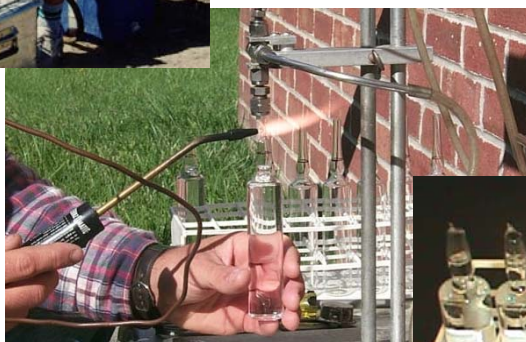




# The Stability of Chlorofluorocarbons (CFCs) in Ground-Water Samples Archived in Borosilicate Ampoules

Open-File Report 04-1392



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

Cover photos (left to right):

1. U.S. Geological Survey Hydrologist collects a water sample in a borosilicate ampoule
2. Flame-sealing of borosilicate ampoule
3. Set of water samples sealed in borosilicate ampoules

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*By Stephanie Dunkle Shapiro, Eurybiades Busenberg, L. Niel Plummer*

**Open-File Report 2004-1392**

**Reston, Virginia  
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**U.S. Department of the Interior**

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**U.S. Geological Survey**

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## Conversion Factors

Multiply	By	To obtain
Cubic centimeters (cm <sup>3</sup> )	0.06102	Cubic inch
Gram (g)	0.03527	Ounce
Kilogram (kg)	2.205	Pound
Milligram (mg)	0.001	Gram
Picogram (pg)	1x10 <sup>-12</sup>	Gram
Femtogram (fg)	1x10 <sup>-15</sup>	Gram

For temperature, degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by using the formula  $F=(1.8)(^{\circ}\text{C}) + 32$ .

Abbreviated units used in report: L (liter), mL (milliliter), kg (kilogram), pg (picogram), mol (mole),  $\mu\text{mol}$  (micromole), fmol (femtomol), fg (femtogram), pptv (parts per trillion by volume), mg/L (milligrams per liter),  $\mu\text{g/L}$  (micrograms per liter).

## Abbreviations and Acronyms

CFC	Chlorofluorocarbon
CFC-11	Trichlorofluoromethane
CFC-12	Dichlorodifluoromethane
CFC-113	1,1,2-trichloro-1,2,2-trifluoroethane
GC-ECD	Gas Chromatograph-Electron Capture Detector
USGS	United States Geological Survey
VOC	Volatile Organic Compound
DOC	Dissolved Organic Carbon
$\mu\text{g/L}$	Micrograms per liter
pg/kg	Picograms per kilogram
<sup>3</sup> H	Tritium
<sup>3</sup> He	Helium-3

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## Abstract

The U.S. Geological Survey (USGS) Chlorofluorocarbon (CFC) Laboratory in Reston, Va., has been measuring concentrations of CFCs in ground-water samples since 1989 to estimate the year that a water sample was recharged to a ground-water flow system. The water samples have been collected in flame-sealed borosilicate ampoules. Typically for each site, three samples were analyzed within days to a few months after collection, and additional samples were archived for extended periods of time (up to four years). The stability of CFC concentrations in the archived water samples from the USGS CFC Laboratory was investigated by analyzing the CFC concentrations in archived water samples and comparing them with the CFC concentrations that were obtained soon after the samples were collected. The archived samples selected for analysis were chosen from sites with a wide variety of hydrogeologic and geochemical conditions. For CFC-11 and CFC-12 concentrations, approximately 14% and 10.5%, respectively, of the archived samples were statistically different (both higher and lower) from the concentrations obtained from analyses conducted soon after the sample collection. Most of the extraneous values were attributed to natural variability of CFC concentrations originally in the water discharged from wells, rather than to microbial degradation within the ampoule on storage.

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## Introduction

Since 1989, the United States Geological Survey (USGS) Chlorofluorocarbon (CFC) Laboratory in Reston, Virginia, has been measuring concentrations of trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12) in ground-water samples from throughout the U.S. Concentrations of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) have been measured since 1992. The CFC concentrations have been converted to atmospheric partial pressures and related to historic atmospheric concentrations of CFCs to estimate the year that a given water sample was recharged to a ground-water flow system (Busenberg and Plummer, 1992; Plummer and Busenberg, 2000; Plummer and Friedman, 1999; <http://water.usgs.gov/lab/cfc> (accessed on January 19, 2005)).

Water samples have been collected from over 6,000 field sites, which include a wide range of hydrogeologic, land-use and geochemical conditions. The water samples were collected and flame-sealed in borosilicate ampoules to isolate them from the atmosphere (Busenberg and Plummer, 1992; Plummer and Busenberg, 2000; Plummer and Friedman, 1999; <http://water.usgs.gov/lab/cfc> (accessed on January 19, 2005)). The samples were transported to the USGS CFC Laboratory and stored in a dark location at room temperature (~23°C). They were not refrigerated or acidified. Typically, five or six samples were collected at each sampling location, and three of the samples were analyzed for CFC concentrations using purge-and-trap gas chromatography (GC) with an electron-capture detector (ECD) (Busenberg

and Plummer, 1992; Plummer and Busenberg, 2000; Plummer and Friedman, 1999; <http://water.usgs.gov/lab/cfc> (accessed on January 19, 2005)). The remaining samples were archived, or in the event that there were discrepancies in the CFC concentrations among the first three samples analyzed, additional samples may have been analyzed.

### ***Purpose and Scope***

The purpose of this study was to determine whether CFC analyses of ground-water samples after months to years of storage could be used to represent CFC concentrations in the ground-water flow system at the time of sampling. This report describes the results of analyzing CFC-11 and CFC-12 concentrations using GC-ECD for 356 archived ground-water samples stored in borosilicate ampoules to assess the stability of the CFCs in the ampoules during storage. The archived samples were stored up to four years prior to their analysis. The measured CFC concentrations for the archived samples were compared to the concentrations of the CFCs from the samples originally analyzed. CFC-113 analyses were not included due to an interference problem during analysis that occurred from December 1999 through February 2001 when some of the samples were analyzed.

### ***Degradation of CFC Concentrations***

In aerobic ground water (typically found in sand aquifers), CFC-11, CFC-12, and CFC-113 concentrations have been shown to be conservative, and under piston-flow conditions, concentrations calculated using the three CFC tracers are generally in agreement (Dunkle and others, 1993; Ekwurzel and others, 1994; Katz and others, 1995; Szabo and others, 1996; Plummer and others, 1998b; Busenberg and Plummer, 2000). Small losses of CFC-11 and CFC-12 were detected in aerobic microcosm experiments with autoclaved sediment and peat (Lovely and Woodward, 1992; Bauer and Yavitt, 1996), but the losses may have been due to sorption (Bauer and Yavitt, 1996). Many aerobic ground-water samples that have infiltrated through soils with organic matter indicate loss of CFC-11 relative to CFC-12

(Lindsey and others, 2003; Plummer and others, 2001). The mechanism of CFC-11 loss in soils is not known.

