Dating young groundwater with sulfur hexafluoride: Natural and anthropogenic sources of sulfur hexafluoride

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Abstract. Sulfur hexafluoride (SF_6) is primarily of anthropogenic origin but also occurs naturally. The troposphere concentration of SF_6 has increased from a steady state value of 0.054 ± 0.009 to more than 4 parts per trillion volume during the past 40 years. An analytical procedure was developed for measuring concentrations of SF_6 to less than 0.01 fmol/L in water. Groundwater can be dated with SF_6 if it is in equilibrium with atmospheric SF_6 at the time of recharge and does not contain significant SF_6 from other sources. The dating range of SF_6 is currently 0 to 30 years. The tracer was successfully used to date shallow groundwater of the Atlantic Coastal Plain sand aquifers of the United States and springs issuing near the top of the Blue Ridge Mountains of Virginia. Significant concentrations of naturally occurring SF_6 were found in some igneous, volcanic, and sedimentary rocks and in some hydrothermal fluids.

1. Introduction

SF_6 is a colorless, odorless, nonflammable, nontoxic, stable gas with excellent electrical insulating and arc-quenching properties. It is mainly used as an electrical insulator in high-voltage switches and transformers and as a blanket gas in the melting operations of magnesium metal production [*Maiss and Brenninkmeijer*, 1998]. Industrial production of SF_6 began in 1953 with the introduction of SF_6-filled electrical switches, and annual production has increased from nearly zero in 1953 to 85,700 t of SF_6 in 1995 [*Ko et al.*, 1993; *Maiss and Brenninkmeijer*, 1998]. SF_6 is released to the atmosphere predominantly in the middle latitudes of the Northern Hemisphere and is subsequently incorporated into the hydrosphere. The SF_6 atmospheric mixing ratio has rapidly increased because of (1) the long lifetime in the atmosphere, with estimates of 1935 [*Patra et al.*, 1997] to 3200 [*Ravishankara et al.*, 1993] years, (2) the low solubility of the tracer in water [*Ashton et al.*, 1968; *Cosgrove and Walkey*, 1981; *Mroczek*, 1997], (3) the apparent high stability in soils [*Maiss and Brenninkmeijer*, 1998], and (4) the lack of other significant natural sinks [*Maiss and Brenninkmeijer*, 1998]. The SF_6 atmospheric mixing ratio increased from 0.6 parts per trillion volume (pptv) in 1976 [*Maiss and Brenninkmeijer*, 1998] to more than 4 pptv in 1999.

SF_6 received significant recent interest because of its high greenhouse-warming potential, which was estimated to be 23,900 times that of CO_2, the highest value measured for any gas [*Intergovernmental Panel on Climate Change*, 1995]. It was one of the gases covered by the Kyoto Protocol to the United Nations Framework Convention on Climate Change (access address http://www.unfccc.de/resource/docs/convkp/kpeng.html). Production and release controls for SF_6 are expected to be set after the protocol is ratified by at least 55 counties; these controls, however, will become applicable only for developed countries. Atmospheric concentrations of SF_6 are expected to continue to increase into the 21st century [*Ko et al.*, 1993].

SF_6 has been extensively used in many studies as a natural

atmospheric tracer [*Lovelock and Ferber*, 1982; *Levin and Hesshaimer*, 1996; *Patra et al.*, 1997; *Geller et al.*, 1997; *Hall and Waugh*, 1998; *Zahn et al.*, 1999]. The gas has been injected into the oceans to determine longitudinal dispersion, diapycnal and isopycnal diffusion, and mixing [*Ledwell et al.*, 1986; *Watson et al.*, 1987; *Ledwell and Watson*, 1988, 1991; *Watson et al.*, 1991; *Law et al.*, 1998; *Ledwell et al.*, 1998] and air-sea gas exchange and dispersion [*Watson et al.*, 1991; *Wanninkhof*, 1992; *Wanninkhof et al.*, 1993, 1997; *Asher and Wanninkhof*, 1998]. SF_6 has been used to study longitudinal dispersion, gas exchange, and mixing in lakes, rivers, and estuaries [*Wanninkhof et al.*, 1985, 1987; *Clark et al.*, 1994; *Maiss et al.*, 1994a, 1994b; *Clark et al.*, 1996; *Cole and Caraco*, 1998; *Hibbs et al.*, 1999]; in the study of soil venting [*Olschewski et al.*, 1995]; and as a hydrologic tracer [*Wilson and Mackay*, 1993; *Upstill-Goddard and Wilkins*, 1995; *Wilson and Mackay*, 1995, 1996].

Because of its high rate of increase in the atmosphere (7% per year), its known atmospheric history [*Maiss et al.*, 1996; *Geller et al.*, 1997; *Maiss and Brenninkmeijer*, 1998], its apparent stability in soils [*Maiss and Brenninkmeijer*, 1998], and the relatively simple analytical and sampling procedures [*Wanninkhof et al.*, 1991; *Busenberg and Plummer*, 1997], SF_6 is being studied as a potential environmental tracer for dating young groundwater [*Busenberg and Plummer*, 1997; *Plummer and Busenberg*, 1999]. SF_6 appears to be resistant to biodegradation and does not significantly sorb onto organic matter [*Watson et al.*, 1991; *Wilson and Mackay*, 1996] or significantly degrade under highly reducing conditions, as is the case with chlorofluorocarbons [*Plummer and Busenberg*, 1999]. Contamination of urban groundwaters with SF_6 is less likely than contamination with CFCs, because SF_6 is not present in any commonly used household product, though *Ho and Schlosser* [2000] reported significant excess of SF_6 in air from the New York City vicinity. In addition, SF_6 does not readily sorb into rubber and polymers; therefore groundwater is less likely to be contaminated with SF_6 from contact with these materials during sampling [*Reynolds et al.*, 1990; *Wilson and Mackay*, 1995]. Dating of young groundwater with SF_6 can, in some instances, be complicated by the presence of a natural background source of SF_6 [*Busenberg and Plummer*, 1997; *Harnisch and Eisenhauer*, 1998] and by addition of excess air during recharge.

A

WATER STRIPPING SYSTEM
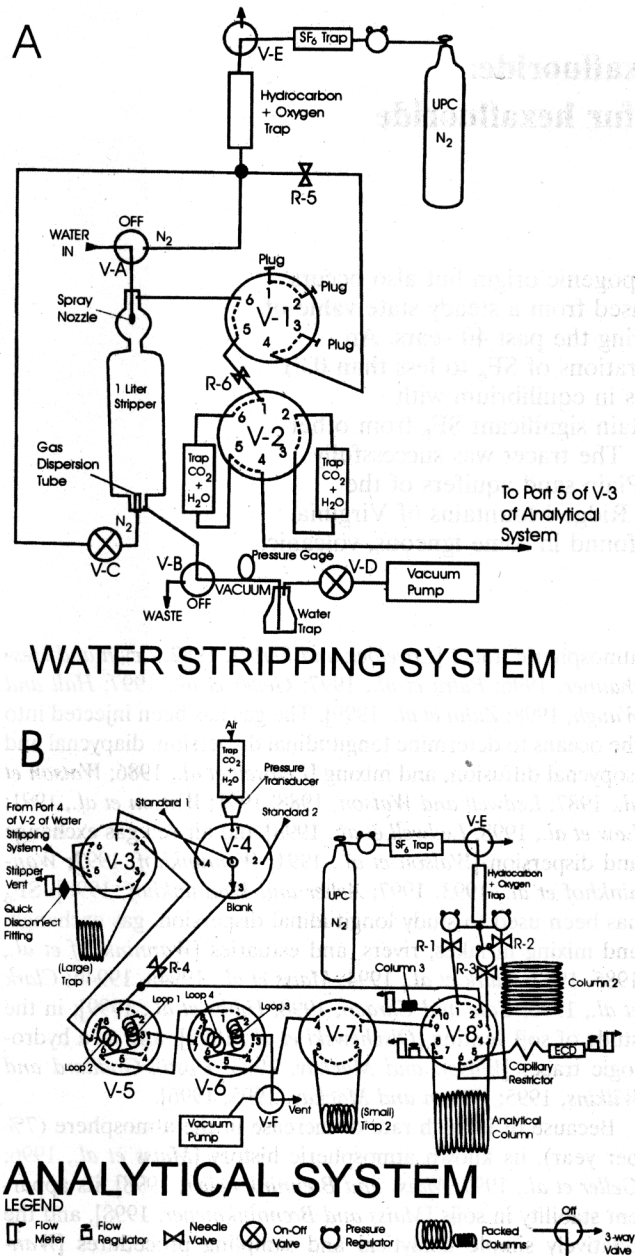
B

ANALYTICAL SYSTEM

LEGEND

Figure 1. (a) Schematic of apparatus used for the vacuum extraction of SF$_6$ from groundwater (see text). (b) Schematic of apparatus used to measure environmental concentrations of SF$_6$ (see text).

2. Methods

The low atmospheric mixing ratio of SF$_6$ and its low solubility in water complicate the analytical methodology of measuring environmental concentrations of SF$_6$ in groundwater. The concentration of SF$_6$ in the 1999 troposphere was approximately 20 times less than the concentration of CFC-113 and was more than 130 times less than the concentration of CFC-12. Consequently, relatively large volumes of groundwater are needed to extract a sufficient amount of the tracer for analysis. Four procedures were investigated for sampling environmental concentrations of SF$_6$ in groundwater. The simplest and most useful of these is given below, and the others, which have some

potential field applications, are summarized briefly in Appendix A.

2.1. Field Collection of Water Samples

The preferred sampling method was the collection of groundwater in 2.5- or 4-L plastic-coated glass bottles (see Appendix A and Figure 16a). The water in-flow tube was placed in the bottom of the bottle displacing the air with water. After at least 3 L of overflow, the tube was slowly removed. The bottles were sealed with screw caps with conical liners without headspace. The cone liners in the caps allowed for some expansion of the water on warming. However, caps were slightly loosened periodically to prevent the glass bottles from breaking when the groundwater temperature was significantly lower than the ambient air temperature. The analysis was performed in a laboratory near the sampling site or the bottles were shipped to the U.S. Geological Survey (USGS) laboratory in Reston, Virginia, for analysis.

2.2. Field Collection of Gas Samples

Gas samples were collected in stainless steel cylinders using 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. The cylinders were filled with pressurized SF$_6$-free N$_2$ in the laboratory prior to sampling. In the field the ultrapure N$_2$ was released by opening the outflow valves, then the inflow valves were opened to allow airflow through the cylinders for several minutes. After the cylinders were completely flushed with air, the outflow valves were closed, and pumping continued in order to pressurize the cylinder to about 2 atm before inflow valves were closed. Alternatively, gas samples were collected in 100-mL borosilicate glass ampoules using procedures developed for sampling gases for CFC analysis [*Busenberg and Plummer*, 1992]. The gas samples were heat sealed in the borosilicate glass ampoules with a torch. The cylinders and ampoules were returned and analyzed at the USGS laboratory.

2.3. Extraction of SF$_6$ From Natural Waters

The apparatus used for vacuum extraction of SF$_6$ from groundwater (Figure 1a) was similar to the system described by *Law et al.* [1994] and *Wanninkhof et al.* [1991]. The apparatus consisted of a 1-L glass stripping vessel and various valves that controlled the flow of gases, water, and the vacuum. First, valves V-1, V-A, and V-C were turned to the closed positions, then V-B was turned to the vacuum position and V-D was opened. A high vacuum was pulled into the 1-L gas stripper cylinder. The stripper was isolated from the vacuum by closing of valves V-B and V-D. The water sampling tube, a 3.2-mm OD copper tube, was placed in the bottle, and V-A was turned from the off position to the water-in position. The water intake tube was slowly lowered into the bottom of the 2.5- or 4-L bottle. The vacuum in the stripping cylinder pulled the water in and sprayed the water into the vessel through six nozzles. After about 100 mL of water was sprayed into the vessel, valve V-A was turned into the N$_2$ position, and the stripper was pressurized with SF$_6$-free N$_2$. The N$_2$ pressure expelled the water to waste from the stripper when V-B was turned from the off to the waste position. This procedure cleaned the intake tube and valves and prevented carryover of SF$_6$ from the previous sample. The stripper was then reevacuated. One liter of water was

sprayed into the cell; the vacuum spraying of the sample extracted about 90% of the SF_6 from the water. N_2 was introduced at the bottom of the stripper through a stainless steel gas-dispersion tube when valve V-C was slowly opened. After the stripper was pressurized with N_2, V-1 was turned allowing the N_2 and stripped SF_6 to pass through the Ascarite-magnesium perchlorate drier, and then the SF_6 was trapped on a 60-cm 3.2-mm OD Porapak Q trap (Figure 1b). The CO_2, H_2S, and H_2O trap were replaced when exhausted without interruption of the analysis by means of valve V-2. The SF_6 trap was precooled to a temperature of between $-70°$ and $-79°C$ in a dry ice and isopropyl alcohol mixture. After exactly 6 min of stripping at precisely 250 mL/min, the trap was switched from the stripping system to the analytical system by turning valve V-3. The stripping cell was emptied and prepared for the next sample.

A large volume of N_2 was needed to efficiently strip the SF_6 from the 1-L of water; however, breakthrough of SF_6 occurred on short Porapak Q traps; thus a longer trap (60 cm) was used to quantitatively trap the SF_6. To significantly improve the chromatography of SF_6, the sample was transferred from the 60-cm trap into the 10-cm precooled trap by placing the 60-cm trap in 95°C water. The transfer was completed in 1 min, trap 2 was isolated from the carrier flow by turning valve V-7, and then trap 1 was switched from the analytical system to the water stripping system by turning valve V-3. Trap 1 was cooled and was prepared to receive the next sample.

