Low-Level Detections of Halogenated Volatile Organic Compounds in Groundwater: Use in Vulnerability Assessments

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Abstract: Concentrations of halogenated volatile organic compounds (VOCs) were determined by gas chromatography (GC) with an electron-capture detector (GC-ECD) and by gas chromatography with mass spectrometry (GC-MS) in 109 groundwater samples from five study areas in the United States. In each case, the untreated water sample was used for drinking-water purposes or was from a monitoring well in an area near a drinking-water source. The minimum detection levels (MDLs) for 25 VOCs that were identified in GC-ECD chromatograms, typically, were two to more than four orders of magnitude below the GC-MS MDLs. At least six halogenated VOCs were detected in all of the water samples analyzed by GC-ECD, although one or more VOCs were detected in only 43% of the water samples analyzed by GC-MS. In nearly all of the samples, VOC concentrations were very low and presented no known health risk. Most of the low-level VOC detections indicated post-1940s recharge, or mixtures of recharge that contained a fraction of post-1940s water. Concentrations of selected halogenated VOCs in groundwater from natural and anthropogenic atmospheric sources were estimated and used to recognize water samples that are being impacted by nonatmospheric sources. A classification is presented to perform vulnerability assessments at the scale of individual wells using the number of halogenated VOC detections and total dissolved VOC concentrations in samples of untreated drinking water. The low-level VOC detections are useful in vulnerability assessments, particularly for samples in which no VOCs are detected by GC-MS analysis.

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Introduction

Approximately one-half of the U.S. population relies on groundwater as a source of drinking water, and groundwater is the primary source of drinking water in rural areas. Today, a substantial portion of the Nation's groundwater resources are impacted by a large number of contaminants from industrial, agricultural, commercial, and residential sources. Increasingly, there is a need to conduct assessments of the vulnerability of groundwater systems to contamination from anthropogenic sources (Focazio et al. 2002), particularly, groundwater systems used as a source of drinking water. Most vulnerability assessments rely on statistical evaluations that utilize combinations of hydrogeologic, land-use, and other environmental data (Aller et al. 1987; Rupert 2001; Nolan and Hitt 2006), or more complex process-based analyses utilizing groundwater models (Eberts et al. 2005). Measurements of the chemical and isotopic composition of water in well discharge can be used to test the reliability of vulnerability models (Mahlknecht et al. 2006), or to evaluate trends in water-quality parameters (MacDonald et al. 2003).

Detections of selected environmental tracers, such as tritium (^3H), chlorofluorocarbons (CFCs), other selected halogenated volatile organic compounds (VOCs), pesticides, nitrate, pharmaceuticals, caffeine, and other substances of anthropogenic origin in discharge from drinking-water wells indicate the presence of recent recharge (typically, post-1940s) or groundwater mixtures containing at least a fraction of recent water (Plummer et al. 1993; Dörr et al. 1997; Seiler et al. 1999; Shelton et al. 2001; Stewart and Morgenstern 2001; Focazio et al. 2002; Belitz et al. 2003; MacDonald et al. 2003; Nelms et al. 2003; Oudijk 2003; Shapiro et al. 2003, 2004a; Manning et al. 2005; Morris et al. 2005a, 2006; Verstraeten et al. 2005; IAEA 2006). The "low-level" detections of CFCs and other selected halogenated VOCs can be quite useful in determining whether fractions of post-1940s water are present in well discharge. Here, the term "low level" refers to concentrations that, typically, are below the minimum detection level (MDL) for VOCs determined by purge and

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trap capillary column gas chromatography with mass spectrometry (GC-MS), and can be at concentrations as low as two to more than four orders of magnitude below the commonly reported GC-MS MDL of 0.01–0.2 $\mu g/L$. Preliminary results of the use of low-level concentrations of CFCs and other halogenated VOCs in detecting anthropogenic inputs in drinking water were presented by Shapiro et al. (2003, 2004a).

The purpose of this study was to develop a quantitative procedure for using measurements of low-level concentrations of halogenated VOCs in drinking water as a means of conducting assessments of vulnerability of drinking-water sources to contamination. This study extended the earlier work of Shapiro et al. (2004a) for a set of 109 groundwater samples collected from five study areas in the United States that are being intensively investigated as a part of the U.S. Geological Survey (USGS) program, Transport of Anthropogenic and Natural Contaminants (TANC) (Eberts et al. 2005), which is part of the USGS National Water-Quality Assessment (NAWQA) program. Land uses in the study areas included rural, agricultural, urban, and industrial settings, and the groundwater sampled was used for drinking-water purposes or was from a monitoring well near a drinking-water source.

Methods

Sample Collection

All water samples were collected before chlorination or any other form of disinfection treatment. Water samples for GC-MS analysis were collected in triplicate in 40-mL baked amber ampoules with Teflon-lined caps following NAWQA protocols (Koterba et al. 1995). A closed Teflon path from the well to the vial was established. The flow rate during filling (within a sampling chamber) was less than 0.5 L/min to minimize degassing associated with bubble formation. The samples were acidified to a pH of 2 with VOC-free HCl, capped without a headspace, and stored on ice.

Three to five replicate water samples for gas chromatography with an electron-capture detector (GC-ECD) analysis were collected at each well without contact with the atmosphere in 125-mL glass bottles with aluminum-foil lined caps. Refrigeration-grade copper or nylon tubing was used to establish a closed path from the well discharge to the bottom of the bottle, which was submerged in an overflowing container. The bottles were capped under water without a headspace. The samples were not acidified and were stored at room temperature (http://water.usgs.gov/lab/chlorofluorocarbons/sampling/bottles/). Repeated analyses of replicate bottles showed no evidence of degradation of the VOCs identified as a part of this study in groundwater samples on storage for up to four months. The stability of the VOCs in the present study was attributed to the low particulate organic carbon (POC) content in the drinking-water samples, and in many samples, the presence of dissolved oxygen. Previous studies have shown CFCs to degrade on storage of surface-water samples with an elevated POC content (Plummer et al. 1998). Another study indicated that CFCs in groundwater were stable in flame-sealed glass vials of untreated drinking water for up to 10 years (Shapiro et al. 2004b).

Analytical

Water samples were analyzed for VOCs using (1) the USGS purge and trap capillary column GC-MS procedure (Rose and Schroeder 1995; Connor et al. 1998) at the USGS National Water-Quality Laboratory (NWQL), Lakewood, Colo., and (2) using a purge and trap GC-ECD method similar to that of Busenberg and Plummer (1992) at the USGS Chlorofluorocarbon Laboratory, Reston, Va.

The NWQL analytical method corresponds closely to USEPA Method 524 for drinking-water samples (Moran et al. 2006). The NWQL method uses a set of unique fragmentation masses and patterns to identify individual compounds to a high degree of confidence. The method currently measures 85 VOCs with a tentative identification of additional unknown compounds. The minimum reporting level was defined as two times the long-term method detection level (LT-MDL) (Childress et al. 1999). In computing detection frequencies of VOCs from NWQL purge and trap capillary column GC-MS analyses, an assessment level of 0.2 $\mu g/L$ is normally assigned. Further improvements to the GC-MS method are now capable of producing results that can be evaluated at an assessment level of 0.02 $\mu g/L$ (Moran et al. 2006, 2007), an order of magnitude lower than the earlier measurements.

Details of low-level VOC sampling and analyses from the USGS Chlorofluorocarbon Laboratory are given at http://water.usgs.gov/lab/chlorofluorocarbons/lab/analytical_procedures/ and in IAEA (2006). The analytical system is calibrated daily for quantitative analysis of CFC-11, CFC-12, and CFC-113 using an air standard calibrated on the SIO-98 scale (Walker et al. 2000) (http://water.usgs.gov/lab/chlorofluorocarbons/lab/analytical_procedures/#sta). A sample volume of approximately 34 cm^3 was stripped of VOCs for a period of 4 min using ultrapure N_2 that has passed through a mole sieve. The system and analytical procedure is nearly identical to that of Busenberg and Plummer (1992), with these few exceptions: the analysis time was extended from 10 to 30 min to detect a larger suite of VOCs; the 3-m analytical column was packed with Porasil C and heated at 72°C in the GC oven; a constant flow of about 25 cm^3/min of ultrapure N_2 carrier gas was used; and the ECD was maintained at 300°C.

Although the MDLs can be as low as 1 picogram per liter (pg/L, 1×10^{-6} ug/L, or 1 part per quadrillion) for some halogenated VOCs using purge and trap GC-ECD methods, the ECD does not detect most nonhalogenated hydrocarbons. High concentrations [tens of parts per billion (ppb)] of some halogenated VOCs can be difficult to quantify by GC-ECD because of the nonlinear response of ECDs, especially at higher concentrations. The sensitivity of the ECD also varies with the electron affinity of different halogenated VOCs. The identification of compounds in groundwater samples by GC-ECD is based on retention time, and for the compounds identified, concentrations were determined using calibration standards. Many purgeable halogenated VOCs were detected in GC-ECD chromatograms of untreated drinking water, but were not present in any of the commercially available standards analyzed and were, therefore, unidentified.

Because of the limitations of GC-ECD methods for analyzing a wide range of VOCs, mass-spectrometric methods are more commonly used in identifying and quantifying concentrations of VOCs in groundwater. With assessment levels on the order of about 0.2–0.02 ug/L, the mass-spectrometric method is sufficient to meet U.S. Environmental Protection Agency (USEPA) regulatory requirements for drinking water. The primary advantage of purge and trap GC-ECD methods relative to the mass spectrometric analysis is the extremely low MDL, which allows vulnerable waters to be detected more frequently than they would be using GC-MS.

GC-ECD Peak Identification

Compound retention times in the purge and trap GC-ECD analytical system were determined by (1) analyzing commercial gas mixtures containing concentrations of 100 ppb of specific VOCs in nitrogen; (2) analyzing commercially available single VOC compounds dissolved in methanol that were then diluted in ultrapure nitrogen; (3) comparing chromatograms of commercial standards containing various combinations of the more common halogenated VOCs; and (4) comparing detections in GC-ECD chromatograms of groundwater samples with the corresponding GC-MS compound identifications and analyses for the same sample. Sixty-three VOCs, with retention times between 2.0 and 28.1 min, were detected by GC-ECD in groundwater. Twenty-five of these compounds were identified (Table 1) by retention time. Peak identification by GC-ECD may not be unique for a specific compound, and depending on instrumental conditions and peak area, compound identification can be obscured by overlapping peaks (multiple VOCs with similar retention times). For example, using the present instrumental configuration, methyl bromide and vinyl chloride have nearly identical retention times and cannot be resolved in GC-ECD chromatograms. Because of the low sensitivity of the ECD to vinyl chloride, such detections were assumed to be methyl bromide, which has an ECD sensitivity six times that of vinyl chloride (Table 1).

As an example, Fig. 1 shows a 30-min GC-ECD chromatogram of water from a monitoring well in the glacial aquifer system, Woodbury, Conn. Fourteen compounds were detected, and 11 were identified (CFC-12, CFC-11, methyl chloride, 1,1-dichloroethlyene, CFC-113, methyl iodide, carbon tetrachloride, methylene chloride, TCE, PCE, and methyl chloroform) based on retention time data for the analytical system. The compounds corresponding to three other peaks in the chromatogram are unknown. The concentrations of the 11 VOCs quantified with the GC-ECD were below the LT-MDL for GC-MS analysis; that is, there were no VOC detections reported by the GC-MS analysis of this sample.

GC-ECD Relative Sensitivity to Halogenated VOCs

The relative sensitivities of VOCs to the ECD of the identified compounds were estimated as factors relative to the ECD sensitivity of an equivalent concentration of methyl chloride (Table 1). The sensitivity factors were computed as the ratio of the peak areas of a 100 ppb gas standard measured on the ECD relative to the peak area of a 100 ppb methyl chloride standard. The sensitivity factors ranged from 1 (methyl chloride) to about 650 for tetrachloroethene (PCE) and CFC-11 relative to methyl chloride. Common VOCs that have particularly high sensitivity to the ECD (in addition to PCE and CFC-11) are Halon-1211, methyl iodide, CFC-113, TCE, carbon tetrachloride, chloroform, and CFC-12 (Table 1). Because of their high relative sensitivity to the ECD, their widespread persistence in the environment (Zogorski et al. 2006), and predominant anthropogenic origins, PCE, TCE, CFC-11, and CFC-12 are ideal compounds for performing vulnerability assessments at low-level concentrations.

Chloroform was the most frequently detected VOC in water from 3,500 drinking-water wells analyzed by GC-MS procedures, at an assessment level of 0.2 ug/L (Zogorski et al. 2006; Rowe et al. 2007). With the GC-ECD method, chloroform also is frequently detected in water from drinking-water wells, but there are some complications with ECD detection of chloroform. Chloroform has a relative sensitivity that is approximately three times smaller than that of TCE, and TCE has a retention time of only 0.5 min greater than that of chloroform in the analytical system used here. Consequently, the TCE peak can overlap with the chloroform peak, if even a small concentration of TCE is present in the sample, often obscuring the presence of chloroform or the cooccurrence of chloroform and TCE. As the mixture (TCE-chloroform) was the third most-frequently occurring in aquifers sampled by NAWQA (Zogorski et al. 2006), the detection frequency of chloroform in GC-ECD analyses can be underestimated.