CFC concentrations have been shown to be nonconservative under anaerobic conditions in a variety of settings. CFCs are electron acceptors, as are nitrate, iron (III), sulfate, and CO<sub>2</sub> in ground water. Under sulfate-reducing conditions, CFC-11 and CFC-113 have been shown to undergo dehalogenation (Sonier and others, 1994; Lesage and others, 1990). Previous investigations have found CFC-11 to be more rapidly degraded than CFC-12 under reducing conditions in termite mounds (Khalil and Rasmussen, 1989), under simulated landfill conditions (Deipser and Stegmann, 1997), in organic-rich soils (Oster et al., 1996; Plummer and others, 2001), and in anaerobic ground-water flow systems (Cook and others, 1995; Dunkle and others, 1993; Goode and others, 1999; Katz and others, 1995; Plummer and others, 1998a&b; and Semprini and others, 1992). Plummer and others (1998b) found good agreement between CFC-11 and CFC-12 concentrations in aerobic ground water from the Upper Floridan aquifer in south Georgia, but CFC-11 and CFC-113 were nearly absent throughout anaerobic (sulfate-reducing and methanogenic) parts of the aquifer that were impacted by seepage of dissolved organic carbon (DOC)-rich river water. CFC-12 persisted in aerobic and anaerobic zones of the Upper Floridan aquifer and apparent CFC-12 ages were within 5 years of apparent ages obtained using tritium (<sup>3</sup>H) and helium-3 (<sup>3</sup>He) in seven of nine co-dated samples. Rowe and others (1999) and Shapiro and others (1998) found significant degradation of CFC-11 and CFC-12 under methanogenic conditions, as determined by comparisons to <sup>3</sup>H-<sup>3</sup>He data and modeling, in a buried-valley aquifer near Dayton, Ohio. Using tritium measurements to determine apparent ages, Parks and others (1995) found CFC-11 and CFC-12 completely degraded under methanogenic conditions in the Memphis Sand aquifer near the Mississippi River in southwest Tennessee. Happell and others (2003) found a 50 to 90 percent decrease in concentrations of CFC-11, CFC-12, and CFC-113 in a high-methane interval just below the



ground-water/surface-water interface in Everglades National Park, Florida. Deipser and Stegmann (1997) found that under methanogenic conditions, CFC-11 degradation was nearly 16 times that of CFC-12 and CFC-113. Sulfate (and nitrate) in anaerobic environments slows the rates of dehalogenation reactions by competing with highly halogenated aliphatic compounds as terminal electron acceptors (Mohn and Tiedje, 1992; Sylvestre and others, 1997). Inhibition of dehalogenation by sulfate may explain the persistence of CFC-12 in sulfate-reducing environments (as in Cook and others, 1995; Shapiro and others, 1997; and Plummer and others, 1998a&b) where dissolved sulfate is still present, and more rapid degradation of CFC-12 in methanogenic environments (Deipser and Stegmann, 1997; Happell and others, 2003; Oster and others, 1996) where sulfate concentrations are usually very low.

Field and laboratory observations of CFC degradation in ground-water flow systems raised the question of whether reductive dehalogenation is likely to occur during storage in the flame-sealed borosilicate ampoules for either aerobic or anaerobic ground-water samples. An investigation of degradation of CFCs during storage in ampoules was conducted by Plummer and others (1998b). Plummer and others (1998b) conducted a series of laboratory microcosm experiments using river water with high DOC content and high concentration of suspended sediment. These samples were not representative of ground water, which typically has low DOC content. Ampoules were analyzed at the time of filling and periodically over 2.5 years. Plummer and others (1998b) found that CFC-11 and CFC-113 were completely removed within 400 days in ampoules stored in the dark at room temperature and under refrigerated conditions, due to microbial degradation under anaerobic conditions that developed during dark storage. CFC-12 was stable in the ampoules. Samples stored in the light showed no change in CFC-11, CFC-12, or CFC-113 due to growth of green algae, which likely sustained aerobic conditions (Plummer and others, 1998b). Other than the investigation by Plummer and others (1998b), no specific study had been conducted

on degradation of CFCs in ground-water samples stored in ampoules.

## Approach

Water from stored ampoules from 356 sites was analyzed by GC-ECD. The samples were from sites in 19 states, including Hawaii, and are from a wide variety of hydrogeologic environments, including sand and gravel, karst, and fractured rock aquifers; and confined and unconfined aquifers. Depths ranged from near land surface to almost 1,000 feet below land surface. Samples were obtained from recharge and discharge areas of ground-water flow systems. Redox conditions were often known and were noted as either high in dissolved oxygen (concentrations > 0.5 mg/L) or low in dissolved oxygen (concentrations < 0.5 mg/L); or having methane. Methane concentrations were not routinely measured on all CFC samples, but were noted when detected on the basis of dissolved gas samples that were sometimes collected along with CFC samples. Because methane concentrations were not available for all samples and were not used in any quantitative analyses, they are simply presented as a 'detect' when known. CFC concentrations in the water samples ranged from below the detection limit of approximately 0.3 picograms per kilogram of water (pg/kg,  $0.3 \times 10^{-12}$  grams per kilogram, or 0.3 parts per quadrillion) to thousands of pg/kg.

Some variability in the CFC concentrations can be expected from one ampoule to the next for a single sampling event due to the variability in the water withdrawn during pumping (Barcelona and Helfrich, 1986; Gibs and Imbrigiotta, 1990; Busenberg and Plummer, 1992), insufficient purging (Pankow, 1990), or over-purging (Gibs and Imbrigiotta, 1990). Gibs and Imbrigiotta (1990) found that typical purging criteria are not reliable for sampling volatile organic compounds (VOCs) and that over-purging is common because VOCs are not usually distributed uniformly throughout an aquifer, but can be in small plumes of limited vertical and horizontal extent in discrete sections of the aquifer. Although CFCs are classified as VOCs, Gibs and Imbrigiotta (1990) primarily considered VOCs from point sources of

contamination. CFCs in ground water, for the most part, are derived from pervasive atmospheric inputs that are incorporated into ground–water recharge. Nevertheless, spatial variability in aquifer properties can result in a nonuniform distribution of CFCs in an aquifer system.

With the inclusion of the analysis of the archived sample from this investigation and the three ampoules analyzed after the samples were originally collected, each site typically had four ampoules analyzed for CFC concentrations. The results of these four analyses were used to assess changes in the CFC concentrations in the ampoules over time. The method of Dean and Dixon (1951) was used to estimate central values and set confidence limits for data with small numbers of observations. Dean and Dixon (1951) used the Q-test to eliminate questionable observations with 90% confidence for data sets with two to ten observations. The observations were assumed to be independent random samples from a normally distributed population. In this report, the CFC concentrations were assumed to be distributed about a mean value, and questionable values may be the result of degradation or other processes.

## **Stability of CFCs in Archived Ground-Water Samples**

A summary is presented in table 1 of site, laboratory, geochemical, and chlorofluorocarbon data. For CFC-11, 27 of the 356 sampling sites could not be evaluated because the concentrations for all samples from a given site were above the calibration range (1,000 pg/kg) of the instrument. Of the remaining 329 sites, 81 (24.6% of the 329 sites) failed the Q-test for an extraneous value for concentrations from 0 to 925 pg/kg. Of the 81 sites that failed, 62 (76.5% of failed sites) had an extraneous value that was higher than the other values from the site; however, 19 (23.5% of failed sites) had an extraneous value that was lower than the other values from the site. Of the 81 sampling sites that failed the Q-test, the archived sample was the one that failed at 46 (56.8% of failed sites). Fifteen of those archived samples had lower concentrations than the other values from the

site, although 31 of the archived samples had higher concentrations than the other values from the site. Because a larger percentage of sites had an extraneous value that was higher rather than lower than the others from the same site, this indicated that systematic degradation of CFC-11 in the ampoules was not the cause of the variations in CFC concentrations. In addition, of the 15 sites with lower concentrations, 7 had high dissolved oxygen concentrations, 7 had low concentrations of dissolved oxygen and/or methane, and one had an unknown geochemical condition. Because CFC-11 degradation does not occur when dissolved oxygen concentrations are high, the lower CFC-11 values, at least for 7 of the samples, cannot be attributed to degradation.