2.4. Extraction of SF_6 From Minerals and Rocks

An apparatus was constructed to extract gases from fluid inclusions in rocks and minerals (Figure 2a) and inject the trace gas into the SF_6 analytical system, which consisted of a 1.9-cm OD and 35-cm-long stainless steel cylinder that was attached as shown to three-way valve. Samples were crushed to pieces of 0.5 cm or smaller and dried overnight at 125°C. The samples were placed in the cylinder and then were heated to 250°C with a heating tape, and the system was evacuated for at least 30 min. The system was isolated from the vacuum by closing valve V-H, and the vacuum was monitored with a pressure transducer. If no pressure changes were observed, V-G was turned allowing ultrapure carrier (UPC) grade N_2 to enter the cylinder with the sample. The gas was pulled through V-G and V-H and through the precooled large SF_6 trap, providing a sample blank. The system was then again evacuated, V-G was closed, and V-G and the cylinder were disconnected from the system by releasing the two quick-disconnect fittings. The heating tape was removed, and the sample in the stainless steel tube was crushed to a fine powder with a large vise. The tube was reattached to the apparatus, the system was evacuated and isolated from the vacuum, and then V-G was opened to the system. The change in pressure was recorded; the heating tape was rewrapped around the crushed stainless steel tube which was heated to 250°C for at least 30 min or more, until no further pressure changes were observed. N_2 was added to the stainless steel tube containing the crushed sample through valve V-G. The SF_6 released from the powdered sample was collected on trap 1. The volume of the system was determined after each run by connecting V-H to a known volume of gas at atmospheric pressure and observing the drop in pressure, and the unknown volume was calculated from the gas law. Calibration with SF_6 was performed by injecting known volumes of standards through the injection port and into the evacuated cylinder, trapping and then measuring the concentrations.
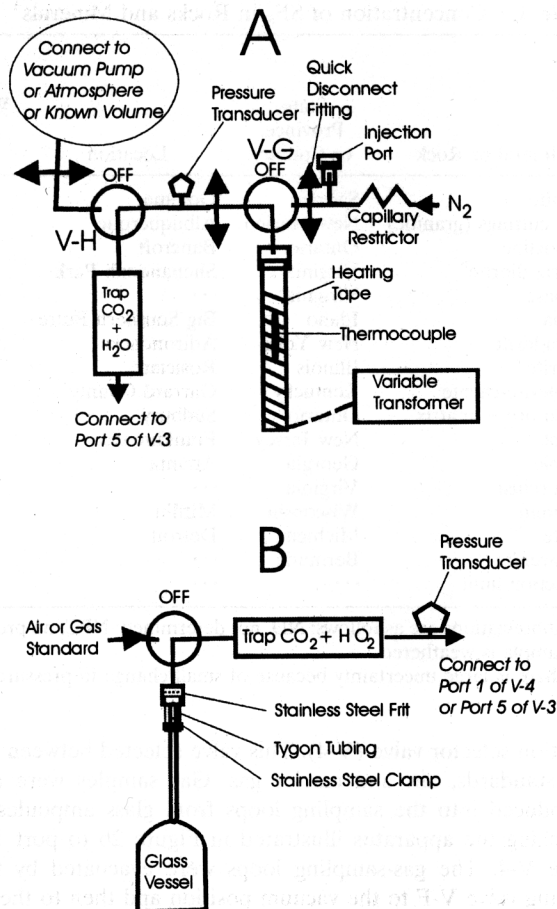

Figure 2. (a) Schematic of apparatus used to extract SF_6 from rocks and minerals (see text). (b) Diagram showing apparatus used to sample gases sealed in glass ampoules (see text).

2.5. Measurement of SF_6

The analytical system (Figure 1b) bears similarities to other analytical instruments used to measure SF_6 [*Law et al.*, 1994; *Wanninkhof et al.*, 1991; *Maiss et al.*, 1994a]; however, most analytical systems described in the literature were inadequate for the routine measurement of very low concentrations of SF_6 normally found in groundwater. Modifications were made to control flow and improve the regulation of the carrier pressure. The analytical system (Figure 1a) was modified to allow the stripping of 1 L of water. The design of the gas distribution system was critical for obtaining good chromatograms from very small signals that were obtained from natural levels of SF_6.

UPC grade N_2 was used throughout the system. The carrier gas was purified with a charcoal and a hydrocarbon-O_2 trap. The pressure of the gas was controlled with four ultraclean pressure regulators, and the flow was adjusted by three needle valves. Additional pressure and flow regulation was achieved by using dummy columns and a capillary restrictor. A flow controller was added after the electron capture detector to maintain constant carrier flow through the detector. All these measures prevented flow and pressure fluctuations during the switching of valves, which had caused background drift and signal noise without pressure and flow control.

The gas sample introduction system consisted of the four-

Table 1. Concentration of SF$_6$ in Rocks and Minerals[a]

Mineral or Rock	State, Province, or Country	Location	Weight of Sample, g	Volume of Gas Released at 23°C, cm^3 STP/g × 100	Volume of Gas Released at 250°C, cm^3 STP/g × 100	Concentration of SF$_6$ in Sample, mol/g × 10^{18}	Concentration of SF$_6$ in Gas Released at 250°C, pptv
Granite	Sweden	Gotemar	56.5	1.11	1.19	9000	19000
Well cuttings (granitic)	New Mexico	Albuquerque	37	0.075	2.19	0.92	10
Microcline	Ontario	Bancroft	49.5	1.81	2.66	12	11
Quartz diorite[b]	Virginia	Shenandoah Park	62	0.032	0.84	0.49	1.4
Diabase	Virginia	...	59	0.003	ND	<0.2	BDL
Scoria	Idaho	Big Southern Butte	26.5	NPC	0.009	0.65	180[c]
Labradorite	New York	Adirondacks	61.5	0.053	1.09	0.59	1.3
Fluorite	Illinois	Rosiclare	98.5	1.01	ND	7600	ND
Sphalerite-calcite	Kentucky	Garrard County	40	2	ND	7.9	ND
Ni-Cu ore + matrix	Ontario	Sudbury	70	0.022	0.42	3	17
Marble	New Jersey	Franklin area	71.5	1.52	ND	27	ND
Marble	Georgia	Atlanta	45	0.085	ND	0.25	ND
Mica schist	Virginia	...	59	NPC	0.034	<0.2	0
Dolomite	Wisconsin	Mifflin	65.5	0.34	1.76	10	14
Halite	Michigan	Detroit	62.5	0.021	1.18	14	29
Calcarenite	Bermuda	...	40	0.021	0.41	<0.2	BDL
Detection limit	...	...	40	0.017	...	0.17	...

[a]Abbreviations are as follows: ND, not determined; NPC, no pressure change observed after crushing sample; and BDL, below detection limit.
[b]Sample is weathered.
[c]There is large uncertainty because of small change in pressure after crushing sample.

position selector valve (V-4). This valve selected between two gas standards, air, and carrier gas. Gas samples were also introduced into the sampling loops from glass ampoules by attaching the apparatus illustrated in Figure 2b to port 1 of valve V-4. The gas-sampling loops were evacuated by first turning valve V-F to the vacuum position and then to the off position. The sample was released by breaking the prescored tip of the ampoule. The samples were injected into the carrier gas stream by valves V-5 or V-6 of the analytical system at ambient, subambient, or greater than atmospheric pressures. All volumes in the gas-introduction system were measured, and the pressures were determined with a pressure transducer. The gas injection system consisted of two valves and four sampling loops with volumes ranging from 0.1 to 15 mL. The SF$_6$ in the loops was directly injected into the analytical column, or the SF$_6$ was trapped at about −75°C on the 10-cm Porapak Q trap. Alternatively, SF$_6$ concentrations were measured from large volumes of gas by attaching the apparatus shown in Figure 2b to port 5 of V-3 and a vacuum pump to port 4 of V-3. First, the lines were evacuated, then the prescored tips of the ampoules were broken, and the sample was slowly pulled through the large precooled trap by the vacuum pump. The SF$_6$ collected on trap 1 and then was transferred from the water stripping system to the analytical system through V-3, and the SF$_6$ was collected on trap 2.

Trap 2 was isolated by turning valve V-7, then trap 2 was heated to 95°C, valve V-8 was switched from the back flush position to the run position, and then trap 2 was injected into the analytical column. The SF$_6$ entered the analytical column, and the chromatography phase began. After the SF$_6$ concentration was measured, valve V-8 was switched to the back flush position preventing O$_2$ and other highly retentive compounds from reaching the electron capture detector. This procedure significantly reduced the analytical time.

2.6. Calibration and SF$_6$ Standards

The instrument was calibrated using a blank and 0.1, 0.3, 0.5, and 0.6 cm^3 of a 100 pptv Scott master gas standard. The gas

was directly injected into the analytical column or was trapped on the Porapak Q trap and then injected onto the analytical column. Both procedures yielded identical results indicating 100% efficiency in the trapping of SF$_6$. The system also was calibrated using a blank and 5, 10, 15, 30, and 45 mL of a National Oceanic and Atmospheric Administration air standard. The SF$_6$ in all the air samples and standards was collected in trap 2 and then injected into the analytical column.

2.7. Precision and Accuracy of Measurements

Standard deviations of about 1% were routinely obtained for repeated measurements of standards. The calibration was linear through the entire measuring range. Standards used were prepared by gravimetric procedures; the accuracy of the standards was about 1%. The analytical precision of the water analyses was about 20% near the detection limit of less than 0.01 fmol/L and about 3% for concentrations greater than 0.1 fmol/L.

3. Natural SF$_6$

Recently, *Harnisch et al.* [1996] and *Harnisch and Eisenhauer* [1998] reported the presence of SF$_6$ in fluorite and in two of eight granites analyzed. *Busenberg and Plummer* [1997] found large concentrations of SF$_6$ in hot springs from volcanic and igneous areas and low concentrations in pre-1940s groundwaters from Maryland. These results indicated the existence of a natural source of SF$_6$ and the presence of small concentrations of the tracer in the atmosphere before the industrial production of SF$_6$.

SF$_6$ was measured in a suite of minerals and rocks of various origins in an attempt to determine the source of the SF$_6$ (Table 1). The detection limit of SF$_6$ using this procedure was 1.7 × 10^{-19} mol/g of sample. SF$_6$ was present in almost all the samples that were analyzed in this study because the detection limit was 10^4 times lower than the detection limit of *Harnisch and Eisenhauer* [1998]. *Harnisch and Eisenhauer* [1998] detected SF$_6$ in nearly all the fluorites they analyzed and in only two of eight granites.

The highest concentrations of SF_6 found in this study were in a fluorite and granite; however, significant concentrations of SF_6 were also found in other mineral and rock types (Table 1). SF_6 was present in many samples from hydrothermal mineral deposits. The results of this study and the data of *Harnisch and Eisenhauer* [1998] apparently indicate that SF_6 concentrations are generally lower in mafic and higher in silicic igneous rocks. Relatively high concentrations of SF_6 were present in a sedimentary dolomite and in a Silurian salt from the Michigan basin, but no SF_6 was detected in a Bermuda calcarenite, suggesting that high concentrations of SF_6 may also be present in some diagenetic fluids.

4. Natural Background Concentrations of SF_6 in the Atmosphere

There is widespread evidence of the occurrence of low concentrations of SF_6 in minerals and rocks (Table 1) [*Harnisch and Eisenhauer*, 1998] and in igneous fluids [*Busenberg and Plummer*, 1997]; consequently, a background concentration of SF_6 must have existed in the atmosphere prior to the introduction of the anthropogenic source of SF_6. *Kranz* [1966] and *Harnisch and Eisenhauer* [1998] propose that SF_6 and CF_4 form in fluorite through the reaction of fluorine with the organic matter present. They suggest that the energy for the reaction is provided by α particles produced by the radioactive decay of U and Th and their daughter elements. The background concentration of SF_6 in the atmosphere has likely varied over geologic time, being higher during times of increased tectonic and volcanic activity. During periods when the natural flux of SF_6 to the atmosphere was approximately constant, a quasi steady state concentration may have existed where the natural input rate was equal to the removal rate of SF_6 from the atmosphere.

Old atmospheric gases can be obtained from air bubbles trapped in glacier ice; however, it is difficult to obtain and process the large sample of ice required for SF_6 analysis without contaminating the samples with modern air. Alternatively, old air can be extracted from firn [*Butler et al.*, 1999; *Battle et al.*, 1996]. A 1900 air sample extracted from firn from a depth of 120 m at the South Pole was reported to have an SF_6 concentration near the detection limit of about 0.1 pptv [*Butler et al.*, 1999; *Elkins et al.*, 1996, Figure 5.37]. The natural SF_6 background atmospheric concentration was estimated as less than 0.04 pptv [*Maiss and Brenninkmeijer*, 1998] based on observed atmospheric concentrations since 1978, cumulative sales, and model emissions. *Harnisch and Eisenhauer* [1998] estimated the natural atmospheric SF_6 background to be between 0.001 and 0.01 pptv. *Harnisch and Eisenhauer* [1998] assumed that SF_6 together with CF_4 was produced radiochemically in natural fluorite minerals.