For more than 30 years, concentrations of CFCs (CFC-11, CFC-12, and later, CFC-113) have been measured in groundwater using GC-ECD analyses at MDLs that, today, are on the order of 1 pg/L, equivalent to water in equilibrium with air from the late 1940s (see, for example, IAEA 2006, and references therein). The high sensitivity of the ECD to CFC-11, CFC-12, and CFC-113 has permitted the wide use of these compounds in dating groundwater (IAEA 2006).

Concentration Ranges Detected by GC-ECD

The concentration ranges detected by GC-ECD depend on a number of factors, including sensitivity of the compound to the ECD, instrument operating conditions, and VOC stripping efficiency. The efficiencies of stripping VOCs during the 4-min purge of water samples were measured for many of the compounds identified in Table 1 and ranged from about 40 to 100%. Stripping efficiencies were highest (70–100%) for VOCs with retention times of less than about 6 min and decreased to about 40–50% for compounds with retention times greater than 6 min (Table 1). Stripping times of more than 4 min resulted in partial loss of VOCs with low retention times (<3 min). An empirical relation was fitted to measurements of stripping efficiency during 4-min purges as a function of retention time and was used to calculate concentrations from peak areas, introducing a correction factor that, typically, was less than 2. The GC-ECD was calibrated daily for CFC-11, CFC-12, and CFC-113 using air standards as described previously. Concentrations of these CFCs are well known, and have MDLs of about 1, 5, and 9 pg/L for CFC-11, CFC-12, and CFC-113 in water, respectively (Table 1). The MDLs for CFCs determined by GC-ECD were more than four orders of magnitude lower than the LT-MDL for CFC-11 (80,000 pg/L) and CFC-12 (180,000 pg/L) obtained in GC-MS analysis at the USGS NWQL (Table 1).

The concentrations of most of the VOCs identified in Table 1 were quantified using commercially available halogenated VOC gas standards. The GC-ECD MDL was defined for each VOC as two times the peak area of the smallest peak that could be quantified for that VOC above background (Table 1). The lower concentration MDLs of several VOCs were confirmed by comparing peak areas determined by GC-ECD with the mass spectrometric concentrations determined for the same sample at the USGS NWQL, with extrapolation to the GC-ECD MDL peak area. The minimum concentrations detected by GC-ECD are given in Table 1, where they are compared to the LT-MDL from the GC-MS analysis. For many VOCs, there were an insufficient number of detections to permit compound identification or quantification of MDLs. Furthermore, correlation of many VOC peak areas from the GC-ECD with GC-MS analyses could not be made because the concentrations were below the LT-MDL of the GC-MS analysis.

The GC-ECD analytical procedure was not designed for quantitative analysis of contaminated samples. For example, large con-

Table 1. Halogenated VOCs Identified in GC-ECD Chromatograms

Compound	Retention time (Min)	Alternate name	Approximate peak area of 1.0 cc of 100 ppb[a]	ECD sensitivity relative to methyl chloride	Minimum peak area integrated by GC-ECD	Stripping efficiency 4-min purge in percent	GC-ECD MDL (pg/L)[b]	GC-MS LT-MDL (ug/L)	Ratio of MDL values (GC-MS/GC-ECD)
Sulfur hexafluoride[c]	1.99		407,525	15	498	86.6	25	ND	ND
Dichlorodifluoromethane	2.53	CFC-12	1,887,281	71	604	84.1	5.5	0.180	32,582
Halon 1211	3.36	Halon 1211	15,027,000	565	766	80.5	1.3	ND	ND
Dichlorotetrafluoroethane	3.52	CFC-114	924,148	35	797	79.9	22	ND	ND
Trichlorofluoromethane	4.34	CFC-11	17,388,501	654	958	76.6	1.2	0.080	67,355
Chloromethane	4.88	Methyl chloride	26,584	1.0	1,063	74.5	326	0.170	522
1,1-dichloroethene	6.00		294,415	11	1,282	70.4	72	0.024	333
Bromomethane	6.64	Methyl bromide	66,143	2.5	1,407	68.2	356	0.260	730
Vinyl chloride	6.66		10,847	0.4	1,411	68.1	1,435	0.080	56
Trichlorotrifluoroethane	7.13	CFC-113	5,398,569	203	1,503	66.6	9.4	0.466	49,483
Trans-1,2-dichloroethene	8.53		36,791	1.4	1,777	62.4	902	0.032	35
Methyl iodide	9.45		7,466,743	281	1,957	59.9	7.5	0.500	66,975
Carbon tetrachloride	10.17		3,563,684	134	2,098	58.1	19	0.060	3,203
Dichloromethane	12.42	Methylene chloride	85,969	3.2	2,538	53.4	564	0.060	106
Chloroethane	12.49		26,698	1.0	2,552	53.3	1,390	0.120	86
Trichloromethane	15.93	Chloroform	1,821,791	69	3,225	48.8	52	0.024	461
Trichloroethene	16.52	TCE	5,380,886	202	3,340	48.4	20	0.038	1,875
1,1,2-trichloroethane	16.54		43,975	1.7	3,344	48.4	2,522	0.130	52
1,1,2,2-tetrachloroethane	16.72		303,590	11	3,379	48.2	466	0.080	172
Cis-1,2-dichloroethene	18.84		28,270	1.1	3,794	47.5	3,292	0.024	7
Tetrachloroethene	20.35	PCE	17,173,121	646	4,089	47.7	9.9	0.030	3,015
1,2-dichloroethane	20.50		235,812	8.9	4,119	47.8	435	0.130	299
Bromochloromethane	20.77		3,691,808	139	4,171	47.9	37	0.120	3,269
1,1,1-trichloroethane	23.24	Methyl chloroform	930,185	35	4,654	49.8	161	0.032	199
1,1-Dichloroethane	28.11		4,649,677	175	5,607	58.4	25	0.035	1,425
Average VOC (for unidentified peaks)			3,474,801	NA	109	96.2	0.5	NA	NA

Note: NA=not applicables; ND=not determined.

[a] Gas standard calibration (2006).

[b] Sample volume of 34 cc.

[c] Sulfur hexafluoride was not included in the summation of halogenated VOCs in this study, but is given here because it commonly is detected in GC-ECD chromatograms.

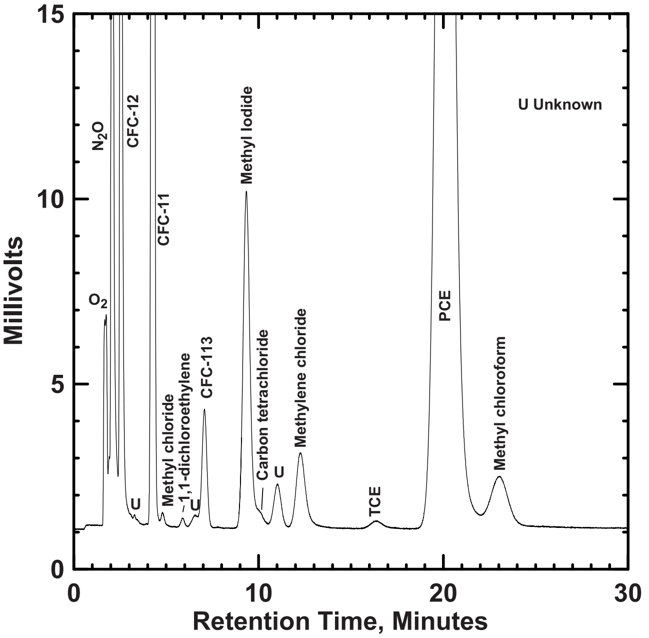

Fig. 1. GC-ECD chromatogram of water from a monitoring well in the glacial aquifer system at Woodbury, Conn., showing detections of at least 14 halogenated VOCs. U=unknown. There were no VOC detections in this sample from the GC-MS analysis.

centrations (greater than a few ug/L) can be underestimated by GC-ECD analysis due to peak "clipping" during peak integration. Further, large contaminant peaks can obscure detection and quantification of other VOCs on chromatograms.

Blanks and Replicate Samples

Both gas and water blanks were analyzed. The gas blanks were analyzed daily and consisted of ultrapure nitrogen that was passed through a VOC trap. Gas blanks were run following highly contaminated (ppb concentrations) samples to assure that there was no carryover between samples. Water from some deep wells that discharge old water can be VOC free and provide confirmation that sampling and analytical protocols do not introduce VOCs to the samples at the trace levels of concentration detected with the GC-ECD (Table 1). Groundwater samples were analyzed in duplicate or triplicate to confirm sample collection and analytical reproducibility.

Four GC-ECD chromatograms that were blank, or nearly blank (containing only a few VOCs near their MDLs) are compared in Fig. 2. Fig. 2(a) shows a chromatogram for blank carrier gas (ultrapure N_2) after injection through the purge cell and columns to the ECD; no halogenated VOCs were detected. Fig. 2(b) is a chromatogram of water from a flowing well in the Upper Floridan aquifer (UFA) at Oslo, Fla., near the Atlantic coast, where the UFA is confined by approximately 122 m of Miocene sediment. The well has 259 m of PVC casing with a 15 m screen to 274 m total depth, and was allowed to flow for several hours before sampling. The water sample was fused in glass in May 1991 and analyzed in January 2006 as a part of this study. Traces of CFC-12, CFC-11, and other (unknown) VOCs with low retention times were present. Traces of TCE and PCE also were present [Fig. 2(b)] corresponding to concentrations of approximately 0.0004 and 0.0001 ug/L, respectively. The extremely low concentrations of VOCs could have been introduced in the drilling process, or possibly released from the PVC casing. Regardless, the water from the monitoring well was nearly blank with respect to halogenated VOCs. The chromatograms shown in Figs. 2(c and d) are from a public-supply well in Albuquerque, N.M., sampled initially in 1996 and then nine years later. The pump discharged 225 L/s. The total depth of the well was 321.6 m, with a screened interval of 175.6 m. The unsaturated-zone thickness was approximately 146 m and the water level was within the open interval of the well. The chromatogram shown in Fig. 2(c) is of water sampled from this well in June 1996 and fused into a glass ampoule with an ultrapure N_2 head space. The sample was analyzed in January 2006. A gas blank was analyzed prior to analysis of this sample, to confirm that there was no possibility of carryover of trace VOCs from a previous sample. The trace TCE and PCE concentrations were approximately 0.00005 and 0.00007 ug/L, respectively. Water from the same public-supply well was sampled in July 2005 and analyzed 20 days later [Fig. 2(d)]. In the nine intervening years between sampling, the TCE was no longer present, and the concentration of PCE decreased to about 0.00002 ug/L; however, trace concentrations of CFC-11 (0.000019 ug/L) and a peak with retention time of 9.46 min (identified as methyl iodide, retention time 9.45 min) appeared [Fig. 2(d)]. Trace VOC contaminants can be expected near the water table beneath metropolitan areas such as Albuquerque. The sample likely remained aerobic in the fused ampoule [field dissolved oxygen (DO) concentration was 3.9 mg/L], so TCE in the sample from 1996 was probably not a degradation product of the PCE.

The two chromatograms shown in Fig. 3 are of water samples collected in glass bottles only minutes apart in July 2005 from a production well in Albuquerque, N.M., near an arroyo where storm runoff infiltrates to the aquifer. The well had a total depth of 383 m, with an open interval of 190 m. The unsaturated zone was 179 m in the vicinity of the well, which had 13 m of water above the open interval. The well discharge rate was 101 L/s. The chromatograms shown in Figs. 3(a and b) are nearly identical and show that the combined effects of field collection in glass bottles with foil-lined caps, shipping, handling, and laboratory analytical procedures are reproducible. Although some of the VOC peaks in the chromatograms appear to be relatively large, they actually represent very small concentrations of CFC-12, CFC-11, CFC-113, and PCE of approximately 0.00025, 0.00007, 0.00022, and 0.0023 ug/L, respectively.

Description of Field Sites

A total of 109 wells were sampled in five USGS study areas that are being intensively investigated as a part of TANC, within the USGS NAWQA Program (Fig. 4) during 2004–2005. The study areas and number of wells sampled include a glacial aquifer system in the Pomperaug River Basin near Woodbury, Conn. (11), the Floridan aquifer system in the Temple Terrace section of Tampa, Fl. (19), the Edwards aquifer in the San Antonio region, (24), the High Plains aquifer near York, Neb. (16), and the Santa Fe Group aquifer system of the Middle Rio Grande Basin in the vicinity of Albuquerque, N.M. (39).

Glacial Aquifer System, Woodbury, Conn.

