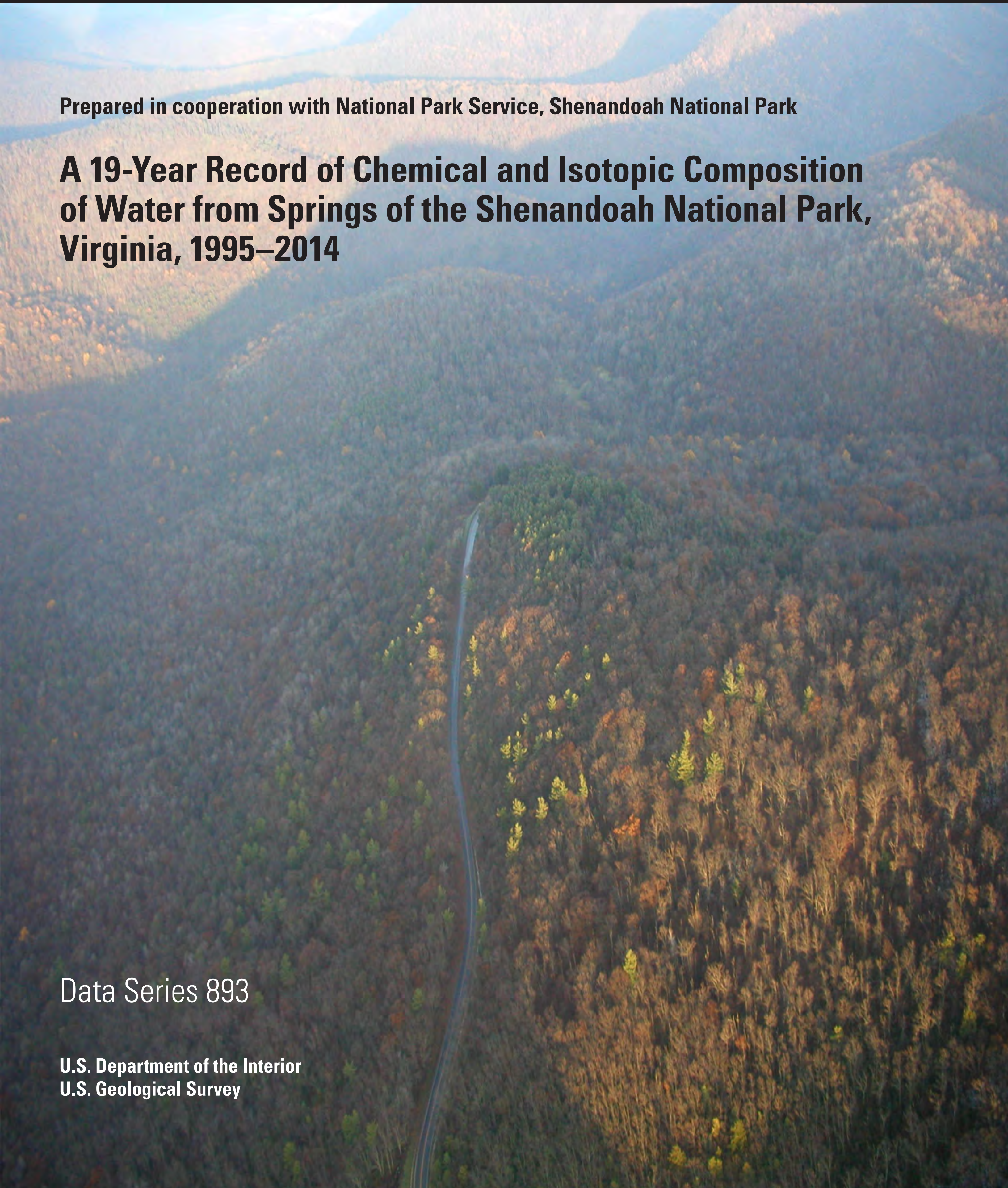

Prepared in cooperation with National Park Service, Shenandoah National Park

A 19-Year Record of Chemical and Isotopic Composition of Water from Springs of the Shenandoah National Park, Virginia, 1995–2014

Data Series 893

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

Cover: Skyline Drive south of Elkwallow Wayside in Shenandoah National Park, Virginia. Aerial view looking to the northeast. Photograph by David L. Nelms, U.S. Geological Survey

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U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
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Tables (*available at http://pubs.usgs.gov/ds/2014/893/*)

Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
meter (m)	3.281	foot (ft)
meter (m)	1.094	yard (yd)
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
micrometer (µm)	0.000001	meter
kilometer (km)	0.6214	mile (mi)
kilometer (km)	0.5400	mile, nautical (nmi)
	Area	
square kilometer (km^2)	247.1	acre
square centimeter (cm^2)	0.001076	square foot (ft^2)
square meter (m^2)	10.76	square foot (ft^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	0.2642	gallon (gal)
milliliter (mL)	0.001	liter
cubic meter (m^3)	264.2	gallon (gal)
cubic meter (m^3)	0.0002642	million gallons (Mgal)
cubic centimeter (cm^3)	0.06102	cubic inch (in^3)
liter (L)	61.02	cubic inch (in^3)
cubic meter (m^3)	35.31	cubic foot (ft^3)
	Flow rate	
liter per minute (L/min)	0.2642	gallon per minute (gal/min)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
milligram (mg)	0.001	gram (g)
microgram (µg)	0.000001	gram (g)
picogram (pg)	10^{-12}	gram (g)
femtogram (fg)	10^{-15}	gram (g)
kilogram (kg)	2.205	pound avoirdupois (lb)
	Pressure	
kilopascal (kPa)	0.009869	atmosphere, standard (atm)
kilopascal (kPa)	0.01	bar

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Altitude, as used in this report, refers to distance above the vertical datum.

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

°F=(1.8×°C)+32

Specific conductance (SC) is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

φ_A Volume fraction of gas *A* in a mixture.