Background SF_6 air concentrations can be calculated from groundwater older than 60 years before anthropogenic SF_6 was introduced into the atmosphere because these waters were in equilibrium with the atmosphere at the time of recharge. Groundwater samples were selected from the Coastal Plain sand aquifers of Maryland, New Jersey, North Carolina, and Virginia to calculate the natural background concentration of SF_6. A criterion used for the selection of samples was the absence of CFCs or a minimum age of 60 years. The maximum age of the groundwater was estimated from the ^{4}He concentrations, using an age-helium relation [*Solomon et al.*, 1996; *Andrews*, 1985; *Schlosser et al.*, 1989] derived from the younger
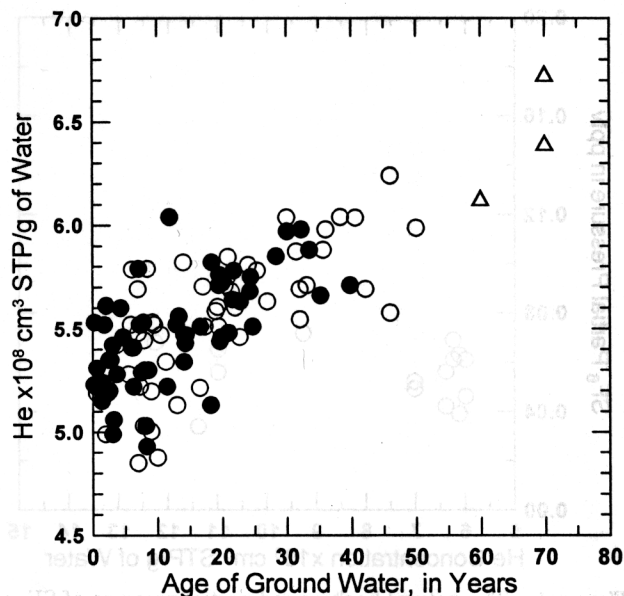

Figure 3. Helium concentration as a function of the age of the groundwater, Atlantic Coastal Plain aquifer of Maryland and Virginia. Groundwater ages were determined by the ^{3}H/^{3}He (solid circles), CFC-12 (open circles), and numeric simulation (triangles) procedures.

dated waters in the Coastal Plain aquifers. Figure 3 shows the correlation between the concentration of ^{4}He in the groundwaters from the Coastal Plain of Virginia, Maryland, and New Jersey as a function of the groundwater ages. ^{3}H/^{3}He ages were primarily used when available, otherwise CFC-12 model ages were used. In a few cases, ages were derived from a groundwater flow model. The scatter in the data in Figure 3 results from differences in the amount of excess air present in the water and analytical uncertainties for samples analyzed by gas chromatography. The rate of ^{4}He accumulation in the groundwater can be approximated from the following equation:

$$C_{He} = a + bA, \tag{1}$$

where C_{He} is the ^{4}He concentration in cm^3 STP/g of water, a is the constant that represents the solubility of He in water (4.7×10^{-8} cm^3 STP/g of water at 12°C) plus the ^{4}He contributed by excess air (5.24×10^{-9} cm^3 STP/g of water for each cm^3 STP of excess air per kilogram of water), b is another constant, and A is the age of the water (time since recharge) in years. The fitted values of constants a and b to the field data are 5.25×10^{-8} and 1.8×10^{-10} cm^3 of He at STP/g of H_2O, respectively. Helium concentrations and (1) were used to estimate the apparent age of the other Coastal Plain water samples that had not been dated or were older than the dating range of CFCs and ^{3}H/^{3}He. *Solomon et al.* [1996] reported similar ^{4}He accumulation rates for other aquifers.

The atmospheric background partial pressure of SF_6 was calculated from measured SF_6 concentrations in groundwaters of the Atlantic Coastal Plain with estimated ages of 60 years to about 400 years (Figure 4). Groundwaters containing CFCs, regardless of their ^{4}He concentrations, were considered to be either younger than 60 years old or mixtures of old and young water and were not plotted in Figure 4. The average natural background atmospheric concentration of SF_6 was 0.054 ± 0.009 pptv.
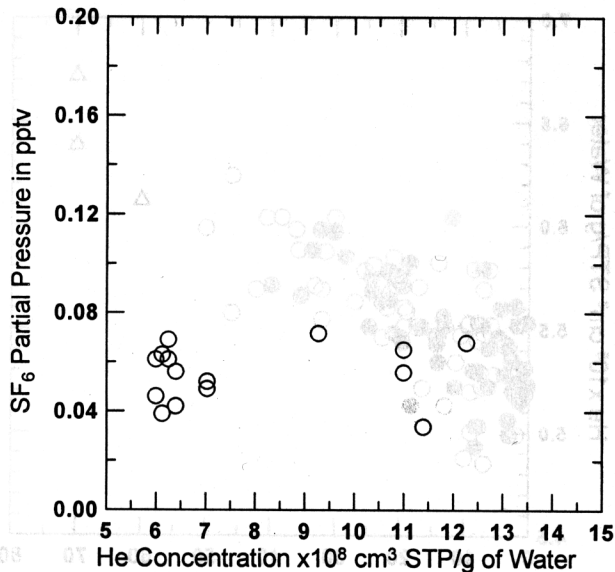
Figure 4. The natural background partial pressure of SF$_6$ as a function of the helium concentration of groundwater from the Atlantic Coastal Plain aquifer of Virginia and Maryland.

5. Anthropogenic Sources and Atmospheric History of SF$_6$

Lovelock [1971] first recognized the potential of SF$_6$ as a useful tracer in atmospheric and marine studies and made the first atmospheric measurement. *Watson and Liddicoat* [1985] were the first to attempt to reconstruct the atmospheric history from an oceanic depth profile. The atmospheric growth history of SF$_6$ has been described by *Ko et al.* [1993], *Rinsland et al.*
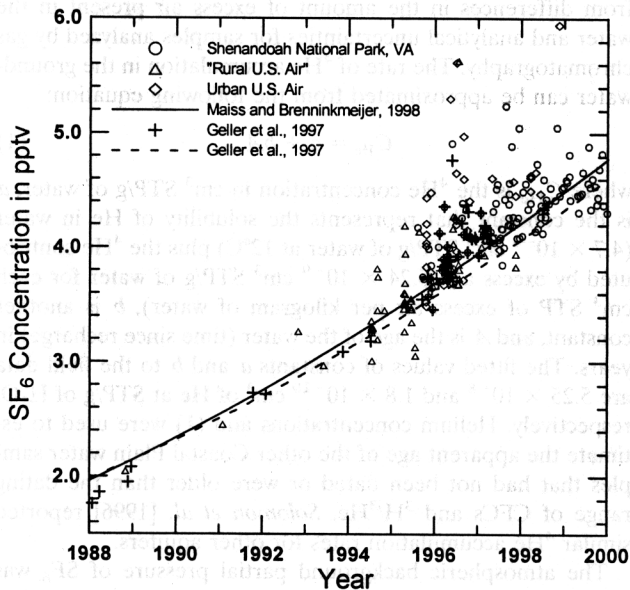

Figure 5. Concentration of SF$_6$ in air as a function of time in North American atmosphere. The Shenandoah National Park air was collected from a 10-m tower; all the other samples were collected 2 m above ground surface. Samples collected from sites located more than 20 km from major metropolitan areas and their suburbs are designated as "rural air." The National Oceanic and Atmospheric Administration air samples were from Niwot Ridge, Colorado [*Geller et al.*, 1997].

[1993], *Maiss and Levin* [1994], *Law et al.* [1994], *Geller et al.* [1997], and *Maiss et al.* [1996]. Recently, *Maiss and Brennink-meijer* [1998] recognized the presence of a natural background concentration of atmospheric SF$_6$ and that the concentration extrapolated back to the year of 1970 did not equal zero, as was assumed in their earlier work [*Maiss et al.*, 1996].

Figure 5 compares more than 250 measurements of SF$_6$ in air from various parts of the United States, measured as a part of this study, with the Northern Hemisphere growth curve (dashed curve) calculated from the equation given by *Geller et al.* [1997] and the Northern Hemisphere growth curve calculated from the equation of *Maiss and Brenninkmeijer* [1998] (solid curve). The value of 0.054 pptv was used as the natural background concentration of SF$_6$ (the c_0 term in the equation of *Maiss and Brenninkmeijer* [1998]. The data on Figure 5 include weekly flask measurements from the Big Meadows Air Station, Shenandoah National Park, Virginia (38°31'22"N, 78°26'09"W, and elevation 1085 m) which is located 105 km west of Washington, D. C. *Maiss and Brenninkmeijer* [1998] calculated the pre-1970 atmospheric history of the tracer from production data, their estimated natural background, and atmospheric measurements (solid curve on Figure 5). The atmospheric history of SF$_6$ was slightly revised using the natural background measured in this study (Figure 4) and is shown in Figure 6a. The solid curve in Figure 5 gives a slightly better fit to the North American air data and was used to date U.S.
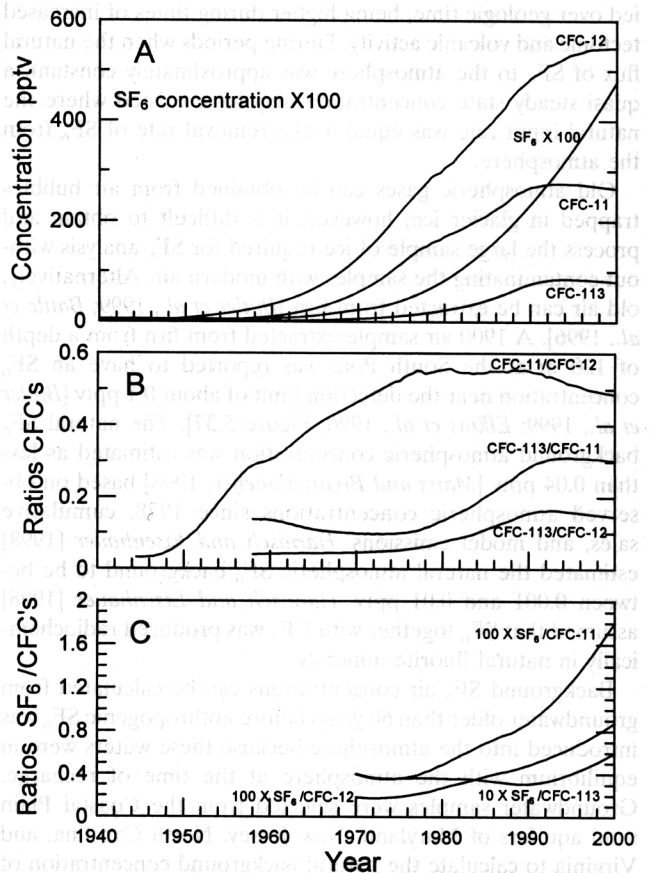

Figure 6. (a) Concentration of CFC-11, CFC-12, CFC-113, and SF$_6$ as a function of time in North American air. (b) Ratio of the partial pressures of CFCs in North American air as a function of time. (c) Ratio of the partial pressures of SF$_6$ to CFCs in North American air as a function of time.

Table 2. Concentration of SF₆ in Water From Springs Emanating From Crystalline Rocks at or Near Faults Separating Crystalline-Sedimentary Rocks[a]

Spring	State	Location	Date Sampled	SF₆ Concentration, fmol/L	He Concentration, cm³/g at STP
Lidy Hot Springs[b] (site 1)	Idaho	44°08'32"N, 112°33'10"W	7/20/96	4.6	ND
Lidy Hot Springs[b] (site 2)	Idaho	44°08'32"N, 112°33'10"W	7/20/96	2.2	ND
Lidy Hot Springs[b]	Idaho	44°08'32"N, 112°33'10"W	5/11/97	ND	54×10^{-8}
Island Park (big spring)	Idaho	44°30'06"N, 113°54'58"W	7/20/96	3.5	ND
Island Park (small spring)	Idaho	44°30'06"N, 113°54'58"W	7/20/96	3.5	ND
Big Springs	Idaho	44°30'06"N, 113°54'58"W	5/21/97	2.2	68×10^{-8}
Condie Hot Spring	Idaho	43°19'58"N, 113°54'58"W	7/20/96	4.6	ND
Condie Hot Spring	Idaho	43°19'58"N, 113°54'58"W	5/22/97	ND	470×10^{-8}
Tunnel Spring	New Mexico	35°17'28"N, 106°26'24"W	6/18/96	12	4.04×10^{-8}
Embudo Spring	New Mexico	35°08'05"N, 106°28'29"W	7/2/96	1.6	ND
Eubudito Spring	New Mexico	35°05'54"N, 106°27'44"W	7/2/96	1.2	ND
Coyote Spring[b]	New Mexico	34°59'57"N, 106°28'12"W	7/1/96	0.02	9.23×10^{-8}
Trout Spring[c]	Pennsylvania	40°09'44"N, 77°00'47"W	9/9/96	5.1	ND
Alexander Spring[c]	Pennsylvania	40°10'05"N, 77°15'53"W	9/10/96	5.0	7.31×10^{-8}
Big Spring[c]	Pennsylvania	40°07'42"N, 77°24'28"W	9/10/96	4.3	ND
Dykman Spring[c]	Pennsylvania	40°02'32"N, 77°30'55"W	9/10/96	9.0	ND
Harver Spring[c]	Maryland	39°40'39"N, 77°34'18"W	9/25/96	5.5	ND
Hillbilly Spring[c]	Maryland	39°23'16"N, 77°28'28"W	11/14/96	7.4	ND
Keedyville Spring[c]	Maryland	39°29'16"N, 77°41'33"W	11/18/96	3.5	ND
Arthur Weiss[c]	Virginia	39°08'39"N, 77°54'58"W	9/19/96	5.8	ND
Arthur Weiss[c]	Virginia	39°08'39"N, 77°54'58"W	8/12/96	ND	6.03×10^{-8}
Elkton Spring[c]	Virginia	38°24'15"N, 78°36'12"W	9/18/96	4.3	ND
Elkton Spring[c]	Virginia	38°24'15"N, 78°36'12"W	8/5/97	ND	6.53×10^{-8}
Coyner Spring[c]	Virginia	38°03'10"N, 78°55'54"W	9/11/96	3.6	ND

[a]Modern air-water equilibrium is <2 fmol/L for SF₆ and about 4.7×10^{-8} cm³/g of water for He. ND is not determined.
[b]Some degassing occurred prior to sampling.
[c]Springs are located at or near the crystalline-sedimentary fault contact.

groundwater. *Hurst et al.* [1997, 1998] give additional atmospheric measurements of SF₆ from a 496-m tower in North Carolina, and *Ho and Schlosser* [2000] give atmospheric data from New York City vicinity; however, the data are not shown in Figure 5. SF₆ concentration in approximately 5% of our samples exceeded by more than 10% the mean North Ameri-

can air curve (Figure 5) and probably represents pollution events near the sample collection station.