The glacial aquifer system consists of relatively shallow (to 30 m in thickness), unconfined, valley-fill glacial deposits (Meinzer and Stearns 1929) that overlie fractured Mesozoic bedrock beneath

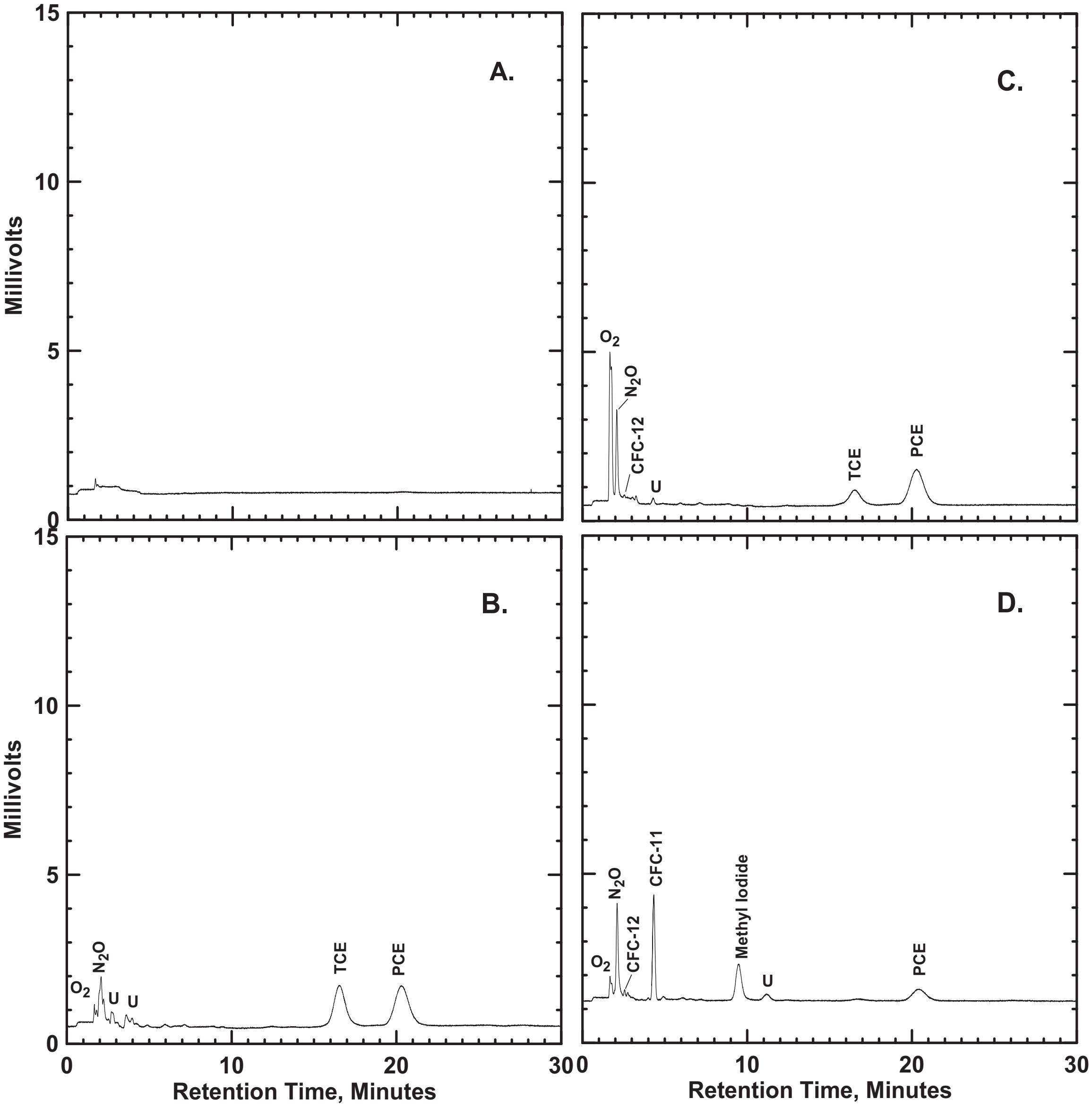

Fig. 2. Comparison of GC-ECD chromatograms for blanks and nearly blank old groundwater, U, unknown: (a) blank carrier gas entered through the water-stripping cell; (b) water from a deep monitoring, flowing well with PVC casing from the Floridan aquifer near Oslo, Fla.; (c) water from a public-supply well at Albuquerque, N.M. (sampled June 22 1996); and (d) water from a public-supply well at Albuquerque, N.M. (sampled on July 27, 2005)

the town of Woodbury, Conn. (population 9,200), in the Pomperaug River Basin of west-central Connecticut. Groundwater is the predominant source of drinking water in the area. Land use in the Pomperaug River watershed is primarily residential, with some commercial, light industrial, and agricultural use. All residences and businesses are unsewered and rely on septic-tank drainfields to dispose of human waste. Several organic contaminant sources have been identified within the study area, including spills or leaks of chlorinated solvents, a methyl tertiary butyl ether (MTBE) plume emanating from a gas station, infiltration from septic-tank drainfields, and chemical applications to lawns (Brown et al. 2007; Starn and Brown 2007). Drinking water is obtained from either private domestic wells or public-supply wells completed in valley-fill deposits. One public-supply well in the Pomperaug River Basin was selected for detailed study. This well has a total depth of 16.5 m and 4.6 m of open interval, with the top of the open interval approximately 11 m below the water table. GC-MS analysis detected 11 VOCs in water from this well, including TCE (5.2 ug/L), methyl chloroform (4.5 ug/L), and PCE (0.31 ug/L). Ten monitoring wells with depths of 4.3–8.5 m, and 0.6 m open intervals at depths of 0.9–4.8 m below the water table also were sampled in the vicinity of Woodbury. A range of 3–9 VOCs were detected by GC-MS analysis in water from one-half of the monitoring wells, although no VOCs were detected by GC-MS in water from the other five monitoring wells.

Floridan Aquifer System, Temple Terrace, Fla.

The Floridan aquifer system provides drinking water to millions of people throughout the southeastern United States. In the city of Temple Terrace (population 20,918 in 2000), in the northeastern part of the Tampa metropolitan area of west-central Florida, the principal source of freshwater is the UFA, a highly productive,

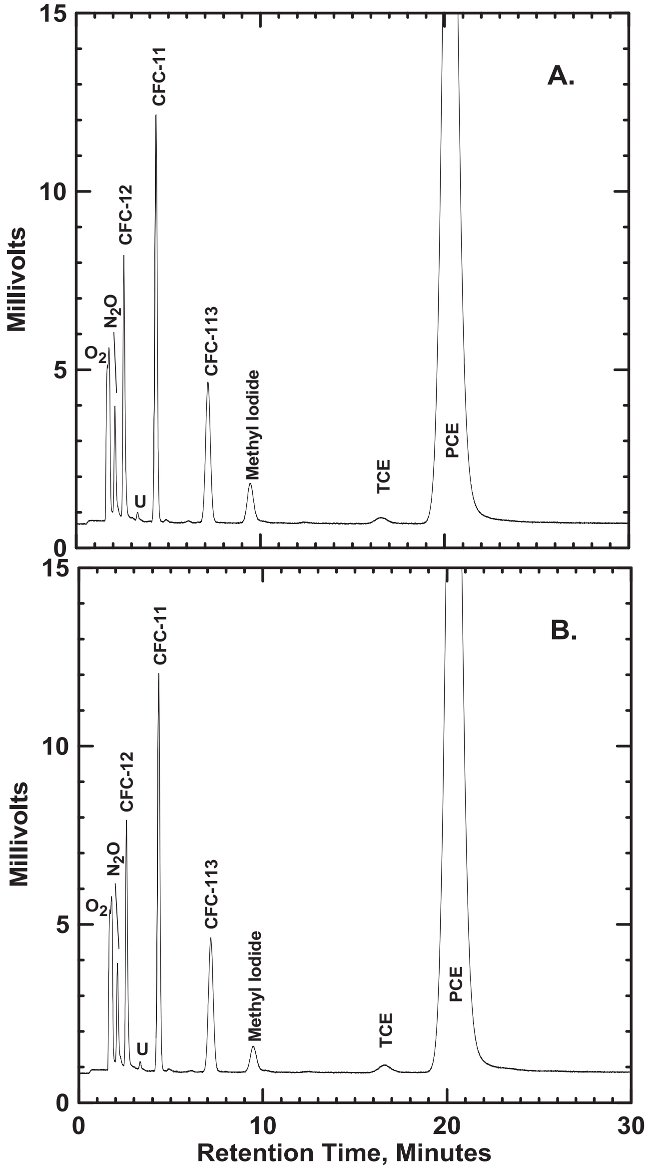

Fig. 3. Separate samples collected minutes apart from a public-supply well in Albuquerque, N.M.

karstic, carbonate aquifer (Miller 1986). Principal hydrogeologic units that lie above the UFA are the intermediate confining unit and surficial aquifer. The surficial aquifer is an unconfined sand and clayey aquifer that is separated from the UFA by a clay-rich intermediate confining unit that, in the Temple Terrace area, generally is less than 3 m in thickness. The intermediate confining unit may limit downward leakage from the surficial aquifer to the UFA in places. The extent, thickness, and permeablity of the intermediate confining clay unit are highly variable throughout the study area. Breaches formed in this clay unit from localized subsidence associated with karst development in the UFA, and local permeable zones in the intermediate confining unit provide paths for recharge to the UFA.

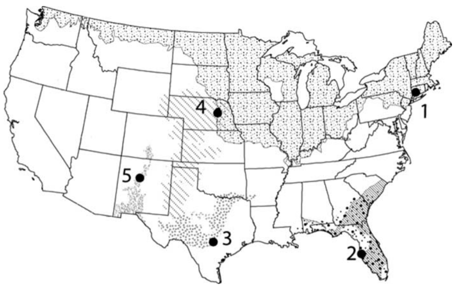

Fig. 4. Location of selected NAWQA/TANC study areas from which ground-water samples were analyzed for VOCs: (1) glacial aquifer system at Woodbury, Conn., in glacial deposits; (2) Floridan aquifer system near Tampa, Fla., in karst limestone; (3) Edwards aquifer near San Antonio, in karst limestone; (4) High Plains aquifer near York, Neb., in alluvial and glacial deposits; and (5) Santa Fe Group aquifer system near Albuquerque, N.M., in basin-fill alluvial deposits. The patterns show the regional extent of each hydrogeologic setting or aquifer system.

The area is entirely served by a municipal sewer system, and storm runoff within Temple Terrace is routed to a series of storm-water retention basins. Potential sources of contaminants to the surficial aquifer and UFA at Temple Terrace include leakage from underground storage tanks, dry cleaners, and other commercial operations that use solvents, chemicals applied to golf courses and lawns, infiltration from storm-water retention ponds, and a hazardous-waste site.

Eighteen monitoring wells within the contributing area of production wells in the Temple Terrace area, and one public-supply well were sampled. All of the monitoring wells had 3 m openings; 11 of the wells were completed in the surficial aquifer and seven in the UFA. The production well had a total depth of 53 m with a screened interval of 16.5 m in the UFA. The thickness of the unsaturated zone at the 11 monitoring wells sampled in the surficial aquifer averaged 6.4 ± 2.4 m. The average total depth of the wells sampled in the surficial aquifer was 9.1 m (range of 6–14 m). The average total depth of the wells in the UFA was 38 m (range 19–58 m).

GC-MS analysis detected at least 1 VOC in 13 of the 18 monitoring wells sampled. The maximum number of VOCs detected in a single sample was four and the median number of VOCs detected was two. Detections included chloroform, PCE, TCE, dichloromethane, carbon disulfide, bromodichloromethane, and toluene at concentrations generally less than 1 ug/L and well below the USEPA maximum contaminant level (MCL). Traces of chloroform (0.08 ug/L), and TCE (0.04 ug/L) were detected by GC-MS analysis in water from the public-supply well.

Edwards Aquifer, San Antonio, Tex.

The Edwards aquifer was, until recently, the sole source of water supply for the metropolitan area of San Antonio (population 1.4 million) in south-central Texas. The aquifer also is used extensively for agricultural irrigation and ranches in areas west of San Antonio. The highly productive Edwards aquifer is in fractured, karstic limestone of lower Cretaceous age that ranges in thickness from 137 to 274 m at San Antonio (Lindgren et al. 2004). Regionally, the Edwards aquifer is bordered on the north by the Edwards Plateau, a rugged, “Texas Hill Country” catchment area that provides direct recharge to the unconfined Edwards–Trinity and Trinity aquifers. Although less productive than the Edwards aquifer, the Trinity aquifer is the predominant source of water supply on the Edwards Plateau, an area experiencing rapid residential/suburban growth in the San Antonio region. Streams that drain the Edwards Plateau recharge the unconfined Edwards aquifer as they flow across the karst of the Balcones Fault Zone in the San Antonio region. Surface-water reservoirs or recharge structures constructed across the karstic and fractured limestone in the recharge zone further enhance recharge to the Edwards aquifer. Most of the recharge to the Edwards aquifer is in rural/agricultural outcrop areas of Medina and Uvalde counties to the west of San Antonio. Flow from there is southward and then east along long flow paths that discharge at a series of springs on or close to faults within the Balcones Fault Zone to the east and northeast of San Antonio, including Comal and San Marcos springs in Comal and Hays counties. Further to the south and southeast, within the Balcones Fault Zone, the Edwards aquifer is confined by Cretaceous (and further south by Tertiary age) Gulf Coastal Plain clays and siliclastics. Where confined, the Edwards aquifer is artesian. The southern boundary of the active flow system of the Edwards aquifer generally is placed at the freshwater/saltwater interface of 1,000 mg/L of dissolved solids (Lindgren et al. 2004).