For CFC-12, 12 of the 356 sites could not be evaluated because the concentrations for all samples from each of these sites were above the calibration range (2,500 pg/kg) of the instrument. Of the 344 sites left to evaluate, 82 (23.8% of the 344 sites) failed the Q-test for an extraneous value for concentrations from 0 to 2,306 pg/kg. Of the 82 sites that failed, 60 (73.2% of failed sites) had an extraneous value that was higher than the other values from the site, and 22 (26.8% of failed sites) had an extraneous value that was lower than the other values from the site. Of the 82 sites that failed the Q-test, 36 (43.9% of failed sites) were the archived sample, and 7 of those had lower concentrations; however, 29 had high concentrations, which eliminated the possibility of any systematic degradation in the ampoules. In addition, of the seven sites with lower concentrations, two had high dissolved oxygen concentrations, four had low concentrations of oxygen and/or methane, and one had an unknown geochemical condition. Because CFC-12 degradation does not occur when dissolved oxygen concentrations are high, the lower CFC-12 values, at least for two of the samples, cannot be attributed to degradation.

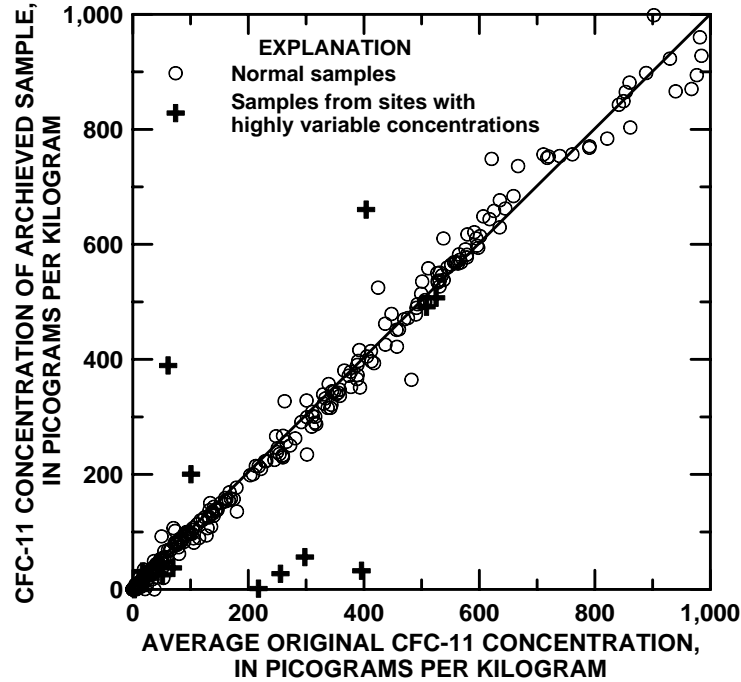
Of the 81 and 82 sites that failed the Q-test for CFC-11 and CFC-12, respectively, 21 were the same sample for both CFC-11 and CFC-12. Nineteen had higher concentrations than the other samples from the same site, indicating that the outlier resulted from variability in the CFC

concentrations in ground water during pumping rather than from degradation during storage in the ampoule. Of the two samples that had lower concentrations, only one was from an archived sample. This archived sample also had low dissolved oxygen and degradation in the ampoule could have affected concentrations of CFC-11 and CFC-12. In some cases, a site failed the Q-test for CFC-11 or CFC-12, but not both. However, in some cases, both showed the same trend yet one did not fail by a small margin. In these cases, variations during well purging would likely explain the failure because both compounds showed a similar trend. For example, for site 18, CFC-11 failed the Q-test for the archived sample, but CFC-12 did not, yet both are lower in the archived sample for a site that originally had a high dissolved oxygen concentration. The slightly larger variability in the CFC-12 values for this site caused the archived sample to pass the Q-test.

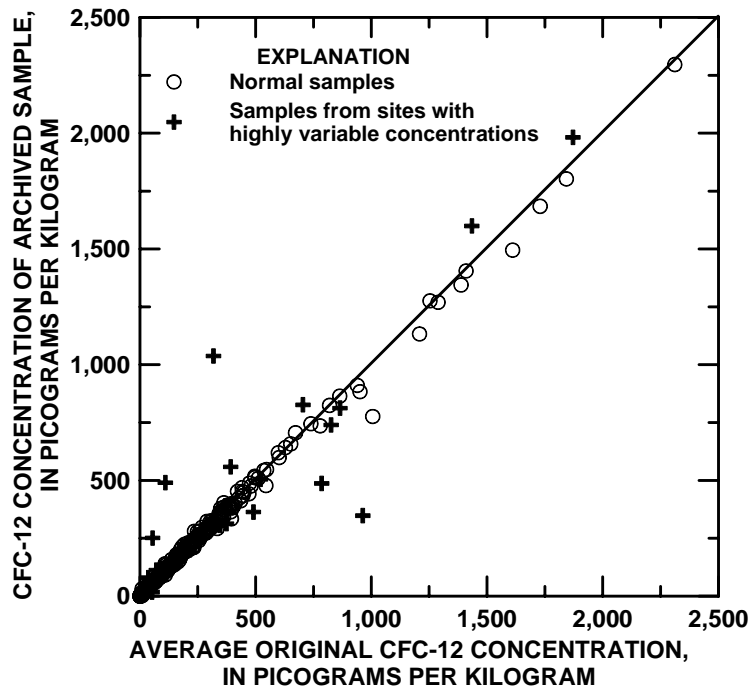
After eliminating those samples that were considered to be extraneous values with 90% confidence using the Q-test, the samples representing the original analyses were averaged and plotted against the sample that was analyzed specifically for the present investigation and represents the archived sample. The original analyses are those considered most representative for the site from the original sampling; however, these were often analyzed over a significant period of time (days to months) as well, but were averaged for plotting purposes. It should be noted that samples were not analyzed in the field and were often stored for months in the CFC Lab, so there are no representative starting concentrations. The point of the present study was to determine whether CFC concentrations were stable over long periods of time. If the archived sample analyzed for the present investigation was eliminated because it failed the Q-test, then the very first sample (or the average of the first samples if more than one was analyzed originally) was plotted against the sample analyzed at a later time (or the average of samples analyzed at a

later time). The CFC-11 and CFC-12 concentrations in the original analyses and the archived samples are shown in figures 1a and 1b, respectively. Each site is represented by one point that is the average of the original analyses plotted against the analysis for the archived sample. The concentrations are plotted to the calibration limits of 1,000 pg/kg for CFC-11 and 2,500 pg/kg for CFC-12.

In figures 1a and 1b, the data points represented by the '+' symbol are those that are from sites with highly variable analyses. These sites likely never stabilized during sampling and may be affected by mixing of water with variable CFC concentrations. For example, site 296 has a high concentration of dissolved oxygen and has detectable methane, indicating that the sample could be a mixture of relatively old methanogenic water and relatively young oxygenated water. The majority of the variable sites were from fractured-rock aquifers, as might be expected; however, it should be noted that the hydrogeologic environment was not known for all sites included in this investigation, so no statistical evaluation was possible. Examples of selected sites that either never stabilized during sampling, showing purging trends with concentrations increasing or decreasing over time, or were drawing water with variable concentrations of CFCs are shown in table 2. With the exception of a few of the more variable sites identified on figures 1a and 1b the remaining sites appear to have maintained relatively stable concentrations of CFC-11 and CFC-12 over the storage period.



**Figure 1a.** Comparison of original analyses of CFC-11 to analysis of CFC-11 in archived sample. The concentrations are shown only for samples that plot within the calibration limit of 0 to 1000 pg/kg for CFC-11. The data points represented by the '+' symbol are those that are from sites with highly variable analyses.