6. Concentration of SF₆ in Natural Waters

Nearly 3000 natural waters from throughout the United States were analyzed. Results indicate that many factors can influence the concentrations of SF₆ in natural water including rock type, geologic history, geologic age, and other aquifer characteristics. Results from natural waters from various geological environments are used to illustrate the distributions of SF₆ in the United States.

6.1. Springs and Groundwater From Igneous and Volcanic Areas

SF₆ concentrations greater than that possible for equilibrium with modern air (excess SF₆) were detected in discharge from springs throughout the United States in areas of igneous and volcanic rocks (Table 2). A large excess of SF₆ was detected in many springs issuing from igneous rocks at or near fault contacts separating crystalline and sedimentary rocks in Maryland, Pennsylvania, Virginia, West Virginia, and New Mexico (Table 2 and Figures 7 and 8). Excess SF₆ was detected in springs influenced by volcanic activity at Big Springs, Idaho (temperature 13.1°C), located about 12 km west of Yellowstone National Park and 35 km west of Old Faithful Geyser, and Lidy Hot Springs (Figure 9) and Condie Hot Spring in southeast Idaho, where water temperatures are 60° and 50°C, respectively.

6.2. Eastern Snake River Plain Aquifer, Southeast Idaho

The Eastern Snake River Plain aquifer lies within a northeast trending structural basin and is about 320 km long and 80
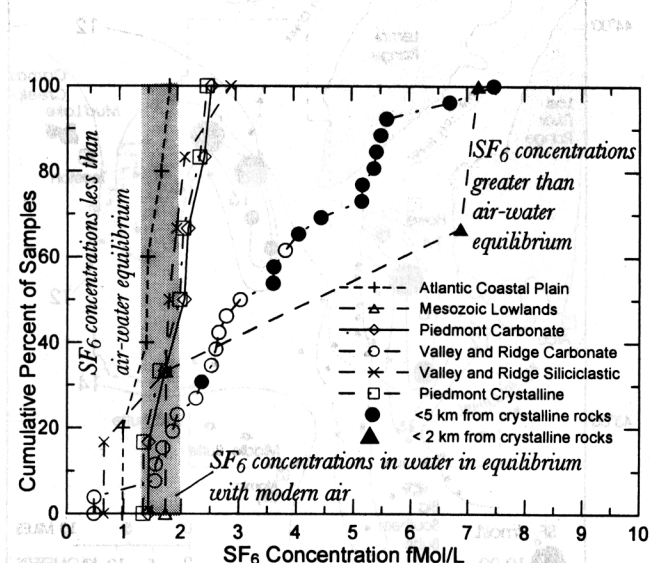

Figure 7. Cumulative percent of concentrations of SF₆ in fmol/L for samples collected from springs within the Chesapeake Bay Watershed of the eastern United States. Many of the samples are near equilibrium with modern air or have some apparent age. Solid circles represent samples located within 5 km of a thrust fault separating the Valley and Ridge sedimentary rocks from the Blue Ridge crystalline rocks and are likely enriched from terrestrial sources.
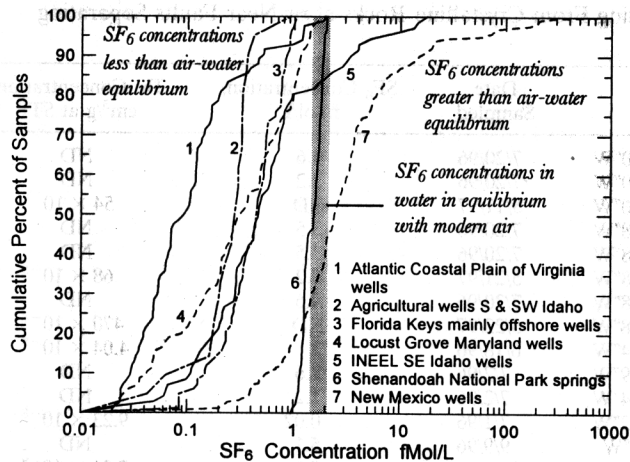
Figure 8. Cumulative percent of concentrations SF₆ in fmol/L for groundwater samples collected through out the United States. Most samples have measurable apparent groundwater ages, though 20% of the samples from Idaho National Engineering and Environmental Laboratory (INEEL) in Idaho and 50% of the samples from New Mexico have large excesses of SF₆.

to 110 km wide in the Eastern Snake River Plain. The plain is underlain by a layered sequence of basaltic lava flows and cinder beds interbedded with thin sedimentary deposits. The basaltic lava flows and interbedded sedimentary deposits combine to form the Snake River Plain aquifer, which is the main source of water on the Snake River Plain [Olmsted, 1962; Mundorff et al., 1964; Robertson et al., 1974]. The thick Snake River Plain basalts are believed to have been formed by a mantle hot spot as it moved from the Columbia Plateau volcanic area to its present location beneath Yellowstone National Park, Wyoming [Murphy et al., 1998; Dodson et al., 1997]. The concentrations of SF₆ were measured in 51 groundwater samples collected in the vicinity of the Idaho National Engineering and Environmental Laboratory (INEEL) [Busenberg et al., 1998], which is located near the northern border of the Eastern Snake River Plain (ESRP). An additional 13 groundwaters were collected from ESRP, an agricultural area located south and southwest of INEEL.

All groundwaters from the agricultural parts of the ESRP had concentrations of SF₆ that were significantly lower than modern air-water equilibrium (Figure 8). Most of the wells sample the top of the ESRP aquifer, which has been shown to contain predominantly irrigation water diverted from the Snake River [Plummer et al., 2000], and the groundwaters are low in SF₆ content. At INEEL, however, concentrations of SF₆ ranged from 0.00 to about 17 fmol/L. Even though most groundwaters sampled in and near the INEEL contained less than 1 fmol/L [Busenberg et al., 1998], several samples had SF₆ concentrations that exceeded modern air-water equilibrium concentrations of 1.4 to 2 fmol/L (Figures 8 and 9). The high concentrations of SF₆ in these samples were likely derived from natural sources, because no industrial sources could be identified in this undeveloped, rural area. There appears to be a close correlation between the groundwater temperature and the high SF₆ concentrations in the aquifer (Figure 9). All the groundwaters from INEEL with high SF₆ concentrations were found at or near the northern boundary of the basin and near the contact of the basalts with rhyolitic volcanic rocks [Robertson et al., 1974]. Rhyolite and granitic rocks have higher fluo-

ride concentrations than basalts and mafic rocks, and the silicic rocks may be the source of the natural SF₆, as is suggested by the data presented in Table 1. SF₆ concentrations greater than equilibrium with modern air and very high concentrations of He were also present in a number of cold springs in Idaho that issue from the western flank of the Yellowstone Caldera (Table 2). The Yellowstone hot spot is a source of He with high ³He/⁴He ratio [Craig et al., 1978] and possibly a source of SF₆.

6.3. Middle Rio Grande Basin, New Mexico

SF₆ concentrations were determined in a large number of water samples from the Santa Fe Group system of the Middle Rio Grande Basin, New Mexico [Plummer et al., 1997]. Of the 272 SF₆ measurements in groundwater, 149 measurements exceeded 2.0 fmol/L (Figure 10). SF₆ concentrations of 10 to 200 fmol/L were common in groundwater derived from the pre-Cambrian granitic rocks of the Sandia Mountains east of Albuquerque, New Mexico (Figure 8). High concentrations of SF₆ were also detected in a monitoring well near a landfill (203 fmol/L), though water from monitoring wells near another landfill had only 2 to 5 fmol/L of SF₆. The highest concentration of SF₆ (753 fmol/L) was of unspecified origin from groundwater at a high-energy research test facility in a remote area of Kirtland Air Force Base.

There is little correlation between dissolved He and SF₆ concentrations in groundwater in this area. For example, most multidepth piezometer nests sampled show significant increases in dissolved helium with depth, but the increase was usually not associated with an increase in SF₆. An exception is that east of Albuquerque along the Sandia Mountains (Figure
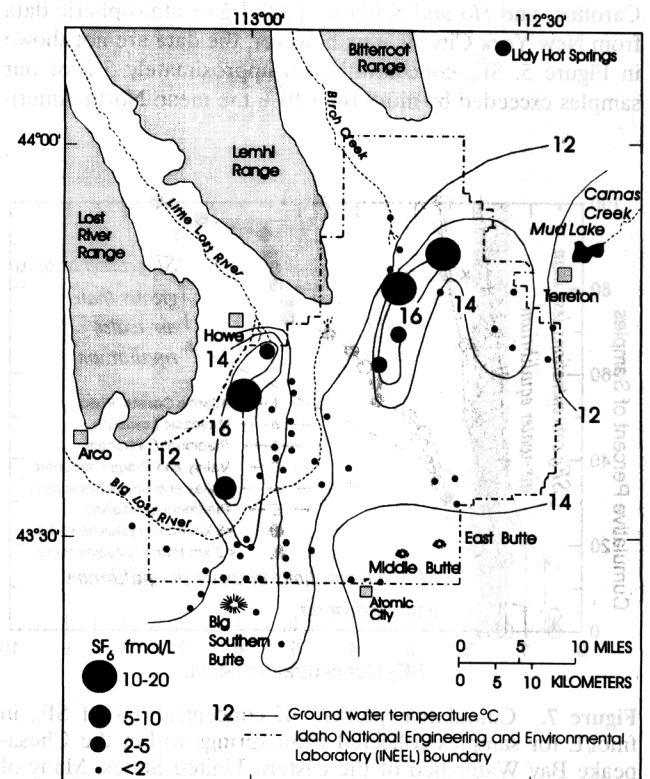

Figure 9. Map showing the groundwater temperature and concentration of SF₆ in groundwater from the eastern Snake River Plain aquifer in the vicinity of the Idaho National Engineering and Environmental Laboratory (INEEL), Idaho.
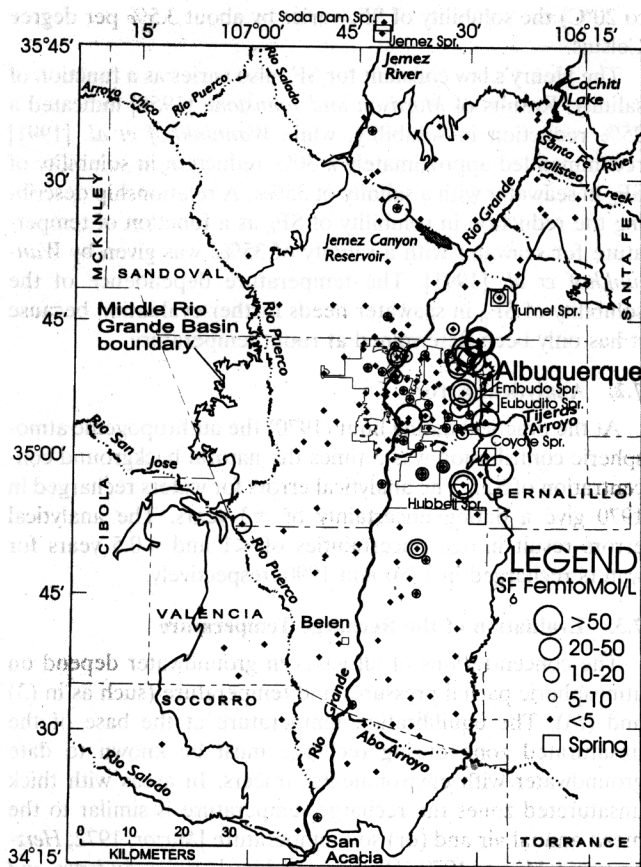
Figure 10. Map showing the concentration of SF₆ in groundwater from the Middle Rio Grande Basin, New Mexico. The diamond symbols show the location of wells and springs sampled for SF₆. Circles of various sizes indicate SF₆ concentrations greater than 5 fmol/L.

10), where water is likely derived from mountain front recharge through crystalline rocks, and concentrations of both SF₆ and He increased with depth in some well nests.

6.4. Blue Ridge Mountains, Shenandoah National Park, Virginia

Springs near the top of the Blue Ridge Mountains in Shenandoah National Park were sampled for SF₆ from 1996 to 1999. All the springs issuing from the overburden near the top of the Blue Ridge Mountains had concentrations of SF₆ that were near the equilibrium concentration between modern air and water [*Plummer et al.*, 1999] (see Figure 8).