Increasing urban development and associated vulnerability to inputs of contaminants from the land surface across the Edwards aquifer recharge zone is a subject of concern for the future of this water supply. In one of the first applications of chlorofluorocarbons in hydrologic investigations, Thompson and Hayes (1979) traced a narrow plume of CFC-11 from an apparent point source on the northwest edge of San Antonio approximately 80 km northeast of San Antonio to discharge at San Marcos Spring. Fahlquist and Ardis (2004) reported the detection of chloroform, bromodichloromethane, chlorodibromomethane, and several other VOCs (by GC-MS analysis) in waters from unconfined parts of the Edwards aquifer, at concentrations generally less than 1 ug/L. The two most frequently detected halogenated VOCs (by GC-MS analysis) in the recharge zone of the Edwards aquifer were chloroform and PCE, but at concentrations well below the USEPA drinking-water MCLs (Bush et al. 2000).

This study includes analytical results from 24 public-supply wells in unconfined parts of the Edwards aquifer in the vicinity of San Antonio, Bexar County, Tex., and in rural parts of Uvalde and Medina Counties, extending approximately 88 km to the west of San Antonio, and to Comal County, approximately 48 km to the east and northeast of San Antonio. Land use includes rural or rural/residential, agricultural, urban or urban/residential, domestic/residential, industrial, and military. The total depths of the public-supply wells range from 65 to 716 m with open intervals of 16–453 m. Waters from six of these 24 wells had no VOC detections by GC-MS analysis, and the highest number of VOC detections by GC-MS in a single sample was five (bromodichloromethane, bromoform, chloroform, toluene, and PCE). No monitoring well samples were collected from the Edwards aquifer.

High Plains Aquifer, York, Neb.

The High Plains aquifer in eastern Nebraska consists of unconsolidated Quaternary deposits of eolian loess, and alluvial and glacial sand, gravel, silt, and clay (Gutentag et al. 1984), and is the major source for agricultural irrigation and public-water supply in eastern Nebraska and Kansas. Near the town of York (population 8,100) in east-central Nebraska, the uppermost hydrogeologic unit is mostly unsaturated loess. Sand and gravel, with discontinuous silt and clay lenses, underlie the loess and form a regionally extensive unconfined aquifer. A clay–silt confining layer underlies the unconfined aquifer and provides a locally effective barrier to downward leakage to an upper confined aquifer layer comprised of fine- to medium-grained sand. Discontinuous deeper sand layers, separated from the upper confined aquifer by clay–silt confining units, locally comprise a lower confined aquifer.

Regionally, groundwater withdrawals are predominantly for agricultural irrigation purposes, and groundwater is the sole source for municipal and domestic supply. Along the regional direction of groundwater flow (from northwest to southeast), land use changes from mostly irrigated agricultural; through a transition zone of increasing density of households, businesses, and livestock facilities along the western edge of York; to low-density residential and commercial/transportation areas of York. Many irrigation, commercial, and some public-supply wells are perforated in both the unconfined and confined aquifers, providing potential pathways for downward leakage of contaminants from the unconfined aquifer. Hydraulic measurements indicate that the clay–silt unit between the unconfined and upper confined aquifers locally isolates the two aquifers. However, downward leakage through the confining layer through wellbores is quantitatively significant (Clark et al. 2006) and alters water chemistry in parts of the confined aquifers (Landon et al. 2006), including two of the monitoring wells sampled. The upper confined sand aquifer generally is anoxic, undergoing Mn and Fe reduction.

Of the 16 monitoring wells sampled in the High Plains aquifer near York, seven were in agricultural areas (1 confined, 6 unconfined) and nine were in the urban area of York, Neb. (five confined, four unconfined). The monitoring wells were selected from a larger set of 36 monitoring wells in the area because they had a low frequency of detection of halogenated VOCs from the GC-MS analysis. PCE concentrations of 0.02–0.04 ug/L were measured in water from only three monitoring wells from the set of 16, and one of these waters contained 0.015 ug/L of TCE. All detections were near the LT-MDL for the GC-MS procedure. Within the overall set of 36 monitoring wells in the area, 17 VOCs were detected, and most were at trace concentrations by GC-MS analysis. At least one VOC was detected by GC-MS analysis in 21 of the 36 monitoring wells. In this larger set of wells, three wells (urban, unconfined) were identified that had concentrations of PCE of 6–12 ug/L, which exceeded the USEPA MCL of 5 ug/L for PCE. One urban well contained elevated concentrations of 1,2-dichloroethane. The most frequently detected VOCs were PCE, TCE, and degradation products cis-1,2-dichloroethene and trans-1,2-dichloroethene. TCE also is used as a degreaser that is commonly added to septic tanks, providing an additional source to groundwater (Katz et al. 2007).

For the subset of 16 monitoring wells included in this study, all had 1.5-m open intervals. Total depths averaged 57 m for the wells in the upper confined aquifer and 15 m for the wells in the unconfined aquifer. Unsaturated zone thickness ranged from 4 to 23 m above the unconfined aquifer. No public-supply well samples from the High Plains aquifer were included in this study.

Santa Fe Group Aquifer System, Albuquerque, N.M., and Vicinity

Historically, groundwater from the Santa Fe Group aquifer system of the Middle Rio Grande Basin, central New Mexico, has been essentially the sole source of public supply for domestic, industrial, and commercial uses in the metropolitan area of Albuquerque, N.M. (population 713,000). The basin-fill alluvial deposits of the aquifer system are composed primarily of unconsolidated to moderately consolidated sand, gravel, silt, and clay that were deposited in fluvial, lacustrine, or piedmont-slope environments from the late Oligocene to the middle Pleistocene. Post-Santa Fe

Group valley and basin-fill deposits of Pleistocene to Holocene age, typically, are in hydraulic connection with the Santa Fe Group deposits. Sustained groundwater withdrawals from the Middle Rio Grande Basin have resulted in water-level declines that exceed 36 m in eastern Albuquerque (Bexfield and Anderholm 2002).

The Santa Fe Group aquifer system generally is unconfined and depths to water range from less than 1 m in the low-lying flood plain of the Rio Grande (average depth to water in the inner valley of the Rio Grande is less than about 8 m), to more than 213 m beneath upland areas both east and west of the river (and at least 274 m beneath parts of Rio Rancho northwest of Albuquerque). As a result of high evaporation rates and generally large depths to groundwater in this semiarid region, aerial infiltration of precipitation to the Santa Fe Group aquifer system is thought to be minor (Anderholm 1988). Most recharge to the aquifer system occurs as infiltration of surface water along the Rio Grande and its main tributary, the Jemez River, with lesser amounts of recharge from other surface–water features and from infiltration along the basin margins (Sanford et al. 2004a,b; McAda and Barroll 2002; Plummer et al. 2004a,b). With urbanization, new sources of recharge to the groundwater system at Albuquerque include seepage from septic tanks, sewer and distribution lines, and turf irrigation; there also have been changes to the quality of some important sources of recharge, such as arroyo infiltration. Localized water-quality issues include infiltration from landfills, industrial operations, military operations, and underground storage tanks.

Anthropogenic compounds that have been detected in groundwater of the basin include VOCs (particularly chlorinated solvents and petroleum hydrocarbons) (Earp 1991; Anderholm 1997; USEPA 2006). Most detections of these compounds have been in monitoring wells that are in or near the inner valley of the Rio Grande, an area that intrinsically is susceptible to groundwater contamination because of shallow depths to groundwater (Anderholm 1997).

Thirty-nine public-supply wells in Albuquerque and vicinity were sampled as a part of this study. Land use in the vicinity of the wells is classified as predominantly urban or domestic/residential, and to a lesser degree military. Based on proximity to domestic septic systems, 11 of the 39 wells could potentially be influenced by septic-tank effluent. Total well depths averaged 325 m (range was 64–631 m) with water levels that average 110 m (range was 3–268 m). The length of the open interval for the 39 wells averaged 161 m (range was 3–447 m) with an average of 50.6 m of water (range was 0–175 m) above the open interval. Five of the water-supply wells were within the inner valley of the Rio Grande, with water levels that averaged 4 m below land surface. Eleven wells were on the fringe of the inner valley, where water levels averaged 55.7 m. The remaining water-supply wells were in upland areas outside the inner valley, and water levels averaged 158.5 m. No VOCs were detected by GC-MS in 22 of the 39 water-supply wells sampled. One VOC was detected by GC-MS analysis in water from 12 of the 39 wells. Water from only one well had GC-MS detections of more than two VOCs (six detections) and this was from a production well located about 1.2 km east of the inner valley of the Rio Grande at Albuquerque (1,2-dichloroethane, 0.08 ug/L; PCE 0.05 ug/L; 1,1-dichloroethane, 0.53 ug/L; 1,1-dichloroethene 0.19 ug/L; TCE, 0.17 ug/L; cis-1,2-dichloroethene, 0.04 ug/L). No monitoring well samples were collected from the Santa Fe Group aquifer system for this study.

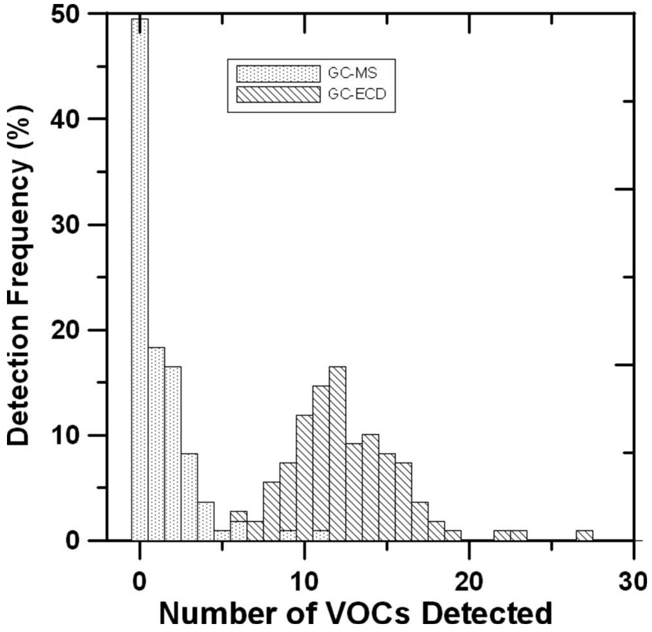

Fig. 5. Frequency and distribution of VOCs detected in 109 drinking-water samples analyzed using GC-MS and GC-ECD procedures

Results

VOC Detection Frequency

Halogenated VOCs were detected in 43% of the 109 water samples analyzed by GC-MS from the five study areas. At least six halogenated VOCs were detected in every water sample analyzed by GC-ECD (Fig. 5). The maximum number of VOCs detected in any sample by GC-MS was 11, compared to a maximum of 27 VOCs detected in the same sample (Connecticut study area) by GC-ECD (Table 2). The median and average number of detections by GC-MS analysis were 0.5 and 1.2 per sample, compared to 12 and 12.6 per sample, respectively, for GC-ECD analyses. With the lowered detection limit of the GC-ECD compared to that of the GC-MS analysis, the distribution in frequency of detections shifted from a highly skewed function obtained from the GC-MS data to an approximately normal distribution obtained from the GC-ECD data (Fig. 5).

The frequency of detection of individual halogenated VOCs in the 109 water samples determined by GC-MS and GC-ECD analysis is compared in Fig. 6. Chloroform was the most frequently detected VOC determined by GC-MS analysis, and was detected in 33% of the samples. The frequency of detection of chloroform by GC-ECD analysis (29%) was slightly lower than that by GC-MS due to interference from TCE.

Tetrachloroethene was detected in 24% of the samples by GC-MS, but was detected in every sample analyzed by GC-ECD (Fig. 6, see, also, Fig. 7). The ECD has a very high sensitivity to PCE, a sensitivity that is approximately 650 times that of methyl chloride. The MDL for PCE determined by GC-ECD was approximately 1.0×10^{-5} ug/L, which is approximately 3,000 times below the LT-MDL of the GC-MS analysis. The smallest peak area integrated for PCE among the 109 samples was about 33,800 counts, corresponding to a concentration in water of about 4 $\times 10^{-5}$ ug/L, a factor of 4 above the GC-ECD MDL for PCE. In a few cases, it was possible that there was some trace carryover of

Table 2. Summary of VOC Detections for Each Study Area

		Number of VOC detections								Average concentration determined by GC-ECD		
		Detections by GC-MS				Determined by GC-ECD						
Study area	Number of samples	Minimum	Maximum	Median	Average	Minimum	Maximum	Median	Average	CFC-12 (pg/L)	TCE (pg/L)	PCE (pg/L)
CONN (MW)	10	0	9	1.5	2.5	13	27	15.5	16.7	1,967	2,668	12,152
CONN (PSW)	1	11	11	11	11	19	19	19	19	3,416	419,229	149,947
GAFL [unconfined (MW)]	11	0	3	1	1.3	14	23	16	16.6	597	2,170	16,614
GAFL UFA (MW)	7	0	4	2	2.1	12	17	16	15.3	505	2,917	8,303
GAFL (PSW)	1	2	2	2	2	12	12	12	12	2,407	104,534	23,365
GAFL (total)	19	0	4	2	1.6	12	23	16	16.1	658	7,832	14,065
SCTX (PSW)	24	0	5	2	1.7	9	15	12	11.9	863	1,726	34,541
HPGW [unconfined (MW)]	10	0	0	0	0.0	10	13	11	11.2	534	2,613	12,288
HPGW [upper confined (MW)]	4	0	0	0	0	12	14	11.5	11.3	68	977	1,863
HPGW [lower confined (MW)]	2	0	0	0	0	11	13	12	12	39	5,189	5,916
HPGW (total)	16	0	2	0	0.3	10	14	11.5	11.8	374	2,620	8,931
RIOG (PSW)	39	0	6	0	0.6	6	16	10	10.5	629	5,840	2,985
All	109	0	11	0.5	1.2	6	27	12	12.6	796	8,310	14,927
Air–water equilibrium (2005)[a]										286	22	85
Air–water equilibrium (1975)[a]										118	325	727

Note: CONN=glacial system (Woodbury, Conn.); MW=monitoring well; PSW=public-supply well; GAFL=Floridian aquifer system (Tampa, Fla.); UFA=Upper Floridian aquifer; SCTX=Edwards aquifer (San Antonio, Tex.); HPGW=High Plains aquifer (York, Neb.); and RIOG=Santa Fe Group aquifer system (Albuquerque, N.M., and vicinity).

