



## Dating groundwater with trifluoromethyl sulfurpentafluoride ( $\text{SF}_5\text{CF}_3$ ), sulfur hexafluoride ( $\text{SF}_6$ ), $\text{CF}_3\text{Cl}$ (CFC-13), and $\text{CF}_2\text{Cl}_2$ (CFC-12)

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[1] A new groundwater dating procedure using the transient atmospheric signal of the environmental tracers  $\text{SF}_5\text{CF}_3$ , CFC-13,  $\text{SF}_6$ , and CFC-12 was developed. The analytical procedure determines concentrations of the four tracers in air and water samples.  $\text{SF}_5\text{CF}_3$  and CFC-13 can be used to date groundwaters in some environments where the CFCs and  $\text{SF}_6$  have previously failed because these new tracers have increasing atmospheric input functions, no known terrigenous source, and are believed to be stable under reducing conditions.  $\text{SF}_5\text{CF}_3$  has a dating range from 1970 to modern; the mixing ratio (mole fraction) in North American air has increased from the detection limit of 0.005 parts per trillion (ppt) to the 2006 mole fraction of about 0.16 ppt. No evidence was found for degradation of  $\text{SF}_5\text{CF}_3$  in laboratory anaerobic systems. The solubility of  $\text{SF}_5\text{CF}_3$  was measured in water from 1 to 35°C. Groundwater samples that contained large amounts of terrigenous  $\text{SF}_6$  did not contain terrigenous  $\text{SF}_5\text{CF}_3$ . CFC-13 is a trace atmospheric gas with a dating range in groundwater of about 1965 to modern. CFC-13 has been used primarily in very low-temperature refrigeration; thus groundwater environments are less likely to be contaminated with nonatmospheric sources as compared to other widely used CFCs. Because of the low solubility of  $\text{SF}_5\text{CF}_3$  and CFC-13 in water, an excess air correction must be applied to the apparent ages. The new dating procedure was tested in water samples from wells and springs from Maryland, Virginia, and West Virginia.

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### 1. Introduction

[2] The dating of groundwater is used to determine recharge rates to aquifers, to calibrate models of groundwater flow, and to extract information on the rates of geochemical and microbiological processes occurring in aquifers. The dating can also be used to evaluate the contamination potential, retrieve historical records of contaminant loading, and determine remediation times of contaminated aquifer systems, information that can improve management strategies for groundwater systems [Plummer, 2005].

[3] Analyses of chlorofluorocarbons (CFCs—CFC-11, CFC-12, and CFC-113) have been widely used to interpret groundwater age information for waters recharged as early as the 1940s [see Busenberg and Plummer, 1992, 2000; Plummer and Busenberg, 2000; Plummer, 2005; International Atomic Energy Agency (IAEA), 2006, and references therein]. In dating with CFCs and other atmospheric gases, it is assumed that infiltration water maintains equilibrium with the unsaturated zone air during recharge. Date of recharge is derived from the temporal history of atmospheric concentrations. Age is defined as the time since recharge and confinement from the unsaturated zone air [Cook and Solomon, 1997]. Most environmental tracers used to obtain

age information from groundwater differ in their advantages and limitations [Plummer, 2005; IAEA, 2006]. For example, CFCs have had widespread use in industrial and domestic applications, and consequently, CFC excesses are present in many urban environments; that is, they contain concentrations that are greater than possible from an atmospheric source and cannot be dated. In some anaerobic groundwater environments, all CFCs can be degraded by microbiological processes, again limiting the usefulness of dating with CFCs [Plummer and Busenberg, 2000; Happell et al., 2003]. Atmospheric concentrations of CFCs were rapidly increasing before the 1990s, but as a result of the Montreal Protocol on Substances that Deplete the Ozone Layer adopted in 1987, atmospheric concentrations are now declining, making it impossible to resolve the more recent, post-1990s age information from CFC data.

[4]  $\text{SF}_6$  continues to have important applications in dating post-1990s waters because atmospheric concentrations of  $\text{SF}_6$  are currently increasing [Geller et al., 1997; Maiss and Brenninkmeijer, 1998], and there are relatively few industrial and domestic uses of  $\text{SF}_6$ , in comparison to applications of CFCs. Furthermore,  $\text{SF}_6$  appears to be stable in anoxic environments. The dating range of water with  $\text{SF}_6$  is from 1970 to modern, and concentrations of  $\text{SF}_6$  are particularly useful in dating very young (post-1993) groundwater [Busenberg and Plummer, 2000; Sliwka and Lasa, 2000; Bauer et al., 2001; Zoellmann et al., 2001].

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[5] In dating with SF<sub>6</sub> in some urban environments, it is often necessary to correct for local SF<sub>6</sub> enrichment in urban air [Ho *et al.*, 1998]. Although SF<sub>6</sub> is primarily of anthropogenic origin, it also occurs naturally [Harnisch and Eisenhauer, 1998; Harnisch *et al.*, 2000; Busenberg and Plummer, 2000]. High terrigenous concentrations of SF<sub>6</sub> have been measured in groundwater from fractured silicic igneous rocks, from some carbonate aquifers, from some hot springs, and in some groundwater from volcanic areas [Busenberg and Plummer, 2000; Koh *et al.*, 2007]. Where the terrestrial flux of SF<sub>6</sub> from igneous rocks and mineral grains is high, groundwater cannot be dated with SF<sub>6</sub>. Further, low levels of SF<sub>6</sub> enrichment, below concentrations corresponding to modern air-water equilibrium, are difficult to recognize and can lead to a young bias in apparent SF<sub>6</sub> age in some water samples or in mixtures with fractions of old water that contain significant amounts of terrigenous SF<sub>6</sub> [Busenberg and Plummer, 2000; Koh *et al.*, 2007].

[6] This paper describes the possible use of SF<sub>5</sub>CF<sub>3</sub> and CFC-13 as new tools for dating young groundwater. SF<sub>5</sub>CF<sub>3</sub> has been measured in the atmosphere [Sturges *et al.*, 2000a, 2000b] and determined in air extracted from firn at Concordia Dome, Antarctica. SF<sub>5</sub>CF<sub>3</sub> has received considerable attention because it is the most effective greenhouse gas known with a warming potential of about 18000 times that of CO<sub>2</sub> [Sailor *et al.*, 2002]. The source of SF<sub>5</sub>CF<sub>3</sub> in the atmosphere is still uncertain. Sturges *et al.* [2000b] speculated that SF<sub>5</sub>CF<sub>3</sub> is produced by the reaction of SF<sub>6</sub> with fluoropolymers in high-voltage equipment. Huang *et al.* [2004] were not able to produce SF<sub>5</sub>CF<sub>3</sub> from SF<sub>6</sub> and fluoropolymers or from SF<sub>6</sub> and CF<sub>4</sub>. SF<sub>5</sub>CF<sub>3</sub> was produced from SF<sub>6</sub> and CHF<sub>3</sub> when excited SF<sub>6</sub><sup>\*</sup> and CHF<sub>3</sub><sup>\*</sup> combined to form the transient SF<sub>6</sub>CHF<sub>3</sub><sup>-</sup> which converted to SF<sub>5</sub>CF<sub>3</sub> and HF during spark discharge. SF<sub>5</sub>CF<sub>3</sub> was also produced during arcing from SF<sub>6</sub> and CH<sub>2</sub>F<sub>2</sub> through a series of more complex reactions [Huang *et al.*, 2004]. SF<sub>5</sub>CF<sub>3</sub> also is a by-product in the manufacture of some fluorochemicals [Santoro, 2000] and possibly a by-product in the manufacture of SF<sub>6</sub>. Recent experimental results suggest that another potential source of SF<sub>5</sub>CF<sub>3</sub> might be the recombination of SF<sub>5</sub> and CF<sub>3</sub> radicals on aerosol particles in the atmosphere [Carrier *et al.*, 2007]. Regardless of source, SF<sub>5</sub>CF<sub>3</sub> is ultimately released to the atmosphere and becomes incorporated into the hydrosphere.

[7] SF<sub>5</sub>CF<sub>3</sub> is potentially a very useful environmental tracer for dating groundwater because (1) the SF<sub>5</sub>CF<sub>3</sub> atmospheric mixing ratio (mole fraction in dry air) was increasing at about 6 percent per year between 1970 and 2000 [Sturges *et al.*, 2000b], (2) SF<sub>5</sub>CF<sub>3</sub> has a relatively long atmospheric lifetime; estimates range from about 1000 years [Chim *et al.*, 2003] to the range of 650 to 950 years [Takahashi *et al.*, 2002], (3) SF<sub>5</sub>CF<sub>3</sub> has high stability in soils and sediments (this study), and does not degrade in anaerobic environments, (4) except for the hydrosphere, there are no other significant natural sinks of SF<sub>5</sub>CF<sub>3</sub> [Ravishankara *et al.*, 1993], (5) there does not appear to be a natural terrigenous source of SF<sub>5</sub>CF<sub>3</sub> (this study), and (6) because there are no industrial uses of SF<sub>5</sub>CF<sub>3</sub>, groundwater is unlikely to be contaminated with SF<sub>5</sub>CF<sub>3</sub> from anthropogenic point sources. Thus it may be possible to use SF<sub>5</sub>CF<sub>3</sub> to date some waters that cannot be dated with CFCs (CFC-11, CFC-12, CFC-113), owing to CFC con-

tamination from nonatmospheric anthropogenic sources, or with SF<sub>6</sub>, owing to contamination from terrigenous sources.

[8] CFC-13 was used mainly as a refrigerant in very low-temperature cascade systems (below -70°C) and was a by-product in the production of other halocarbons. CFC-13 was first detected in the atmosphere in the late 1970s [Penkett *et al.*, 1981]; however, the atmospheric history of CFC-13 is not well known [Rasmussen and Khalil, 1980; Penkett *et al.*, 1981; Fabian *et al.*, 1996; Intergovernmental Panel on Climate Change (IPCC), 2001; Urhan and Ballschmitter, 2000; Montzka and Fraser, 2003; Culbertson *et al.*, 2000, 2004]. CFC-13 is thought to be stable in most groundwater environments and has an atmospheric lifetime of 640 years [IPCC, 2001]. The atmospheric mixing ratio of CFC-13 is currently increasing at a rate of about 2.5 percent per year [IPCC, 2001]. The source of CFC-13 is entirely anthropogenic in origin.

## 2. Methods

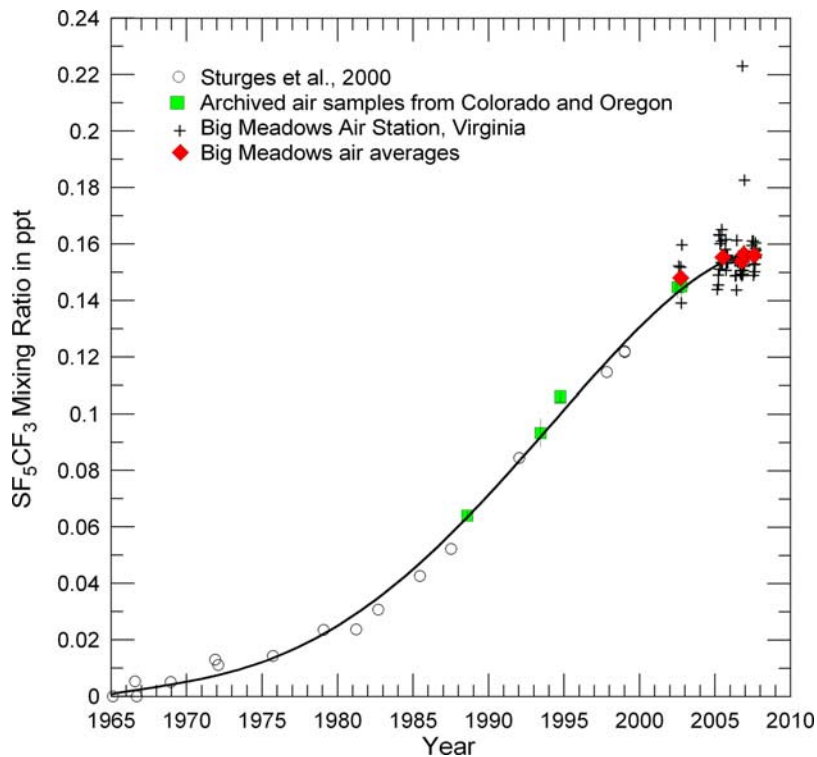
[9] The low atmospheric mixing ratio of SF<sub>5</sub>CF<sub>3</sub>, and its low solubility in water complicate the analytical methodology of measuring environmental concentrations of SF<sub>5</sub>CF<sub>3</sub>. The mixing ratio of SF<sub>5</sub>CF<sub>3</sub> in the 2005 troposphere was more than 30 times less than the mixing ratio of SF<sub>6</sub> and about 2700 times less than the mixing ratio of CFC-12. Consequently, because of low solubility of SF<sub>5</sub>CF<sub>3</sub> in water, a large volume of groundwater is needed to extract a sufficient amount of the tracer for analysis. CFC-13 mixing ratios in the atmosphere are similar to those of SF<sub>6</sub>; however, because of the low electron affinity of CFC-13, it is difficult to measure environmental concentrations of the tracer by gas chromatography with electron-capture detector (GC-ECD). Appendix A summarizes methods that were developed as a part of this study for (1) field collection of water samples for combined determination of SF<sub>5</sub>CF<sub>3</sub>, SF<sub>6</sub>, CFC-12, and CFC-13, (2) laboratory analysis of SF<sub>5</sub>CF<sub>3</sub>, SF<sub>6</sub>, CFC-12, and CFC-13, (3) determination of the solubility of SF<sub>5</sub>CF<sub>3</sub> in water, and (4) investigation of the potential for microbial degradation of SF<sub>5</sub>CF<sub>3</sub> in anoxic systems.