^{i}E, ^{j}E The symbols *i* and *j* represents the atomic number (sum of protons plus neutrons in the nucleus) of element *E*.

Stable isotope ratios are expressed in $\delta^{i}E$ where $\delta^{i}E$ in per mil (o/oo or 1/1000) is given by the equation:

$$\delta^{i}E = \left[\frac{n_X(^{i}E)/n_X(^{j}E)}{n_{ref}\left(^{i}E\right)/n_{ref}(^{j}E)} - 1 \right] \times 1000$$

where *i* refers to the delta value of the isotope number of element *E* of sample *X* relative to the reference *ref*, and $n_x(^{i}E)/n_x(^{j}E)$ and $n_{ref}(^{i}E)/n_{ref}(^{j}E)$ are the ratios of the isotope amounts in the unknown *X* and the reference standard *ref*.

A tritium unit (TU) is equal to 3.22 picocuries per liter or a tritium to hydrogen ratio of 10^{-18}.

One mole contains 6.022×10^{23} atoms or molecules of a substance.

Concentrations in gases are expressed as a mixing ratio, that is, volume of gas per volume of dry air, in parts per trillion [parts per trillion by volume (pptv)]

Abbreviations

Al	aluminum
Ar	argon
B	boron
Ba	barium
C	carbon
Ca	calcium
CFC	chlorofluorocarbon
CFC-11	trichorofluoromethane ($CFCl_3$)
CFC-12	dichlorodifluoromethane (CF_2Cl_2)
CFC-113	trichlorotrifluoroethane ($C_2F_3Cl_3$)
CF_3Br	trifluorobromomethane (H-1301)
CH_4	methane
CMDL	Climate Monitoring and Diagnostic Laboratory
CO_2	carbon dioxide
HCO_3^-	bicarbonate
H_2CO_3	carbonic acid
Cl^-	chloride
Cu	copper
DO	dissolved oxygen
F^-	fluoride
Fe	iron
H	hydrogen
^2H	hydrogen-2, deuterium
^3H	hydrogen-3, tritium
He	helium
^3He	helium-3
^4He	helium-4
K	potasium
Mg	magnesium
Mn	manganese
N_2	nitrogen (in the form of dinitrogen)
Na	sodium
Ne	neon
Ni	nickel

NO_3^-	nitrate
NOAA	National Oceanic and Atmospheric Administration
O_2	oxygen (in the form dioxygen)
^{16}O	oxygen-16
^{18}O	oxygen-18
Pb	lead
PF	piston flow
ppt	parts per trillion
pptv	part per trillion by volume
Rb	rubidium
SC	specific conductance
SF_6	sulfur hexafluoride
SF_5CF_3	trifluoromethyl sulfurpentafluoride
SIO	Scripps Institution of Oceanography
SiO_2	silicon dioxide
SO_4^{2-}	sulfate
Sr	strontium
TU	tritium unit
USGS	U.S. Geological Survey
V	vanadium
Zn	zinc

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Abstract

During October 1995 through March 2014, the U.S. Geological Survey in cooperation with the National Park Service, Luray, Virginia Station collected and analyzed samples of selected springs, air and unsaturated-zone gases in Shenandoah National Park, Virginia. The 19-year record of measurements of chemical and isotopic composition of water discharging from 34 springs located along the crest of the Blue Ridge Mountains in Shenandoah National Park, Virginia, is reported. These data include field measurements of water temperature, specific conductance, concentrations of dissolved oxygen (O_2), and pH. Laboratory measurements included major-, minor-, and trace-element chemistry; concentrations of dissolved gases (nitrogen, [N_2] argon [Ar], oxygen, and carbon dioxide [CO_2]); concentrations of dissolved trace atmospheric gases, including trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), and trichlorotrifluoroethane (CFC-113) and sulfur hexafluoride (SF_6); and hydrogen stable isotopic composition (δ^2H) and oxygen isotopic composition ($\delta^{18}O$) of water. The data include an up to 14-year time series record of monthly sampling at five springs collected between 1995 and 2013. The measurements included temperature, specific conductance, pH, and discharge recorded at 30-minute intervals. Atmospheric mixing ratios of CFC-11, CFC-12, CFC-113, trifluorobromomethane (CF_3Br), SF_6, and trifluoromethyl sulfur pentafluoride (SF_5CF_3) in air from the Big Meadows Air Monitoring Station, Shenandoah National Park, were measured at approximately weekly intervals from September 1995 through March 2014.