[a] Air values of 544, 1, and 5 ppt for CFC-12, TCE, and PCE, respectively (calculated water concentrations in pg/L at 15°C).

[b] Air values of 224, 14.5, and 43 ppt for CFC-12, TCE, and PCE, respectively (calculated water concentrations in pg/L at 15°C).

PCE from a previous sample, but it was unlikely in most samples because a gas blank was usually run following samples with relatively large (ppb) concentrations of PCE or other VOCs. As most of the detections of PCE were more than an order of magnitude above the GC-ECD MDL, it was likely that PCE, at very low concentrations, was present in every sample analyzed.

Trichloroethylene (TCE) was detected in 11 of the 109 samples analyzed by GC-MS (10% of the samples), although it was detected in 100 samples (92%) analyzed by GC-ECD. The GC-ECD MDL for TCE was about 2×10^{-5} ug/L, which was 1,900 times below the GC-MS LT-MDL for TCE (of approximately 0.038 ug/L). The smallest peak integrated for TCE by GC-ECD in the set of 109 samples was about 2,500 counts, which corresponded to a concentration of about 1.8×10^{-5} ug/L, just below the GC-ECD MDL for TCE. Other halogenated VOCs detected by GC-MS in a few samples included methyl chloride; 1,1-dichloroethylene; methylene chloride; cis-1,2-dichloroethylene; methyl chloroform; and 1,1-dichloroethane [Fig. 6(a)].

In addition to PCE, other halogenated VOCs that were detected in every sample analyzed by GC-ECD [Fig. 6(b)] include CFC-12, CFC-11, and methyl iodide. There were no detections of CFCs or methyl iodide in any sample analyzed by GC-MS. Other VOCs identified by GC-ECD with high detection frequencies were methyl chloride (86%); 1,1-dichloroethylene (83%); CFC-113 (81%); carbon tetrachloride (39%); methylene chloride (51%); methyl chloroform (35%); and chloroform (29%). Many other VOCs were detected by GC-ECD, but further investigation is needed for compound identification.

The frequencies of VOC detections by GC-ECD in the 63 samples having no VOC detections by GC-MS were remarkably similar to the frequencies of detection in the entire dataset of 109 samples (Fig. 8). The distribution in the frequency of detection of VOCs also is little changed between the set of all samples, and those having no GC-MS detections (Fig. 9). In the subset of 63 samples with no GC-MS detections, the minimum and maximum number of detections in any sample analyzed by GC-ECD were 6 and 27, respectively, as for the set of 109 samples. The median and average number of VOCs detected by GC-ECD were only slightly smaller, 11 and 11.9, respectively, for the 63 samples with no GC-MS detections, compared to 12 and 12.6 for the complete set of 109 samples (Fig. 9). As expected, the detection frequencies of the commonly recognized VOCs are considerably above those reported previously for drinking water (Zorgorski et al. 2006), because of the low MDLs of the GC-ECD analysis (Shapiro et al. 2004a).

Although the frequency of detection of halogenated VOCs in the subset of samples with GC-MS detections was nearly identical to that in the subset with no GC-MS detections, the measured VOC concentrations were considerably higher in the set with GC-MS detections than in the set with no GC-MS detections. The average concentrations of CFC-12, CFC-11, CFC-113, carbon tetrachloride, chloroform, TCE, and PCE were factors of 1.8, 3.4, 25.1, 2.7, 16.3, 8.0, and 11.0 times higher, respectively, in the set of samples with GC-MS detections than in the set without GC-MS detections. The average concentration of methyl iodide was nearly identical in the two sets of samples.

Air–Water Equilibrium

CFC-11, CFC-12, and PCE have relatively long histories of release to the environment, and have very high sensitivities to the ECD, which contributes to their high frequency of detection in

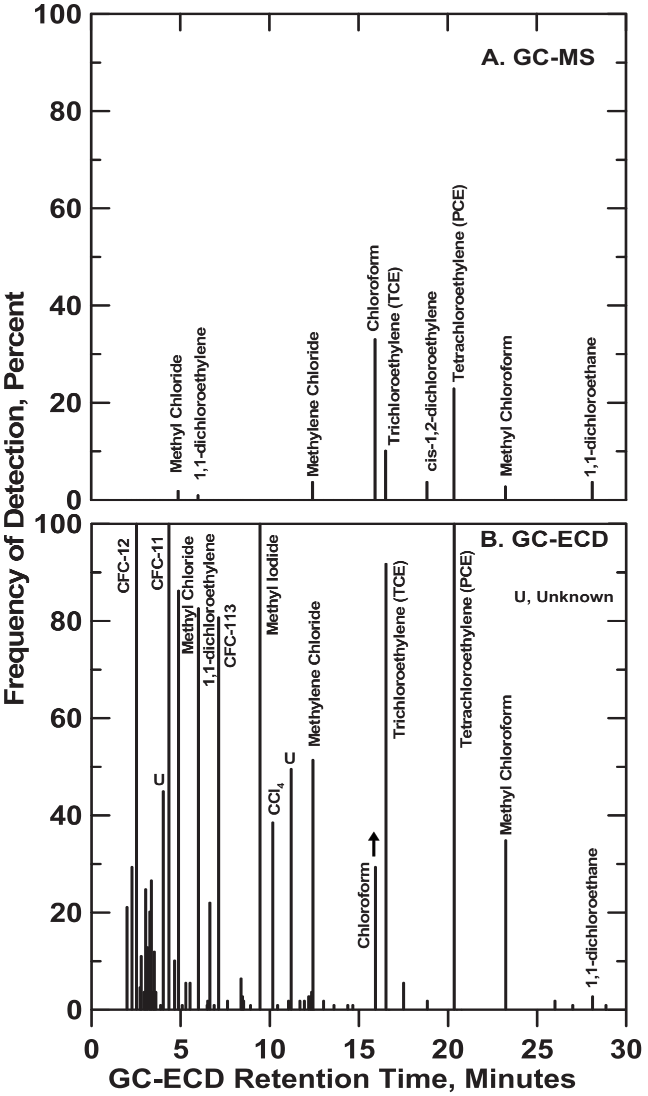

Fig. 6. Comparison of frequency of detection of individual halogenated VOCs determined (a) by GC-MS analysis; (b) by GC-ECD in 109 drinking-water samples from the five study areas

groundwater. The lowest concentrations of these halogenated VOCs were near those expected for water in equilibrium with air. The atmospheric mixing ratio of PCE varies seasonally and, in rural parts of the northern hemisphere, was between 7 (late summer) and 26 parts per trillion (ppt) in late winter in the late 1980s (Wang et al. 1995), but can be considerably higher (to about 100 ppt) in air from urban centers such as Boston (Kleiman and Prinn 2000). PCE has been widely used as a dry-cleaning solvent and in industrial degreasing since the 1930s. Production in the United States more than tripled in the 1960s and peaked during the 1970s (Doherty 2000).

Concentrations of CFC-12 and PCE in the 109 groundwater samples are compared in Fig. 7. Waters recharged in 1940 having only an atmospheric source of PCE contained about 84 pg/L of PCE and only about 0.2 pg/L of CFC-12. The concentration of PCE in air peaked in 1975 with an air–water equilibrium concentration of about 730 pg/L. Atmospheric concentrations of CFC-12 continued to rise until about 1995 and have decreased slightly since then, although PCE concentrations fell after 1975 (Fig. 7). Many of the samples from the Santa Fe Group aquifer system plot along the air–water equilibrium line corresponding to the rise in atmospheric mixing ratios of PCE and CFC-12 from the 1940s to about 1975. Although the lowest concentrations of PCE in the groundwater samples corresponded to equilibrium with the modern atmosphere, the associated CFC-12 concentrations were too low for modern air–water equilibrium. These samples may represent dilutions of post-1950 water with old tracer-free water. Many of the Albuquerque water-supply wells have large intervals open to the aquifer that permit mixing of young and old water. Most of the PCE and CFC-12 detections in the groundwater samples (Fig. 7) represent excesses above air–water equilibrium, indicating anthropogenic inputs in excess of air–water equilibrium. All of the water samples contained CFC-12, which indicated that all samples contained a fraction of post-1940's water.

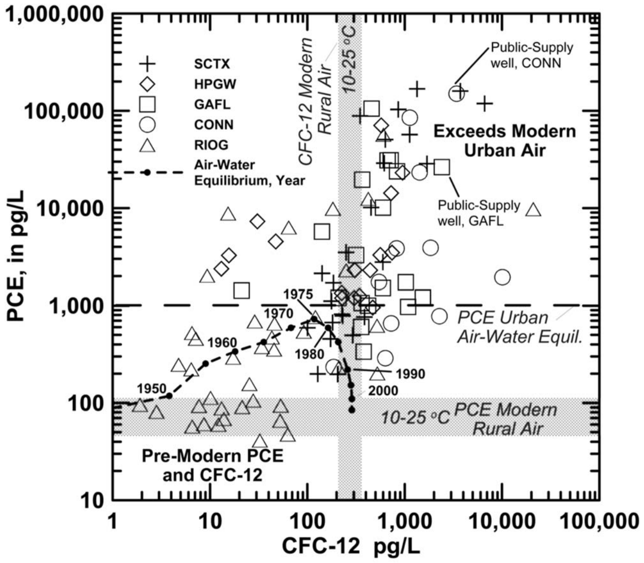

Fig. 7. Comparisons of the concentrations of PCE and CFC-12 in 109 drinking-water samples. SCTX, South Central Texas (San Antonio and vicinity); HPGW, High Plains aquifer, York, Neb.; and GAFL, Floridan aquifer at Tampa, Fla.; CONN, glacial aquifer system at Woodbury, Conn.; and RIOG, Santa Fe Group aquifer system at Albuquerque, N.M., and vicinity. The horizontal and vertical shading patterns show the ranges of PCE and CFC-12 concentrations, respectively, consistent with equilibrium with the modern rural atmosphere at 10 to 25 °C. The upper horizontal dashed line corresponds to the maximum PCE concentration in water in equilibrium with urban air recharged at 13 °C. The dashed curve gives the concentrations of PCE and CFC-12 in water in equilibrium with air from pre-1950 to 2005 calculated at 15 °C, and plotted at 5-year intervals.

Relation of VOC Occurrence to Land Use and Hydrogeologic Factors

Among the five study areas, some differences were evident in terms of the numbers of VOCs detected, the occurrence of individual compounds, and the actual concentrations present. These differences likely were related primarily to local land-use and hydrogeologic factors. The minimum, maximum, median, and average number of detections of VOCs determined by GC-MS and GC-ECD for the samples from the individual study areas and for the total group of 109 samples are summarized in Table 2. As observed for the total population of samples, the number of VOC detections determined by GC-MS within any particular study area

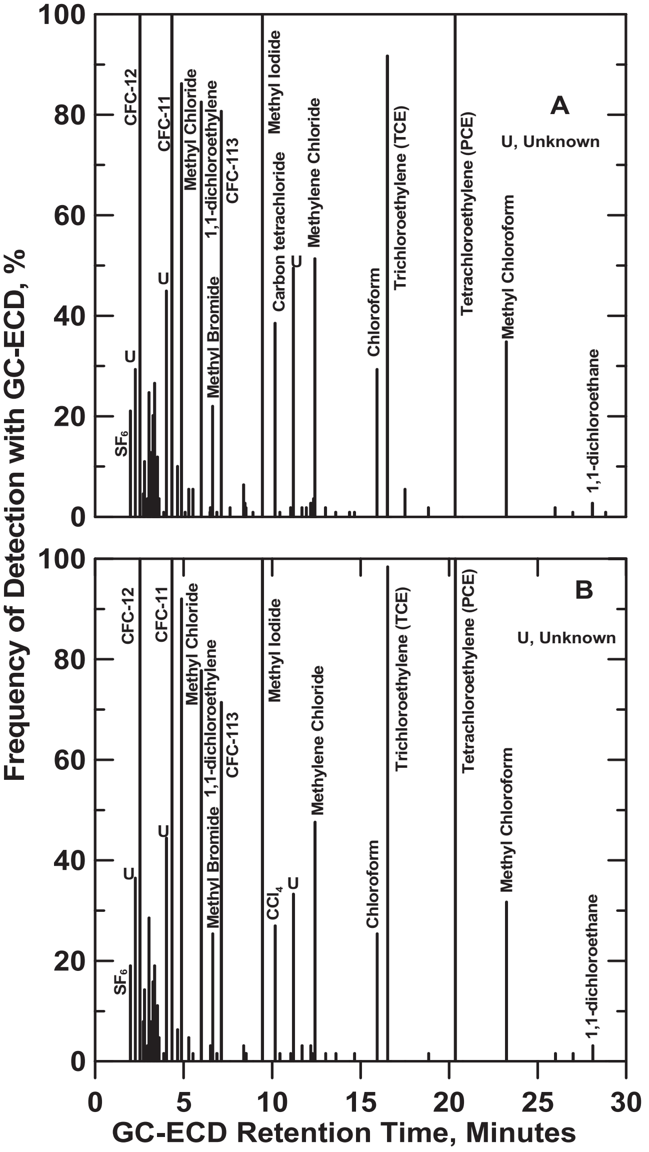

Fig. 8. Frequency of detection of halogenated VOCs from GC-ECD analysis: (a) all samples; (b) samples with no halogenated VOC detections by GC-MS analysis

was considerably lower than that detected by GC-ECD. Utilizing the GC-ECD data, the maximum number of VOC detections (27) was in water from a shallow (water level 2 m below land surface with 5 m of water above the open interval) monitoring well in the glacial aquifer system at Woodbury, Conn. (Table 2). The lowest number of detections (6) was for waters from the Santa Fe Group aquifer system at Albuquerque, N.M. (Table 2).