## 3. Results

### 3.1. Atmospheric Mixing Ratios

[10] The reported mixing ratio of SF<sub>5</sub>CF<sub>3</sub> from Antarctic firn air [Sturges *et al.*, 2000a] are consistent with measured mixing ratios in six archived air standards from the U. S. Geological Survey (USGS) Reston Chlorofluorocarbon Laboratory (Figure 1). Some air samples collected at the USGS in Reston, Virginia, have elevated mixing ratios of both SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub>. SF<sub>5</sub>CF<sub>3</sub> air data from Sturges *et al.* [2000a, 2000b] and from air samples collected at the Big Meadows Air Monitoring Station, Shenandoah National Park, Virginia, are shown in Figure 1. The atmospheric mixing ratios measured in Krakow, Poland, between December 2000 and May 2003 [Rosiek *et al.*, 2007] are slightly higher than the data plotted in Figure 1. The atmospheric mixing ratio of SF<sub>5</sub>CF<sub>3</sub> was increasing at about 6% per year between 1970 and 2000; however, the rate of increase in the atmosphere appears to have decreased somewhat after 2000.

[11] The atmospheric mixing ratio of CFC-13 was reconstructed in this study from analyses of archived NOAA and



**Figure 1.** Increase in atmospheric mixing ratio (mole fraction) of SF<sub>5</sub>CF<sub>3</sub> between 1965 and 2007. The archived air samples as well as the Virginia air concentrations were measured in this study. The atmospheric data were fitted to a second degree polynomial equation (line). The atmospheric mixing ratio of SF<sub>5</sub>CF<sub>3</sub> was increasing at a rate of about 6% per year between 1970 and 2000, but the rate of increase appears to have decreased somewhat after 2000.

Oregon marine air standards and a limited number of published measurements (Figure 2). The post-1993 air data suggest that the atmospheric mixing ratio is increasing at about 0.1 ppt annually [IPCC, 2001] or about 2.5% per year. The pre-1988 mixing ratio of CFC-13 was estimated in this study from CFC-13 partial pressures in dated groundwater from Locust Grove, Maryland. Modern air (2005) contains about 4.7 ppt of CFC-13 and the reconstructed atmospheric mixing ratios of CFC-13 are shown in Figure 2 and tabulated in <http://water.usgs.gov/lab/>.

[12] SF<sub>5</sub>CF<sub>3</sub> was present in two commercial standards of SF<sub>6</sub>. A Scott 1.00 ppb standard gas and a 99.97 ppm gravimetric Master Standard gas contained 0.21% and 0.005% SF<sub>5</sub>CF<sub>3</sub> in the SF<sub>6</sub> from which the standards were prepared, respectively. The constant atmospheric mole ratio of SF<sub>5</sub>CF<sub>3</sub> to SF<sub>6</sub> of 0.028 from 1965 to 1999 [Sturges *et al.*, 2000b] suggests that the SF<sub>5</sub>CF<sub>3</sub> may be predominantly produced in the atmosphere. The historical atmospheric mixing ratios of SF<sub>5</sub>CF<sub>3</sub> are given in <http://water.usgs.gov/lab/>.

[13] The atmospheric history of CFC-12 is well known and can be obtained from the Climate Monitoring and Diagnostics Laboratory of National Oceanic and Atmospheric Administration Web site <http://www.cmdl.noaa.gov/> and from <http://cdiac.esd.ornl.gov/> [Walker *et al.*, 2000; Prinn *et al.*, 2000; Cunnold *et al.*, 1997]. The preindustrial revolution troposphere steady-state mixing ratio of SF<sub>6</sub> was estimated at less than 0.0064 ppt [Vollmer and Weiss, 2002]. The atmospheric history of SF<sub>6</sub> is now known [Maiss and Levin, 1994; Maiss and Brenninkmeijer, 1998] and the

mixing ratio of SF<sub>6</sub> is currently increasing, while those of the CFC-11, CFC-12, and CFC-113 are nearly constant or decreasing.

### 3.2. Solubility of SF<sub>5</sub>CF<sub>3</sub> in Water

[14] The Henry's law solubility constant of SF<sub>5</sub>CF<sub>3</sub> was determined as described in Appendix A6 and calculated using the procedure described by Warner and Weiss [1985] and Bullister *et al.* [2002]. The solubility of SF<sub>5</sub>CF<sub>3</sub> in water was found to be about 2 times lower than that of SF<sub>6</sub> and the temperature dependence of the Henry's law solubility constant is given by the equation:

$$\ln K = A_1 + A_2(100/T) + A_3 \ln(T/100) \quad (1)$$

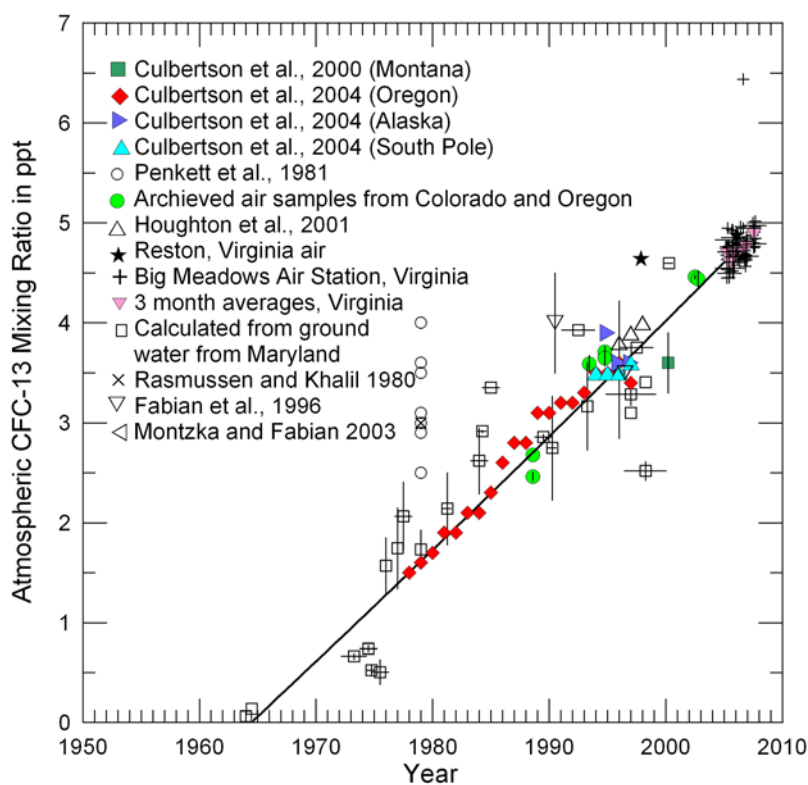
where  $K$  is the Henry's law solubility constant,  $T$  is temperature in degrees Kelvin and the gravimetric constants ( $\text{mol kg}^{-1} \text{atm}^{-1}$ )  $A_1$ ,  $A_2$ , and  $A_3$  are equal to  $-14.9316$ ,  $26.9057$ , and  $-2.9203$ , respectively.

[15] The temperature dependence of the Henry's law constant of SF<sub>5</sub>CF<sub>3</sub> is given in Table 1 and plotted in Figure 3a and compared to SF<sub>6</sub> [Bullister *et al.*, 2002], CFC-13 [Scharlin and Battino, 1995], CFCs, and other atmospheric gases in Figure 3b.

### 3.3. Modification of SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> Concentrations by Microbial Activity

[16] The concentrations of SF<sub>5</sub>CF<sub>3</sub> and SF<sub>6</sub> in closed microcosms containing soils and organic-rich sediment (Appendix A7) decreased slightly over the duration of the





**Figure 2.** Increase in the atmospheric mixing ratio (mole fraction) of CFC-13. The measurements of Penkett *et al.* [1981] are inconsistent with more recent results. The archived air samples as well as the Virginia air concentrations were measured in this study. The atmospheric data were fitted to a second degree polynomial equation. The calculated partial pressures of CFC-13 for groundwaters from Locus Grove, Maryland are also shown.

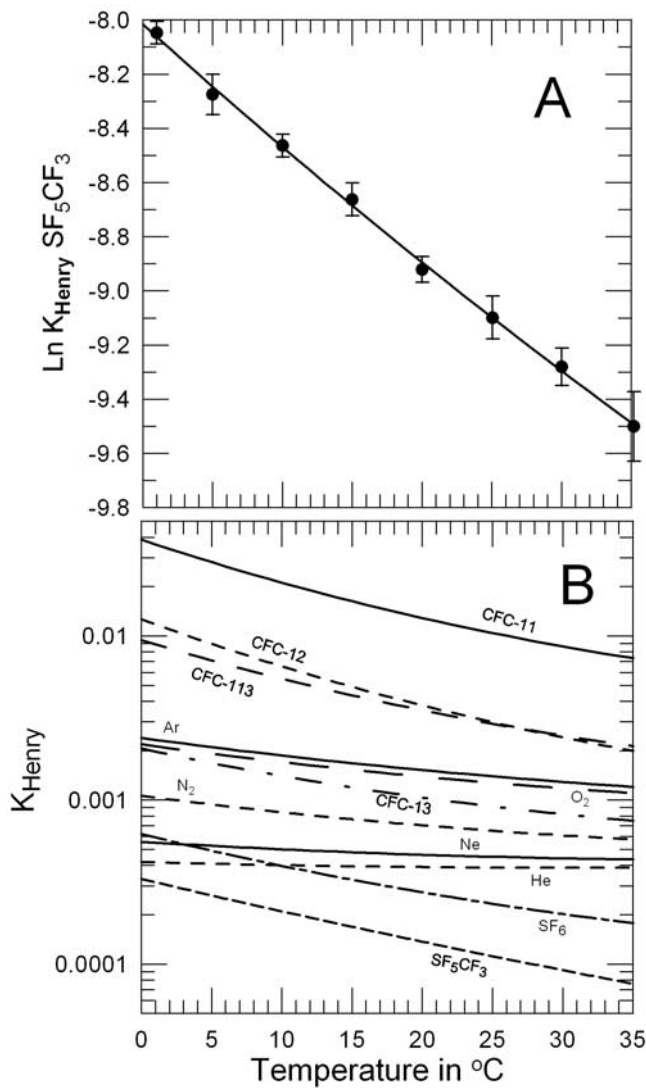
experiment (335 days) in all the samples and in the blank controls (Figure 4). The line in Figure 4a is a linear fit showing a decrease in concentrations between the initial and final concentrations of the blank controls. Figure 4b shows that CH<sub>4</sub> accumulated in the headspace of the bottles containing sediments from Lake Newport and Julian's Pond (Appendix A7), but no methane was found in bottles containing the Reston soil samples. CO<sub>2</sub> concentrations increased in the headspace of all bottles containing samples (Figure 4c).

[17] The results from the microcosm experiments indicate that there was significant biological activity in all bottles with sediment samples, but there were no detectable differences in the tracer concentrations in the bottles of the controls and samples. The decrease in concentrations observed in the controls and samples was probably the result of sorption of SF<sub>5</sub>CF<sub>3</sub> and SF<sub>6</sub> into the rubber septum and/or loss by diffusion through the septum. The results indicate that SF<sub>5</sub>CF<sub>3</sub> and SF<sub>6</sub> are useful environmental tracers for dating both aerobic and anaerobic groundwaters.

#### 3.4. Effects of Excess Air on the Model Recharge Dates

[18] Excess air refers to the quantity of air dissolved in groundwater that is in excess of air-water equilibrium [Heaton and Vogel, 1981; Aeschbach-Hertig *et al.*, 2000]. During recharge events, excess air is trapped beneath the rising water table within intergranular spaces or in fractures and dissolved under increased hydrostatic pressure. If the volume of excess air completely dissolves under increased

hydrostatic pressure, the dissolved composition is equal to that of air and is referred to as unfractionated excess air (UA model of Aeschbach-Hertig *et al.* [2000] and Holocher *et al.* [2002]). If the quantity of excess air is only partially dissolved, a fractionation results due to the changing composition of the remaining excess air (CE model of Aeschbach-Hertig *et al.* [2000] and Holocher *et al.* [2002]). Several models were considered to account for the effects of excess air on the interpretation of groundwater age. The procedure of Busenberg and Plummer [1992, 2000] for CFCs and SF<sub>6</sub> corrects the tracer model-ages for the presence of unfractionated excess air. The amount of excess air in groundwater and various environments that are favorable to the dissolution of large quantities of excess air are discussed by Busenberg and Plummer [2000] and Holocher *et al.* [2002]. Vertical advective flow favors the formation of unfractionated excess air; however, episodic recharge events favor the formation of fractionated excess air [Holocher *et al.*, 2002]. Other factors that control the composition of the excess air include bubble size and distribution, amount of entrapped air, and its composition [Holocher *et al.*, 2002]. The amount of excess air and degree of fractionation influences the calculated model ages obtained with all dating methods that use transient environmental gas tracers. The effects on the calculated model ages are inversely proportional to the solubility of the tracer in water and are significant for sparsely soluble tracers. The fractionation factors can be evaluated from noble gas measurements and



**Figure 3.** (a) Experimental measured solubility of SF<sub>5</sub>CF<sub>3</sub> in water as a function of temperature was measured between 1 and 35°C. See Appendix A6 for details. (b) Also shown is a graph showing the temperature dependence of Henry's law constants of SF<sub>5</sub>CF<sub>3</sub>, SF<sub>6</sub>, CFC-11, CFC-12, CFC-13, CFC-113, N<sub>2</sub>, O<sub>2</sub>, Ar, He, and Ne as a function of temperature. The solubility of all CFCs in water is greater than that of N<sub>2</sub> while the solubility of SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> in water is significantly less than the solubility of the major atmospheric gases.

effects on calculated model ages are discussed in detail in Appendix A8.