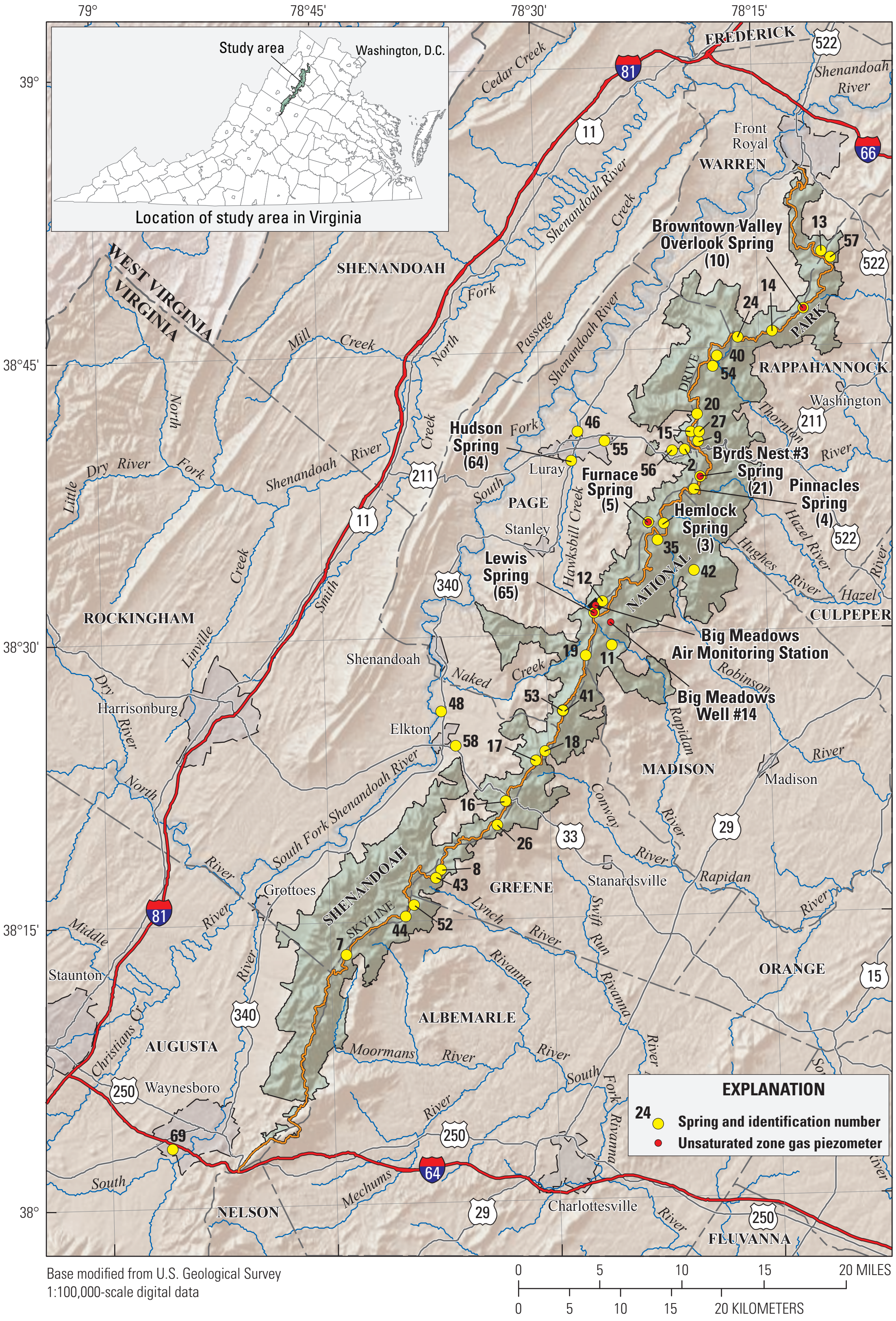
Additional data include monthly (between May 2001 and August 2003) measurements of temperature, N_2, O_2, Ar, CO_2, CFC-12, CFC-11, CFC-113, and SF_6 concentrations in unsaturated-zone air from seven multilevel piezometers in Shenandoah National Park and at the U.S. Geological Survey National Center in Reston, Virginia. All samples were analyzed at the U.S. Geological Survey Laboratories in Reston, Virginia.

Introduction

Shenandoah National Park is located in the western part of the Blue Ridge province (Tollo and others, 2004) and covers an area of approximately 800 square kilometers (km^2) in Virginia (fig. 1). The altitude above sea level ranges from 170 meters (m) at the northeastern part of the park near Front Royal, Virginia, and increases to 1,230 m in the center of the park. The Shenandoah National Park (DeKay, 1972) area is underlain with fractured Mesoproterozoic- to Cambrian-age rocks. The bedrock consists of granitic gneisses, metabasalts, and granitoid crystalline rocks that often are overlain by a thin layer of residuum of between 0 to 9 m thick (Southworth and others, 2009). The limited water resources of the park reside mainly in the overburden (DeKay, 1972).

Water from springs and wells is the sole source of public and staff supply for Shenandoah National Park, which receives approximately 1.2 million visitors annually (National Park Service, 2013). The only information about the quality of groundwater in the Park, its susceptibility to contamination, the response times of springs and wells to transient chemical inputs, and lag times (groundwater ages, groundwater residence times) necessary for flushing of contaminants from groundwater is provided by Plummer and others (2000, 2001) and Busenberg and Plummer (2014).

Approximately 850 springs and seeps have been identified throughout the park, but most of these have discharges of less than several liters per second, and most are located at elevations significantly below park facilities, limiting their usefulness as water supplies to park facilities (DeKay, 1972). Approximately 70 springs are known to occur above or near Skyline Drive, the principal route of travel in the park that traverses 170 km along the crest of the Blue Ridge Mountains (fig. 1).



Base modified from U.S. Geological Survey 1:100,000-scale digital data

Figure 1. Location of springs and unsaturated zone gas piezometers in the Shenandoah National Park.

The potential for contamination of water supplies in Shenandoah National Park is compounded by two factors. First, water discharged from shallow, unconfined springs can be easily contaminated from surficial sources, and fractured rock is difficult to protect from contamination because of the multiplicity and unknown connections of flow paths available to waters infiltrating from the land surface. Secondly, the potential for contamination of water supplies is increased by the location of facilities in the park. The result is that most public water supplies are located in the most populated parts of the park, and at higher altitudes that lack surface-water sources.

Springs used for public water supply were modified by subsurface construction in the 1930s to enhance discharge and collection (DeKay, 1972). In some cases, the development was fairly extensive, with underground construction of "wing walls," gravel packs, and terra cotta pipes that channel water, often from multiple subsurface sources, to a weir box and then to a central collection and distribution system where the water is chlorinated. Construction records indicate that some springs combine discharge from shallow fractures in bedrock with water draining from shallow colluvium and residuum that overlies the bedrock (DeKay, 1972).

The measurement of the concentrations of atmospheric environmental tracers and other chemical and isotopic substances in water from springs and wells gives information on groundwater quality, groundwater age, and travel time. Environmental tracers (chlorofluorocarbons [CFCs], tritium [^{3}H], tritiogenic helium-3 [^{3}He], sulfur hexafluoride [SF_6]) have known historical atmospheric concentrations (Plummer and Busenberg, 1999; International Atomic Energy Agency, 2006). Elevated concentrations of chlorofluorocarbons (Plummer and Busenberg, 1999) can be used to identify water supplies that are being affected by human activities (Plummer and others, 2001).