**Figure 1b.** Comparison of original analyses of CFC-12 to analysis of CFC-12 in archived sample. The concentrations are shown only for samples that plot within the calibration range of 0 to 2,500 pg/kg for CFC-12. The data points represented by the '+' symbol are those that are from sites with highly variable analyses.





















**Table 1.** Summary of site, laboratory, geochemical, and chlorofluorocarbon data (*continued*)

Site	State	Ampoule Number	Sampling Date	Analysis Date	Storage Time in Days	Geochemical Code	CFC-11 pg/kg	CFC-11 pg/kg	CFC-11 pg/kg	CFC-11 Q	New Average CFC-11 pg/kg	CFC-12 pg/kg	CFC-12 pg/kg	CFC-12 pg/kg	CFC-12 Q	New Average CFC-12 pg/kg
173	HI	2	14-Jun-00	1-Nov-00	140	H	576.4	559.4	559.4	0.2		936.4	863.7	855.8	0.6	
173	HI	1	14-Jun-00	4-Jan-01	204	H	549.7					847.7				
173	HI	3	14-Jun-00	4-Jan-01	204	H	542.3					806.8				
173	HI	1	14-Jun-00	20-Mar-01	279	H	569.0					863.8				
174	HI	2	26-Jun-00	30-Oct-00	126	H	479.1	475.2	474.9	0.3		127.7	122.7	122.0	0.4	
174	HI	4	26-Jun-00	27-Dec-00	184	H	472.8					119.2				
174	HI	5	26-Jun-00	27-Dec-00	184	H	477.0					119.4				
174	HI	3	26-Jun-00	20-Mar-01	267	H	472.0					124.5				
175	VA	2	16-Jul-97	10-Nov-97	117	H	388.7	407.4		1.0	389.5	176.5	181.0		0.7	
175	VA	4	16-Jul-97	10-Nov-97	117	H	390.3					179.3				
175	VA	3	16-Jul-97	18-Apr-01	1372	H	443.1					187.1				
176	WV	2	22-May-97	16-Oct-97	147	L,M	89.3	97.9	99.6	0.5		135.1	142.5	142.1	0.3	
176	WV	4	22-May-97	16-Oct-97	147	L,M	102.7					146.2				
176	WV	5	22-May-97	30-Oct-97	161	L,M	102.9					150.9				
176	WV	3	22-May-97	18-Apr-01	1427	L,M	96.5					137.9				
177	WV	2	27-May-97	15-Oct-97	141	L	12.9	14.6		0.3		221.8	211.6		0.5	
177	WV	4	27-May-97	15-Oct-97	141	L	16.0					207.8				
177	WV	3	22-May-97	16-Oct-97	147	L	13.0					213.2				
177	WV	5	27-May-97	5-Nov-97	162	L	17.3					204.0				
177	WV	1	27-May-97	18-Apr-01	1422	L	13.8					211.2				
178	NC	2	2-Jul-97	6-Nov-97	127	NA	12.2	44.8	40.2	0.4		184.0	184.9	185.5	0.5	
178	NC	4	2-Jul-97	6-Nov-97	127	NA	55.2					187.0				
178	NC	5	2-Jul-97	10-Nov-97	131	NA	86.7					180.4				
178	NC	3	2-Jul-97	18-Apr-01	1386	NA	25.2					188.3				
179	WV	3	6-May-97	16-May-97	10	L,M	34.4	17.1		0.4		103.0	79.2		0.5	
179	WV	5	6-May-97	16-May-97	10	L,M	22.4					71.6				
179	WV	6	6-May-97	16-May-97	10	L,M	5.6					35.9				
179	WV	7	6-May-97	16-May-97	10	L,M	22.6					73.1				
179	WV	1	6-May-97	18-Apr-01	1443	L,M	0.5					112.3				
180	VA	2	29-Jul-97	7-Nov-97	101	H,M	452.9	449.7	459.5	0.6		203.5	200.6	206.7	0.7	
180	VA	4	29-Jul-97	7-Nov-97	101	H,M	466.1					209.9				
180	VA	5	29-Jul-97	12-Nov-97	106	H,M	354.9					165.7				
180	VA	3	29-Jul-97	18-Apr-01	1359	H,M	524.7					223.3				
181	WV	2	13-May-97	15-Oct-97	155	L,M	35.7	33.9	34.9	0.7		56.9	49.5	48.6	0.6	
181	WV	4	13-May-97	15-Oct-97	155	L,M	34.1					48.1				
181	WV	5	13-May-97	5-Nov-97	176	L,M	29.8					43.9				
181	WV	3	13-May-97	18-Apr-01	1436	L,M	36.0					49.1				
182	WV	1	28-May-97	6-Oct-97	131	L	100.5	130.3		0.3		80.8	103.1		0.2	
182	WV	2	28-May-97	30-Oct-97	155	L	114.1					91.5				
182	WV	4	28-May-97	30-Oct-97	155	L	151.6					118.0				
182	WV	5	28-May-97	5-Nov-97	161	L	176.2					129.5				
182	WV	3	28-May-97	18-Apr-01	1421	L	109.2					95.6				
183	WV	2	13-May-97	27-Oct-97	167	L	GCR					269.5	252.0		0.3	
183	WV	4	13-May-97	27-Oct-97	167	L	GCR					260.1				
183	WV	5	13-May-97	5-Nov-97	176	L	GCR					235.5				
183	WV	1	13-May-97	6-Nov-97	177	L	GCR					255.1				
183	WV	3	13-May-97	18-Apr-01	1436	L	GCR					240.0				
184	WV	2	6-Jul-00	5-Dec-00	152	L	4.0	1.8		0.8		15.6	15.1		0.9	
184	WV	3	6-Jul-00	5-Dec-00	152	L	1.1					14.1				
184	WV	5	6-Jul-00	17-Apr-01	285	L	0.4					15.7				
185	WV	2	27-Jun-00	5-Dec-00	161	H	231.3	457.8		1.0	227.4	167.9	210.0		1.0	
185	WV	4	27-Jun-00	12-Feb-01	230	H	223.4					171.9				
185	WV	3	27-Jun-00	17-Apr-01	294	H	918.7					290.3				
186	WV	2	11-Jul-00	5-Dec-00	147	H	33.2	49.5	45.6	0.7		30.8	36.3	37.5	0.7	
186	WV	4	11-Jul-00	12-Feb-01	216	H	46.0					38.0				
186	WV	5	11-Jul-00	12-Feb-01	216	H	73.7					39.3				
186	WV	3	11-Jul-00	17-Apr-01	280	H	45.1					36.9				
187	WV	4	18-Jul-00	12-Feb-01	209	L	ERR					8.5	10.4		0.6	
187	WV	5	18-Jul-00	12-Feb-01	209	L	ERR					10.2				
187	WV	3	18-Jul-00	17-Apr-01	273	L	41.8					12.6				
188	WV	2	20-Jul-00	5-Dec-00	138	L	7.8	7.9	7.5	0.5		5.7	7.2	6.9	0.6	
188	WV	4	20-Jul-00	12-Feb-01	207	L	1.7					7.2				
188	WV	5	20-Jul-00	12-Feb-01	207	L	14.7					6.6				
188	WV	3	20-Jul-00	17-Apr-01	271	L	7.2					9.3				
189	WV	2	7-Jul-00	5-Dec-00	151	L	55.9	20.1	10.9	0.7		8.6	4.0		0.9	
189	WV	4	7-Jul-00	12-Feb-01	220	L	5.2					1.3				
189	WV	5	7-Jul-00	12-Feb-01	220	L	2.9					2.0				
189	WV	3	7-Jul-00	17-Apr-01	284	L	16.5					ERR				
190	WV	2	4-Aug-00	5-Dec-00	123	L	71.0	64.0		0.7		16.0	16.1		0.5	
190	WV	4	4-Aug-00	5-Dec-00	123	L	28.7					14.4				
190	WV	5	4-Aug-00	17-Apr-01	256	L	92.2					17.8				