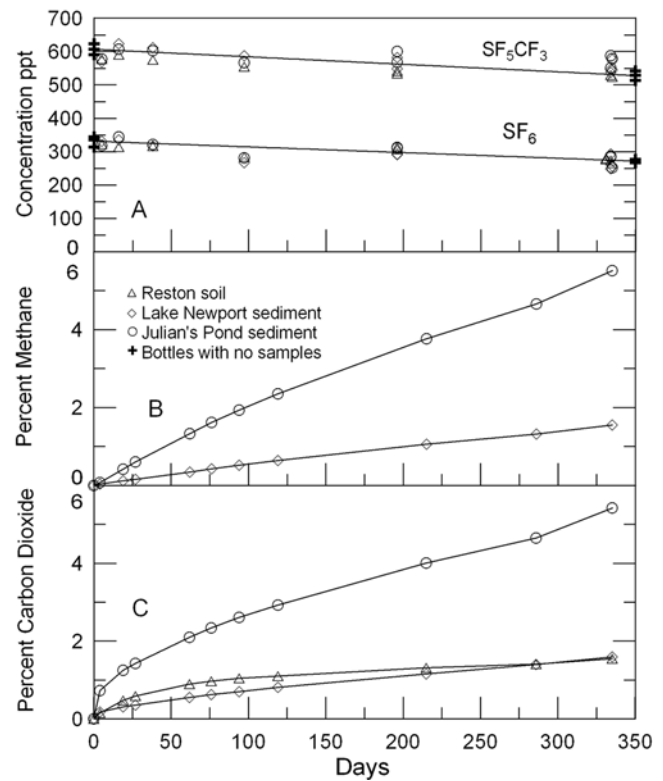
#### 4. Field Examples

[19] Eighty five groundwater samples from more than 30 wells and springs from the eastern United States were analyzed for CFC-12, SF<sub>6</sub>, SF<sub>5</sub>CF<sub>3</sub>, and CFC-13 using the GC-ECD method (Appendix A3). In each case, separate water samples were analyzed for dissolved N<sub>2</sub> and Ar to estimate recharge temperature and quantities of excess air (UA model), which were used in calculating the apparent age from the environmental tracer data. Most of the wells sampled were shallow monitoring wells in Atlantic Coastal

**Table 1.** Solubility of CF<sub>3</sub>SF<sub>5</sub> in Water From 1.0 to 35.15°C

Temperature, °C	K Henry	Standard Deviation	Number
1.0	0.000320	0.0000133	5
5.0	0.000255	0.0000190	7
10.0	0.000211	0.0000895	6
15.0	0.000173	0.0000104	5
20.0	0.000134	0.00000945	8
25.05	0.000112	0.00000880	11
30.0	0.0000932	0.00000646	8
35.15	0.0000748	0.00000960	8

Plain sediments of Maryland in the eastern United States. Water from some of these wells was previously dated with CFCs [Dunkle *et al.*, 1993; Plummer *et al.*, 1993; Böhlke and Denver, 1995], <sup>3</sup>H/<sup>3</sup>He, <sup>85</sup>Kr, and CFCs [Ekwurzel *et al.*, 1994], and CFCs and SF<sub>6</sub> [Busenberg and Plummer, 2000]. Other sites included were (1) two springs from the Blue Ridge Mountains, Virginia, which are known to discharge water of nearly modern apparent age [Plummer *et al.*, 2000, 2001]; (2) a spring at the base of the Blue Ridge Mountains in the Valley and Ridge Province of Virginia which has been dated repeatedly since 1994 using CFCs and



**Figure 4.** (a) Microcosm experiments under anaerobic conditions, in which the concentrations of SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> do not differ from the controls. The results indicate that SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> did not degrade under methanogenic anaerobic conditions after a period of 335 days. (b) The methane concentrations in the bottles increased as a function of time in bottles containing sediments from Lake Newport and Julian's Pond. Methane was not detected in the bottles containing the Reston Virginia soil samples. (c) The concentrations of CO<sub>2</sub> increased in all three sets of bottles containing sediments, indicating significant biological activity in all bottles with sediment samples.

<sup>3</sup>H/<sup>3</sup>He yielding apparent ages of 24 to 33 years [Plummer *et al.*, 2000, 2001]; (3) a spring in the Valley and Ridge Province of West Virginia which has a <sup>3</sup>H/<sup>3</sup>He apparent age of 7.1 years but cannot be dated with CFCs or SF<sub>6</sub> (L. N. Plummer *et al.*, unpublished data, 2005); and (4) a deep well in the Atlantic Coastal Plain of Virginia (L. N. Plummer and E. Busenberg, unpublished data, 2005) that discharges water that is nearly free of CFCs.

[20] Only the apparent (piston-flow) age was calculated for comparison among the various environmental tracers. Most of the monitoring wells have narrow openings of typically less than 1 m. The excess air was assumed not to be fractionated ( $f = 1$ ).

[21] During the past 12 years, over which some of the samples have been collected, there has likely been some variation in recharge rate in the study areas, and some variation in apparent age over time is possible because in the Maryland site the land use has changed from crops of corn and soybeans to irrigated ornamental shrubs and trees. However, to a first approximation, the results indicate nearly constant apparent age among the various environmental tracers. All ages of water samples collected prior to the present study were recalculated from the original measurements using the same air curves and calculation procedures as used with the new measurements. Table 2 summarizes all apparent ages obtained from the various tracers at the 30 sites since 1994.

#### 4.1. Groundwater Samples Contaminated With SF<sub>6</sub> and/or CFCs

[22] Two springs, Hudson Spring, located in Luray, Virginia, and Kilmer Spring, located in Martinsburg, West Virginia, were selected for study because they contain large amounts of terrigenous or excess SF<sub>6</sub> and/or excess CFCs and cannot be dated by the SF<sub>6</sub> or CFC methods.

[23] Water from Hudson Spring contains significant amounts of terrigenous SF<sub>6</sub>. The <sup>3</sup>H/<sup>3</sup>He apparent age from a sample collected in 1997 from Hudson Spring was 24.4 ± 0.8 years [Plummer *et al.*, 2000]. Eleven CFC-11 and CFC-12 apparent ages and four CFC-113 apparent ages of water from Hudson Spring collected in 1997 and 1999 averaged 28.7 ± 1.8, 27.4 ± 1.6, and 26.2 ± 1.3 years, respectively [Plummer *et al.*, 2000]. Water from Hudson Spring sampled in 1999 contained an excess of SF<sub>6</sub> of about 40% greater than that of modern air water equilibrium and more than 15 times the amount of SF<sub>6</sub> corresponding to recharge in 1974, as implied by the <sup>3</sup>H/<sup>3</sup>He apparent age. The apparent age of water from Hudson Spring determined with SF<sub>5</sub>CF<sub>3</sub> was 21.9 ± 3.2 years (Table 2) and consistent with the <sup>3</sup>H/<sup>3</sup>He age of 24.4 ± 0.8 years. The CFC-13 and CFC-12 ages based on the new procedure were older than that from SF<sub>5</sub>CF<sub>3</sub>, averaging 34.6 ± 1.7 and 31.6 ± 0.0 years, respectively, but in the range of the previously determined CFC ages of 27.5 to 34.2 years. Within the uncertainties of the measurements, the SF<sub>5</sub>CF<sub>3</sub> data from Hudson Spring indicate that there is no terrigenous source of SF<sub>5</sub>CF<sub>3</sub>, nor anthropogenic source of CFC-13 other than the atmosphere.

[24] Water from Kilmer Spring contains large excesses of nonatmospheric CFCs and terrigenous SF<sub>6</sub>. The CFC-11, CFC-12, and CFC-113 ppt values, calculated from the measured dissolved concentrations and Henry's law solubility, exceed that of modern air by factors of 7.1, 3.2, and 4.6 times, respectively, in water from Kilmer Spring. The

calculated SF<sub>6</sub> partial pressure is some 5.6 times greater than that in modern air. Although water from Kilmer Spring cannot be dated with CFCs or SF<sub>6</sub>, a <sup>3</sup>H/<sup>3</sup>He apparent age for a water sample collected in July 2004 was 7.1 ± 0.5 years (L. N. Plummer *et al.*, unpublished data, 2005). The reconstructed initial tritium in the sample (tritium plus tritiogenic <sup>3</sup>He) was 10.6 TU, consistent with that of tritium in precipitation in the late 1990s in the region. Therefore the <sup>3</sup>H/<sup>3</sup>He age for water from Kilmer Spring appears valid, and the sample is likely not significantly mixed with older water. Water from Kilmer Spring was dated with CFC-13 and SF<sub>5</sub>CF<sub>3</sub> yielding apparent (piston flow) ages of 4.9 ± 3.2 and 6.1 ± 0.7 years, respectively (Table 2), and, within the uncertainties, consistent with the <sup>3</sup>H/<sup>3</sup>He age. Apparently, this sample, though contaminated with CFC-11, CFC-12 and CFC-113, is not contaminated with CFC-13, and again, there appears to be no terrigenous source of SF<sub>5</sub>CF<sub>3</sub>.

#### 4.2. Blue Ridge Mountains, Shenandoah National Park, Virginia

[25] Two springs from the Blue Ridge Mountains in Shenandoah National Park, Virginia, were sampled for SF<sub>6</sub> and CFCs from 1996 to 1999. The springs issue from the base of the overburden near the top of the mountains and have concentrations of SF<sub>6</sub> and CFCs that are near values for water in equilibrium with air (at the time of sampling) [Plummer *et al.*, 2000, Figure 8]. CFC ages were uncertain because of the leveling off the atmospheric input of CFCs, but average SF<sub>6</sub> apparent ages of 1.4 ± 1.1 (n = 13) and 1.5 ± 1.7 (n = 14) years were determined for water from Furnace and Lewis Springs, respectively. The <sup>3</sup>H/<sup>3</sup>He apparent ages of water from Furnace and Lewis springs averaged 0.1 ± 0.2 and 0.0 ± 0.2 years, respectively, in four determinations from each spring during 1996–1997 [Plummer *et al.*, 2000]. Piston-flow apparent ages based on cosmogenic <sup>35</sup>S averaged about 1.5 years but were near the maximum detectable dating range of <sup>35</sup>S [Plummer *et al.*, 2001]. All previous environmental tracer data indicate nearly modern ages for water from Furnace and Lewis Springs, yet there is a young bias of perhaps 1 year in the <sup>3</sup>H/<sup>3</sup>He ages relative to those based on SF<sub>6</sub> and <sup>35</sup>S. When sampled in July 2005, modern ages also were confirmed with CFC-13 and SF<sub>5</sub>CF<sub>3</sub>. The CFC-13 ages at Furnace and Lewis Springs were modern and 0.3 ± 1.2 years, respectively, and those based on SF<sub>5</sub>CF<sub>3</sub> were modern and modern, respectively (Table 2). The model ages are within the uncertainties of the various dating methods; all apparent ages at these springs are approximately modern.

#### 4.3. Atlantic Coastal Plain of Maryland and Virginia

##### 4.3.1. Gas Exchange Between the Headspace and Old Water

[26] The Milford 2 well, located in Caroline County, Virginia, is in Cretaceous sands from the confined Middle Potomac aquifer and draws water from a 9 m screened interval some 80 m below the land surface. Water from the Milford 2 well is free of CFCs and one tritium determination from 1998 was <0.3 TU [Nelms and Harlow, 2003], indicating recharge before the 1940s. Nelms *et al.* [2003] reported a radiocarbon age of 16.7 ± 3.1 ka for water from the Milford 2 well. Because the water is old and contains little or no postbomb fraction, the water also should be free from CFC-13 and SF<sub>5</sub>CF<sub>3</sub>.