The water from the overburden enters the fractures in the crystalline rocks and was sampled in wells completed in crystalline rocks. Four of the wells completed in fractured crystalline rocks had SF₆ concentrations that were higher than modern air-water equilibrium. The SF₆ concentration in the water from eight wells was significantly higher than required for their age, which was calculated from CFCs or ³H/³He. This implies that SF₆ was added to the groundwater as it traveled through the fractures in the crystalline rock. The data suggest that the crystalline rocks are the natural source of SF₆, which was present in a rock sample from this area (Table 1). The flux of SF₆ from the igneous rocks into the groundwater cannot be evaluated at this time because (1) the groundwaters are mixtures of waters of various ages, (2) the residence times of the

various fractions of water are not known, and (3) the distances and paths traveled by the various fractions are uncertain because of the complexity of the fracture network and the extreme variability in the hydraulic properties of the rocks.

6.5. Chesapeake Bay Watershed of Eastern United States

Springs were sampled throughout the Chesapeake Bay Watershed of the eastern United States, an area of approximately 166,000 km² with more than 240,000 km of streams draining six major physiographic provinces [*Focazio et al.*, 1998]. Significant differences in SF₆ concentrations and ranges of concentration were observed in water of springs from the different physiomorphic and lithologic parts of this watershed (Figure 7).

In the crystalline rock provinces, springwaters that had the highest specific conductance and the highest dissolved solid content also had the highest concentrations of SF₆. These waters were probably derived from fractured crystalline rocks and Paleozoic rocks. All other springs in this region had SF₆ concentrations at or near equilibrium with modern air (Figure 7), and these waters are believed to be mainly derived from regolith, which is composed of saprolite, colluvium, alluvium, and soil.

The springs in the Valley and Ridge carbonate rocks have generally higher and a greater range of SF₆ concentrations than the springs in Piedmont carbonates (Figure 7). The Valley and Ridge carbonates are intensely folded limestones and dolomites of Cambrian to Devonian age, and about 80% of the springs exceeded the modern air-water equilibrium concentration as shown in Figure 7. The proximity of the springs to the thrust fault separating the Valley and Ridge Province from the Blue Ridge Mountains may have contributed to the high SF₆ concentrations in some of the waters. Springs that are less than 5 km from the thrust fault are represented by solid circles in Figure 7. It is likely that a small fraction of the springwater moved through the fractures network of the Blue Ridge Mountains [*Nutter*, 1974; *Focazio et al.*, 1998], and thus waters may have acquired some of the SF₆ from the crystalline rocks.

Springwater from the Coastal Plain is derived from unconsolidated clastic and marine sediments, and SF₆ concentrations range from less than to near equilibrium between water and modern air (Figures 7 and 8 and Atlantic Coastal Plain and Locust Grove wells).

7. Dating Groundwater With SF₆

The procedures used to date groundwater with SF₆ are similar to those used to date with chlorofluorocarbons [see, e.g., *Busenberg and Plummer*, 1992; *Cook and Solomon*, 1997; *Plummer and Busenberg*, 1999]. Water recharging an aquifer is assumed to be in equilibrium with the unsaturated-zone atmosphere. If the unsaturated zone is relatively thin (less than approximately 10 m), the concentration of SF₆ in the unsaturated-zone air should be nearly identical to that of the troposphere. Confinement occurs through recharge, because diffusion coefficients of the gas in water are approximately 5 orders in magnitude smaller in water than in air. Age is the time elapsed from the time of confinement.

Other processes can influence the transport of dissolved gases through an aquifer and can affect the calculated model age. Reaction, sorption, or any other process that can impede the transport of the environmental tracer has to be considered when dating with the tracer. SF₆ behaves like an ideal gas and does not react with the substrate [*Wilson and Mackay*, 1993;

Upstill-Goddard and Wilkins, 1995] or sorb onto aquifer organic matter [*Wilson and Mackay*, 1996] and apparently does not biodegrade even in highly reducing environments. In this study, SF$_6$ was present in groundwater containing both methane and hydrogen sulfide and did not appear to significantly degrade under reducing conditions. The low reactivity of SF$_6$ is the result of kinetic factors and is not due to thermodynamic stability. The inertness, especially to hydrolysis, is attributed to the octahedral coordination of the sulfur, the high S-F bond strength, the complete saturation of the sulfur, the steric hindrance, and the lack of polarity of the molecule [*Cotton and Wilkinson*, 1972].

The concentration of SF$_6$ in groundwater (SF$_{6_{total}}$) is given by the mass balance equation:

$$SF_{6_{total}} = SF_{6_{eq}} + SF_{6_{exc}} + SF_{6_{terr}} + SF_{6_{cont}} - SF_{6_{loss}}, \quad (2)$$

where SF$_{6_{eq}}$ is the air-water equilibrium concentration, SF$_{6_{exc}}$ is the supersaturation concentration of SF$_6$ derived from the dissolution of air bubbles trapped in the aquifer during a rise in the water table (excess air), SF$_{6_{terr}}$ is the concentration of SF$_6$ added to the water from natural sources, SF$_{6_{cont}}$ is the SF$_6$ introduced by anthropogenic contamination of the groundwater, and SF$_{6_{loss}}$ is the SF$_6$ removed by biodegradation, sorption, dispersion, matrix diffusion, or any other removal process. If the last three terms in (2) are small and the amount of excess air can be determined independently, it is possible to date groundwater with SF$_6$ using the known atmospheric input function.

7.1. Solubility of SF$_6$ in Water

The solubility of SF$_6$ in water as a function of temperature has been measured by *Friedman* [1954], *Morrison and Johnstone* [1955], *Ashton et al.* [1968], *Cosgrove and Walkley* [1981], and *Wanninkhof et al.* [1991] and at temperatures between 75° and 230°C by *Mroczek* [1997]. Recently, *Strotmann et al.* [1999] measured the thermodynamic properties of the H$_2$O-SF$_6$ system. The solubility of SF$_6$ in freshwater is given by the following equation [*Wilhelm et al.*, 1977]:

$$\ln x_2 = (A + B/T + C \ln T)/R, \quad (3)$$

where x_2 is the mole fraction of SF$_6$ in solution, T is the temperature in kelvins, and R is the gas constant. The constants A, B, and C are equal to -877.854, 42,051, and 125.018, respectively.

The Henry's law constant is calculated from the mole fraction x_2 and is equal to

$$K_H = 55.50868/[(1/x_2) + 1], \quad (4)$$

where K_H is Henry's law constant.

The partial pressure of SF$_6$ (p_{SF_6}) in air is defined [*Warner and Weiss*, 1985] as

$$p_{SF_6} = x_{SF_6}(P - p_{H_2O}), \quad (5)$$

where p_{SF_6}, p_{H_2O}, P, and x_{SF_6} are the partial pressure of SF$_6$, the partial pressure of water, the total atmospheric pressure, and the dry air mole fraction of SF$_6$, respectively. The atmospheric partial pressure is calculated from the expression:

$$p_{SF_6} = c_{SF_6}/K_H, \quad (6)$$

where c_{SF_6} is the concentration of SF$_6$ in mol/kg of water. In the recharge temperature range of most U.S. groundwaters (5° to 20°C) the solubility of SF$_6$ varies by about 3.5% per degree Celsius.

The Henry's law constant for SF$_6$ also varies as a function of salinity. Results of *Morrison and Johnstone* [1955] indicated a 25% reduction in solubility, while *Wanninkhof et al.* [1991] recommended approximately a 30% reduction in solubility of SF$_6$ in seawater with a salinity of 35‰. A relationship describing the reduction in solubility of SF$_6$ as a function of temperature for seawater with a salinity of 35‰ was given by *Wanninkhof et al.* [1991]. The temperature dependence of the solubility of SF$_6$ in seawater needs further evaluation because it has only been determined at room temperature.

7.2. Analytical Error

At the practical dating limit (1970) the anthropogenic atmospheric contribution was 3 times the natural background concentration of SF$_6$. The analytical errors for waters recharged in 1970 give a dating uncertainty of ±3 years. The analytical errors result in age uncertainties of <1 and <0.5 years for waters recharged in 1980 and 1990, respectively.

7.3. Evaluation of the Recharge Temperature

The concentrations of all gases in groundwater depend on atmospheric partial pressures and temperature (such as in (3) and (6)). The equilibration temperature at the base of the unsaturated zone during recharge must be known to date groundwater with environmental tracers. In areas with thick unsaturated zones the recharge temperature is similar to the mean annual air and (or) soil temperature [*Mazor*, 1972; *Herzberg and Mazor*, 1979; *Heaton and Vogel*, 1981; *Andrews and Lee*, 1979; *Andrews et al.*, 1989; *Busenberg et al.*, 1993]. The recharge temperature can be different from the mean annual temperature where the unsaturated zone is thin and the temperature just above the water table responds to the seasonal variations in the air temperature [*Matthess*, 1982]. For most studies reported in the literature, however, recharge occurs below the neutral zone [*Mazor*, 1972; *Herzberg and Mazor*, 1979; *Heaton and Vogel*, 1981; *Andrews and Lee*, 1979]. The recharge temperature is not the mean air temperature during the rainy season nor the temperature of the shallow groundwater [*Stute and Schlosser*, 1993]. The concentrations of noble gases and N$_2$ in oxic waters are excellent indicators of the recharge temperature [*Heaton*, 1981; *Heaton and Vogel*, 1981; *Andrews et al.*, 1989; *Stute and Schlosser*, 1993; *Aeschbach-Hertig et al.*, 1999].

Unlike He and Ne, SF$_6$ shows a significant variation in solubility with temperature. However, because of the rapid increase of the atmospheric SF$_6$ mixing ratio of about 7% per year [*Geller et al.*, 1997], an uncertainty in the recharge temperature of 1° to 2°C introduces an error in the model groundwater age of only ≤0.5 year.

7.4. Excess Air

Almost all groundwaters are apparently supersaturated with air at the temperature of recharge; the supersaturation has been attributed to air entrainment during recharge [*Heaton and Vogel*, 1981; *Andrews*, 1991]. Many factors can influence the amount of excess air present in groundwater such as lithology, recharge temperature, annual precipitation, and climate [*Wilson and McNeill*, 1997; *Heaton*, 1981; *Heaton et al.*, 1983, 1986; *Aeschbach-Hertig et al.*, 1999; *Ballentine and Hall*, 1999]. The excess air concentrations are normally from nearly zero to 3 cm^3 STP/kg of water [*Wilson and McNeill*, 1997]; however,

concentrations as high as 18 cm³ STP/kg of water were found in water recharged during floods in the semiarid climates in Arizona [*Glynn and Busenberg*, 1996].

The addition of excess air to groundwater increases the SF_6 concentration of the water above the air-water equilibrium concentration. For this reason, if the presence of excess air is not considered in the calculation of an SF_6 model age, then the apparent age will be too young. The error in the age due to the presence of excess air is less than 1 year for pre-1990 waters dated with CFCs [*Busenberg and Plummer*, 1992] but can be significant for younger waters. Excess air can introduce a significant error when dating groundwater with SF_6 because the Henry's law constant of SF_6 is approximately 55 and 13 times smaller than that of CFC-11 and CFC-12, respectively.

In the calculations mentioned previously, it was assumed that the excess air was introduced at recharge and not during sampling and that the air had the same mixing ratio as tropospheric air at the date of recharge. As a first approximation, the recharge date of the groundwater was calculated by assuming no excess air was present. The date was recalculated using the first approximation, the excess air, and the SF_6 mixing ratio of the first date approximation. The procedure was repeated several times to obtain the recharge date of the water. If the excess air present in the groundwater was not known and was underestimated by 1 cm³ STP/kg of water for typical U.S. groundwaters, the date of recharge between 1970 and 1990 was underestimated by 1 to 2 years. The underestimation of the excess air by 1 cm³ STP/kg of water resulted in the underestimation of the date of recharge by 1 to 2.5 years for waters that were recharged after 1990. In all cases the error in the apparent date of recharge was higher for the waters that were recharged at the higher temperature. Groundwaters recharged prior to 1970 contain low SF_6 concentrations and are very difficult to date with the SF_6 method.

7.5. Elevation Error

An uncertainty of 100 m in the recharge elevation introduces an error of about 1.3% in the SF_6 concentration. An uncertainty of 300 m in the recharge elevation is required to introduce errors of a half year in the SF_6 model age of waters that recharge after 1970. Overestimation of the recharge elevation will result in a younger apparent age.

7.6. Unsaturated-Zone Processes

When the unsaturated zone is relatively thin, the unsaturated-zone air composition tracks that of the troposphere [*Oster et al.*, 1996]. It is reasonable to assume that unsaturated-zone SF_6 concentrations closely track tropospheric concentrations to unsaturated-zone depths of less than 10 m [*Weeks et al.*, 1982; *Busenberg et al.*, 1993]. In deeper unsaturated zones, there is a lag time for diffusive transport of SF_6 through the unsaturated zone. The time lag is largely a function of the tracer diffusion coefficients, tracer solubility in water, and soil water content [*Weeks et al.*, 1982; *Cook and Solomon*, 1995]. Figure 11 shows the lag time of SF_6 (solid curve) and three CFCs as a function of the depth to the water table. Figure 11 was calculated with a one-dimensional flow equation, assuming instantaneous gas liquid exchange at 10°C, with gas- and liquid-filled porosities of 0.15 and 0.2, respectively, using the model of *Cook and Solomon* [1995]. If a groundwater was recharged by infiltration through a deep unsaturated zone while maintaining equilibrium with the diffusion-modified unsaturated-zone air profile,
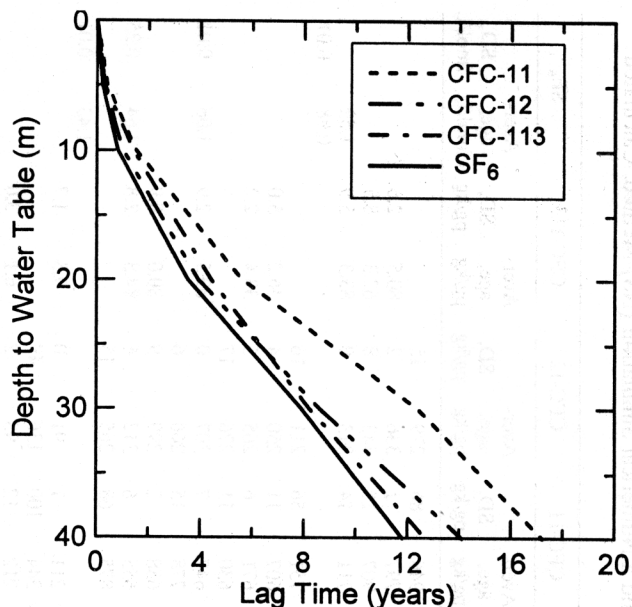

Figure 11. Lag times for water recharged through tracer-diffusion profiles in unsaturated-zone air with different depths to the water table. CFC results are from *Cook and Solomon* [1995]; SF_6 results were calculated under the same conditions.

then the apparent tracer age will be older than the true age of recharge.