During October 1995 through May 2014, the U.S. Geological Survey in cooperation with National Park Service completed several synoptic samplings of selected springs and wells in Shenandoah National Park, along with other studies of air and precipitation chemistry. This report tabulates the chemical and isotopic data obtained by the U.S. Geological Survey for water from shallow springs in Shenandoah National Park. Additional data are given on the chemical and isotopic composition of water samples from selected surface waters at the base of the Blue Ridge Mountains surrounding Shenandoah National Park, and for trace gases (chlorofluorocarbons and SF_6) in air from the Big Meadows Air Monitoring Station, Shenandoah National Park (Plummer and others, 2000).

For samples from springs and wells, the data in the Plummer and others (2000) report include field measurements of water temperature, SC, concentrations of dissolved oxygen (O_2), and pH, and laboratory measurements of major- and trace-element chemistry, concentrations of dissolved gases nitrogen (N_2), argon (Ar), helium (He), neon (Ne), O_2, carbon dioxide (CO_2), ^{3}H of water. Also measured were concentrations of dissolved trace atmospheric gases, including chlorofluorocarbons (CFC-11, CFC-12, and CFC-113) and SF_6, the $^3He/^4He$ isotope ratio (given as δ^3He) of dissolved helium, hydrogen and oxygen isotope deltas (δ^2H and δ^{18}O) of water. Surface-water samples include measurement results of δ^2H, δ^{18}O, ^{3}H concentration in tritium units. Air samples include analyses of CFC-11, CFC-12, and CFC-113, and SF_6.

Climatic Data for Shenandoah National Park

An almost complete record of precipitation and temperature is available in the Great Valley of Virginia at Luray, located about 10 km west of the crest of the Blue Ridge Mountains, and at Front Royal, located about 6 km north of the park. A partial record also is available at the Big Meadows Air Monitoring Station, which is located within Shenandoah National Park (fig. 1). No trend in mean daily temperature is discernible in the Luray and Big Meadows Air Monitoring Station records between 1995 and 2012, but an annual warming of 0.107 degrees Celsius (°C) between 1996 and 2011 was evident in the Front Royal record (Busenberg and Plummer, 2014). This station is located within an urban area and the increase is attributed to local factors rather than climatic changes. The mean, maximum, and minimum annual temperatures at Big Meadows during this period were 8.5, 9.5, and 7.4 °C respectively (National Climate Data Center, 2013). The average annual precipitation at the Big Meadows Air Monitoring Station (elevation 1,070 m) for the years 1995 through 2011 was 143.5 centimeters (cm), with an annual maximum of 193.7 and a minimum of 103.7 cm (National Atmospheric Deposition Program, 2011).

Sample Locations

All springs are shown on figure 1 by site identification number, and also identified by site name and site identification number in tables 1–15. The site numbers from figure 1 are used throughout this report. Samples may also be distinguished by site name, and site identification number in the tables. A total of 40 springs were sampled (table 1). Water from selected springs and wells was sampled in April 1996 and August–December 2011. Lewis Spring and Furnace Spring were sampled monthly between March 1999 and April 2014. Byrds Nest No. 3 Spring, Browntown Valley Overlook Spring, and Hudson Spring were sampled monthly between March 1999 and November 2011.

The site number, latitude, longitude, altitude, and the principal geologic formation for the springs are included in table 1. Latitude and longitude were determined using the NAVSTAR Global Positioning System (GPS) Precise Positioning Service (PPS) equipment. Site locations are based on averages of approximately 1,000 readings from the GPS/PPS in "Continuous Mode" operation and are accurate to within approximately 0.01 seconds (table 1).

The principal geologic formation was based on data of Gathright (1976), DeKay (1972), and Southworth and others (2009). All samples from within the boundaries of Shenandoah National Park are located on the surficial geologic map (Gathright, 1976; Southworth and others, 2009).

Sample Collection and Analytical Procedures

The methods used to sample springs and wells were selected to minimize or eliminate contact with air. For developed springs, a stainless steel piston displacement pump (Bennett pump) was inserted in the discharge pipe for the spring. If possible, flow from the spring was then blocked, flooding the below-land-surface construction. A closed path from the pump to the sample container prevented subsequent contact with air. Spring discharge was measured by capturing timed flow in a calibrated bucket. Stability in field parameters including water temperature, SC, pH, and dissolved oxygen provided additional guidelines in determining when to sample. A closed path was established between the spring and sampling equipment to prevent contact of the sample with air.

Calculated Field Parameters

Calculated dissolved oxygen (DO) in the tables equals the sum of the equilibrium solubility of O_2 at the discharge temperature plus the O_2 contribution of excess air measured in this study. In many instances, the measured and calculated DO are nearly identical. When the calculated DO is higher than the measured DO, it indicates that O_2 was consumed by bacterial oxidation of organic matter, oxidation reactions of mineral phases, or both.

The pH can be easily calculated from the measured partial pressure of CO_2 obtained from the dissolved gas analyses, the measured bicarbonate alkalinities, and the calculated activity coefficients. The activity coefficients of these dilute waters were calculated using the Davies equation (Garrels and Christ, 1965). The calculated activities (a) are defined as the measured molal concentrations (m) multiplied by the calculated activity coefficients (γ) of about 0.99 for these springs. The activity of species i is defined by the equation $a_i = \gamma_i . m_i$. K_{Henry} is Henry's law constant for the dissolution of $CO_{2(gas)}$ in water as a function of temperature, and K_1 is the first dissociation constant of carbonic acid ($H_2CO_{3(aq)}$). The activity of H^+ can be calculated by combining the equations 1 and 2 below:

$$K_{Henry} = \frac{a_{H_2CO_{3(aq)}}}{P_{CO_2}} \qquad (1)$$

and

$$K_1 = \frac{a_{H^+} \times a_{HCO_3^-}}{a_{H_2CO_{3(aq)}}} \qquad (2)$$

to obtain,

$$a_{H^+} = \frac{K_{Henry} \times K_1 \times P_{CO_2}}{a_{HCO_3^-}} \qquad (3)$$

In these dilute waters, the alkalinity can be substituted for the concentration of the bicarbonate.