**Table 2.** Calculated Average Model Ages in Years and Standard Deviations in Parenthesis When Determined, Using Eight Environmental Tracers and a Numerical Simulation Method (NS)<sup>a</sup>

Location and Well Name	Date Sampled	1994 <sup>b</sup> <sup>3</sup> H/ <sup>2</sup> He	1994 <sup>b</sup> <sup>85</sup> Kr	1994 <sup>c</sup> NS	2000 <sup>d</sup> CFC-11	2005 <sup>e</sup> CFC-11	2000 <sup>d</sup> CFC-12	2005 <sup>e</sup> CFC-12	New <sup>f</sup> CFC-12	2000 <sup>d</sup> CFC-113	2005 <sup>e</sup> CFC-113	2000 <sup>g</sup> SF <sub>6</sub>	2005 <sup>e</sup> SF <sub>6</sub>	New <sup>f</sup> SF <sub>6</sub>	New <sup>f</sup> CFC-13	New <sup>f</sup> SF <sub>5</sub> CF <sub>3</sub>
<i>Locust Grove, Delmarva Peninsula, Maryland</i>																
KeBe 050	08/23/05				9.6(0.7)	<15	7.1(0.0)	<15	<15	9.1(1.0)	<15	10.7(0.3)	8.6(0.0)	14.1(4.9)	11.1	10.1(3.5)
KeBe 052	08/22/05	7.1(0.7)	7.7(1.0)	8.1	9.6(0.0)	<15	7.1(0.0)	<15	<15	9.8(0.3)	<15	7.8(0.8)	9.6(0.0)	7.4(1.0)	6.9(6.7)	8.4(2.8)
KeBe 059	11/01/05			6.0	C	<15	6.6(1.3)	<15	<15	—	<15	2.6(2.0)	7.6(1.1)	5.3	8.3	9.8
KeBe 059	08/23/05			6.0	C	<15	6.6(1.3)	<15	<15	—	<15	5.9(0.0)	8.1(1.4)	7.1(4.2)	8.6(5.7)	8.4(1.4)
KeBe 061	08/22/05	16.0(0.6)	14.4(1.0)	17.5	16.6(0.0)	16.1(0.7)	17.6(0.3)	18.4(0.4)	19.7(0.4)	18.6(0.0)	18.1(0.4)	17.0(2.7)	20.6(0.7)	17.6(2.1)	12.9(6.0)	14.6(0.7)
KeBe 062	08/22/05	3.1(0.8)	5.4(0.6)	3.9	10.6(0.0)	<15	7.6(0.0)	<15	<15	8.6(0.0)	<15	3.7(0.9)	5.4(0.4)	5.4(0.4)	4.1(0.0)	3.1
KeBe 063	08/23/05			12.3	21.1(0.0)	24.4(0.4)	23.1(0.0)	25.2(0.0)	23.6(2.8)	22.6(0.0)	24.8(1.0)	24.2(0.3)	26.6(0.4)	20.6(0.7)	24.4(1.8)	19.9(2.1)
KeBe 064	08/23/05			2.6	11.8(0.3)	<15	11.3(0.3)	<15	<15	12.1(0.0)	<15	10.2(0.3)	15.4(0.4)	14.1(2.1)	14.6(4.9)	12.1(0.0)
KeBe 159 N <sub>2</sub>	11/01/05			65.6	>53	52.8(0.7)	>56	57.6(0.4)	52.1(1.8)	>41	55.3	34.9(0.0)	41.8	49.8(4.2)	40.3(0.0)	40.1(1.1)
KeBe 159 air	11/01/05			65.6	>53	52.8(0.7)	>56	57.6(0.4)	52.8	>41	55.3	34.9(0.0)	41.8	49.8(4.2)	40.3(0.0)	40.1(1.1)
KeBe 160 N <sub>2</sub>	11/01/05	19.8(0.6)		27.1	28.1(0.3)	27.8(0.0)	24.6(0.0)	28.4(0.0)	26.3(2.8)	29.1(0.5)	30.1	29.6(1.8)	31.3(0.7)	33.1(0.4)	34.1(0.4)	27.3(0.0)
KeBe 160 air	11/01/05	19.8(0.6)		27.1	28.1(0.3)	27.8(0.0)	24.6(0.0)	28.4(0.0)	25.8(3.5)	29.1(0.5)	50.8	29.6(1.8)	31.3(0.7)	30.1(0.4)	34.1(0.4)	33.8(0.7)
KeBe 160	08/22/05	19.8(0.6)		27.1	28.1(0.3)	28.8(0.0)	24.6(0.0)	28.4(0.0)	29.1(0.5)	29.1(0.5)	28.6(0.4)	29.6(1.8)	32.4(1.1)	26.6(0.0)	34.4(0.4)	25.1(1.4)
KeBe 161	08/22/05	14.4(0.7)		15.6	13.3(0.3)	17.1(0.7)	12.6(0.5)	15.4(1.8)	19.4(1.8)	13.8(0.3)	16.9(0.4)	12.9(0.9)	16.1(0.7)	15.6(0.0)	13.4(0.4)	13.9(1.1)
KeBe 162 N <sub>2</sub>	11/01/05	40.6(1.4)		36.7	34.8(0.3)	36.0(0.3)	33.6(0.5)	35.2(0.6)	33.6(0.4)	13.8(0.3)	31.5(0.8)	26.4(0.3)	30.3(0.7)	31.3(0.7)	36.1(1.1)	34.8(4.9)
KeBe 162 air	08/22/05	40.6(1.4)		36.7	34.8(0.3)	36.0(0.3)	33.6(0.5)	35.2(0.6)	34.9(1.1)	42.6(0.0)	32.8(0.8)	26.4(0.3)	30.9(0.4)	25.1(0.7)	35.9(0.4)	22.9(2.1)
KeBe 163 air	11/01/05	7.8(0.7)	5.7(1.6)	8.8	11.1(0.0)	16.3(0.0)	9.5(0.0)	<15	<15	10.1(0.0)	<15	10.1(1.0)	13.3(1.4)	11.8(1.4)	8.6(7.4)	13.3(2.1)
KeBe 163	08/22/05	7.8(0.7)	5.7(1.6)	8.8	11.1(0.0)	<15	9.5(0.0)	<15	<15	10.1(0.0)	<15	10.1(1.0)	12.4	12.9(0.4)	10.6(4.2)	11.4(1.4)
KeBe 164	11/01/05			23.5	18.1(0.9)	23.3(0.0)	24.0(2.0)	23.1(0.0)	19.3(0.7)	—	23.6(0.4)	23.7(0.3)	28.3(0.7)	29.1(1.1)	21.1(3.2)	22.1(0.4)
KeBe 164 air	08/23/05			23.5	18.1(0.9)	23.3(0.0)	24.0(2.0)	22.0	21.4(1.1)	—	23.8(0.6)	23.7(0.3)	28.6	16.9(4.6)	23.9(3.9)	17.6(1.4)
KeBe 165	08/23/05	18.4(0.8)			24.1(0.0)	21.2(0.0)	24.6(0.0)	17.4	16.1(3.5)	26.6(1.0)	18.7(0.0)	25.1(2.3)	21.6(0.7)	17.6(2.1)	15.9(3.2)	16.6(0.4)
KeBe 166	08/23/05				9.6(0.0)	<15	3.3(0.8)	<15	<15	7.6(0.0)	<15	9.2(0.4)	8.6(2.1)	8.1(2.8)	9.4(1.1)	7.4(0.4)
KeBe 167	08/23/05				10.1(0.0)	<15	4.1(1.0)	<15	<15	8.8(0.3)	<15	4.1(0.0)	7.4(1.8)	9.4(3.2)	16.6(0.7)	6.9(3.5)
KeBe 206	11/02/05				16.9(0.2)	18.2(0.0)	16.4(0.2)	18.8(1.0)	18.2(3.3)	17.9(0.6)	17.7(0.8)	19.4	7.4(1.8)	23.3(0.7)	13.1(0.4)	21.8(0.4)
KeBe 206 air	08/23/05				16.9(0.2)	18.2(0.0)	16.4(0.2)	18.8(1.0)	17.1(2.5)	17.9(0.6)	17.1	19.4	20.9(0.4)	16.6(2.8)	16.4(6.0)	8.1(0.4)
KeBe 207	11/02/05				21.8(0.2)	21.6(0.0)	21.1(0.2)	21.8(0.0)	17.1(2.5)	19.3(0.2)	20.3	22.4(0.5)	24.6(0.4)	29.6(1.1)	20.3(3.5)	30.3(4.9)
KeBe 208	11/02/05				30.9(0.0)	28.8(0.0)	34.4(0.0)	28.2(0.3)	19.3(3.5)	31.9(0.8)	26.3	30.4(0.5)	29.8(0.0)	30.8(0.7)	26.1(2.5)	36.8(6.0)
KeBe 210	11/02/05				31.2(2.2)	51.3(0.0)	46.1(5.0)	56.3(0.7)	46.3	>43	52.8	46.9(0.0)	41.3(2.1)	40.3	39.8	34.3
<i>Blue Ridge Mountains, Shenandoah National Park, Virginia</i>																
Furnace Spring	07/20/05	0.1 <sup>hi</sup> (0.2)			<15	<15	<15	<15	<15	<15	<15	1.7 <sup>h</sup> (2.1)	1.5(0.3)	—	M	M
Lewis Spring	07/20/05	0.0 <sup>hi</sup> (0.3)			<15	<15	<15	<15	<15	<15	<15	1.7 <sup>h</sup> (1.8)	—	0.3(1.2)	M	M
<i>Valley and Ridge Province, Virginia</i>																
Hudson Spring	07/20/05	24.4 <sup>h</sup> (0.8)			28.7 <sup>h</sup> (1.8)	34.2(0.3)	27.5(1.6)	33.0	31.6(0.0)	C to 28 <sup>h</sup>	32.0	C <sup>h</sup>	C	C	34.6(1.7)	21.9(3.2)
Dices Spring	03/08/06	Cannot be dated <sup>j,k</sup>			C	C	C	C	C	C	C	C	C	C	36.9(0.4)	25.7(4.9)
Bolar Spring	03/08/06	Cannot be dated <sup>j,k</sup>			C	C	C	C	C	C	C	C	C	C	27.4(0.4)	18.2(5.7)
<i>Valley and Ridge Province, West Virginia</i>																
Kilmer Spring	08/17/05	7.1(0.5) <sup>j</sup>			C	C	C	C	C	C	C	C	C	C	4.9(3.27)	6.1(0.7)



Table 2. (continued)

Location and Well Name	Date Sampled	1994 <sup>b</sup> <sup>3</sup> H/ <sup>3</sup> He	1994 <sup>b</sup> <sup>85</sup> Kr	1994 <sup>c</sup> NS	2000 <sup>d</sup> CFC-11	2005 <sup>e</sup> CFC-11	2000 <sup>d</sup> CFC-12	2005 <sup>e</sup> CFC-12	2000 <sup>d</sup> CFC-113	2005 <sup>e</sup> CFC-113	2000 <sup>g</sup> SF <sub>6</sub>	2005 <sup>g</sup> SF <sub>6</sub>	New <sup>f</sup> SF <sub>6</sub>	New <sup>f</sup> CFC-13	New <sup>f</sup> SF <sub>5</sub> CF <sub>3</sub>
<i>Atlantic Coastal Plain, Virginia</i>															
Milford 2 air	10/12/05					>61		>65		>56		>56	36.5(2.5)	>40.8	29.8(0.0)
Milford 2 He	10/12/05					>61		>65		>56		>56	>52.8	>40.8	>40.8
Milford 2 N <sub>2</sub>	10/12/05					>61		>65		>56		>56	>52.8	>40.8	>40.8
USGS 20	05/05/05					<15		<15		<15		4.7(0.4)	—	M	2.6

<sup>a</sup>The results were calculated using equation (A15) and unfractonated excess air ( $f = 1$ ). C means that age could not be determined; calculated partial pressure exceeds 2005 air mixing ratio. M refers to modern; calculated partial pressure is within the range of the modern atmosphere. Air, N<sub>2</sub>, He = headspace gas used in the spray chamber. Here <15 refers to young water, age cannot be accurately determined because of the flattening and turnover of the CFC mixing ratios in the atmosphere. Dashed lines or blank spaces means not possible or not determined. The original data on which these ages were based can be obtained from *Dunkle et al.* [1993], *Plummer et al.* [1993], *Ekurzel et al.* [1994], *Reilly et al.* [1994], *Böhlke and Denver* [1995], *Plummer et al.* [2000], *Busenberg and Plummer* [2000], and L. N. Plummer and E. Busenberg, unpublished data, 2005.

<sup>b</sup>Data are taken from *Ekurzel et al.* [1994].

<sup>c</sup>Data are taken from *Reilly et al.* [1994].

<sup>d</sup>Data are taken from *Busenberg and Plummer* [2000].

<sup>e</sup>Data are determined by the method of *Busenberg and Plummer* [1992].

<sup>f</sup>Data are determined by the new procedure.

<sup>g</sup>Data are taken from *Plummer et al.* [2000].

<sup>h</sup>Minimum <sup>35</sup>S piston flow age is 1.5 years [*Plummer et al.*, 2001].

<sup>i</sup>Data are taken from L. N. Plummer et al. (unpublished data, 2005), corrected for terrigenous helium.

<sup>k</sup>Very high terrigenous helium cannot be dated by the <sup>3</sup>H/<sup>3</sup>He method.

[27] In three separate tests, water from the Milford 2 well was equilibrated for one hour with initial headspace gases of air, He, and N<sub>2</sub>. When air was used, complete exchange equilibrium was not achieved and very low concentrations of SF<sub>6</sub>, CFC-13, and SF<sub>5</sub>CF<sub>3</sub> were present in the headspace after 1 h (Table 2). With initial headspace gas compositions of He or N<sub>2</sub>, concentrations of CFC-12, SF<sub>6</sub>, CFC-13, and SF<sub>5</sub>CF<sub>3</sub> were below the detection after 1 h of spray equilibration, indicating apparent ages of >56, >53, >41, and >41 years, respectively, for water from the Milford 2 well.