7.7. Modification of SF_6 Concentrations in Water by Microbial Activity

In this study, no perceptible degradation of SF_6 was observed in highly reducing waters from several locations. A comparison of CFC and SF_6 model ages from groundwater at Locust Grove, Maryland, provided evidence that SF_6 apparently does not degrade under anaerobic conditions. Water in well KeBe 53, the shallowest well at Locust Grove, screened between 0.95 and 1.55 m below the water table, was very young as indicated by the model ages obtained with SF_6 and numerical simulation [*Reilly et al.*, 1994]. In contrast, model CFC ages for this groundwater were too old compared to the SF_6 and numerical simulation ages, suggesting that degradation of CFCs may have occurred. At another site in the Florida Keys, SF_6 was present in reducing waters containing up to 17 mg/L of H_2S and traces of CH_4. In studies from Virginia, New Mexico, and Idaho the natural background SF_6 concentration was present in waters believed to be several thousand years old that contained Fe(II), H_2S, and up to 4.3 mg/L of CH_4.

8. Field Example: Dating Groundwater With SF_6

Locust Grove, Maryland, was selected to study the feasibility of the use of SF_6 as an environmental dating tool because of the relatively simple hydrology of the aquifer [*Back*, 1966; *Bachman*, 1984; *Reilly et al.*, 1994; *Böhlke and Denver*, 1995], the presence of a network of multidepth wells installed by the U.S. Geological Survey [*Hamilton and Shedlock*, 1992; *Hamilton et al.*, 1989, 1993], the low natural SF_6 background in the aquifer (Figure 4), and the proximity of the site to the laboratory. The age of groundwater in this watershed has been intensely studied with environmental tracers including CFC-11 and CFC-12 [*Dunkle et al.*, 1993; *Plummer et al.*, 1993; *Böhlke*

Table 3. Calculated Model Ages of Groundwater From Locust Grove, Maryland, Using Six Environmental Tracers and a Numerical Simulation (NS) Method, Calculated Recharge Temperatures, and Excess Air Concentrations[a]

Sample Name	Date Sampled	CFC-11 Aver-age, years	CFC-11 SD, years	CFC-12 Aver-age, years	CFC-12 SD, years	CFC-113 Aver-age, years	CFC-113 SD, years	SF$_6$ Aver-age, years	SF$_6$ SD, years	^{3}H/^{3}He[b] Aver-age, years	^{3}H/^{3}He[b] SD, years	^{85}Kr[b] Aver-age, years	^{85}Kr[b] SD, years	NS[c], years	CFC-11 Aver-age, pg/kg	CFC-11 SD, pg/kg	CFC-12 Aver-age, pg/kg	CFC-12 SD, pg/kg	CFC-113 Aver-age, pg/kg	CFC-113 SD, pg/kg	SF$_6$ Aver-age, fmol/L	SF$_6$ SD, fmol/L
KEBE 050	11/19/90	C		5.4	1.1	2.9	0.5								946	86	279	15	80.5	2.6		
KEBE 050	11/14/91	C		-4.6	0.5	5.6	1.1								797	1	336	2	62.3	8.5		
KEBE 050	03/31/92	C		-3.5	0.3	9.1	1.0								907	15	343	8	83.3	5.9		
KEBE 050	07/24/98	9.6	0.7	7.1	0.0			6.6							711	14	313	0			1.32	
KEBE 050	12/10/98							10.7	0.3												0.98	0.01
KEBE 052	11/05/90	4.3	0.5	5.6	0.3	9.5	1.1								751	56	211	16	36.2	5.0		
KEBE 052	11/05/91	6.1	0.3	6.3	0.4	10.4	0.5								607	11	250	4	33.4	2.2		
KEBE 052	03/31/92	4.6	0.2	5.4	0.4	6.2	1.0								671	6	265	5				
KEBE 052	07/21/93	6.9	0.4	6.1	1.3	9.8	0.3			7.1	0.7	7.7	1.0		630	11	276	17	69.5	2.9		
KEBE 052	07/29/97	9.6	0.0	7.1	0.0			7.8	0.8					8.1	647	7	307	0			1.06	
KEBE 053	04/02/91	2.9	0.7	6.8	0.5	4.6	0.0								778	15	266	6	80.0	0.9		
KEBE 053	07/21/93	6.3	0.3	4.1	1.0	8.1	0.5								658	2	299	9	84.3	2.8		
KEBE 053	07/29/97	10.3	0.3	6.6	1.0			2.6	2.0					0.8	655	6	312	6			1.64	0.25
KEBE 059	11/19/90	C		6.6	1.3	18.8	0.0								875	68	265	15	9.3	1.7		
KEBE 059	12/10/98							5.9	0.0					6.0							1.43	0.01
KEBE 061	11/05/90	19.1	0.3	19.8	0.0										211	1	91	0				
KEBE 061	04/02/91	16.5	2.8	17.6	3.8										344	100	136	49				
KEBE 061	11/06/91	20.0	0.5	20.7	0.2	23.7	3.7			16.7	0.6	14.4	1.0		212	12	93	2	6.1	3.0		
KEBE 061	07/21/93	20.6	0.0	20.1	0.0	19.6	0.0			16.0	0.6				251	3	121	0	11.9	0.0		
KEBE 061	07/29/97	16.6	0.0	17.6	0.3	18.6	0.0	17.0	2.7					17.5	487	1	192	2	23.3	0.3	0.47	0.15
KEBE 062	11/06/90	C		2.5	3.3										1380	200	310	34				
KEBE 062	11/06/91	2.8	0.0	1.8	0.0	4.6	1.3								704	4	302	0	66.5	11.0		
KEBE 062	03/31/92	2.7	0.3	2.8	0.7	7.1	0.6								747	34	297	7	51.2	3.5		
KEBE 062	07/21/93	5.8	0.3	3.6	0.0	4.8	0.3			3.1	0.8	5.4	0.6	3.9	677	4	304	1	77.5	2.6		
KEBE 062	04/12/95	7.8	0.4	0.0	0.0	2.25	0.0	4.0	1.3						666	9	366	10	97.4	2.3		
KEBE 062	07/28/97	10.6	0.2	7.6	0.5	8.6	0.0	3.7	0.9					12.3	640	1	303	2	81.2	0.0	1.43	0.01
KEBE 063	11/06/90	16.0	0.2	19.7	0.0										350	7	102	6				
KEBE 063	07/29/97	21.1	0.0	23.1	0.0	22.6	0.0	22.8	1.4						372	2	136	1	13.7	0.3	0.21	0.03
KEBE 063	12/11/98							24.2	0.3												0.20	0.00
KEBE 064	11/06/90	2.1	0.3	9.4	1.5										793	5	231	17				
KEBE 064	07/29/97	11.8	0.3	11.3	0.3	12.1	0.0	12.6	1.2					2.6	604	11	259	4	53.1	0.1	0.69	0.09
KEBE 064	12/11/98							10.2	0.3												1.02	0.03
KEBE 158	11/21/90	2.1	0.5	8.8	1.7	9.6	1.0								788	13	239	20	80.6	7.7		
KEBE 158	07/21/98	12.2	0.6	8.7	2.4										624	19	299	26				
KEBE 159	11/07/90	28.9	0.5	47.1	3.8	21.2	0.8								44	4	1	1	8.1	2.9		
KEBE 159	11/07/91	36.1	0.8	45.5	6.6	>39									13	3	4.1	5	0.0	0.0		
KEBE 159	07/20/93	>49		>54		>41									0	0	0	0	0.0	0.0		
KEBE 159	07/28/97	>53		>56				42.1	3.50						0	0	0	0			0.03	0.01
KEBE 159	12/11/98							34.9	0.00					65.6							0.05	0.00
KEBE 160	11/19/90	21.7	0.9	26.4	1.4	20.9	1.5								140	1	49	2	8.0	1.5		
KEBE 160	11/07/91	22.6	0.3	22.1	0.8	29.7	9.2								144	3	77	7	6.3	5.4		
KEBE 160	03/31/92	21.0	0.6	22.8	0.5	27.1	0.5								196	16	76	7	4.1	0.3		
KEBE 160	07/20/93	25.6	0.0	24.1	0.0	29.1	0.5			19.8	0.6				121	3	75	3	5.5	0.4		
KEBE 160	07/28/97	28.1	0.3	24.6	0.0			29.6	1.78					27.1	160	1	112	7			0.09	0.02
KEBE 161	11/07/90	8.0	0.2	13.5	0.5										601	1	186	7				
KEBE 161	04/02/91	11.5	0.3	12.3	0.5										517	5	206	5				

Sample	Date	Age a	±a	Age b	±b	Other ages	SF₆ model age	±	Conc 1	±	Conc 2	±	Conc 3	±	SF₆ conc	±
KEBE 161	11/07/91	8.6	0.8	8.9	0.5				532	18	223	5	29.4	4.9		
KEBE 161	11/07/91	6.4	0.3	9.4	0.0				601	0	216	0	41.8	4.4		
KEBE 161	07/21/93	9.8	0.3	8.1	0.5	15.6 / 14.4 (0.7) / 11.1	12.9	0.85	552	9	251	7	41.9	0.7	0.62	
KEBE 161	07/28/97	13.3	0.3	12.6	0.5	13.8			560	8	244	8				0.05
KEBE 162	11/06/90	23.7	0.2	38.2	1.2				118	4	9	2				
KEBE 162	11/06/91	28.5	0.9	34.4	0.9	36.7			52	8	16	2				
KEBE 162	07/21/93	36.1	0.0	36.3	0.3	>40			20	1	15	0	0.6	0.0		
KEBE 162	04/12/95	37.0	0.8	34.8	2.0		33.5d	9.50	22	1	23	6	0.0	0.0		0.01
KEBE 162	04/12/95	25.9	4.5	24.6	5.1	18.4	26.8e	0.25	167	84	95	42	19.9	9.6	0.14	
KEBE 162	07/28/97	34.8	0.3	33.6	0.5	42.6	26.7	1.24	49	2	37	2	0.0	0.0	0.15	0.00
KEBE 162	12/11/98						26.4	0.25								
KEBE 163	11/06/90	5.9	0.0	13.7	2.6				778	111	231	3	35.5	7.5		
KEBE 163	11/06/91	7.3	0.0	7.2	0.2	9.7			567	4	239	3	41.6	0.2		
KEBE 163	07/21/93	9.3	0.3	8.6	0.0	8.8 / 10.1			562	4	244	1	64.4	0.9		
KEBE 163	04/12/95	9.8	0.0	6.6	0.9	8.3	12.3e	0.25	600	3	291	9	66.4	0.0		
KEBE 163	07/28/97	11.1	0.0	9.5	0.0	10.1	10.1	1.00	634	1	284				0.85	0.07
KEBE 164	11/19/90	18.1	0.9	24.0	2.0	23.5			280	30	64	15				
KEBE 164	12/10/98	16.2	0.2	20.4	0.4		23.7	0.25							0.22	0.01
KEBE 165	11/07/90	17.0	0.3	18.3	0.3				344	8	98	5	7.9	1.0		
KEBE 165	04/02/91	24.1	0.7	24.6	0.0	0.6			332	13	126	2				
KEBE 165	07/29/97	2.9	0.0	8.4	0.4	26.6	25.1	2.26	269	3	114	2			0.16	0.04
KEBE 166	11/07/90	9.6	0.0	3.3	0.0	7.6	9.2	0.41	726	0	287	1	84.8	0.0		
KEBE 166	11/07/90	C		C					665	0	324				1.06	0.04
KEBE 167	11/07/90	10.1	0.0	4.1	1.0	8.8	4.1	0.0	989	12	352	0.7	91.9	1.4		
KEBE 167	07/29/97	50.0	1.0	45.8	7.8	>43	35.1	0.5	769	2	368	6.4	0.0	0.0	1.73	0.01
KEBE 189	07/21/98	C		C		C	8.8	0.3	1	1	8	1.4			0.05	0.00
KEBE 192	07/21/98	13.1	0.0	1.9	0.5	11.6	11.1	0.3	761	7	342	4.7	106.3	0.4	1.13	0.02
KEBE 194	07/20/98	21.1	0.0	10.9	0.2	19.4	20.6		597	1	279	2.2	65.0	2.3	0.92	
KEBE 195	07/20/98			22.4	0.2		10.2		404	2	155	2.9	24.4	3.8	0.32	
KEBE 198	12/11/98	21.1	0.7	21.9	1.0	22.2	23.6	0.3							1.02	0.03
KEBE 199	07/22/98	44.2	0.6	42.2	6.2	33.1	23.9		401	15	160	12.1	16.1	0.4	0.21	
KEBE 199	12/11/98						32.6	0.5							0.20	0.01
KEBE 200	07/22/98	16.9	0.2	16.4	0.6	17.9	42.2	4.8	9	2	19	15.7	1.2	1.8	0.07	
KEBE 200	12/11/98														0.03	0.01
KEBE 206	07/22/98	20.9	0.2	20.6	0.0	19.4	19.1		501	4	215	4.0	29.7	2.5	0.37	
KEBE 206	12/10/98	21.8	0.2	21.1	0.2		19.4								0.37	
KEBE 207	07/23/98	31.6	0.0	20.6	0.0	19.6	19.1	2.0	408	4	175	1.4	24.1	4.5	0.39	0.09
KEBE 207	12/10/98	30.9	0.0	21.1	0.2	19.3	22.4	0.5	401	5	174	1.9	26.0	0.2	0.25	0.02
KEBE 208	07/23/98	31.6	0.0	31.4	0.0	31.6	31.6		101	0	58	2.1	4.5	0.3	0.10	
KEBE 208	12/10/98	30.9	0.0	30.4	0.0	31.9	31.9	0.5	120	1	67	0.9	4.5	0.5	0.03	
KEBE 210	07/22/98	31.2	22.2	46.1	5.0	>43	30.4 / 40.6		3	4	9	8.0	0.0	0.0	0.02	0.00
KEBE 210	12/10/98						46.9	0.0							0.02	
KEBE 211	12/11/98	>50	>55	>43		45.4			0	0			0.0	0.0		0.00
KEBE 212	07/23/98	11.9	0.3	6.4	0.5	8.6	8.6		633	4	319	2.6	86.3	5.7	1.12	0.00
KEBE 216	07/24/98	11.3	0.3	5.1	0.6	9.3	13.6		653	5	322	5.6	85.5	4.8	0.72	0.00