Two of the study areas, the Floridan aquifer system at Temple Terrace, Fla., and the High Plains aquifer near York, Neb., provided information on water quality in an unconfined aquifer underlain by a deeper confined aquifer. In both study areas, there were only small differences in the numbers of VOC detections between the unconfined and confined aquifers (Table 2). In the Floridan aquifer system, the median number of VOCs detected by GC-ECD was the same in both the unconfined and confined aquifer (16). In the High Plains aquifer, slightly more VOCs were detected in the upper confined aquifer (12) than in the unconfined aquifer (11) (Table 2). In both study areas, it can be argued that the confining layers were leaky. In the Tampa, Fla., area, the confining layer was breached by sinkholes, and in the High Plains aquifer near York, Neb., the confining layer had been penetrated by numerous wells that were open to both aquifers. Model simulations of the York, Neb., study area indicated that although leakage of old water through the matrix of the confining layer accounted for a majority of flow into the confined aquifers, rapid leakage of water through boreholes was the primary mechanism for young water of poor quality to enter the confined aquifers (Clark et al. 2006). The relative extent of leakage between the unconfined and confined aquifers in the Floridan aquifer system and the High Plains aquifer can be inferred from the CFC-12 concentrations (Table 2). In the Floridan aquifer system, the CFC-12 concentrations were nearly identical in the unconfined, surficial aquifer and the confined UFA, with concentrations that exceeded that of modern water by approximately a factor of 2; however, SF_6 and $^3H/^3He$ groundwater ages indicated that water in the UFA was older than that in the unconfined aquifer (Katz et al. 2007).

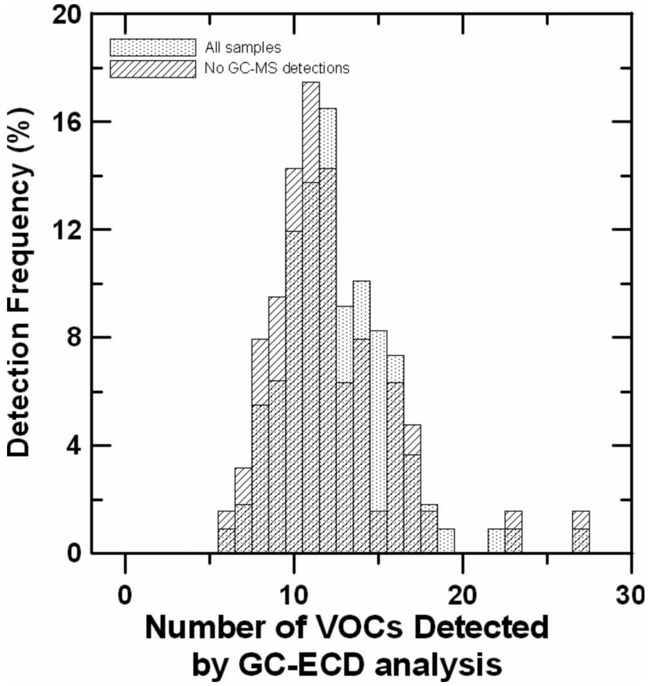

Fig. 9. Comparison of the distribution in frequency of detection of halogenated VOCs in all samples and in those samples in which no halogenated VOCs were detected by GC-MS analysis

In the High Plains aquifer, water from the unconfined aquifer also had CFC-12 concentrations that exceeded that of modern infiltration water, but the CFC-12 concentrations of the upper confined aquifer (average concentration of 68 pg/L) were much lower than those of the unconfined aquifer, consistent with water recharged from the late 1960s, and decreased further (39 pg/L) in the lower confined aquifer, indicating older water with depth (Fig. 10). Microbial degradation of CFC-12 was unlikely in the upper and lower confined aquifers of the High Plains aquifer, which were generally under Mn- and Fe-reducing conditions. Apparently, the confining layer in the High Plains aquifer at York, Neb., was more effective in limiting infiltration from the unconfined aquifer into the upper confined aquifer than was the confining layer above the UFA at Temple Terrace, Fla.

Most of the sampled wells completed in the Santa Fe Group aquifer system at Albuquerque, N.M., were in an urban setting,

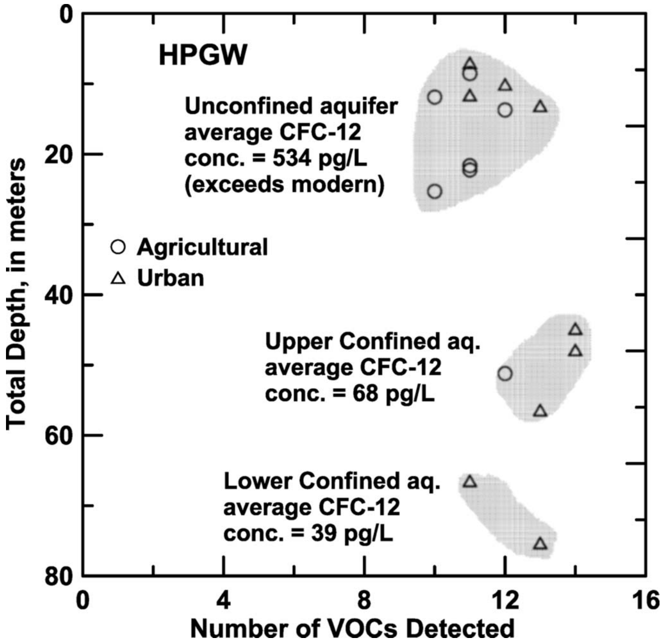

Fig. 10. Plot showing the number of VOC detections in the unconfined aquifer, the upper confined aquifer, and the lower confined aquifer of the High Plains aquifer at York, Neb.

generally, in areas of residential or, in some cases, industrial land use. Despite land-use conditions that can lead to introduction of high numbers and concentrations of VOCs in groundwater, several factors likely contributed to the relatively low number of detections and concentrations of VOCs in the sampled wells. These factors include low recharge rate in this semiarid region, resulting from low precipitation and a generally thick unsaturated zone, and the presence of a municipal sewer system. In addition, the wells that were sampled in the Albuquerque area were all public-supply wells, some with very long screened intervals (up to 447 m), increasing the likelihood that anthropogenic compounds in young water reaching the well screens could be diluted below MDLs with older, tracer-free water. In contrast, the glacial aquifer system at Woodbury, Conn., was in a mostly rural/residential setting, yet had the highest frequency of VOC detections. Factors contributing to the high frequency of detections in the samples from the glacial aquifer study area are the shallow depths to water, shallow well depths, the high permeability of glacial deposits, and the young groundwater ages, coupled with multiple point sources, and the lack of a municipal sewer system.

Depth of water above the open interval of the well and total well depth seem to have little effect on the numbers of VOCs detected in most of the samples (Figs. 10 and 11). For example, at Temple Terrace, Fla., the median number of detections (16) was identical in water from monitoring wells in the unconfined aquifer (total depth 6 to 24 m) and in the UFA to depths near 61 m [Fig. 11(a)], again confirming the leaky nature of the confining layer above the UFA at Temple Terrace.

In the glacial aquifer system at Woodbury, Conn., the maximum number of detections (27) was in water from a monitoring well with 4.6 m of water above the open interval. Detection frequency decreased to 13 for monitoring wells with about 1.5 m of water above the open interval [Fig. 11(b)]. The observations in the glacial aquifer system, again, reflected the young groundwater ages in this shallow aquifer and contributions from point sources in the area. In the Santa Fe Group aquifer system at Albuquerque, the number of VOC detections was mostly independent of depth of water above the open interval [Fig. 11(c)], possibly because of extensive mixing of groundwater withdrawn from public-supply wells in the Albuquerque area. The trace VOCs in discharge from the public-supply wells with 122 to 183 m of water above the open interval [Fig. 11(c)] were, at least in part, atmospheric in origin.

Of the five study areas, the frequency of VOC detections in the Edwards aquifer in the vicinity of San Antonio, was intermediate to those of the other four study areas. All of the samples were from public-supply wells with total depths that ranged from about 61 to nearly 762 m and well screens up to 453 m in length. The minimum number of VOC detections determined by GC-ECD (9) was for water from the deepest well (and two shallower wells). The relatively deep wells in the San Antonio area may intercept regional flowpaths containing high fractions of water recharged in rural areas west of San Antonio. It was expected that the detection frequencies for the unconfined, karstic Edwards aquifer waters closely reflected land use in the recharge area; because of conduit flow, circulation of recent recharge apparently reaches the deepest confined wells sampled.

In addition to differences in detection frequency between study units, the concentrations of VOCs in water also varied between study units. As an example, average concentrations of CFC-12, TCE, and PCE were summarized for each study unit and for confined and unconfined waters in Table 2. The lowest concentrations of PCE were in waters from the Santa Fe Group aquifer system in Albuquerque, N.M., and the upper confined aquifer in the High Plains. The deep unsaturated zone, low recharge rate, public sewer system, and long well-screen lengths in the Albuquerque area apparently were effective in limiting the concentrations of PCE in groundwater withdrawn from the public-supply wells in the Santa Fe Group aquifer system. In the High Plains the confining layer between the upper confined aquifer and unconfined aquifer was effective in isolating the two aquifers. The highest concentrations of PCE were in waters from the Edwards aquifer, the Floridan aquifer system, and the lower confined aquifer in the High Plains (Table 2). The Edwards aquifer is protected by a municipal sewer system over parts of San Antonio, but the northern parts of the city have only septic systems. The Edwards aquifer is recharged directly from streams, and in northern San Antonio and areas outside of the city of San Antonio, contaminants can reach the aquifer by infiltration from septic systems, and other residential, agricultural, and ranch land uses. The average PCE concentration in the unconfined aquifer was elevated relative to those from the upper and lower confined aquifers at York, Neb. In addition, the ratio of PCE/TCE was notably lower in the upper confined aquifer (ratio of 1.9) than in the unconfined aquifer (ratio of 4.7) in the vicinity of York, indicating that although PCE reached the upper confined aquifer, it was more likely to have undergone degradation from PCE to TCE. The concentrations of PCE and TCE in water from the two wells from the lower confined aquifer of the High Plains were approximately 3–5 times that in the upper confined aquifer, resulting, perhaps, from cross-borehole flow.

Factors contributing to the relatively high concentrations of PCE in the glacial aquifer system in Woodbury, Conn., were likely the lack of a municipal sewer system and the commercial and light-industrial activities in the area.