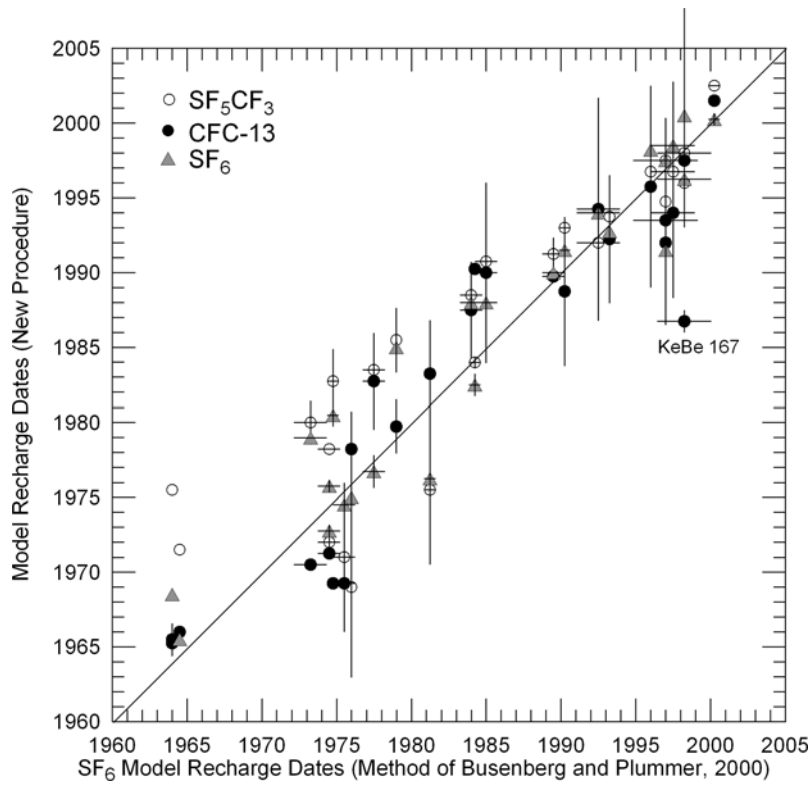
[28] A second test compared equilibration with headspace gases of N<sub>2</sub> or air with water from monitoring well KeBe 160 in shallow Coastal Plain sands in Maryland. The monitoring well is cased to a depth of 10.7 m, below which is a screened opening of 0.9 m. Water from this well contains low, but clearly detectible concentrations of CFCs and SF<sub>6</sub>, with apparent ages that ranged from 25 to 32 years in samples collected between 1994 and 2005. A <sup>3</sup>H/<sup>3</sup>He age from a sample in 1991 was 19.8 ± 0.6 years. When the headspace gas was air, the SF<sub>5</sub>CF<sub>3</sub>, CFC-13, and SF<sub>6</sub> apparent ages were 5.5, 0, and 3 years younger than that obtained from an initial N<sub>2</sub> headspace, with virtually identical results obtained for CFC-12 (Table 2). Apparently, exchange equilibrium was nearly achieved with the trace gases in a water sample of apparent age less than 30 years, when the initial headspace gas was modern air (KeBe 162 and KeBe 163 in Table 2).

#### 4.3.2. Comparison of Apparent Ages, Delmarva Peninsula

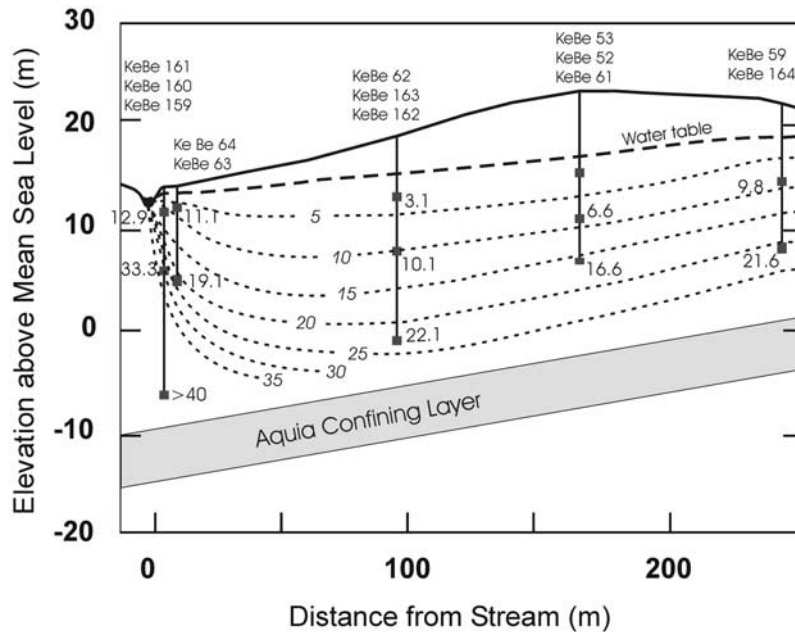
[29] A series of monitoring wells at Locust Grove, Maryland, on the Delmarva Peninsula of Maryland were sampled. The aquifer is unconfined, consists of sands and gravels and is underlain by a confining layer consisting of mainly silt and clay. The location of wells and the flow paths can be found on maps in the work of *Dunkle et al.* [1993], *Reilly et al.* [1994], and *Böhlke and Denver* [1995], and well construction data are given by *Plummer et al.* [1993]. The area is farmed and the groundwater chemistry has been altered by agricultural practices [*Böhlke and Denver*, 1995]. The Locust Grove wells frequently have been selected to test the feasibility of the use of various environmental tracers as dating tools because of the relatively simple hydrology of the aquifer and the presence of a network of multidepth monitoring wells with narrow screens installed by the USGS. The apparent age of the groundwater in the Locust Grove watershed has been determined using CFC-11 and CFC-12 [*Dunkle et al.*, 1993; *Plummer et al.*, 1993; *Böhlke and Denver*, 1995], <sup>3</sup>H/<sup>3</sup>He, <sup>85</sup>Kr, and CFCs [*Ekurzel et al.*, 1994], CFCs and SF<sub>6</sub> [*Busenberg and Plummer*, 2000], and estimated from a groundwater flow model [*Reilly et al.*, 1994]. A summary of the results can be found in the work of *Busenberg and Plummer* [2000]. A comparison of the groundwater ages obtained using various age dating methods with SF<sub>5</sub>CF<sub>3</sub> and CFC-13 is shown in Table 2.

[30] Figure 5 compares 2005 SF<sub>6</sub> model recharge dates obtained using the method of *Busenberg and Plummer* [2000] with the SF<sub>5</sub>CF<sub>3</sub>, CFC-13, and SF<sub>6</sub> ages obtained by the new method. The data are in reasonable agreement with the exception of two wells that were beyond the dating range of SF<sub>5</sub>CF<sub>3</sub> and well KeBe 167 which was pumped dry during sampling.





**Figure 5.** SF<sub>6</sub> piston-flow model ages obtained by the method of *Busenberg and Plummer* [2000] compared to SF<sub>6</sub>, CF<sub>5</sub>CF<sub>3</sub> and CFC-13 ages calculated by the new method for the groundwaters sampled in this study.



**Figure 6.** Cross section showing isochrones of model SF<sub>5</sub>CF<sub>3</sub> ages of the groundwaters at Locust Grove, Maryland. The isochrones are essentially identical to the previously published figure of Locust Grove area based on SF<sub>6</sub> model ages [*Busenberg and Plummer, 2000*]. Well KeBe 53 did not produce sufficient water and could not be sampled in August and November 2005. The solid squares represent the screened interval. See text for further details.

[31] The dashed lines in Figure 6 are isochrones based on the SF<sub>5</sub>CF<sub>3</sub> apparent ages; the isochrones are essentially identical to the previously published figure of Locust Grove area based on SF<sub>6</sub> model ages [Busenberg and Plummer, 2000], CFC model ages [Dunkle et al., 1993; Böhlke and Denver, 1995], <sup>3</sup>H/<sup>3</sup>He and <sup>85</sup>Kr model ages [Ekurzel et al., 1994], and numerical simulation ages [Reilly et al., 1994]. The solid squares on Figure 6 represent the screened interval and the SF<sub>5</sub>CF<sub>3</sub> chronology of this study is in good agreement with the previous measurements.

## 5. Summary and Conclusions

[32] A GC-ECD analytical procedure was developed for determination of environmental concentrations of SF<sub>5</sub>CF<sub>3</sub>, CFC-13, CFC-12, and SF<sub>6</sub> in gases and in gases extracted from groundwater samples. The method was applied to dating of groundwater on the 0–60 year timescale by analysis of headspace gases extracted in the field. The sample collection technique requires about 1 h per sample at spray rates of greater than 1.5 L per minute.

[33] Groundwater dating with SF<sub>5</sub>CF<sub>3</sub> and CFC-13 has not previously been demonstrated but has considerable potential for dating water samples that for various limitations cannot be dated with other CFCs (CFC-11, CFC-12, CFC-113) or SF<sub>6</sub>. SF<sub>5</sub>CF<sub>3</sub> can be used to date young groundwater recharged between 1975 to the present. SF<sub>5</sub>CF<sub>3</sub> is stable under reducing conditions in aquifers and, because there is no terrigenous source of SF<sub>5</sub>CF<sub>3</sub>, many waters that previously could not be dated with SF<sub>6</sub>, because of SF<sub>6</sub> contamination from such sources, can now be dated with SF<sub>5</sub>CF<sub>3</sub>. The solubility of SF<sub>5</sub>CF<sub>3</sub> was determined in water between 1 and 35°C and is about one-half that of SF<sub>6</sub>.

[34] CFC-13 has a dating range of 1965 to modern and, because CFC-13 was used in very specialized ultra-low-temperature refrigeration, it is less likely to exceed air-water equilibrium in groundwaters due to nonatmospheric anthropogenic sources. The atmospheric mixing ratio of CFC-13 is increasing at about 2.5% per year. The atmospheric mixing ratio of SF<sub>5</sub>CF<sub>3</sub> was increasing at about 6% per year between 1970 and 2000; however, the rate of increase in the atmosphere appears to have decreased somewhat after 2000 (Figure 1). In contrast, the mixing ratios of CFC-11, CFC-12, and CFC-113 leveled off or began to decline in the 1990s. Although waters that recharged after about 1990 cannot be accurately dated with CFC-11, CFC-12, or CFC-113, post-1990s water can be dated with SF<sub>5</sub>CF<sub>3</sub>, CFC-13, and SF<sub>6</sub>.

[35] Model groundwater ages calculated with SF<sub>5</sub>CF<sub>3</sub> and CFC-13 are in good agreement with results obtained with other dating techniques. The results calculated with SF<sub>6</sub> and CFC-12 determined by the new analytical procedure are in good agreement with results obtained by the previously established analytical procedures.

## Appendix A

### A1. Field Collection of Gas Samples

[36] Atmospheric gas samples were collected in stainless steel cylinders following the procedure described by Thompson et al. [1985] and Busenberg et al. [1993]. The stainless steel cylinders were equipped with inflow and

outflow stainless steel bellows valves. This design allowed the cylinders to be flushed with a pumped stream of air. In the field the outflow valves and the inflow valves were opened to allow airflow to be pumped through the cylinders for several minutes. After the cylinders were completely flushed with air, the outflow valve was closed and pumping continued in order to pressurize the cylinder to about 2 atmospheres before the inflow valve was closed. Air samples of 60 or 120 cm<sup>3</sup> of were analyzed at the U.S. Geological Survey (USGS) Chlorofluorocarbon Laboratory, Reston, Virginia. (Table A1).

### A2. Extraction of Environmental Tracers From Natural Waters By Spraying Water Into a Headspace

[37] Because of the low concentrations of SF<sub>5</sub>CF<sub>3</sub> and CFC-13 in groundwater, normal purge-and-trap GC-ECD analytical procedures, such as those used for analysis of CFCs [Busenberg and Plummer, 1992] and SF<sub>6</sub> [Busenberg and Plummer, 2000] would require complete extraction from tens of liters of groundwater to obtain sufficient sample for analysis. Collection and transport of such large volumes of water without contamination of the sample is impractical. Therefore in this study, the tracers were extracted from groundwater in the field using a headspace-equilibration procedure [see Busenberg and Plummer, 2000, Appendix A1]. With this procedure, approximately 1 h is required for the headspace partial pressure to equal that of the gas partial pressure in the water sample.

[38] The apparatus used with the headspace spray method is shown in Figure A1a. It consisted of a 0.25 L graduated plastic cylinder that was placed as shown inside a 1 L cylinder. A septum valve was threaded to a small hole in the base of the 0.25 L plastic cylinder (Figure A1a). The larger cylinder was filled with water while septum and cap were not on the valve, allowing the air in the small cylinder to escape as the large cylinder was filled with groundwater. After both cylinders were filled with water, the water flow through the eight spray nozzle tube was initiated. The water flow through the nozzles was maintained for about 3 min before the septum and cap were attached. A gas was injected through the septum with a syringe forming a headspace and exposing the spray nozzles. Several headspace gases were tested including air, He, and N<sub>2</sub>. After equilibration, the headspace gas was removed through the septum of the three-way valve with a 60 mL syringe. The gas sample was injected into an inverted 125 mL bottle in a beaker filled with the same groundwater as shown in Figure A1b, replacing most but not all the water in the bottle. The bottle was capped underwater with an aluminum foil-lined cap. The bottle was dried and the cap was secured with electrical tape and stored upside down. In the laboratory the tape was removed and the bottle was weighed and placed in a beaker filled with water that was stripped with N<sub>2</sub>. The cap was removed underwater. Stainless steel tubing filled with gas-stripped water with a septum at one end was inserted into the bottle and the gas sample was removed with a syringe (Figure A1b). The tubing then was removed and the bottle was capped underwater, dried, and then weighed again to determine the volume of gas in the bottle.