aSD is standard deviation. Blank spaces indicate not determined. C indicates contaminated with one or more CFCs; age could not be determined.
bSource is Ekwurzel et al. [1994].
cNS is numerical simulation [Reilly et al., 1994].
dSF₆ was extracted by equilibration of the water with a gas headspace.
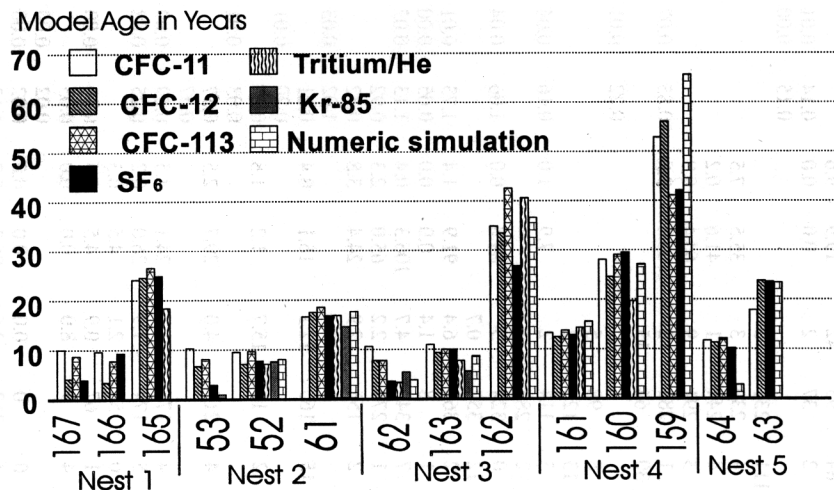eSF₆ was extracted from the sample by spaying the water into a headspace.

Figure 12. Comparison of the model groundwater ages obtained by five different age-dating methods for five well nests at Locust Grove, Maryland (see text for details).

and Denver, 1995], ³H/³He and ⁸⁵Kr [*Ekwurzel et al.*, 1994], and CFC-113 (Figure 13 and Table 3, this study) and with a numerical simulation procedure [*Reilly et al.*, 1994].

8.1. Hydrologic Setting of Locust Grove, Maryland

The Locust Grove Watershed is located on the Delmarva Peninsula on the Atlantic Coastal Plain. The surficial aquifer is unconfined and consists of sands and gravels and ranges in thickness from about 25 m at the Chesterville Branch in the southern part of the watershed to about 5 m in the northern part. The surficial aquifer is underlain by the Aquia confining layer which consists mainly of silt and clay. Maps showing the geographic location, the location of wells, and the flow paths are given by *Dunkle et al.* [1993], *Reilly et al.* [1994], and *Böhlke and Denver* [1995].

The area is intensely farmed; principal crops are corn, soybeans, and ornamental shrubs and trees. The groundwater chemistry has been profoundly altered by the agricultural practices [*Hamilton and Shedlock*, 1992; *Hamilton et al.*, 1993; *Böhlke and Denver*, 1995]. The concentrations of agricultural chemicals in the groundwater can be used to estimate the relative ages of the water at this site [*Böhlke and Denver*, 1995].

8.2. Comparison of SF₆ Model Ages With Model Ages of Other Transient Tracers

The wells at Locust Grove have been sampled numerous times between 1990 and 1998 (Table 3). The early model ages of the groundwater were based on CFC-11 and CFC-12 concentrations using the method of *Busenberg and Plummer* [1992]. These results were presented elsewhere [*Dunkle et al.*, 1993; *Plummer et al.*, 1993; *Ekwurzel et al.*, 1994]. Recently, waters from these wells and some new wells were dated with three CFCs (CFC-11, CFC-12, and CFC-113). The CFC-113 dating method was developed by the authors and has been extensively used by the U.S. Geological Survey to date waters in numerous studies [*Busenberg and Plummer*, 1993; *Cook et al.*, 1995, 1996; *Katz et al.*, 1995; *Szabo et al.*, 1996; *Modica et al.*, 1998; *Plummer et al.*, 1998b; *Plummer and Busenberg*, 1999]. The date of sampling, and the model recharge ages of groundwaters using CFCs, the ³H/³He and ⁸⁵Kr [*Ekwurzel et al.*, 1994], SF₆, and numerical simulation procedures [*Reilly et al.*, 1994] are given in Table 3. The recharge temperatures of 10.5 ±

1.3°C were calculated from the N₂-Ar gas composition of the groundwaters. With the exception of two old samples the volume of excess air present was between 0 and 3 cm³ STP/kg of water. Total He concentrations were measured by gas chromatography and increased with age of the groundwater as shown in Figure 3.

Figure 12 compares the ages of groundwater determined using different methods from five multiwell nests at the Locust Grove study area. Four of the nests are shown in the cross section (Figure 13); wells KeBe 167, 166, and 165 are located north of this cross section, and their groundwater flow direction is to the west toward Morgan Creek. The model ages of all the transient tracers are, for the most part, in good agreement.

The differences between some of the apparent tracer ages are useful in providing clues to some of the processes occurring in the groundwater at this site. For example, comparison of tracer-based ages at different sampling dates may indicate, in part, transient recharge conditions over the approximately 10 years. The CFC-based ages that are older than those based on SF₆ and numerical simulation at well KeBe 53 apparently resulted from the anaerobic biodegradation of CFCs at or near the water table. The discrepancy between the SF₆ and CFC results for the shallow wells KeBe 62 and KeBe 167 may result from the difficulty in dating waters that are less than 10 years old with CFCs. This uncertainty results from the post-1990 rapid decrease in the atmospheric growth rate of CFC-12 (Figure 6a). The growth rate of CFC-12 slowed significantly in mid-1996 and has remained fairly steady since at less than 1% per year [*Butler et al.*, 1998] as a result of the ban of the use of CFCs in developed countries by the Montreal Protocol (Figure 6a); therefore it is possible to resolve only decadal age information in dating post-1993 groundwater with CFC-11 and CFC-113 [*Plummer and Busenberg*, 1999]. Some of the earliest samples (collected in 1990–1991) may have been contaminated with CFC-11 by internal rubber parts used in the sampling pump [*Dunkle et al.*, 1993] leading to ages younger than those obtained in later sampling. Very close agreement was found between other transient tracers and CFCs in the earlier sampling of the some of the wells [*Dunkle et al.*, 1993; *Ekwurzel et al.*, 1994] (Table 3) when CFC concentrations were rapidly rising in the atmosphere. Even though CFC-12 concentrations
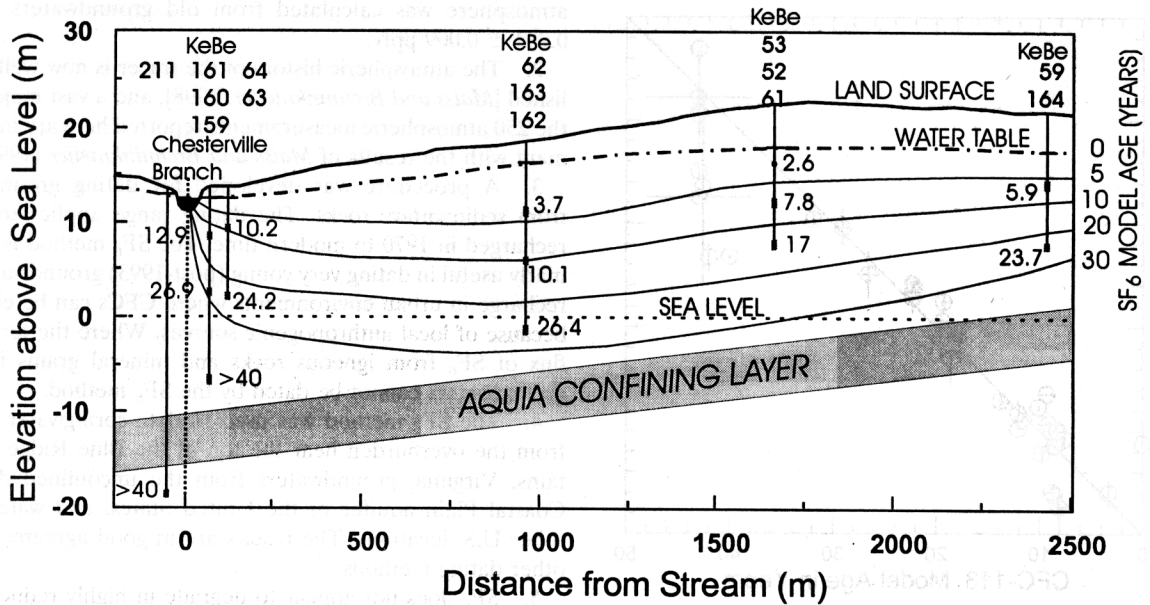
Figure 13. Cross section showing model SF$_6$ ages of the groundwater at Locust Grove, Maryland.

are still increasing, the analytical error of 3% is significantly higher than the present yearly growth rate of about 0.5% per year. Local atmospheric anomalies as well as small uncertainty in the recharge temperature can cause significant error in the calculated model CFC-12 ages in post-1993 water. An advantage in the use of SF$_6$ for dating young groundwaters is the exponential rise of SF$_6$ concentrations in the atmosphere, while CFC-11 and CFC-113 do not give unique ages in post-1993 groundwater (Figure 6a).

Differences of 4 to 6 years in ages based on CFC-12 and ages based on other transient tracers were observed for water from well KeBe 166 (Figure 12). The differences are probably the result of trace contamination of the groundwater with CFC-12. This slight contamination resulted in an age difference of

about 5 years between CFC-12 and other transient tracers. The slight contamination with CFC-12 may have resulted from the use of pesticides where CFC-12 is still present as an inert ingredient [*Plummer et al.*, 2000]. There is better agreement between CFC-113 and the other transient tracers because the uses of CFC-113 were mainly industrial [*Fisher and Midgley*, 1993], and contamination with this compound was less likely at this agricultural site.

Other major discrepancies in age determined from SF$_6$, CFCs, and numerical simulation were observed for water from wells KeBe 159 and 64. KeBe 64 is located near a stream (Figure 13) where the flow lines converge, and the numerical simulation age was uncertain. All transient tracers in the 1998 and previous sampling of this well gave nearly identical ages that were significantly different from the numerical simulation age (Table 3).

Figures 12, 14, and 15 compare the calculated transient tracer ages for the Locust Grove groundwaters. In the SF$_6$ to CFC-12 comparison (Figure 14), about 80% of the model ages agreed to within 3 years. The remaining 20% differed in age by more than 3 years, and most of the waters with the larger differences in age were very young. In the SF$_6$ to CFC-113 comparison (Figure 15), nearly 85% of the ages agreed to within 3 years or better. Waters with ages greater than 30 years are shown in Figures 14 and 15 but were not included in the evaluation above, because the SF$_6$ dating method cannot reliably date water recharged prior to 1970 as a result of tracer concentrations near the detection limit and large uncertainty in the SF$_6$ air curve. Good correlation was also found between the model SF$_6$ age and the nitrate concentration in the groundwater, consistent with the results of *Böhlke and Denver* [1995].