Although there were fewer detections of VOCs by GC-ECD (12) in water from the public-supply well at Temple Terrace, Fla., than in samples from monitoring wells (16), concentrations of CFC-12, TCE, and PCE were considerably elevated in water

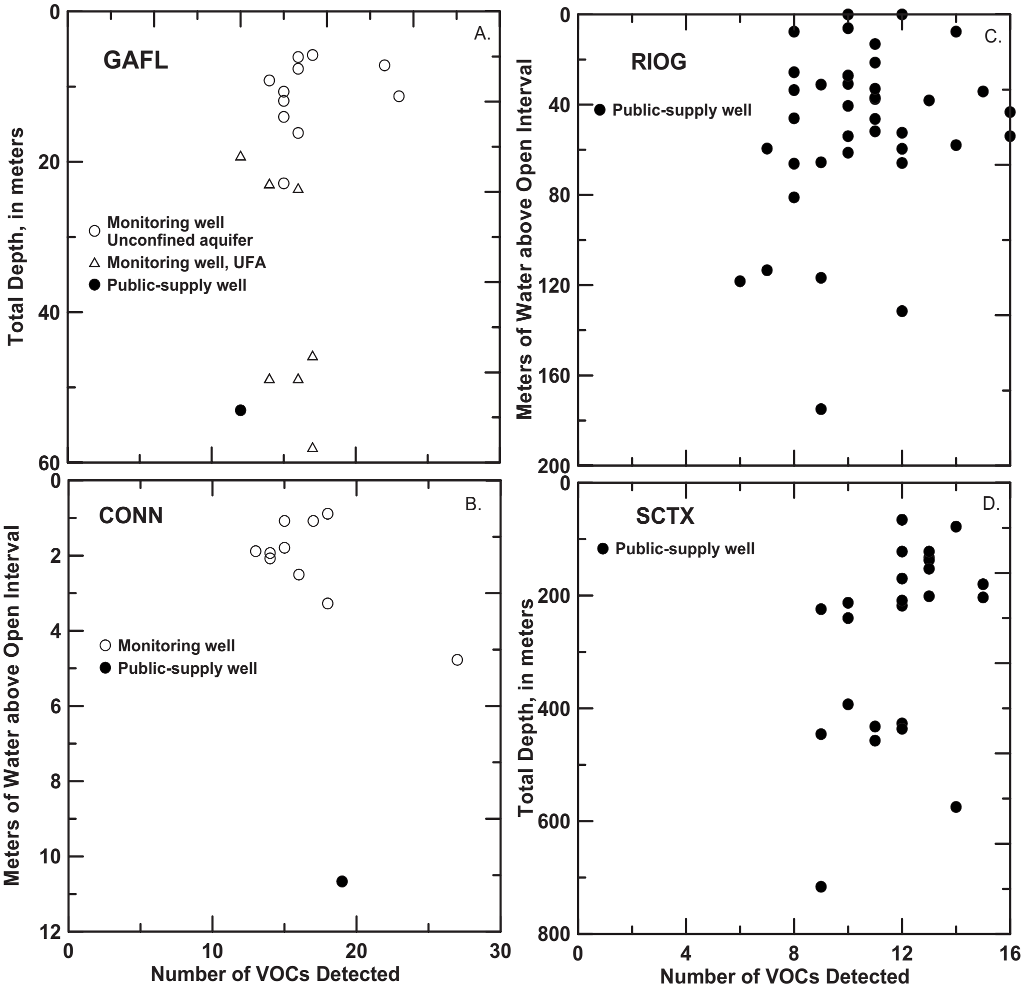

Fig. 11. Plots showing numbers of halogenated VOCs detected as a function of well depth or meters of water above the open interval of the well; solid circles are public-supply wells; open circles are narrow-screened monitoring wells; (a) Floridan aquifer at Tampa, Fla.; (b) glacial aquifer system at Woodbury, Conn.; (c) Santa Fe Group aquifer system at Albuquerque, N.M.; and (d) Edwards aquifer, San Antonio, Tex., and vicinity

from the public-supply well relative to that from the monitoring wells (Table 2). Similarly, concentrations of these three VOCs were elevated in water from the public-supply well at Woodbury, Conn. Apparently, the public-supply wells were particularly effective in drawing water from shallow sources. TCE was considerably elevated in water from the public-supply wells at Temple Terrace, Fla., and Woodbury, Conn. Among the many uses of TCE, it is also a degradation product of PCE and is sometimes used as a degreaser of septic tanks (Katz et al. 2007). The lowest TCE concentrations were in aerobic waters of the Edwards aquifer and in water from the upper confined aquifer at York, Neb. (Table 2).

Vulnerability Classification

As a means of comparing the relative degrees to which the waters from the five study areas have been influenced by natural and anthropogenic inputs, the total concentration of dissolved VOCs (TD-VOC) was approximated by summing the concentrations, in pg/L, of 15 halogenated VOCs detected by GC-ECD and plotted as a function of the number of VOCs detected in the sample (Fig. 12). The subset of 15 halogenated VOCs included Halon-1211, CFC-114, methyl bromide, methyl iodide, CFC-12, CFC-

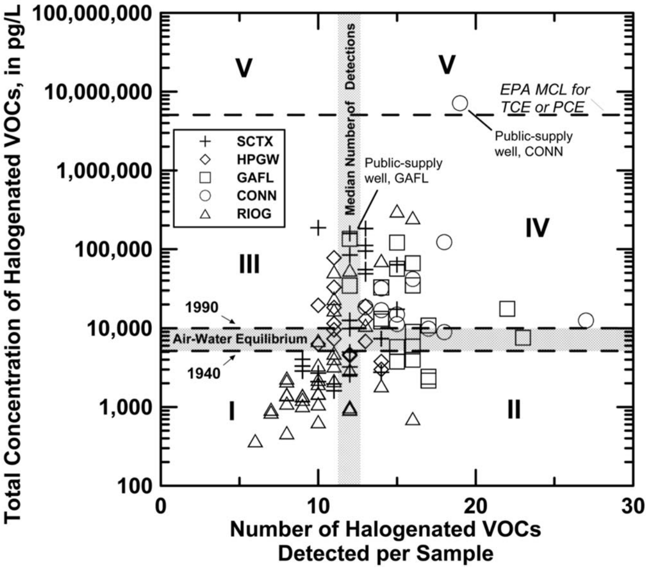

Fig. 12. Estimated total dissolved VOC concentration, in pg/L, for each sample as a function of number of halogenated VOCs detected per sample analyzed by GC-ECD. The sample from the public-supply well at Woodbury, Conn., contains 5.2 ug/L of TCE, with an estimated total dissolved VOC concentration of 7.2 ug/L.

11, methyl chloride, 1,1-dichloroethylene, CFC-113, carbon tetrachloride, methylene chloride, chloroform, TCE, PCE, and methyl chloroform.

An effort was made to estimate the concentrations of the unidentified compounds, and compare the sum of VOC concentrations for all detected peaks with that of the subset of 15 compounds. The peak area of each unidentified VOC in a 100 ppb gas standard was estimated as the median of the peak areas of the identified compounds (6,949,000 counts), and similarly, a median value for the extraction efficiency (47.8%) was assumed. The calculations indicated that the values of TD-VOC computed for the subset of 15 selected compounds accounted for, on average, more than 95% of the total concentration of halogenated VOCs in the set of 109 samples. If included in TD-VOC, the total concentrations of the 10 other compounds identified in Table 1 and those of all the unidentified VOCs would contribute an average of only about 5% to the value of TD-VOC concentration in the samples. The subset of 15 VOCs (listed above) was selected because (1) historical atmospheric concentration data were available for estimation of TD-VOC concentrations in water in equilibrium with air from 1940 to about 2005 for most of these compounds; (2) the concentrations of the other 10 VOCs identified in Table 1 were very low in air and did not contribute significantly to TD-VOC; and (3) the concentrations of the 15 compounds accounted for about 95% of the total concentration of halogenated VOCs in the sample set. The value of TD-VOC calculated for air–water equilibrium at 15°C was about 5,100 pg/L in 1940, about 6,000 in 1960, rose rapidly through the 1970s and 1980s, peaking in 1990 at about 10,000 pg/L, and has since declined to about 8,300 in 2005. The horizontal patterned zone in Fig. 12 encompasses the range of TD-VOC computed for the 15 selected halogenated VOCs between 1940 and 2005. These values correspond to air–water equilibrium, but do not account for microbial degradation of VOCs in soils and groundwater; thus, they represent a maximum threshold of TD-VOC values corresponding to air–water equilibrium.

The horizontal zone for air-water equilibrium, the vertical line for the median number of VOCs detected per sample (12), and the upper horizontal dashed line corresponding to the USEPA MCL for TCE or PCE (5 ug/L) define five classifications in terms of TD-VOC and number of halogenated VOCs detected per sample (Fig. 12): (Class I) low frequency of GC-ECD detection [below the median number of detections (<12)] and TD-VOC at or below air–water equilibrium; (Class II) high frequency of GC-ECD detection (>12) and TD-VOC at or below air–water equilibrium; (Class III) low frequency of GC-ECD detection (<12) and TD-VOC above air–water equilibrium; (Class IV) high frequency of GC-ECD detection (>12) and TD-VOC above air–water equilibrium; and (Class V) contaminated (>5 ug/L). Calculated values of TD-VOC for approximately half of the 109 samples exceeded the possible range of values expected for air–water equilibrium (Fig. 12), and therefore, likely have been influenced by additional, nonatmospheric sources of VOCs.

All of the samples in Class I were from public-supply wells (from the Santa Fe Group aquifer system in Albuquerque and vicinity and from the Edwards aquifer near San Antonio). Factors common to Class I samples are large open intervals of well screens that permit mixing (dilution) with old, low-VOC waters, and aerobic groundwater limiting potential for microbial degradation that could increase the number of halogenated VOCs detected, and could possibly shift the samples into Class II. Further, at Albuquerque, many of the waters are likely old (pre-1940) and transport of VOCs from the land surface to the water table was limited by a deep unsaturated zone. Samples plotting in Class II may be diluted Class IV samples, or samples from areas with increased diversity in land-use activity but still relatively low concentrations, or they could be degraded samples that have an elevated number of VOCs that are degradation products.

Apparently, it is uncommon to find relatively high concentrations of TD-VOC in samples with a relatively low number of VOC detections (Class III). Many of the samples from the High Plains aquifer plot in Class III. Conditions that might lead to samples plotting in Class III include areas of relatively limited diversity in land-use activity, but elevated release to the environment of VOCs from that source.

Two samples from Albuquerque public-supply wells plot in Class IV, along with many of the samples from the glacial aquifer system in Woodbury, Conn., and the Edwards and Floridan aquifers [elevated number of detections, with TD-VOC concentrations that exceed air–water equilibrium concentrations (Fig. 12)]. One sample from the glacial aquifer system in Woodbury, Conn., was contaminated (Class V) due mainly to the presence of 5.2 ug/L of TCE.

The samples from the Edwards aquifer span a wide range in TD-VOC (Fig. 12). Those Edwards aquifer samples with the lowest TD-VOC concentrations (Classes I and II) tended to be waters that were recharged in rangeland settings, or water from wells that intercepted deep, long flowpaths from rangeland/agricultural areas west of San Antonio. Those Edwards aquifer samples with the highest values of TD-VOC (Classes III and IV) were from areas that may be affected by inputs from septic tanks or residential and (or) commercial land use.

Vulnerability increases with increasing TD-VOC; that is, Class V samples were more vulnerable to contamination than those of Classes III and IV, and Class III and IV samples were more vulnerable to contamination than those of Classes I and II. Further, because TD-VOC generally increased with the number of halogenated VOCs detected per sample (Fig. 12), Class II samples were more vulnerable to contamination than Class I samples, and Class IV samples were more vulnerable than Class III samples.

Discussion

VOCs detected in groundwater can be grouped according to three general sources: (1) those of natural, atmospheric origin; (2) those of anthropogenic atmospheric origin; and (3) those of contaminant anthropogenic origin. Samples containing VOCs of contaminant anthropogenic origin are of greatest concern, and of highest vulnerability to contamination. By recognizing preanthropogenic and modern anthropogenic atmospheric concentrations of halogenated VOCs in groundwater, it is possible to identify those samples that contain contaminant anthropogenic sources of VOCs.

Several VOCs are produced naturally in the environment, and, if not degraded or otherwise altered, will be found in unaffected groundwater, i.e., groundwater that has no impact from human sources. Methyl iodide (and methyl bromide) is detected in air and produced naturally by marine and aquatic biological processes (Sturges et al. 2001; Bell et al. 2002; Cox et al. 2005; Chuck et al. 2005). The atmospheric source and high sensitivity of methyl iodide to the ECD (Table 1) contribute, in part, to the widespread detection in groundwater. Natural emissions of other naturally occurring halogenated VOCs have been identified, including methyl chloride, chloroform, PCE, TCE, and methylene chloride (Keene et al. 1999; Khalil et al. 1999). Approximately

90% of global emissions of chloroform are estimated to be of natural origin, divided approximately equally between marine and terrestrial sources (Laturnus et al. 2002; McCulloch 2003). Although most of the chloroform of natural origin is oxidized (to hydrogen chloride and carbon dioxide) in the atmosphere, some low-level detections of chloroform in rural groundwater may be of natural, terrestrial origin (McCulloch 2003). Five percent of the total 1998 global input of PCE and 10% of that of TCE were attributed to the natural, oceanic source (Keene et al. 1999). Given the high sensitivity of the GC-ECD to PCE and TCE, this may contribute to the widespread detection of these compounds in deep groundwater. Values of TD-VOC of natural atmospheric origin, assuming air–water equilibrium and no degradation during infiltration or in groundwater probably do not exceed 5,000 pg/L. Methyl chloride alone constitutes approximately 70% of the atmospheric concentration of naturally occurring halogenated VOCs, and if not degraded, would contribute nearly 4,000 pg/L of methyl chloride in groundwater. However, methyl chloride is degraded readily in soils and groundwater, as evidenced by the median methyl chloride concentration of only 314 pg/L in the 109 groundwater samples analyzed. Consequently, TD-VOC values in groundwater of naturally occurring preanthropogenic halogenated VOCs probably do not exceed 500 pg/L. Waters of preanthropogenic origin are believed to plot in Class I in Fig. 12 and have low vulnerability to contamination from the land surface. However, other samples plotting in Class I may be dilutions of more contaminated waters, and thus, will have higher vulnerability. It is necessary to examine mixing relations among individual atmospheric environmental tracers to recognize samples that have been diluted with old, preanthropogenic water (IAEA 2006).