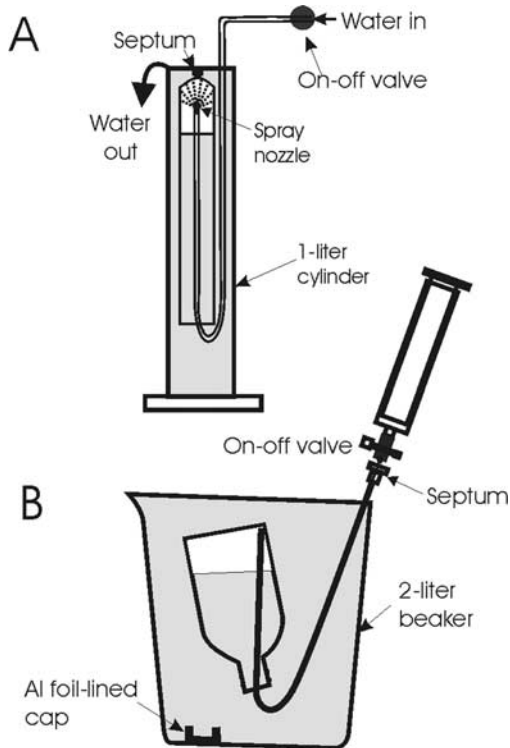
[39] In laboratory experiments, water was sprayed at rates of 2 L/min through eight 0.5 mm diameter nozzles into the

**Table A1.** Concentrations of Six Environmental Tracers Measured in This Study Using Standard Procedures and the New Method<sup>a</sup>

Sample Name	Sampling Date	Elev., m	Exc. Air, cm <sup>3</sup> /kg	Rech T, °C	Field T, °C	CFC-12, pg/kg	CFC-11, pg/kg	CFC-113, pg/kg	SF <sub>6</sub> , fmol/kg	SF <sub>6</sub> , ppt	SF <sub>5</sub> CF <sub>3</sub> , ppt	CFC-13, ppt	CFC-13, Std	SF <sub>5</sub> CF <sub>3</sub> , Std	CFC-12, ppt	CFC-12, Std
KeBe 050	08/23/05	21.3	2.8	7.4	14.7	692.9	3.59	363.3	2.90	95.0	0.07	2.27	0.02	3.79	4.82	0.882
KeBe 052	08/22/05	22.9	2.9	10.8	14.5	749.4	5.92	332.6	5.51	84.1	2.29	1.91	0.02	4.15	4.17	0.111
KeBe 059	11/01/05	21.6	2.4	93.2	14.8	710.7	11.32	363.6	2.52	92.7	0.58	2.10	0.07	4.76	4.34	0.097
KeBe 059	08/23/05	21.6	2.2	10.2	13.5	685.9	3.16	347.8	0.82	87.7	0.53	2.00	0.14	4.85	4.38	0.102
KeBe 061	08/22/05	22.9	2.4	10.6	14.6	624.0	12.82	292.9	6.05	60.7	0.75	0.73	0.03	2.04	3.60	0.070
KeBe 062	08/22/05	18.6	1.8	10.5	13.3	666.3	27.51	328.1	20.93	85.2	5.75	2.23	0.02	4.21	4.17	0.118
KeBe 063	08/23/05	13.7	2.4	10	14.3	512.5	26.90	219.7	16.11	32.6	3.84	0.38	0.01	1.26	1.58	0.17
KeBe 064	08/23/05	13.7	1.7	11.3	16.8	711.1	3.96	309.9	3.58	78.7	1.11	1.10	0.02	2.58	3.86	0.082
KeBe 159	11/01/05	13.7	5.5	13.5	14	5.1	1.70	3.0	0.44	0.0	0.00	0.06	0.00	0.04	0.06	0.01
KeBe 160	11/01/05	13.7	2.9	10.2	14	431.9	2.68	183.3	1.04	19.4	0.29	0.21	0.02	0.32	0.87	0.008
KeBe 160	08/22/05	13.7	3.1	11.1	16.4	390.2	3.46	174.6	2.76	18.5	2.14	0.18	0.02	0.75	0.87	0.026
KeBe 161	08/22/05	13.7	1.5	11.4	14.6	683.6	11.82	308.1	15.88	76.6	3.77	1.00	0.03	2.13	3.37	0.13
KeBe 162	11/01/05	18.6	2	9.9	13.2	170.8	9.78	95.0	6.01	13.3	1.59	0.22	0.01	0.38	0.58	0.14
KeBe 162 air	08/22/05	18.6	1.9	10.1	14.2	156.0	3.45	87.5	3.36	10.7	0.53	0.20	0.01	0.84	0.65	0.06
KeBe 163	11/01/05	18.6	1.6	10.7	13.1	730.2	3.14	330.6	1.62	93.1	0.75	1.32	0.08	2.90	3.71	0.84
KeBe 163	08/22/05	18.6	1.6	10.5	13	713.4	20.18	331.7	11.77	92.8	3.36	1.41	0.01	2.62	3.51	0.48
KeBe 164	11/01/05	21.6	2.8	9.6	13.6	569.4	0.77	247.8	3.73	40.1	1.67	0.32	0.03	0.53	2.46	0.42
KeBe 164	08/23/05	21.6	2.7	9.4	13.6	548.9	6.79	240.1	10.30	38.1	2.37	0.15	0.15	2.10	2.10	0.49
KeBe 165	08/23/05	20.1	2.4	8.8	13.8	646.4	3.94	323.3	4.20	70.5	0.61	0.71	0.03	2.01	4.41	0.43
KeBe 166	08/23/05	20.1	2.3	10.5	13.2	713.1	0.17	354.6	6.89	92.1	0.92	1.96	0.19	3.93	3.63	0.12
KeBe 167	08/23/05	20.1	2.9	8.2	16.1	762.8	13.30	382.9	11.27	101.1	1.83	2.37	0.15	4.26	4.04	0.15
KeBe 206	11/02/05	21.3	2.6	9.9	13.2	680.5	24.61	297.2	16.21	79.4	6.12	0.70	0.01	1.07	3.32	0.01
KeBe 206	08/23/05	21.3	2.5	9.5	14.6	724.5	9.09	303.2	1.05	86.4	0.16	0.76	0.01	2.35	3.44	0.80
KeBe 207	11/02/05	21.3	3.1	11.2	13.4	560.0	4.90	244.8	1.37	52.5	0.40	0.50	0.02	0.50	0.07	0.38
KeBe 208	11/02/05	21.3	2.9	10.4	13.3	400.9	6.92	185.4	4.19	26.1	0.10	0.26	0.00	0.41	0.03	0.31
KeBe 210	11/02/05	21.3	2.5	10.7	13.1	9.0	0.41	4.4	0.54	0.0	0.00	0.06	0.01	0.14	0.15	0.005
Furnace Spr.	07/20/05	1045.5	0.0	7.7	8.3	787.0	6.33	350.5	2.75	95.0	0.54	2.39	0.04	—	5.62	0.41
Lewis Spr.	07/20/05	1011.9	0.2	9.0	9.5	702.4	8.49	354.2	8.56	60.0	49.96	2.26	0.01	—	4.26	0.17
Hudson Spr.	07/20/05	233.2	2	7.7	14.8	196.1	1.02	110.5	5.33	11.6	0.47	2.90	0.08	—	1.00	0.29
Kilmer Spr.	08/17/05	161.5	1.7	10.6	12.7	6530.0	12.00	796.1	4.06	328.9	4.94	10.20	1.10	39.3	3.27	0.91
Dices Spr.	03/08/06	1123			17.6										0.05	0.027
Bolar Spr.	03/08/06	1875			20.4										2.84	0.06
Milford 2 air	10/12/05	61.0	3.1	7	16.2	0.2	0.01	0.0	0.00	0.0	0.00	0.00	0.00	0.30	0.07	0.04
Milford 2 He	10/12/05	61.0	3.1	7	16.2	0.2	0.01	0.0	0.00	0.0	0.00	0.00	0.00	0.02	0.00	0.05
Milford 2 N <sub>2</sub>	10/12/05	61.0	3.1	7	16.2	0.2	0.01	0.0	0.00	0.0	0.00	0.00	0.00	0.01	0.00	0.01
USGS 20	07/05/05	56.4	3	10	12.3	857.6	5.30	373.6	3.20	84.0	2.10	2.53	0.03	—	4.69	0.30

<sup>a</sup>The concentrations shown in the last eight columns of this table were partial pressures measured in the headspace at the stripping temperature and elevation using the new method. The method of Busenberg and Plummer [1992] measures the concentrations of CFCs in water, which are reported as picograms per kilogram (pg/kg). The SF<sub>6</sub> concentrations are also measured in water in the procedure of Busenberg and Plummer [2000] and are reported in femtomoles per kilogram of water (fg/kg). With the new procedure the concentrations are measured in the headspace and are reported in parts per trillion (ppt).





**Figure A1.** (a) Apparatus used for the exchange the dissolved gases in groundwater with a N<sub>2</sub> headspace. The apparatus and procedures for collecting the dissolved gases in groundwater are described in detail in Appendix A2. (b) Also shown is the apparatus and procedures used to transfer samples from the stripping cell into a bottle without contact with air. This procedure also was used to retrieve the samples with a syringe and inject them into the GC.

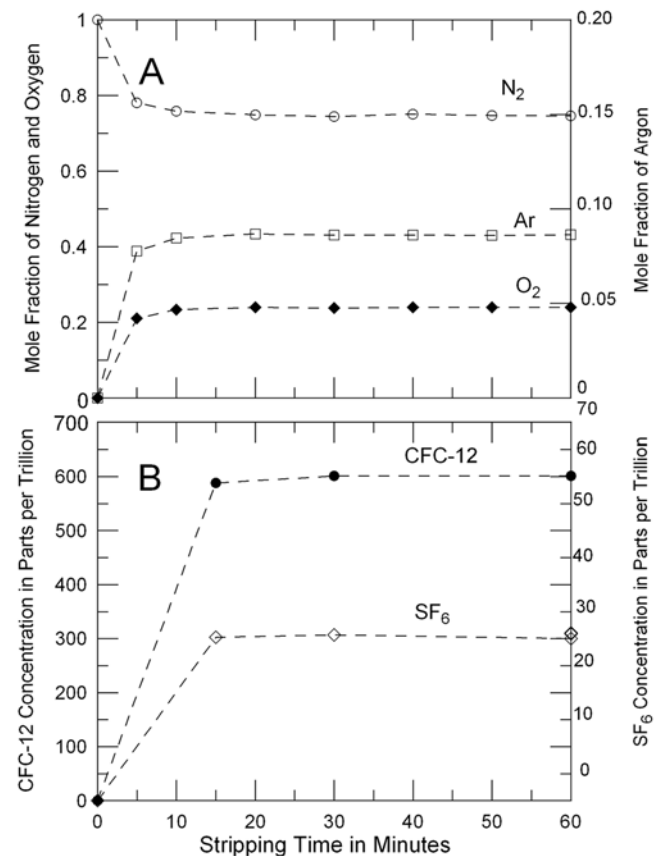
headspace. The composition of the headspace gas was determined by gas chromatography as a function of time. In 10 min or less, equilibrium was reached between dissolved nitrogen, oxygen, and argon (Figure A2a) in the water and the headspace gas. In about 30 min, equilibrium was reached with CFC-12 and SF<sub>6</sub> (Figure A2b). *Busenberg and Plummer* [2000] evaluated the time needed to reach equilibrium with various headspace gases at various spraying rates. Equilibrium with SF<sub>5</sub>CF<sub>3</sub> was reached in 1 h, for samples near the detection limit of SF<sub>5</sub>CF<sub>3</sub> (0.005 ppt; 1970 air). N<sub>2</sub> or He was used as the headspace gas for relatively old samples with low concentrations of SF<sub>5</sub>CF<sub>3</sub>; however, for very young waters, air can be used as the headspace gas which reduces the equilibration time. This equilibration procedure requires spray of at least 120 L of water over a period of about 1 h.

[40] The spray extraction experiments did not reach steady state when (1) the groundwater temperature was significantly different (>10°C) from the groundwater recharge temperature, (2) when the groundwater contained significant amounts of fractionated dissolved excess air (>8 mL/L), and (3) when the groundwater contained a significant excess of N<sub>2</sub> and/or CH<sub>4</sub> [*Busenberg and Plummer*, 2000]. Under these conditions, the headspace volume rapidly increases during the extraction and steady state is never achieved.