Table 1. Summary of site, laboratory, geochemical, and chlorofluorocarbon data (continued)

Site	State	Ampoule	Sampling	Analysis	Storage	Geochemical	Average	Median	New Average			Average	Median	New Average		
		Number	Date	Date	Time		Code	CFC-11	CFC-11	CFC-11	CFC-11	CFC-12	CFC-12	CFC-12	CFC-12	CFC-12
					in Days		pg/kg	pg/kg	pg/kg	Q	pg/kg	pg/kg	pg/kg	pg/kg	Q	pg/kg
191	WV	2	19-Jul-00	5-Dec-00	139	H	575.7	688.5	614.0	0.9	601.2	301.7	287.9	288.7	0.3	
191	WV	4	19-Jul-00	12-Feb-01	208	H	950.2					272.5				
191	WV	5	19-Jul-00	12-Feb-01	208	H	606.7					297.2				
191	WV	3	19-Jul-00	17-Apr-01	272	H	621.2					280.2				
192	WV	2	13-Jul-00	5-Dec-00	145	L	33.1	76.7	38.6	0.9	35.8	38.8	39.2	39.2	0.5	
192	WV	4	13-Jul-00	12-Feb-01	214	L	44.1					32.6				
192	WV	5	13-Jul-00	12-Feb-01	214	L	199.1					39.5				
192	WV	3	13-Jul-00	17-Apr-01	278	L	30.3					45.7				
193	NE	3	9-Sep-98	26-Jan-99	139	M	1.0	0.8	0.9	0.6		0.7	1.3	1.0	0.6	
193	NE	4	9-Sep-98	26-Jan-99	139	M	1.0					0.7				
193	NE	5	9-Sep-98	28-Jan-99	141	M	0.5					1.3				
193	NE	1	9-Sep-98	9-Mar-01	912	M	0.8					2.3				
194	NE	2	10-Sep-98	26-Jan-99	138	L	47.5	49.3	48.7	0.5		73.9	75.7	74.9	0.6	
194	NE	4	10-Sep-98	26-Jan-99	138	L	47.2					73.3				
194	NE	5	10-Sep-98	29-Jan-99	141	L	49.9					79.5				
194	NE	3	10-Sep-98	9-Mar-01	911	L	52.6					75.9				
195	NE	2	10-Sep-98	27-Jan-99	139	L,M	2.2	0.9	0.6	0.7		84.1	87.9	87.2	0.6	
195	NE	4	10-Sep-98	27-Jan-99	139	L,M	0.6					87.6				
195	NE	5	10-Sep-98	29-Jan-99	141	L,M	0.6					86.7				
195	NE	3	10-Sep-98	9-Mar-01	911	L,M	0.0					93.1				
196	NE	2	10-Sep-98	26-Jan-99	138	L	132.4	70.1	50.5	0.9	49.3	75.5	45.8	37.1	0.8	35.9
196	NE	4	10-Sep-98	26-Jan-99	138	L	47.1					33.7				
196	NE	5	10-Sep-98	28-Jan-99	140	L	48.4					33.4				
196	NE	3	10-Sep-98	9-Mar-01	911	L	52.5					40.5				
197	NE	2	10-Sep-98	26-Jan-99	138	NA	177.1	183.9	179.5	0.8	178.7	158.3	166.3	168.5	0.8	169.0
197	NE	4	10-Sep-98	26-Jan-99	138	NA	181.9					169.2				
197	NE	5	10-Sep-98	28-Jan-99	140	NA	199.7					167.7				
197	NE	3	10-Sep-98	9-Mar-01	911	NA	177.0					170.1				
198	NE	2	12-Sep-98	27-Jan-99	137	NA	3.2	2.5	2.9	0.6		14.8	15.0	15.2	0.5	
198	NE	4	12-Sep-98	27-Jan-99	137	NA	2.6					13.8				
198	NE	5	12-Sep-98	1-Feb-99	142	NA	3.7					15.6				
198	NE	1	12-Sep-98	9-Mar-01	909	NA	0.6					15.7				
199	NE	2	12-Sep-98	27-Jan-99	137	NA	9.8	6.1	5.1	0.8	4.8	24.6	26.1	26.1	0.5	
199	NE	4	12-Sep-98	27-Jan-99	137	NA	4.8					26.2				
199	NE	5	12-Sep-98	1-Feb-99	142	NA	5.4					27.6				
199	NE	1	12-Sep-98	9-Mar-01	909	NA	4.3					25.9				
200	NE	2	11-Sep-98	26-Jan-99	137	L,M	121.3	108.5	111.6	0.6		220.4	220.4	222.1	0.6	
200	NE	4	11-Sep-98	26-Jan-99	137	L,M	114.3					230.5				
200	NE	5	11-Sep-98	29-Jan-99	140	L,M	108.9					223.7				
200	NE	0	11-Sep-98	9-Mar-01	910	L,M	89.4					206.8				
201	NE	3	11-Sep-98	28-Jan-99	139	L,M	0.6	88.4	1.0	1.0	0.8	147.1	152.2	147.4	0.8	145.2
201	NE	5	11-Sep-98	28-Jan-99	139	L,M	0.5					140.9				
201	NE	4	11-Sep-98	29-Jan-99	140	L,M	1.3					147.6				
201	NE	2	11-Sep-98	9-Mar-01	910	L,M	351.3					173.3				
202	MN	4	15-May-98	29-Sep-98	137	L	3.6	4.7	4.6	0.4		1576.2	1581.9	1599.5	0.6	
202	MN	2	14-May-98	29-Sep-98	138	L	6.1					1633.6				
202	MN	5	14-May-98	1-Oct-98	140	L	5.1					1622.7				
202	MN	3	14-May-98	18-Apr-01	1070	L	4.0					1494.9				
203	MN	2	12-May-98	29-Sep-98	140	H	GCR					955.9	710.6	699.9	0.5	
203	MN	4	12-May-98	29-Sep-98	140	H	GCR					676.4				
203	MN	5	12-May-98	1-Oct-98	142	H	GCR					723.4				
203	MN	3	12-May-98	18-Apr-01	1072	H	GCR					486.6				
204	MN	2	6-May-98	30-Sep-98	147	H	902.2	950.4				274.2	213.7	194.7	0.9	193.5
204	MN	4	6-May-98	30-Sep-98	147	H	GCR					197.6				
204	MN	5	6-May-98	1-Oct-98	148	H	GCR					191.8				
204	MN	3	6-May-98	18-Apr-01	1078	H	998.6					191.2				
205	MN	2	13-May-98	29-Sep-98	139	H	835.8	841.9	839.4	0.5		484.6	463.6	464.1	0.3	
205	MN	4	13-May-98	28-Sep-98	138	H	820.7					454.0				
205	MN	5	13-May-98	30-Sep-98	140	H	868.2					474.2				
205	MN	3	13-May-98	18-Apr-01	1071	H	842.9					441.7				
206	MN	2	12-May-98	28-Sep-98	139	H	847.8	856.3	856.3	0.1		653.3	653.1	655.4	0.7	
206	MN	4	12-May-98	28-Sep-98	139	H	849.3					658.8				
206	MN	5	12-May-98	30-Sep-98	141	H	863.2					642.9				
206	MN	3	12-May-98	18-Apr-01	1072	H	865.0					657.4				
207	MN	2	5-May-98	28-Sep-98	146	H	46.8	49.4		0.2		81.9	83.7		0.9	81.7
207	MN	3	5-May-98	28-Sep-98	146	H	47.8					81.0				
207	MN	4	5-May-98	28-Sep-98	146	H	47.6					81.3				
207	MN	5	5-May-98	1-Oct-98	149	H	52.9					91.9				
207	MN	1	5-May-98	18-Apr-01	1079	H	51.7					82.6				
208	MN	2	6-May-98	30-Sep-98	147	H	GCR					116.8	117.4	116.0	0.7	
208	MN	4	6-May-98	30-Sep-98	147	H	GCR					113.7				
208	MN	5	6-May-98	1-Oct-98	148	H	GCR					123.9				
208	MN	3	6-May-98	18-Apr-01	1078	H	GCR					115.2				