The pH is defined as the following equation:

$$\mathrm{pH} \equiv -\log_{10}(\gamma_{H^+} \times m_{H^+}) \equiv -\log_{10} a_{H^+}. \qquad (4)$$

The pH was calculated at the discharge temperature of the springs, and the temperature dependence of the equilibrium constants was obtained from Plummer and Busenberg (1982). The calculated pH values are believed to be more accurate than the measured pH because it is very difficult to measure pH in very dilute waters with glass electrodes (Bates, 1973; Busenberg and Plummer, 1987).

The SC of dilute solutions is the sum of the limiting ionic conductance (l_{0i}) times equivalent concentrations of the ions in solution $c_i z_i$ where c_i and z_i are the molar concentration and charge of the ions (i) in solution, respectively. The ionic strengths of the springs in Shenandoah National Park range from 0.0001 for Hemlock Spring to a maximum 0.0006 for Lewis Spring. The calculated SC determined from limiting conductance were as much as 1 percent too high (MacInnes, 1939). The calculated SC is more reliable than the field-measured conductance in these cold and dilute solutions (Maron and others, 1974).

Air Samples

Ambient air samples were collected in 800-cubic-centimeter (cm^3) stainless steel flasks with electro-polished internal surfaces using an ultra-pure diaphragm-type pump and analyzed for concentrations of CFCs, CF_3Br, SF_6, and SF_5CF_3. The flasks were prepared in the laboratory and filled with air. At the Big Meadows Air Monitoring Station, the flasks were flushed with air for 15 minutes before filling. Total sample pressure was typically 2 atmospheres. Air samples were pumped through 3.1-millimeter (mm) outer diameter refrigeration-grade stainless steel tubing from a point approximately 10 m above land surface. The gas samples were analyzed by electron capture detector (ECD) gas chromatography, with a precision of better than 5 percent.

Unsaturated Zone Gases

Piezometers were augered into the unsaturated zone. Refrigeration-grade 0.3175-cm (1/8-inch) copper tubing and a thermocouple were inserted into the augered holes. A few centimeters of coarse sand was added followed by a few centimeters of powdered silica and then some of the soil that was removed by the auger. The soil was compacted by tamping with a metal rod. Additional sampling ports were added to the augered hole by repeating the previous steps. The sampling copper tubes were capped at the surface.

Unsaturated zone gases were collected in borosilicate ampoules using the apparatus and procedures described in Busenberg and Plummer (1992) and Busenberg and others (2000). The 60- and 100-cm^3 ampoules were flame sealed with an O_2-propane gas torch. Several ampoules were collected at each port; the sampling proceeded from the shallowest to the next deeper port. In the laboratory, the ampoules were scored then inserted into the evacuated port and sampling loops, the scored neck broken, and the pressure measured with a transducer. The concentrations of CFC-11, CFC-12, CFC-113, SF_6, N_2, O_2, Ar, and CO_2 were measured by the procedures described in Busenberg and Plummer (1992, 2000) and Busenberg and others (1998). The pressures were normalized to 1 atmosphere and reported as dry volume fractions.

Water Chemistry

The procedures and guidelines established by the USGS were followed in the collection and preservation of the water samples (Wilde and others, 1998). Samples for analysis of cations were filtered (0.45 micrometers [µm]) and collected in acid-rinsed 250-milliliter (mL) polyethylene bottles. The samples were acidified with 1 mL of ultra-pure nitric acid. The samples for analysis of anions were filtered and collected in 250-mL polypropylene containers. The containers, filters, and acid were obtained from USGS National Water Quality Laboratory in Lakewood, Colorado. Further details of field collection procedures are described elsewhere (Busenberg and Plummer, 1992; Dunkle and others, 1993; Busenberg and others, 1998, 2000; Plummer and others, 2000, 2003).

Samples collected before 1997 were analyzed for major cations and silica at the USGS Water Chemistry Laboratory in Reston, Virginia, using the ARL SpectraSpan V, a multielement direct-current plasma spectrometer (DCP). The instrument was equipped with the Adam analytical manager and background corrector. The analytical detection limits in parts per million for calcium (Ca), magnesium (Mg), strontium (Sr), silicon dioxide (SiO_2), sodium (Na), potassium (K), iron (Fe), manganese (Mn), and aluminum (Al) by the DCP were less than 0.1, 0.01, 0.005, 0.1, 0.05, 0.1, 0.01, 0.005, and 0.005, respectively. Reproducibility of the measurements by the DCP were 3 to 5 percent for Ca, Mg, Sr, and Na; 5 percent for SiO_2 and Mn; 5 to 10 percent for K and Fe; and 10 to 15 percent for Al.

Post-1997 samples were analyzed with a Perkin Elmer Optima 4300DV inductively coupled plasma-optical emission spectrophotometer with a Burgener Mira-Mist nebulizer and cyclonic spray chamber. The detection limits in parts per million for Ca, Mg, Sr, SiO_2, Na, K, Fe, Mn, and Al are 0.1, 0.1, 0.005, 0.2, 0.1, 0.1, 0.02, 0.01, and 0.01, respectively. The reproducibility of measurements was on the order of 3 to 5 percent.