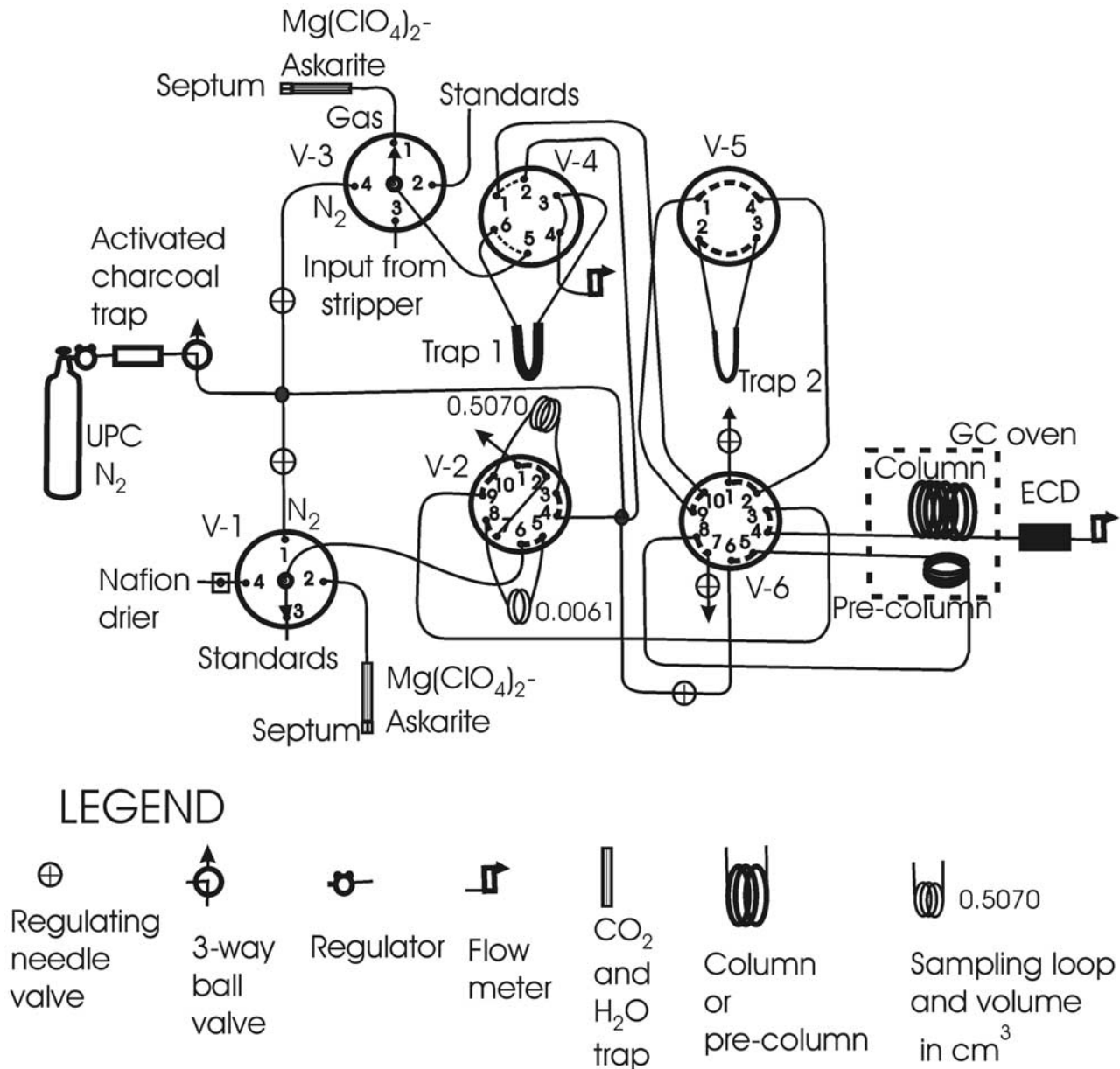
### A3. Measurement of the Environmental Tracers

[41] A commercial GC-ECD is used in the analytical system (Figure A3) and was designed to measure concentrations of SF<sub>6</sub>, CFC-13, SF<sub>5</sub>CF<sub>3</sub>, and CFC-12 in gas samples ranging in volume from 6 μL to hundreds of mL. The high concentration segment of the system includes the sample selector valve V-1, and valve V-2 that has two calibrated loops. Standards, blanks, and samples can be injected into the loops through a Nafion<sup>®</sup> drier or a trap that removes both water and CO<sub>2</sub>. The sample can be directly injected into the analytical column or the sample can be trapped in trap 2 (V-5) cooled to -70°C in an ethanol-dry ice bath. After trapping, trap 2 is closed and heated to 95°C. The sample then is injected into the precolumn and column by first turning valve V-6 followed by opening the trap. Trap 2 is 15 cm long with an outer diameter (OD) of 0.3175 cm and is packed with 6 cm of Porasil C<sup>®</sup> and 6 cm of Porapak T<sup>®</sup> separated with glass wool.

[42] Environmental concentrations of the tracers are injected into the analytical system through selector valve V-3. Air and headspace samples are injected by syringe through a trap that removes both the moisture and CO<sub>2</sub>. The water stripping system used for SF<sub>6</sub> analysis [*Busenberg and Plummer*, 2000] can be attached to input 3 of V-3 when



**Figure A2.** (a) Mole fraction of N<sub>2</sub>, O<sub>2</sub> and Ar in the headspace as a function of the stripping time. A steady state composition was achieved in the headspace in about 10 min. (b) Also shown is the mole fraction of CFC-12 and SF<sub>6</sub> as a function of the stripping time. A steady state composition was achieved in the headspace in about 20 min at a flow rate of 2 L/m.



**Figure A3.** Apparatus used to measure environmental concentrations of the four tracers in air and groundwater samples. See Appendix A3 for a detailed description of the system.

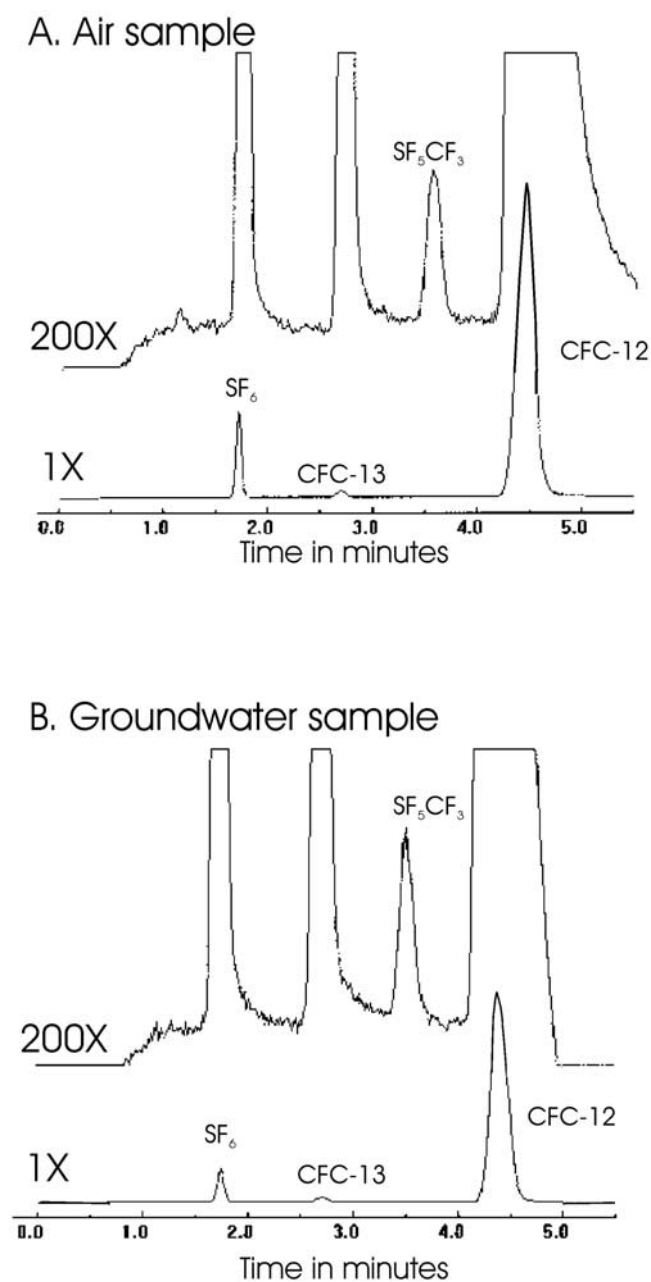
needed. The tracers are trapped on a 1 m, 0.3175 cm OD stainless steel trap packed with Porapak Q<sup>®</sup> immersed in an ethanol-dry ice bath at  $-70^{\circ}\text{C}$ . After trapping the sample in Trap 1, V-3 is turned to position 4 which allows N<sub>2</sub> to pass through the trap at 60 cm<sup>3</sup> per minute for 2 min to remove all the trapped O<sub>2</sub>. Valve V-3 is turned and Trap 2 is opened. Trap 1 then is placed in 95°C water releasing the tracers which then are transferred to the  $-70^{\circ}\text{C}$  cooled trap 2. This step transfers the tracers from the larger to the smaller trap in about 1 min. Trap 2 is closed, placed in 95°C water, V-6 is turned, and then trap 2 is opened, injecting the tracers through the pre-column into the column and the electron capture detector. V-6 is turned after 45 s, flushing out the highly retentive VOCs. Both the pre-column and column are of 0.3175 cm OD stainless steel tubing; all other tubing of the system is 0.158 cm OD stainless steel. The pre-column is

30 cm long and packed with washed 60–80 mesh 5 angstrom molecular sieve (Alltech). The column is 3 m long and packed with 60–80 mesh Carboxograph 1AC coated with 1% AT-1000 (Alltech). The ultra pure N<sub>2</sub> carrier flow is 30 cm<sup>3</sup> per minute. The GC oven is maintained at 65°C and the ECD at 265°C. The analytical time is 6 min per sample. The data are given in Table A1.

[43] Recently, *Rosiek et al.* [2007] published a GC-based procedure using a special homemade modulator-detector system with two ECDs for measuring SF<sub>5</sub>CF<sub>3</sub> in 200 cm<sup>3</sup> of air. The detector system is not commercially available.

#### A4. Calibration of Standards

[44] The instrument was calibrated using a blank and various volumes of a NOAA standard air with known



**Figure A4.** (a) Chromatogram of 120 cm<sup>3</sup> of 2006 air from Big Meadows Air Monitoring Station, Shenandoah National Park, Virginia. The amounts injected were  $3.2 \times 10^{-14}$ ,  $2.1 \times 10^{-14}$ ,  $8.8 \times 10^{-16}$ , and  $2.8 \times 10^{-12}$  moles of SF<sub>6</sub>, CFC-13, SF<sub>5</sub>CF<sub>3</sub>, and CFC-12, respectively. (b) Also shown is a chromatogram of a young groundwater sample from Locust Grove, Maryland.

CFC-12 and SF<sub>6</sub> concentrations. A gravimetric standard was prepared in house from pure SF<sub>5</sub>CF<sub>3</sub> and SF<sub>6</sub> and diluted with ultrapure N<sub>2</sub>. The SF<sub>6</sub> was added to check the prepared standard with a 1000 ppt Scott Master Gas Standard. The concentrations of the SF<sub>5</sub>CF<sub>3</sub> were calculated in archived air standards and were consistent with the atmospheric mixing ratios of SF<sub>5</sub>CF<sub>3</sub> reported by *Sturges et al.* [2000a]. There are no commercial gas standards of SF<sub>5</sub>CF<sub>3</sub> or CFC-13. Since there is no primary CFC-13 standard, an atmospheric mixing

ratio of 4 ppt in 1998 clean air [*IPCC, 2001*] was assumed, and all measurements were normalized to this 1998 clean air mixing ratio.

#### A5. Precision and Accuracy of Measurements

[45] Standard deviations of about 3 percent were routinely obtained for repeated measurements of standards. The calibrations were nearly linear within the measuring range. The analytical precision of the water analyses was about 20 percent near the detection limit of about 0.005 ppt of SF<sub>5</sub>CF<sub>3</sub> in 1970 air and about 5 percent for groundwater recharged after 1985. Chromatograms from the GC-ECD system of an air sample and a groundwater sample are shown in Figures A4a and A4b.

#### A6. Determination of the Solubility of SF<sub>5</sub>CF<sub>3</sub> in Water

[46] The solubility of SF<sub>5</sub>CF<sub>3</sub> was measured in water between 1.0 and 35.2°C at 1 atmosphere total pressure using a static headspace method similar to the procedure described by *Robbins et al.* [1993]. Approximately 20 L of ultrapure water was stripped with N<sub>2</sub>, and then small volumes of SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> were bubbled through the solution. The SF<sub>6</sub> measurements were used to check the validity of the procedure by comparison with the previous determinations of SF<sub>6</sub> solubility [*Bullister et al.*, 2002]. The solution was stirred and homogenized, and then various volumes (20 to 40 mL) were transferred into 60 mL vials. The volume of the solution was determined by weight. The solution in the vials was equilibrated with the N<sub>2</sub> headspace in temperature-controlled baths. After equilibration of the solution with the headspace, the concentrations of SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> were determined in the headspace gas. The headspace gas was then replaced with N<sub>2</sub> and the solution reequilibrated with the headspace and the two tracers were again measured in the headspace. From these two sets of measurements, Henry's law constants were determined as a function of temperature. Five to 11 determinations were made at each temperature.

#### A7. Stability of SF<sub>5</sub>CF<sub>3</sub> and SF<sub>6</sub> in Anoxic Soils

[47] Four sets of experiments were performed to evaluate the potential for microbial degradation of SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> in closed systems of soils and organic-rich lake sediments. The samples consisted of a sandy forest soil collected in Reston, Virginia (USGS); a tan mud from Lake Newport (LN), Reston, Virginia; a dark gray mud from Julian's Pond (JP), Lovettsville, Virginia. The USGS, LN, and JP samples contained 3.65, 0.39, and 1.21 percent carbon (dry weight), respectively. The nitrogen concentrations for the USGS, LN, and JP samples were 0.13, 0.04, and 0.09 percent, respectively. Fifteen grams of air-dried soil and 21 g of wet LN and JP sediments were placed in 160 ml bottles which were first purged with N<sub>2</sub> and then filled with N<sub>2</sub> gas containing SF<sub>5</sub>CF<sub>3</sub> and SF<sub>6</sub>. Three sets of control blanks were prepared similarly but without addition of sediments. Each set of points were obtained from a fresh set of bottles. The 160 ml bottles were discarded after sampling of the headspace for SF<sub>5</sub>CF<sub>3</sub>, SF<sub>6</sub>, and dissolved gases.