8.3. Dating With Multiple Transient Tracers: Ratios of Two Tracers

Figures 6b and 6c show the ratios of partial pressures of different tracer combinations that were used to date binary mixtures. The CFC-11 to CFC-12 ratio can be used to date 1950 to 1976 waters and post-1992.5 waters. The ratio method gives dual ages for waters recharged between 1972 and 1976
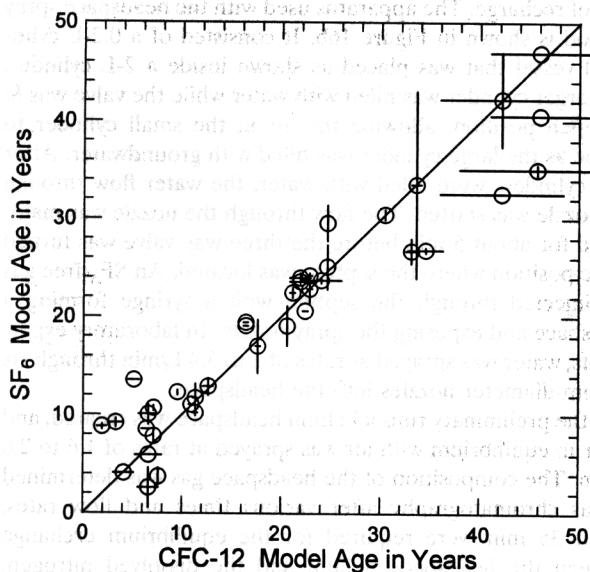

Figure 14. Model SF$_6$ ages as a function of the model CFC-12 ages of groundwaters from Locust Grove, Maryland. Vertical and horizontal lines represent one standard deviation.
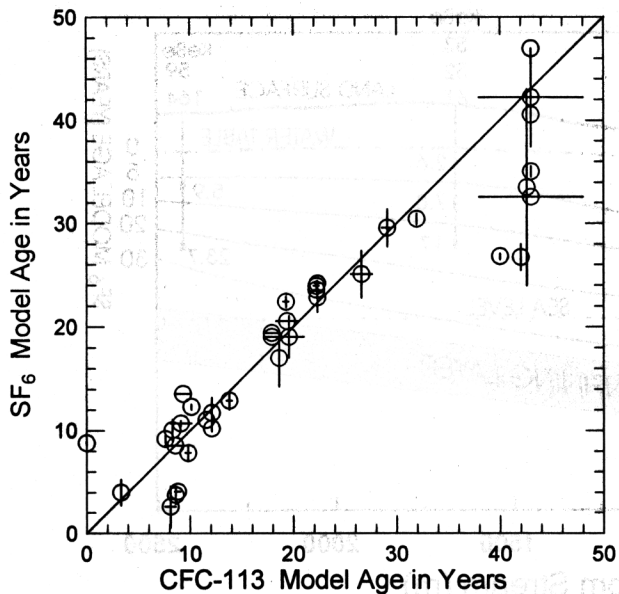
Figure 15. Model SF$_6$ ages as a function of the model CFC-113 ages of groundwaters from Locust Grove, Maryland. Vertical and horizontal lines represent one standard deviation.

and post-1992.5 waters. The dating of waters recharged between 1976 and 1992.5 is not possible because the ratio of these two tracers remained nearly constant in the atmosphere during this time. The CFC-113 to CFC-12 ratio can be used to date 1965 to 1992.5 waters, and the CFC-113 to CFC-11 ratio can be used to date 1980 to 1992 waters [Plummer et al., 1998a, 1998b, 2000; Plummer and Busenberg, 1999]. The CFC ratio method was used extensively in oceanographic studies but was rarely used in groundwater studies because one or more CFC concentrations were often modified by contamination or other physical/chemical processes. Recently, the ratio method has been used to date groundwater and binary mixtures of young and of pre-1940 waters [Plummer et al., 2000; Plummer and Busenberg, 1999]. The SF$_6$ to CFC partial pressure ratio method can be used to date very young groundwater. The SF$_6$ to CFC-11 partial pressure ratio is rapidly increasing and has a useful dating range of 0 to 25 years. The rate of change of the partial pressure ratio is expected to increase as SF$_6$ concentrations increase, while CFC-11 concentrations decline. The SF$_6$ to CFC-12 dating range is also 0 to 25 years; however, the SF$_6$ to CFC-113 dating range is only 0 to 8 years. The SF$_6$ to CFCs partial pressure ratios are ideal for dating the young fraction in mixtures of post-1970s water with older water.

9. Summary and Conclusions

Methodologies were developed for collecting water samples and measuring environmental concentrations of SF$_6$ in groundwater, gases, and rocks. The analytical procedure can measure concentration to less than 0.01 fmol/L in groundwater. SF$_6$ concentrations were measured in more than 250 North American air samples, in minerals and rocks, and in about 3000 natural waters and groundwater samples.

1. Two sources of SF$_6$ were identified, a small natural background and a large anthropogenic component. The natural background concentration constitutes about 1.2% of the 1999 total atmospheric partial pressure of more that 4 pptv. The steady state natural background SF$_6$ concentration in the

atmosphere was calculated from old groundwaters and is 0.054 ± 0.009 pptv.

2. The atmospheric history of the tracer is now well established [Maiss and Brenninkmeijer, 1998], and a vast majority of the 250 atmospheric measurements reported here are in agreement with the results of Maiss and Brenninkmeijer [1998].

3. A procedure was developed for dating groundwater from sedimentary rocks. The dating range applies to water recharged in 1970 to modern time. The SF$_6$ method is particularly useful in dating very young (post-1993) groundwater and recharge in urban environments where CFCs can be elevated because of local anthropogenic sources. Where the terrestrial flux of SF$_6$ from igneous rocks and mineral grains is high, groundwaters cannot be dated by the SF$_6$ method.

4. The SF$_6$ method was used to date springwater issuing from the overburden near the top of the Blue Ridge Mountains, Virginia, groundwaters from the unconfined Atlantic Coastal Plain aquifer of the United States, and water from other U.S. locations. The results are in good agreement with other dating methods.

5. SF$_6$ does not appear to degrade in highly reducing environments.

6. Small but significant concentrations of SF$_6$ were measured in 16 minerals and rocks of igneous, metamorphic, hydrothermal, and sedimentary origin. Concentrations of SF$_6$ were generally highest in silicic igneous rocks and lowest in mafic rocks. Significant concentrations of SF$_6$ may be present in some diagenetic fluids.

7. Concentrations of SF$_6$ significantly higher than equilibrium with modern air and water were measured in groundwater from fractured silicic igneous rocks, from some hot springs, and in some groundwaters from volcanic areas. Concentrations of SF$_6$ may be a useful natural tracer of igneous and volcanic fluids.

Appendix A

A1. Extraction of SF$_6$ by Spray Equilibration of a Headspace With Groundwater

With this procedure the headspace partial pressure eventually equals that of the unsaturated-zone atmosphere at the time of recharge. The apparatus used with the headspace spray method is shown in Figure 16b. It consisted of a 0.2-L cylindrical vessel that was placed as shown inside a 2-L cylinder. The larger cylinder was filled with water while the valve was in the open position, 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 nozzle was started. The flow through the nozzle was maintained for about 5 min before the three-way valve was turned to the position where the septum was located. An SF$_6$-free gas was injected through the septum with a syringe forming a headspace and exposing the spray nozzle. In laboratory experiments, water was sprayed at rates of 1 to 3.4 L/min through six 0.5-mm-diameter nozzles into the headspace.

In the preliminary runs a helium headspace was created, and water in equilibrium with air was sprayed at rates of 1.6 to 2.8 L/min. The composition of the headspace gas was determined by gas chromatography after various times and flow rates. About 35 min were required for the equilibrium exchange between the headspace helium and the dissolved nitrogen, oxygen, and argon in the water.

In the next set of experiments, nitrogen, room air, helium, and nitrogen containing 100 pptv of SF$_6$ were injected into the

headspace. These runs were used to determine the equilibrium exchange time between the SF₆ dissolved in the water and the headspace gas. At a spray rate of 2 L/min a little more than 30 min are required to reach exchange equilibrium with the helium headspace, but more than 1 hour is required with the nitrogen headspace (Figure 17, linear scale). In the next set of experiments (Figure 17, logarithmic scale), nitrogen with a concentration of 100 pptv SF₆ was injected in the headspace. About 1 hour was required to reduce the 100 pptv SF₆ concentration to the equilibrium concentration of the water. In other experiments the water spray rates were investigated. The exchange equilibrium time decreased with increasing spray rates; the time was cut in half when the spray rate was increased from 2.0 to 3.4 L/min. In other runs the physical placement of the nozzle in the headspace was investigated. The placement of the nozzle was found to significantly influence the exchange equilibrium time.

Even though it is theoretically possible to use this method to collect SF₆ samples, the time required to reach exchange equilibrium was about 1 hour and at least 120 L of water were required, which makes this method impractical under most field conditions. The exchange runs never reached equilibrium (1) when the groundwater temperature was significantly different from the groundwater recharge temperature, (2) when the groundwater contained significant amounts of dissolved excess air, and (3) when the groundwater contained significant excess N₂, H₂S, and CH₄. Under these conditions the headspace volume rapidly increased during the run, and exchange equilibrium was never achieved.

A2. Extraction of SF₆ by the Equilibration of Groundwater With a Headspace

In oceanographic studies, high concentrations of SF₆ tracer were added to seawater. Seawater was sampled with a glass

Figure 17. Concentration of SF₆ in a headspace as a function of time.

Figure 16. Diagram of apparatus used to extract SF₆ from groundwater (see Appendix A for details): (a) bottles used for the collection of SF₆ samples (section 2.3), (b) apparatus used to equilibrate a headspace with the gases present in groundwater (section 10.1) (c) apparatus used to extract SF₆ into a headspace (section 10.2), and (d) trap used for the collection of SF₆ samples at the well site (section 10.3).
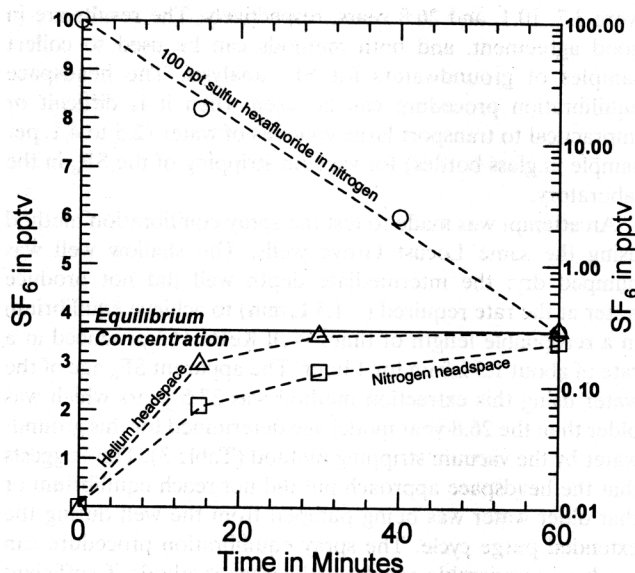
syringe, and a nitrogen headspace was added. The syringe was shaken, then the headspace gas was injected into a gas chromatograph. The procedure was discussed in detail by Sliwka and Lasa [2000], Law et al. [1994] and Wanninkhof et al. [1991]. A variation of this procedure was used in this study. Since natural levels of SF₆ are low, the transient tracer was extracted from 4 L of water. The extraction bottle (Figure 16c) was filled from the tube placed near the bottom of the bottle. After the bottle was filled and was allowed to overflow for at least one bottle volume, the water in three-way valve was closed. A headspace of known volume was created with the injecting SF₆-free N₂ or He and the second three-way valve was closed. The water was vigorously shaken for about 10 min, and the headspace was equilibrated with the water in the bottle. The headspace gas then was removed from the bottle and was flame sealed into glass ampoules for SF₆ analysis in the laboratory. The concentration of SF₆ in the groundwater was calculated from the volume of the headspace, the volume of the water, and the temperature of the water in the bottle.

A3. Extraction of SF₆ by Vacuum Stripping of SF₆ From Groundwater at the Well Site

SF₆ was vacuum extracted in the field and collected in precleaned traps (Figure 16d) using the vacuum stripping procedure of Law et al. [1994] and an apparatus similar to that shown in Figure 1a. The vacuum stripping procedure was discussed in section 2.3. Technical problems with the vacuum pumps often occurred in the field when air temperatures dropped below 10°C.

A4. Comparison of the SF₆ Sampling Methods

A comparison of the headspace equilibration and vacuum stripping procedures was performed at Locust Grove, Maryland. A three-well nest was selected with a shallow (KeBe 62), an intermediate (KeBe 163), and a deep well (KeBe 162) to test the procedure with groundwater containing high, intermediate, and low SF₆ concentrations. The model SF₆ recharge ages of the groundwaters, obtained by the headspace equilibration method, were 4.0, 12.3, and 26.8 years, respectively. The results from the vacuum stripping method for the samples

were 3.7, 10.1, and 26.8 years, respectively. The results are in good agreement, and both methods can be used to collect samples of groundwaters for SF$_6$ analysis. The headspace equilibration procedure can be used when it is difficult or impractical to transport large volumes of water (2.5 to 4 L per sample in glass bottles) for vacuum stripping of the SF$_6$ in the laboratory.

An attempt was made to test the spray equilibration method using the same Locust Grove wells. The shallow well was pumped dry; the intermediate depth well did not produce water at the rate required (~1.5 L/min) to achieve equilibrium in a reasonable length of time. Well KeBe 162 produced at a rate of about 1.5 L/min for 1 hour. The apparent SF$_6$ age of the water using this extraction method was 33.5 years which was older than the 26.8-year model age determined for this groundwater by the vacuum stripping method (Table 3). This suggests that the headspace approach but did not reach equilibrium or that older water was being pumped from the well during the extended purge cycle. The spray equilibration procedure can produce comparable results with other methods if sufficient time is allowed for the water to reach equilibrium with the headspace (Figure 17). This method is impractical for most field use applications because of the large volume of water needed (>120 L), the length of time required (>1 hour) to reach exchange equilibrium at groundwater temperatures of 10°C, and the assumption of constant water composition in discharge from the well for periods of >1 hour.

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