Samples were analyzed for trace cations using a Perkin Elmer ELAN6000 and a Perkin Elmer ELAN9000 (post-2008) inductively coupled plasma-mass spectrometer (ICP-MS) with a Scott-type cross flow nebulizer for sample introduction and a quadrupole mass separator. The detection limits in parts per billion for barium (Ba), copper (Cu), Mn, nickel (Ni), rubidium (Rb), and vanadium (V) were 0.1. The detection limits in parts per billion for Al, lithium (Li), and zinc (Zn) were 1. The detection limits in parts per billion for lead (Pb) and boron (B) were 0.05 and 20, respectively. The reproducibility of measurements was generally 3 to 5 percent for all elements analyzed by ICP-MS.

A Dionex series 4000i ion chromatograph (IC) equipped with a Dionex AS4 column (1996 data), and a Dionex DX-120 equipped with a Dionex AS14 column (post-1996 data) were used for the analysis of samples for fluoride, chloride, nitrate, and sulfate. Bromide was measured with a Dionex DX-120 ion chromatograph. Detection limits in parts per million for chloride, sulfate, nitrate, and fluoride were less than 1, 2, 0.1, and 0.05, respectively. The bromide detection limit depended on the volume of the sampling loop used to inject the sample into the ion chromatograph and ranged from less than 0.005 to less than 0.02 parts per million. The reproducibility of measurements of chloride, sulfate, nitrate, fluoride, and bromide were 3, 3–5, 3–5, 3, and 10 percent, respectively.

Major Dissolved Gases

Water samples for analysis of major dissolved gases were collected in 150-cm^3 septum bottles without headspace. Concentrations of N_2, Ar, O_2, and CO_2 were measured in the USGS Dissolved Gas Laboratory, Reston, Va., using gas chromatography (see U.S. Geological Survey Chlorofluorocarbon Laboratory, 2014 at URL *http://water.usgs.gov/lab/cfc/*). Replicate analyses of N_2 and Ar in laboratory standards prepared by equilibrating water samples with air were typically within 1 percent and yielded calculated equilibration temperatures within ±0.5 °C (see Busenberg and others, 1998 for further details). The dissolved O_2 and CO_2 analyses have uncertainties similar to dissolved N_2 and Ar, but can deviate as much as 10 percent between replicate samples because of varying extents of microbiological processes occurring in the sample bottles. The concentrations of the major dissolved gases in groundwater in Plummer and others (2000, 2001) were calculated using Henry’s law constants given in Wilhelm and others (1977). All the dissolved gas data were recalculated using the Henry’s Law constants of Weiss (1970) for N_2, Ar, and O_2, and Weiss (1974) for CO_2.

Chlorofluorocarbons

Water samples for analysis of CFCs were sealed into borosilicate ampoules in the field using collection procedures that prevent contact with air (Busenberg and Plummer, 1992; International Atomic Energy Agency, 2006). Concentrations of the CFCs, CFC-11 (trichlorofluoromethane, $CFCl_3$), CFC-12 (dichlorodifluoromethane, CF_2Cl_2), and CFC-113, (trichlorotrifluoroethane, $C_2F_3Cl_3$) were determined using purge and trap gas chromatography with an electron-capture detector at the USGS Chlorofluorocarbon Laboratory, Reston, Va. (Busenberg and Plummer, 1992; *http://water.usgs.gov/lab/cfc/*). The concentrations of CF_3Br (erroneously identified as CFC-13 in Busenberg and Plummer, 2008, 2014) and SF_5CF_3 were determined by the procedure of Busenberg and Plummer (2008). The CFC concentrations are referenced to average air compositions measured at Niwot Ridge, Colo. (Climate Monitoring and Diagnostics Laboratory [CMDL] of the National Oceanic and Atmospheric Administration [NOAA], U.S. Department of Commerce [*http://www.esrl.noaa.gov/gmd/hats/index.html*]). The concentrations are reported on the Scripps Institution of Oceanography SIO-2005 Scale (Prinn and others 2000, 2001; Miller and others, 2008; *http://agage.eas.gatech.edu/data.htm*). The detection limit for the determination of mass fractions of CFC-11 and CFC-12 is near 0.3 picograms per kilogram of water (pg/kg), and approximately 1 pg/kg for CFC-113. The primary standard is air collected at Trinidad Head, California, on March 12, 2008, and stored in a stainless steel cylinder. The tank was calibrated on September 9, 2008, at Scripps Institution of Oceanography in the laboratory of Ray Weiss. The volume fractions of SF_6, CFC-12, CFC-11, and CFC-113 on the SIO-95 scale are 6.55 ±0.016, 539.58±1.35, 245.24±0.061, and 76.87±0.16 part per trillion (10^{-12}), respectively. To convert from the SIO-95 scale to the SIO-2005 for CFC-12, CFC-11, and CFC-113, multiply the SIO-95 values by 1.000, 0.995, and 1.004, respectively (*http://agage.eas.gatech.edu/data.htm*). Further details on interpretation of CFC-based apparent age are in International Atomic Energy Agency (2006). The CFC concentrations in Plummer and others (2000, 2001) were recalculated using the revised N_2/Ar recharge temperatures and excess air concentrations given in this report.

Sulfur Hexafluoride

Water samples for analysis of SF_6 were collected in 1.0-liter (L) plastic-coated glass bottles. The tube carrying water from the sample pump was placed in the bottom of the bottle, displacing the air above the water. After at least 3 L of overflow, the tube was slowly removed. The bottles were sealed with polycone-seal lined screw caps without headspace. The cone liners in the caps allowed for some expansion of the water on warming. The water samples were analyzed for sulfur hexafluoride in the USGS Chlorofluorocarbon Laboratory in Reston, Va., by purge and trap gas-chromatographic procedures (Busenberg and Plummer, 2000). The SF_6 detection limit was approximately 1.5 femtograms per liter (fg/L). The concentrations are reported on the NOAA-2006 scale (*http://www.esrl.noaa.gov/gmd/ccl/SF6_scale.html*). There is little to no difference between the NOAA-2006 and SIO-95 scales for SF_6. The SF_6 concentrations were recalculated using Henry's law constants of Bullister and others (2002) and the revised recharge temperatures and excess air concentrations given is this report. The SF_6 ages were recalculated using local air curve (Busenberg and Plummer, 2014).