Most waters plotting in Classes I and II (Fig. 12) have TD-VOC values greater than 500 pg/L and either contain VOCs of anthropogenic atmospheric origin, or could be dilutions of more concentrated samples with old, preanthropogenic water, or may be contaminated samples in which many of the VOCs have been degraded. More can be determined regarding the source of VOCs by examining concentrations of individual compounds in relation to their historical air–water equilibrium concentrations, as shown for CFC-12 and PCE in Fig. 7. Samples with highest vulnerability to contamination plot above the line for air-water equilibrium with the 1990 atmosphere (Fig. 12) and contain contaminant anthropogenic sources of halogenated VOCs.

In a recent investigation (Shapiro et al. 2004a), low levels of at least three different VOCs were detected using GC-ECD in all samples of untreated groundwater from 413 domestic and public-supply wells from 19 states in the U.S. The Shapiro et al. (2004a) study focused on drinking-water wells with no obvious nearby sources of VOCs. Most of the VOC concentrations detected by Shapiro et al. (2004a) were qualitatively assessed (Shapiro et al. 2003), and were very low; none were above existing drinking-water standards. Shapiro et al. (2003) were the first to report VOC detections in 100% of samples of untreated drinking water analyzed on a National scale, indicating the widespread presence of very low concentrations of these compounds in the Nation's drinking water that is derived from groundwater sources. Shapiro et al. (2004a) related relative peak area and frequency of detection to apparent groundwater age based on CFC-12 concentrations and showed that the number of "large" peaks detected per sample decreased with increase in age of groundwater.

Using mass-spectrometric analyses, the USGS recently reported that, at an assessment level of 0.2 ug/L, about 20% of approximately 3,500 untreated water samples collected from various types of wells analyzed between 1985 and 2001 contained one or more of a subset of 55 VOCs (Zogorski et al. 2006). The detection frequency increased to about 50% in a subset of the samples when a modified, low-level mass-spectrometric method with an assessment level of 0.2 ug/L was used (Zogorski et al. 2006), and increased to about 65% in a subset of these samples from domestic wells that were analyzed by the low-level mass-spectrometric method (Rowe et al. 2007). Similar observations were found in this study for the USGS GC-MS analyses of 109 untreated water samples. This study confirms the findings of Shapiro et al. (2004a,b) that, as the MDLs of VOCs are lowered to levels that are two to more than four orders of magnitude below the GC-MS LT-MDL, trace concentrations of VOCs can be detected in a high proportion of water samples from public-supply wells.

There are many possible sources of low-level VOCs in water from public-supply wells, including recharge of recent water containing a contaminant or input from anthropogenic atmospheric sources of VOCs (Pankow et al. 1997, 2003). Most public-supply wells are constructed to produce relatively large quantities of water; as a result, they usually have large intervals over which they withdraw water, including, in many cases, the shallow parts of unconfined aquifers. Large amounts of extraction from aquifers beneath confining layers may induce leakage from unconfined aquifers through leaky confining layers. Other sources of contaminants may reach the screens of wells in fractured rocks that intercept networks of openings that can connect the well bore to shallow water that may be contaminated or contain relatively high concentrations of VOCs. Additional factors contributing to the occurrence of trace VOCs in discharge from public-supply wells include leaky well casings; improperly grouted wells; introduction of VOCs during the drilling operation; introduction of lubricants, solvents, and other VOCs to the aquifer and well fixtures during service and maintenance of pumps; and short or rapid flow paths that water can take in reaching the open interval of high-capacity production wells (Zinn and Konikow 2007).

For some of the public-supply wells in the Santa Fe Group aquifer system in Albuquerque, the presence of trace VOCs in discharge from wells with more than 100 m of water above the opening probably represents dilution of very small fractions of young, shallow water that has been contaminated and is drawn into the capture zone of the well. However, other factors also must be considered because, in three of the study areas (glacial aquifer system, Floridan aquifer system, and High Plains aquifer), most of the samples were obtained from monitoring wells. These monitoring wells were completed with narrow openings in the same depth ranges of the aquifers that are used for the drinking-water source, and were pumped at rates of only a few tenths of a liter per second; yet, water from these monitoring wells also has a high frequency of detection of trace VOC concentrations. It appears that, at least in these cases, water across large parts of the aquifers has been affected by anthropogenic sources.

The atmosphere is a likely source for some of the VOCs detected in untreated groundwater (Baehr et al. 1999; Shapiro et al. 2004a; Chan and Chu 2007). From Fig. 7, 45% of the PCE detections could be attributed to an atmospheric (rural or urban) source, and 55% of the PCE detections exceed equilibrium with modern (urban) air. It has been shown that the occurrence of CFCs in many groundwater samples can be related to groundwater age (see IAEA 2006, and references therein) as determined from CFC concentrations in air, and this seems to be supported by the CFC data. For example, CFC-12, CFC-113, and CFC-11 could have an atmospheric source in 78, 82 and 80% of the samples, respectively. Similar relations were observed for other halogenated VOCs. For example, 71% of the TCE detections and 79% of the methyl chloroform detections were in the range of concentrations expected for air–water equilibrium (allowing for elevated air concentrations in urban settings). Estimated concentrations of CFC-12, TCE, and PCE in water in equilibrium with the 2005 and the 1975 atmosphere at 15°C are given in Table 2. The average concentrations of CFC-12, TCE, and PCE given for the various study units (Table 2) tend to be biased high by a few highly contaminated samples. For example, the median concentrations of CFC-12, TCE, and PCE for all 109 samples were 250, 221, and 1,200 pg/L, respectively; mostly in the range of the calculated air–water equilibrium values.

Other VOCs are at least in part of natural origin, such as methyl iodide. Approximately 46% of the methyl iodide detections were in the range of values expected from an atmospheric source, although the remaining 54% exceeded the atmospheric threshold, with concentrations as much as 70 times that expected for an atmospheric source. Median concentrations of methyl iodide were 420 pg/L in the Edwards aquifer in Texas, 150 pg/L in Connecticut and New Mexico, and 80 and 90 pg/L, respectively, in the High Plains and Floridan aquifer study units. A small fraction of many other halogenated VOCs (including methyl chloride, chloroform, PCE, TCE, and methylene chloride) also have a natural source (Keene et al. 1999) and may contribute to the widespread trace detections of these compounds in groundwater. Further studies would be needed to reconstruct atmospheric histories of halogenated VOCs, relate concentrations in groundwater to groundwater age, recognize those VOCs that have a natural (e.g., atmospheric) source, and identify VOCs that are products of microbial degradation in aquifers.

Low-level detections of halogenated VOCs in groundwater present no known health risk. Although the process(s) responsible for introduction of many of the halogenated VOCs in drinking-water sources are complex (Moran et al. 2007), the ability to detect many of these compounds at extremely low concentrations and separate those that exceed the natural, preanthropogenic concentration of about 500 pg/L, provides a direct observation of vulnerability to contamination, i.e., an awareness that, in these cases, groundwater is influenced by anthropogenic sources. And samples containing more than about 10,000 pg/L of TD-VOC exceed that possible for modern air–water equilibrium and are being impacted by a contaminant anthropogenic source(s). Regular monitoring may establish trends that yield advanced knowledge of contaminants that could reach the well opening in the future (Baehr et al. 1999; Morris et al. 2005b).

Conclusions

Measurements of concentrations of halogenated VOCs in untreated drinking water can provide a direct vulnerability assessment for individual wells—information that is not always available from modeling approaches to vulnerability assessments. This study developed a semiquantitative GC-ECD procedure for analysis of halogenated VOCs in water and compared GC-MS and GC-ECD analyses in a set of 109 drinking-water samples from five study areas across the United States. Although there are many limitations to the GC-ECD procedure in comparison to GC-MS analysis, one advantage is the very low MDLs of halogenated VOCs that can be obtained by GC-ECD analyses in comparison to GC-MS. MDLs of many common halogenated VOCs determined by GC-ECD can be two to more than four orders of magnitude below those determined by GC-MS analysis. The low-level detections can provide vulnerability assessments for the many groundwater samples in which no VOCs are detected by GC-MS procedures.

Of the 63 halogenated VOCs detected in GC-ECD chromatograms, 25 VOCs were identified based on comparison of retention times of VOCs in standards. VOCs with the lowest MDLs by GC-ECD were CFC-11, CFC-12, and CFC-113, with MDLs that were approximately four orders of magnitude below the GC-MS LT-MDL. PCE had a GC-ECD MDL that was approximately three orders of magnitude below the GC-MS LT-MDL. The GC-ECD MDL for TCE was approximately 3,000 times below the GC-MS LT-MDL (Table 1). The high sensitivity of the ECD to CFCs has permitted the wide use of these compounds in dating groundwater recharged since the 1940s.

When applied to the 109 groundwater samples, at least 6 halogenated VOCs were detected in every sample analyzed by GC-ECD, although one or more halogenated VOCs were detected in only 43% of the water samples analyzed by GC-MS. The median number of VOC detections determined by GC-MS analysis was 0.5 per sample, compared to 12 per sample for GC-ECD analyses. With the lowered MDLs of the GC-ECD compared to that of the GC-MS analysis, the distribution in frequency of detections shifted from a highly skewed function obtained from the GC-MS data to an approximately normal distribution obtained from the GC-ECD data. The distribution and frequency of detection by GC-ECD in the subset of 63 samples with no GC-MS detections was nearly the same as that for the complete set of 109 samples.

PCE was detected in 24% of the samples analyzed by GC-MS, but was detected in every sample analyzed by GC-ECD. CFC-12 and CFC-11 also were detected in every sample analyzed by GC-ECD, but there were no detections of CFCs in any sample analyzed by GC-MS. VOCs that were detected in approximately 30% or more of the samples analyzed by GC-ECD included CFC-12 (100%); CFC-11 (100%); PCE (100%); methyl iodide (100%); TCE (92%); CFC-113 (81%); methyl chloride (86%); 1,1-dichloroethylene (83%); carbon tetrachloride (39%); methylene chloride (51%); methyl chloroform (35%); and chloroform (29%), and several unidentified compounds with low retention times. Some detection frequencies (such as that for chloroform) were probably higher than determined by GC-ECD due to interference from adjacent peaks that can limit peak separation on chromatograms. Many other VOCs were detected by GC-ECD, but further investigation would be needed for compound identification.

Differences in frequency of detection and VOC concentrations were related to local land-use practices and hydrogeologic factors. Utilizing the GC-ECD data, the maximum number of VOC detections (27) was in water from a shallow monitoring well in the glacial aquifer system at Woodbury, Conn. The lowest number of detections (6) was for waters from the Santa Fe Group aquifer system in Albuquerque, N.M. Factors contributing to the relatively low number of detections of VOCs in the Santa Fe Group aquifer system in Albuquerque include low recharge rates resulting from low precipitation and a generally thick unsaturated zone, a region served by a municipal sewer system, and possibly long well screens that could lead to dilution of contaminants with older water. Factors contributing to the high frequency of detections in the samples from the glacial aquifer system in Woodbury, Conn., include shallow depths to water and well screens; permeable, thin glacial deposits that permit rapid infiltration from the land surface; lack of a municipal sewer system; urban land use; and possibly short well screens that can limit dilution with deep water.

A classification scheme combined frequency of VOC detection by GC-ECD analysis with a semiquantitative estimate of the total concentration of dissolved VOCs to show the degree and extent of natural and anthropogenic influence on the drinking-water source. In a first approximation, the number of VOCs detected would be expected to be proportional to the diversity of land-use activities, and the TD-VOC concentrations would be expected to increase with the extent to which the aquifer is being impacted from atmospheric and anthropogenic sources. TD-VOC concentrations in the 109 samples were related to historical TD-VOC concentrations corresponding to air–water equilibrium between 1940 and 2005, showing that approximately half of the samples had TD-VOC concentrations that exceeded those possible for air–water equilibrium. Five groupings were recognized: (Class I) samples from areas with low frequency of GC-ECD detection, below the median number of detections (<12) and TD-VOC concentrations at or below air–water equilibrium; (Class II) samples from areas with high frequency of GC-ECD detection (>12) and TD-VOC concentrations at or below air–water equilibrium; (Class III) samples from areas with low frequency of GC-ECD detection (<12) and TD-VOC concentrations greater than that corresponding to air–water equilibrium; (Class IV) samples from areas with high frequency of GC-ECD detection (>12) and TD-VOC concentrations greater than that corresponding to air–water equilibrium; and (Class V) samples that likely exceed the USEPA MCL for one or more VOCs (TD-VOC $>5\ \mu g/L$). The results for the 109 samples showed that TD-VOC generally increased with increasing number of detections of halogenated VOCs in untreated drinking-water samples.

Although there are no known health risks associated with the low-level detections of halogenated VOCs in groundwater, the ability to detect many of these compounds at extremely low concentrations, and separate those that exceed the natural, preanthropogenic concentrations of about 500 pg/L, provides a direct observation of vulnerability to contamination, i.e., an awareness that, in these cases, groundwater is influenced by anthropogenic sources. And samples containing more than about 10,000 pg/L of TD-VOC exceed that possible for modern air–water equilibrium and are impacted by a contaminant anthropogenic source(s). Such information could guide management decisions on future utilization, and source–water protection of individual public-supply wells, and is particularly useful in cases in which no VOCs are detected by GC-MS analysis.

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