**Table 1.** Summary of site, laboratory, geochemical, and chlorofluorocarbon data *(continued)*

Site	State	Ampoule Number	Sampling Date	Analysis Date	Storage Time in Days	Geochemical Code	CFC-11 pg/kg	Average CFC-11 pg/kg	Median CFC-11 pg/kg	New Average CFC-11 pg/kg	CFC-12 pg/kg	Average CFC-12 pg/kg	Median CFC-12 pg/kg	New Average CFC-12 pg/kg	
															Q
209	MN	2	13-May-98	28-Sep-98	138	H	GCR				357.1	356.4	358.3	0.6	
209	MN	4	13-May-98	28-Sep-98	138	H	GCR				367.0				
209	MN	3	13-May-98	30-Sep-98	140	H	GCR				359.5				
209	MN	1	13-May-98	18-Apr-01	1071	H	GCR				341.8				
210	MN	2	13-May-98	28-Sep-98	138	H	GCR				168.6	160.9	163.4	0.7	
210	MN	4	13-May-98	28-Sep-98	138	H	GCR				163.5				
210	MN	5	13-May-98	1-Oct-98	141	H	GCR				163.3				
210	MN	3	13-May-98	18-Apr-01	1071	H	GCR				148.3				
211	VA	2	5-Aug-98	16-Dec-98	133	H	GCR				408.0	382.8	385.0	0.4	
211	VA	4	5-Aug-98	16-Dec-98	133	H	GCR				353.2				
211	VA	6	5-Aug-98	16-Dec-99	498	H	GCR				376.8				
211	VA	3	5-Aug-98	12-Mar-01	950	H	GCR				393.2				
212	VA	2	31-Aug-98	18-Dec-98	109	L,M	11.6	11.2	11.3	0.5	20.8	20.9	20.3	0.6	
212	VA	5	31-Aug-98	18-Dec-98	109	L,M	12.2				19.4				
212	VA	6	31-Aug-98	26-Apr-99	238	L,M	11.0				19.8				
212	VA	3	31-Aug-98	12-Mar-01	924	L,M	10.0				23.4				
213	VA	2	13-Sep-99	11-Jan-00	120	H	138.0	103.7	95.0	0.8	92.2	1296.5	1283.9	1284.8	0.5
213	VA	5	13-Sep-99	11-Jan-00	120	H	86.7				1285.2				
213	VA	6	13-Sep-99	11-Jan-00	120	H	93.2				1284.3				
213	VA	4	13-Sep-99	12-Mar-01	546	H	96.7				1269.4				
214	VA	2	23-Aug-99	21-Dec-99	120	H	264.6	247.9		0.7	1197.6	1183.2		0.7	
214	VA	6	23-Aug-99	27-Dec-99	126	H	243.8				1219.3				
214	VA	5	23-Aug-99	12-Mar-01	567	H	235.3				1132.8				
215	VA	2	23-Aug-99	21-Dec-99	120	H	37.3	40.1	39.9	0.2	210.6	210.1	209.4	0.5	
215	VA	4	23-Aug-99	21-Dec-99	120	H	42.4				206.8				
215	VA	6	23-Aug-99	27-Dec-99	126	H	43.7				214.9				
215	VA	5	23-Aug-99	12-Mar-01	567	H	36.8				208.2				
216	VA	2	30-Aug-99	22-Dec-99	114	H	505.8	503.3	502.8	0.4	252.5	254.4	252.2	0.9	251.9
216	VA	4	30-Aug-99	22-Dec-99	114	H	517.7				251.9				
216	VA	6	30-Aug-99	28-Dec-99	120	H	489.8				261.9				
216	VA	5	30-Aug-99	12-Mar-01	560	H	499.8				251.2				
217	VA	2	31-Aug-99	23-Dec-99	114	H	28.2	26.6	26.7	0.3	88.6	88.4	88.2	0.5	
217	VA	4	31-Aug-99	23-Dec-99	114	H	25.2				87.7				
217	VA	6	31-Aug-99	28-Dec-99	119	H	23.0				84.4				
217	VA	5	31-Aug-99	12-Mar-01	559	H	30.1				92.8				
218	VA	2	1-Sep-99	23-Dec-99	113	H	893.9	915.3		0.8	297.6	313.8	317.4	0.7	
218	VA	4	1-Sep-99	23-Dec-99	113	H	985.9				322.7				
218	VA	6	1-Sep-99	28-Dec-99	118	H	GCR				319.2				
218	VA	3	1-Sep-99	12-Mar-01	558	H	866.2				315.6				
219	VA	2	1-Sep-99	23-Dec-99	113	H	GCR				781.7	768.0	770.3	0.4	
219	VA	4	1-Sep-99	23-Dec-99	113	H	GCR				758.9				
219	VA	6	1-Sep-99	28-Dec-99	118	H	GCR				796.1				
219	VA	3	1-Sep-99	12-Mar-01	558	H	GCR				735.3				
220	VA	2	1-Sep-99	23-Dec-99	113	L	3.2	3.8	3.6	0.7	119.3	120.5	120.8	0.4	
220	VA	4	1-Sep-99	23-Dec-99	113	L	3.7				123.3				
220	VA	6	1-Sep-99	28-Dec-99	118	L	4.8				117.1				
220	VA	5	1-Sep-99	12-Mar-01	558	L	3.5				122.3				
221	VA	4	2-Sep-99	23-Dec-99	112	H	550.4	548.5	555.1	0.7	311.2	305.9	308.2	0.6	
221	VA	2	2-Sep-99	27-Dec-99	116	H	563.8				310.7				
221	VA	6	2-Sep-99	28-Dec-99	117	H	520.1				305.7				
221	VA	5	2-Sep-99	12-Mar-01	557	H	559.8				296.0				
222	VA	2	2-Sep-99	23-Dec-99	112	H	465.1	458.6	458.8	0.3	306.2	308.1	307.2	0.5	
222	VA	4	2-Sep-99	23-Dec-99	112	H	473.8				319.4				
222	VA	6	2-Sep-99	28-Dec-99	117	H	442.9				298.7				
222	VA	3	2-Sep-99	12-Mar-01	557	H	452.4				308.1				
223	VA	2	12-Sep-99	21-Dec-99	100	H	2.4	12.1	2.1	1.0	1.9	131.3	129.0	128.9	0.4
223	VA	4	12-Sep-99	21-Dec-99	100	H	1.7				128.5				
223	VA	6	2-Sep-99	27-Dec-99	116	H	1.5				129.3				
223	VA	5	2-Sep-99	12-Mar-01	557	H	42.8				126.8				
224	VA	2	10-Aug-99	21-Dec-99	133	H	5.1	3.6	3.7	0.5	5.8	4.8	4.7	0.3	
224	VA	4	10-Aug-99	21-Dec-99	133	H	3.7				6.7				
224	VA	6	10-Aug-99	27-Dec-99	139	H	1.8				3.6				
224	VA	5	10-Aug-99	12-Mar-01	580	H	3.6				3.2				
225	VA	2	11-Aug-99	21-Dec-99	132	H	10.4	9.6	9.7	0.1	22.2	22.5	22.3	0.8	22.2
225	VA	4	11-Aug-99	21-Dec-99	132	H	8.8				22.0				
225	VA	6	11-Aug-99	27-Dec-99	138	H	8.9				22.3				
225	VA	5	11-Aug-99	12-Mar-01	579	H	10.4				23.3				
226	VA	2	11-Aug-99	21-Dec-99	132	H	578.2	579.8	584.8	0.6	291.3	315.5	318.0	0.5	
226	VA	4	11-Aug-99	21-Dec-99	132	H	591.3				311.1				
226	VA	6	11-Aug-99	27-Dec-99	138	H	558.2				334.7				
226	VA	3	11-Aug-99	12-Mar-01	579	H	591.5				324.9				
227	VA	2	12-Aug-99	21-Dec-99	131	H	18.7	19.1	18.6	0.7	53.0	54.1	54.3	0.4	
227	VA	4	12-Aug-99	21-Dec-99	131	H	18.5				50.0				
227	VA	6	12-Aug-99	27-Dec-99	137	H	17.7				57.6				
227	VA	5	12-Aug-99	12-Mar-01	578	H	21.5				55.6				

