Stable Isotope Ratios of Oxygen and Hydrogen in Water

Water samples for determination of the stable hydrogen and oxygen isotopic compositions were untreated and collected in 60-cm^3 glass bottles with polycone-seal liner caps. The stable oxygen and hydrogen isotope deltas were determined on water samples at the Reston Stable Isotope Laboratory (RSIL; *www.isotopes.usgs.gov*) of the USGS, Reston, Va. The oxygen isotope delta, δ^{18}O, is defined by the following relation (Coplen, 2011):

$$\delta^{18}\mathrm{O} = \frac{N\left(^{18}\mathrm{O}\right)_\mathrm{P}/N\left(^{16}\mathrm{O}\right)_\mathrm{P} - N\left(^{18}\mathrm{O}\right)_\mathrm{std}/N\left(^{16}\mathrm{O}\right)_\mathrm{std}}{N\left(^{18}\mathrm{O}\right)_\mathrm{std}/N\left(^{16}\mathrm{O}\right)_\mathrm{std}} \tag{5}$$

where N(^{18}O)$_P$ and N(^{16}O)$_P$ are the numbers of the two isotopes ^{18}O and ^{16}O of oxygen in specimen P, and equivalent parameters follow for the international measurement standard, "std," which is Vienna Standard Mean Ocean Water (VSMOW). The δ^{18}O scale is normalized (Coplen, 1988, 1996) by assigning a value of –55.5 parts per thousand (‰) to the international reference material Standard Light Antarctic Precipitation (SLAP).

The hydrogen isotope delta, δ^2H, is defined by the following relation (Coplen, 2011):

$$\delta^{2}\mathrm{H} = \frac{N\left(^{2}\mathrm{H}\right)_\mathrm{P}/N\left(^{1}\mathrm{H}\right)_\mathrm{P} - N\left(^{2}\mathrm{H}\right)_\mathrm{std}/N\left(^{1}\mathrm{H}\right)_\mathrm{std}}{N\left(^{2}\mathrm{H}\right)_\mathrm{std}/N\left(^{1}\mathrm{H}\right)_\mathrm{std}} \tag{6}$$

where N(^{2}H)$_P$ and N(^{1}H)$_P$ are the numbers of the two isotopes ^{2}H and ^{1}H of hydrogen in specimen P and equivalent parameters follow for the international measurement standard, "std," which is VSMOW. The δ^2H scale is normalized (Coplen, 1988) by assigning a value of –428 ‰ to the international reference material SLAP.

The RSIL estimates expanded uncertainty that is equal to two times the combined uncertainty (U=2μ_c) of δ^2H measurement results on water (Révész and Coplen, 2008a). The expanded uncertainty provides an envelope that represents a 95-percent probability of encompassing the true value that has been determined from the aggregation of results during a period of years. The "long-term" expanded uncertainty is plus or minus (±)2 ‰ for the reporting of hydrogen isotopic compositions of water. The expanded uncertainty can be determined using the guide to the expression of uncertainty (Joint Committee for Guides in Metrology, Working Group 1, 2010). The application of expanded uncertainty to the reporting of stable isotope measurements is discussed by Coplen and others (2006). The results suggest that if any given sample were resubmitted to the RSIL for hydrogen isotopic analysis, the measured value would fall within the uncertainty bounds of the previous result more than 95 percent of the time.

Similarly, the expanded uncertainty ($U=2\mu_c$) estimated for reporting of $\delta^{18}O$ measurement results has been determined from aggregating measurement results with time (Révész and Coplen, 2008b), and the long-term uncertainty ($2\mu_c$) for water is ±0.2 ‰. Again, if any given sample were resubmitted to the RSIL for oxygen isotopic analysis, the measured value would fall within the uncertainty bounds of the previous result more than 95 percent of the time.

Tables of Analytical Data

Tables 2–9 contain all the field measurements. The analytical data of the springs are in tables 10–15. In tables 16–23 are the mixing ratios of gases in air and the unsaturated zone. The data was collected from October 1995 through March 2014.

Measured and Calculated Field Parameters of Spring Samples

The date and time of sampling, measured discharge temperature, measured and calculated DO concentrations, measured and calculated pH, measured and calculated SC, and discharge of the 34 springs are summarized in tables 2–9.

Water Chemistry

The major-element chemistry of the spring discharge is summarized in table 10. The major element composition includes dissolved Ca, Mg, Sr, SiO_2, Na, K, Fe, Mn, Al, titration alkalinity as bicarbonate (HCO_3^-), chloride (Cl^-), nitrogen as nitrate (NO_3^-), sulfate (SO_4^{2-}) and fluoride (F^-) in the spring discharge. The selected concentrations of trace elements, including dissolved B, Ba, Li, Cu, Ni, Rb, Pb, V, and Zn, are summarized in table 11.

Stable Isotope Ratios of Oxygen and Hydrogen of Water

The stable isotopic composition of the water of the spring discharge is summarized in table 12. The data was collected from April 1996 through April 2014.

Dissolved Nitrogen, Argon, Oxygen, Carbon Dioxide, Recharge Temperature, and Excess Air

The gas-recharge temperature obtained from nitrogen/argon concentrations, the calculated excess air concentrations (cubic centimeters per kilogram of water at STP), and the dissolved concentrations of N_2, Ar, O_2, and CO_2 (milligrams per kilogram) are summarized in table 13. The recharge temperature and excess air based on the dissolved N_2 and Ar data and the land-surface altitude of the spring discharge. This procedure leads to a minimum estimate of the average altitude of recharge for springs in Shenandoah National Park. Based on traces of watershed area on topographic maps, recharge altitude of some of the sampled springs could be as much as 200 m higher than that of the discharge point; however, because most of the spring samples are from the higher altitudes in Shenandoah National Park and located near the Skyline Drive, the elevation of recharge cannot be underestimated. Plummer and Busenberg (1999) discuss uncertainties in calculated gas partial pressures and apparent CFC-based ages resulting from uncertainties in recharge elevation. Generally, uncertainties of 200 m in recharge elevation can be ignored.