## A8. Effects of Excess Air Concentrations, Differences in Recharge, and Stripping Temperatures on the Composition of the Headspace Gas and Model Recharge Ages

### A8.1. Equilibrium Between the Headspace and Water Containing Unfractionated Excess Air

[48] When the excess air is not fractionated, the total moles ( $n_i^T$ ) of a gas  $i$  in water is given by the equation:

$$n_i^T = n_i^E + n_i^A, \quad (\text{A1})$$

where the superscripts  $T$ ,  $E$ , and  $A$  represent total, equilibrium, and excess air, respectively. Molal concentration,  $C_i$ , is expressed as  $n_i/\text{kg H}_2\text{O}$ . The equilibrium concentration of any gas dissolved in water is given by:

$$C_i^E = K_i^E x_i^E (P^E - P_{\text{H}_2\text{O}}^E), \quad (\text{A2})$$

where  $K_i^E$  is Henry's law constant at the recharge temperature,  $x_i^E$  is the mole fraction of the  $i$ th gas,  $P$  is the total pressure, and  $P_{\text{H}_2\text{O}}^E$  is the vapor pressure of water.

[49] The total pressure varies as a function of elevation and vapor pressure of water which is temperature dependent. The moles per kg of water of gas  $i$  from the dissolved excess air,  $C_i^A$ , is

$$C_i^A = x_i^A V^A / 22414, \quad (\text{A3})$$

where  $V^A$  is the volume of unfractionated excess air,  $\text{cm}^3/\text{kg H}_2\text{O}$ . Equation (1) becomes

$$C_i^T = K_i^E x_i^E (P^E - P_{\text{H}_2\text{O}}^E) + x_i^A V^A / 22414, \quad (\text{A4})$$

which can be simplified in the case of complete dissolution of the excess (unfractionated) air because  $x_i^E = x_i^A$ :

$$x_i^E = \frac{C_i^T}{K_i^E (P^E - P_{\text{H}_2\text{O}}^E) + V^A / 22414}. \quad (\text{A5})$$

Equation (A4) is used to correct for the presence of unfractionated excess air when the concentration of the tracer is measured in groundwater, and the recharge date is determined by comparing  $x_i^E$  to the atmospheric mixing ratios.

[50] With the stripping method (Appendix A2), the partial pressure of tracer  $i$  is measured at the stripping temperature and if the recharge temperature is the same as the stripping temperature, steady state is approached between the groundwater and the headspace gas. The mole fraction of gas  $i$  in the headspace gas of the stripping chamber,  $S$ , can be written as:

$$x_i^S = \frac{C_i^T}{K_i^S (P^S - P_{\text{H}_2\text{O}}^S)}. \quad (\text{A6})$$

Rearranging and combining with equation (A5), where  $S$  refers to the stripping method (Appendix A2), we obtain:

$$x_i^S (P^S - P_{\text{H}_2\text{O}}^S) K_i^S = x_i^E (P^E - P_{\text{H}_2\text{O}}^E) K_i^E + x_i^A V^A / 22414, \quad (\text{A7})$$

and solving for ( $x_i^E = x_i^A$  for the UA model):

$$x_i^E = \frac{x_i^S (P^S - P_{\text{H}_2\text{O}}^S) K_i^S}{[(P^E - P_{\text{H}_2\text{O}}^E) K_i^E + V^A / 22414]}. \quad (\text{A8})$$

[51] Having independently determined recharge temperature and  $V^A$  from additional dissolved gas measurements such as N<sub>2</sub>-Ar, N<sub>2</sub>-Ar-Ne data and measured  $x_i^S$ , equation (A8) is solved for  $x_i^E$ . Apparent age is then determined by comparing  $x_i^E$  to the historical atmospheric mixing ratios.

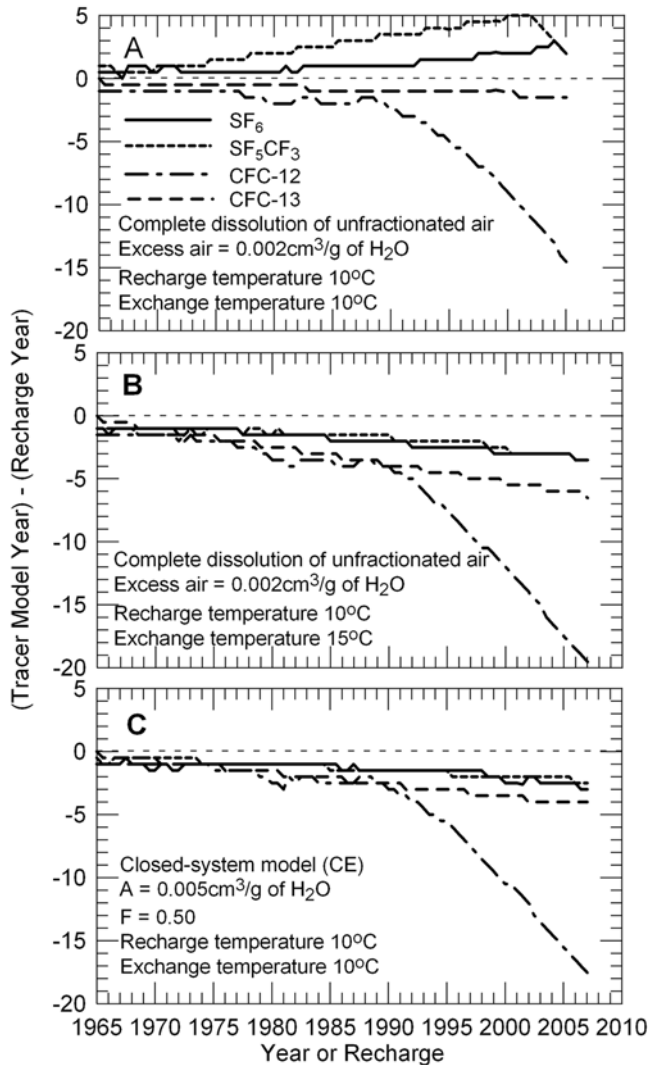
[52] In the derivation of the above equations it was assumed that equilibrium was reached between the headspace and the groundwaters at the stripping temperature and pressure, that the groundwaters were not mixtures, the excess air component was introduced at the time of recharge, that the excess air was completely dissolved, and that the composition of the gas at the water table at recharge was the same as that of the atmosphere at the time of recharge. If no excess air was present and the groundwater and the stripping temperatures were the same, then all the environmental trace gases will give the same piston flow ages. All tracers will give the same model ages when unfractionated excess air is present and the excess air is included in the calculations. If the presence of the excess air is not considered, the apparent tracer model ages will be different from the model piston-flow recharge ages of the groundwater. The trace gases that are less soluble than the major atmospheric gases (Figure 3b) will be enriched in the headspace while trace gases that are more soluble than the major atmospheric gases will be depleted in the headspace (Figure A5a). Figure A5b shows the differences in the recharge and model tracer ages when both the excess air and difference between the recharge and exchange temperature are not considered in the calculation of the apparent tracer ages using the equilibrium exchange model (equation (A8)).

### A8.2. Fractionated Excess Air

[53] If the dissolved air is fractionated, then an excess air correction volume is multiplied by a factor  $f$  to correct for fractionation,

$$f = \frac{n_i^D}{n_i^A} \quad (\text{A9})$$

where  $n_i^D$  is the moles of the  $i$ th component in the excess air that was dissolved in a kilogram of water and  $n_i^A$  is the moles of the  $i$ th component in the same volume of unfractionated air, for unfractionated excess air  $f = 1$ . At the other extreme,  $f = 0$ , all of the excess air is lost and the model defaults to the UA model with zero excess air.



**Figure A5.** (a) Difference in years between the tracer model age from the recharge year when the excess air present in the groundwater was not used to calculate the model tracer age. The groundwater contained 0.002 cm<sup>3</sup>/g of unfractionated excess air. The trace gases that are less soluble than the major atmospheric gases are enriched in the headspace and give apparent younger model ages. The program calculates the age of groundwaters to the nearest 0.5 years. The large difference between the post-1990s CFC-12 model dates and the recharge dates is due to the leveling off in the post-1990s atmospheric mole fraction of CFC-12. (b) The exchange conditions are similar to Figure A5a except in this case the stripping temperature was 5°C warmer than the groundwater recharge temperature. (c) This figure shows the error introduced in the model recharge age when fractionated excess air that was present in the groundwater was not included in the calculation of the tracer model ages. In this example, 0.005 cm<sup>3</sup>/g of air was trapped and half of the trapped air ( $F = 0.50$ ) dissolved in the groundwater.

[54] In general, the contribution of the fractionated excess air is  $fV^A/22414$ , and the equilibrium exchange model (equation (A8)) can be written as:

$$x_i^E = \frac{x_i^S K_i^S (P^S - P_{H_2O}^S)}{[K_i^E (P^E - P_{H_2O}^E) + (fV^A/22414)]}. \quad (\text{A10})$$

[55] The fractionation factors can be calculated from the CE model of *Aeschbach-Hertig et al.* [2000]. The above equations can be used when the headspace volume remains constant or the volume change is small maintaining equilibrium between the water and headspace during the extraction procedure.

[56] The fractionation factor  $f$  for every one of the tracers must be evaluated and are needed to correctly solve equation (A10). Various models that can be used to evaluate fractionation factors for the tracers are given in the next section.

### A8.3. Gas Exchange Between a Headspace With Water Containing Fractionated Excess Air

[57] Several models of fractionation of excess air have been introduced [*Stute et al.*, 1995; *Aeschbach-Hertig et al.*, 2000; *Kipfer et al.*, 2002]. In the partial reequilibration model of *Stute et al.* [1995], the initial excess air composition is modified at the water table through the preferential loss of the lighter gases. In the closed-system equilibration (CE) model of *Aeschbach-Hertig et al.* [2000], the volume of the trapped gas bubbles is reduced by partial dissolution of the bubbles by the hydrostatic pressure. This model is described by the equation:

$$c_i^A = \frac{(1-F)Ax_i}{1 + FAx_i/c_i^E}, \quad (\text{A11})$$

where  $c_i^E$  and  $c_i^A$  are the equilibrium and excess air concentrations of gas  $i$  in cm<sup>3</sup>/g of water.  $F$  is equal to  $\nu/q$  where  $\nu$  is the ratio of final to initial of entrapped gas volumes and  $q$  is ratio of dry gas pressure to the pressure of the atmosphere. The term  $A$  is the initial volume of entrapped air per mass of water in cm<sup>3</sup>/g of H<sub>2</sub>O. The results of the CE model approach those of the UA model as the fractionation parameter,  $F$ , approaches 0. For the condition  $F = 0$ , the excess air volume  $A^V$  (UA model) is equal to  $A$  (CE model); for all other conditions  $A > A^V$ .

[58] Figure A5c shows the differences between the recharge age and the apparent tracer ages if the fractionation of the excess air is not considered. In this case 0.05 cm<sup>3</sup>/g of air was trapped and half of the trapped gas ( $F = 0.5$ ) was dissolved as excess air. This figure shows the error in years that will result in the tracer ages if the presence of fractionated air is not included in the calculations of the tracer piston-flow ages.

### A8.4. Steady State Exchange Between a Headspace With Water

[59] In many cases, the volume of the headspace gas changes significantly during the extraction procedure, but a steady-state concentration of the  $i$ th component is eventually reached. The moles of  $i$  released into the headspace ( $n_i^G$ )

for any given time is the difference between the moles of  $i$  in the groundwater ( $n_i^E + n_i^A$ ) and the moles of  $i$  removed by the stripped water ( $n_i^S$ ).  $V^L$  is volume (in liters) of water stripped for any given time. The mass balance equation describes moles of  $i$  released into the headspace:

$$n_i^G = (n_i^E + n_i^A) - n_i^S \quad (\text{A12})$$

where  $n_i^E$  and  $n_i^A$  are the recharge equilibrium and excess air moles of  $i$  in the water, respectively. If the stripped water leaving the cell is in equilibrium with the headspace gas composition, then:

$$n_i^G = V^L \cdot \left\{ \left[ x_i^E (P^E - P_{H_2O}^E) K_i^E + V^A / 22414 \right] - x_i^S (P^S - P_{H_2O}^S) K_i^S \right\} \quad (\text{A13})$$

The moles gas released into the headspace at any given time is

$$n_i^G = \frac{(P^S - P_{H_2O}^S) x_i^S V^G}{RT^S} \quad (\text{A14})$$

where  $V^G$  is the volume of the gas (in liters) released into the headspace for any given stripping time. Combining equations (A13) and (A14), and simplifying them we obtain

$$x_i^E = \frac{\left[ x_i^S V^G (P^S - P_{H_2O}^S) \right] / V^L RT^S + x_i^S K_i^S (P^S - P_{H_2O}^S)}{K_i^E (P^E - P_{H_2O}^E) + (fV^A / 22414)} \quad (\text{A15})$$

The factor  $f$  is a fractionation correction for the excess air composition.

[60] The gas fractionation model of *Brown* [2004], corrected for temperature, pressure, and excess air concentrations was also tested. *Brown's* model assumes that the gas released from the water into the gas phase is fractionated. The fractionation is large at low flow rates but becomes insignificant at the high flow rates similar to those used in this study. Most of the results obtained with *Brown's* model for high  $V^L$  gave comparable results to those obtained with equation (A15). *Brown's* model fails when  $P^S$  is less than  $P^E$ . However, the steady state model described by equation (A15) was found to fit all the data obtained in this study.

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