**Table 2.** Examples of sites that exhibited either variability in CFC concentrations over the sampling period, or purging trends in the CFC concentrations over the sampling period.

VARIABLE				PURGING			
Site	Ampoule Number	Storage Time in Days	CFC-11 pg/kg	Site	Ampoule Number	Storage Time in Days	CFC-11 pg/kg
120	2	85	157.1	178	2	127	12.2
120	3	185	389.3	178	3	1386	25.2
120	4	157	12.7	178	4	127	55.2
120	5	157	13.5	178	5	131	86.7

Site	Ampoule Number	Storage Time in Days	CFC-12 pg/kg	Site	Ampoule Number	Storage Time in Days	CFC-12 pg/kg
84	2	189	21.9	134	2	127	439.5
84	3	193	41.6	134	3	247	390.4
84	4	188	10.2	134	4	198	332.1
84	5	193	18.7	134	5	198	335.6
120	2	85	148.7	176	2	147	135.1
120	3	185	251	176	3	1427	137.9
120	4	157	7	176	4	147	146.2
120	5	157	7.7	176	5	161	150.9
159	2	12	927.2	182	1	131	80.8
159	3	160	812.3	182	2	155	91.5
159	4	12	890	182	3	1421	95.6
159	7	148	776.3	182	4	155	118
179	1	1443	112.3	182	5	161	129.5
179	3	10	103				
179	5	10	71.6				
179	6	10	35.9				
179	7	10	73.1				
296	1	582	347.6				
296	2	121	1390.5				
296	4	121	1133.2				
296	5	121	365.9				
351	1	1044	79.7				
351	2	203	74.1				
351	4	203	0				
351	6	204	34.1				



## Conclusions

The U.S. Geological Survey (USGS) Chlorofluorocarbon (CFC) Laboratory in Reston, Va., has been measuring concentrations of CFCs in ground-water samples since 1989 to estimate the year that a water sample was recharged to a ground-water flow system. The water samples have been collected in flame-sealed borosilicate ampoules. Typically for each site, three samples were analyzed within days to a few months after collection, and additional samples were archived for extended periods of time (up to four years). The stability of the CFC concentrations in archived water samples from the USGS CFC Laboratory was investigated by analyzing the CFC concentrations in archived water samples collected in flame-sealed borosilicate ampoules and comparing the analyses with those that were obtained soon after sample collection. For CFC-11 and CFC-12, approximately 14% and 10.5%, respectively, of the archived samples were statistically different (both higher and lower) than the concentrations

from analyses conducted soon after the sample collection. The extraneous values, however, were primarily related to natural variability of CFC concentrations in the water rather than to microbial degradation. For both CFC-11 and CFC-12, in a majority of the archived samples that failed the Q-test, the concentrations in the archived sample were higher (rather than lower if degradation were occurring) than the concentrations in the original analyses.

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## References Cited

- Barcelona, M.J., and Helfrich, J.A., 1986, Well Construction and Purging Effect on Ground-Water Samples: *Environ. Sci. Technol.*, v. 20, p. 1179-1184.
- Bauer, M.R., and Yavitt, J.B., 1996, Processes and Mechanisms Controlling Consumption of CFC-11 and CFC-12 by Peat from a Conifer-Swamp and Black Spruce-Tamarack Bog in New York State: *Chemosphere*, v. 32, no. 4, p. 759-768.
- Busenberg, E., and Plummer, L.N., 1992, Use of chlorofluorocarbons ( $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ ) as hydrologic tracers and age-dating tools: The alluvium and terrace system of Central Oklahoma: *Water Resources Research*, v. 28, no. 9, p. 2257-2283.
- Busenberg, E., and Plummer, L.N., 2000, Dating Young Ground Water with Sulfur Hexafluoride-Natural and Anthropogenic Sources of Sulfur Hexafluoride: *Water Resources Research*, v. 36, p. 3011-3030.
- Cook, P.G., Solomon, D.K., Plummer, L.N., Busenberg, E., and Schiff, S.L., 1995, Chlorofluorocarbons as Tracers of Groundwater Transport Processes in a Shallow, Silty Sand Aquifer: *Water Resources Research*, v. 31, no. 3, p. 425-434.
- Dean, R.B., and Dixon, W.J., 1951, Simplified Statistics for Small Numbers of Observations: *Analytical Chemistry*, v. 23, no. 4, p. 636-638.
- Deipser, A., and Stegmann, R., 1997, Biological Degradation of VCCs and CFCs Under Simulated Anaerobic Landfill Conditions in Laboratory Test Digesters: *Environmental Science and Pollution Research*, v. 4, no. 4, p. 209-216.
- Dinicola, R.S., Cox, S.E., and Bradley, P.M., 2000, Natural Attenuation of Chlorinated Volatile Organic Compounds in Ground Water at Area 6, Naval Air Station Whidbey Island, Washington: U.S. Geological Survey Water-Resources Investigations Report 00-4060, 86 p.
- Dunkle, S.A., Plummer, L.N., Busenberg, E., Philips, P.J., Denver, J.M., Hamilton, P.A., Michel, R.L., and Coplen, T.B., 1993, Chlorofluorocarbons  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  as Dating Tools and Hydrologic Tracers in Shallow Groundwater of the Delmarva Peninsula, Atlantic Coastal Plain, United States: *Water Resources Research*, v. 29, no. 12, p. 3837-3860.
- Ekwurzel, B., Schlosser, P., Smethie, W.M. Jr., Plummer, L.N., Busenberg, E., Michel, R.L., Weppernig, R., and Stute, M., 1994, Dating of Shallow Groundwater: Comparison of the Transient Tracers  $^3\text{H}/^3\text{He}$ , Chlorofluorocarbons, and  $^{85}\text{Kr}$ : *Water Resources Research*, v. 30, no.6, p. 1693-1708.
- Gibs, J., and Imbrigiotta, T.E., 1990, Well-Purging Criteria for Sampling Purgeable Organic Compounds: *Ground Water*, v. 28, no. 1, p. 68-78.
- Goode, D.J., Busenberg, E., Plummer, L.N., Shapiro, A.M., and Vroblesky, D.A., 1999, CFC's in the Unsaturated Zone and Shallow Ground Water at Mirror Lake, New Hampshire, in Morganwalp, D. W. and Buxton, H. T., eds., U.S. Geological Survey Toxic Substances Hydrology Program- U.S. Geological Survey Water-Resources Investigations Report 99-4018C, p. 809-820.
- Happell, J.D., Price, R.M., Top, Z., and Swart, P.K., 2003, Evidence for the Removal of CFC-11, CFC-12, and CFC-113 at the Groundwater-Surface Water Interface in the Everglades: *Journal of Hydrology*, v. 279, p.94-105.
- Jeffers, P.M., Ward, L.M., Woytowitch, L.M., and Wolf, N.L., 1989, Homogeneous Hydrolysis Rate Constants for Selected Chlorinated Methanes, Ethanes, Ethenes, and Propanes: *Environmental Science and Technology*, v. 23, no. 8, p. 965-969.
- Katz, B.G., Lee, T.M., Plummer, L.N., and Busenberg, E., 1995, Chemical Evolution of Groundwater Near a Sinkhole Lake,

## References Cited (continued)

- Northern Florida. 1. Flow Patterns, Age of Groundwater, and Influence of Lakewater Leakage: *Water Resources Research*, v. 31, no. 6, p. 1549-1564.
- Khalil, M.A.K., and Rasmussen, R.A., 1989, The Potential of Soils as a Sink of Chlorofluorocarbons and other Man-Made Chlorocarbons: *Geophysical Research Letters*, v. 16, p. 679-682.
- Lesage, S., Jackson, R.E., Priddle, M.W., and Riemann, P.G., 1990, Occurrence and Fate of Organic Solvent Residues in Anoxic Groundwater at the Gloucester Landfill, Canada: *Environmental Science and Technology*, v. 24, p. 559-566.
- Lindsey, B.D., Phillips, S.W., Donnelly, C.A., Speiran, G.K., Plummer, L.N., Bohlke, J.K., Focazio, M.J., Burton, W.C., and Busenberg, E., 2003, Residence Times and Nitrate Transport in Ground Water Discharging to Streams in the Chesapeake Bay Watershed: U.S. Geological Survey Water-Resources Investigations Report 03-4035, 201 p.
- Lovley, D.R., and Woodward, J.C., 1992, Consumption of Freon CFC-11 and CFC-12 by Anaerobic Sediments and Soils: *Environ. Sci. Technol.*, v. 26, p. 925-929.
- Mohn, W.W., and Tiedje, J.M., 1992, Microbial Reductive Dehalogenation: *Microbiol. Rev.*, v. 56, p. 482-507.
- Oster, H., Sonntag, C., and Munnich, K.O., 1996, Groundwater Age Dating with Chlorofluorocarbons: *Water Resources Research*, v. 32, no. 10, p. 2989-3001.
- Pankow, J.F., 1990, Minimization of Volatilization Gasses During Sampling and Analysis of Volatile Organic Compounds, in Ram, N.M., Christman, R.N., and Cantor, K.P., eds., *Significance and Treatment of Volatile Organic Compounds in Water Supplies*, Lewis, Chelsea, Michigan.
- Parks, W.S., Mirecki, J.E., and Kingsbury, J.A., 1995, Hydrogeology, Ground-water Quality, and Source of Ground Water Causing Water-Quality Changes in the Davis Well Field at Memphis, Tennessee: U.S. Geological Survey Water-Resources Investigations Report 94-4212, 58 p.
- Plummer, L.N., and Busenberg, E., 2000, Chlorofluorocarbons, in Cook, P.G., and Herzeg, A., eds., *Environmental Tracers in Subsurface Hydrology*, Chapter 15. Kluwer Academic Press, p. 441-478.
- Plummer, L.N., and Friedman, L.C., 1999, Tracing and Dating Young Ground Water: U.S. Geological Survey Fact Sheet 134-99, 4 p.
- Plummer, L.N., Busenberg, E., Bohlke, J.K., Nelms, D.L., Michel, R.L., and Schlosser, P., 2001, Ground-Water Residence Times in Shenandoah National Park, Blue Ridge Mountains, Virginia, U.S.A.: A Multi-Tracer Approach: *Chemical Geology*, v. 179, no. 1-4, p. 93-111.
- Plummer, L.N., Busenberg, E., Drenkard, S., Schlosser, P., McConnell, J.B., Michel, R.L., Ekwurzel, B., and Weppernig, R., 1998b, Flow of River Water into a Karstic Limestone Aquifer-2. Dating the Young Fraction in Groundwater Mixtures in the Upper Floridan Aquifer near Valdosta, Georgia: *Applied Geochemistry*, v. 13, no. 8, p. 1017-1043.
- Plummer, L.N., Busenberg, E., McConnell, J.B., Drenkard, S., Schlosser, P., and Michel, R.L., 1998a, Flow of River Water into a Karstic Limestone Aquifer. 1. Tracing the Young Fraction in Groundwater Mixtures in the Upper Floridan Aquifer Near Valdosta, Georgia: *Applied Geochemistry*, v. 13, no. 8, p. 995-1015.
- Rowe, G.L.Jr., Shapiro, S.D., and Schlosser, P., 1999, Use of Environmental Tracers to Evaluate Ground-Water Age and Water-Quality Trends in a Buried-Valley Aquifer, Dayton Area, Southwestern, Ohio: U.S. Geological Survey Water-Resources Investigations Report 99-4113, 81 p.

## References Cited (continued)

- Semprini, L., Hopkins, G.D., McCarty, P.L., and Roberts, P.V., 1992, In-Situ Transformation of Carbontetrachloride and Other Compounds Resulting from Biostimulation Under Anoxic Conditions: *Environmental Science and Technology*, v. 26, p. 2454-2461.
- Shapiro, S.D., Plummer, L.N., Focazio, M., Busenberg, E., Kirkland, W., and Fernandez, M., 2002, VOC Occurrence in Drinking Water from the United States: Results from Archived Chromatograms and Water Samples, 1989-2000: U.S. Geological Survey Water-Resources Investigations Report 02-4173, 20 p.
- Shapiro, S.D., Rowe, G., Schlosser, P., Ludin, A., and Stute, M., 1998, Tritium-helium 3 Dating Under Complex Conditions in Hydraulically Stressed Areas of a Buried-Valley Aquifer: *Water Resources Research*, v. 34, no. 5, p. 1165-1180.
- Shapiro, S.D., Schlosser, P., Smethie, W.M. Jr., and Stute, M., 1997, The Use of  $^3\text{H}$  and Tritiogenic  $^3\text{He}$  to Determine CFC Degradation and Vertical Mixing Rates in Framvaren Fjord, Norway: *Marine Chemistry*, v. 59, p. 141-157.
- Sonier, D.N., Duran, N.L., and Smith, G.B., 1994, Dechlorination of Trichlorofluoromethane (CFC-11) by Sulfate-Reducing Bacteria from an Aquifer Contaminated with Halogenated Aliphatic Compounds: *Appl. Environ. Microbiol.*, v. 60, p. 4567-4572.
- Sylvestre, M., Bertrand, J.L., and Viel, G., 1997, Feasibility Study for the Potential Use of Biocatalytic Systems to Destroy Chlorofluorocarbons (CFCs): *Critical Reviews in Environmental Science and Technology*, v. 27, no. 2, p. 87-111.
- Szabo, Z., Rice, D.E., Plummer, L.N., Busenberg, E., Drenkard, S., and Schlosser, P., 1996, Age-Dating of Shallow Groundwater with Chlorofluorocarbons, Tritium/Helium 3, and Flow Path Analysis, Southern New Jersey Coastal Plain: *Water Resources Research*, v. 32, no. 4, p. 1023-1038.