The recharge temperature is the temperature at the water table during recharge and was determined by assuming that the dissolved N_2 and Ar concentrations were in solubility equilibrium during recharge with possible dissolution of excess air. Excess air refers to air trapped below a rising water table with subsequent dissolution under increased hydrostatic pressure. Recharge temperatures were determined for individual samples using data of dissolved N_2 and Ar concentrations with correction for excess air (Heaton, 1981; Heaton and Vogel, 1981; Heaton and others, 1983; Busenberg and others, 1993; Stute and Schlosser, 1999). The calculation of recharge temperature and excess air used data on the vapor pressure of water from Wexler (1976) and the Henry's law solubilities of N_2, Ar, O_2, and CO_2 in water were obtained from Weiss (1970, 1974). The calculation was based on the assumption that excess air dissolves completely (that is, without being fractionated during dissolution).

Dissolved O_2 concentrations from the field and laboratory gas chromatographic measurements are given in tables 2–9 and 13. In these tables, often the laboratory measured DO content is less than the field concentrations as a result of aerobic microbial processes occurring in the serum bottle between collection and analysis (serum bottles for dissolved gas analysis were refrigerated for periods of several weeks before analysis). Several samples have laboratory O_2 concentrations that are greater than the field O_2 analysis, which is an indication of an air leak into the sample container following collection, during laboratory analysis, or both. Nearly all the samples were collected and analyzed in duplicate for dissolved N_2, Ar, O_2, and CO_2. Standard deviations of the analyses are given in table 13.

Chlorofluorocarbon Concentrations

The average concentrations of CFC-11, CFC-12, and CFC-113 measured in spring discharge in picograms per kilogram, as well as the standard deviations, are presented in table 14. The average typically is based on three separate analyses (three separate ampoules of water collected sequentially from the spring). The recharge temperature and the excess air used to calculate the tabulated CFC partial pressures, in parts per trillion by volume, also are included in table 14. The elevations used in the calculations are given in table 1. The average recharge temperature, average excess air, and the standard deviations used in the calculation are in table 13. All CFC partial pressures are expressed as dry air mixing ratios at sea level, and can be compared directly with North American air (Plummer and Busenberg, 1999; International Atomic Energy Agency, 2006). Age dating of post-1999 samples is not possible because of the turn-over of all CFC concentrations in the North American atmosphere, and apparent model piston-flow ages are not given in table 14. Table 8 of Plummer and others (2000) summarizes the apparent (piston flow) recharge dates and ages based on CFC-11, CFC-12, and CFC-113 of 1995–99 samples. The recharge date is based on the North American air curves tabulated in table 9 of Plummer and others (2000).

Sulfur Hexafluoride Concentrations and Ages

The measured SF_6 concentrations in femtomol per kilogram, the standard deviation, and the calculated partial pressure corrected for elevation and temperature of recharge, but not corrected for excess air, are summarized in table 15. The calculated SF_6 partial pressure in the sample is based on Henry's law solubilities from Bullister and others (2002). The modeled SF_6 mixing ratio in parts per trillion volume corrected for introduced unfractionated excess air also is included in table 15, in addition to the apparent piston flow year of recharge and age of the sample (Busenberg and Plummer, 2000). The model partial pressures were calculated assuming the recharge temperature was over- and underestimated by 1 ^{o}C. The apparent ages of the spring recharge with the ±1 ^{o}C recharge temperature uncertainty also are given. The local Shenandoah National Park air curve for SF_6 is given in (Busenberg and Plummer, 2014).

Air Samples

Concentrations of gases in air samples are reported as mixing ratios in dry air in units of parts per trillion by volume (pptv). Concentrations of CFC-12, CFC-11, CFC-113, CF_3Br, SF_6, and SF_5CF_3 in air from the Big Meadows Air Monitoring Station and a few other locations. The Big Meadows Air Monitoring Station results are summarized in table 16. The atmospheric mixing ratios at the Big Meadows Air Station in Virginia of CFC-12, CFC-11, CFC-113, and SF_6 were 1.2, 2.5, 0.1, and 3.8 percent higher, respectively, than the Niwot Ridge Colorado data (Busenberg and Plummer, 2014). Although the CFC atmospheric mixing ratios were constant or decreasing, the SF_6 atmospheric mixing ratio increased at an annual rate of 6 percent during the study period (Busenberg and Plummer, 2014).

Unsaturated-Zone Gas Samples

The composition of the unsaturated-zone gases as a function of depth and time in seven piezometers is summarized in tables 17–23. The purpose was to observe seasonal variations in the gas composition of the unsaturated zone as a function of depth. Six of the piezometers were installed in Shenandoah National Park and the seventh in a wooded area located 90 m north of the USGS National Center in Reston, Va. The results for each piezometer are summarized on three pages. On the first page are measured air temperature and the temperature of thermocouples located at the various depths. Many thermocouples failed after some time. Also on this sheet are the measured concentrations of CO_2 and N_2 for the various sampling ports. The abbreviation 'np' indicates unavailable data. On the second sheet are the concentrations of Ar, O_2, and SF_6 for each sampling port of the piezometer. On the third sheet are the concentrations of CFC-12, CFC-11 and CFC-113 for each sampling port of the piezometer.

Summary

The data report summarizes the chemistry of the discharge of 34 springs located in Shenandoah National Park, Virginia. The data include a 12 year record of monthly sampling of five springs, with measurements of temperature, specific conductance, dissolved oxygen and pH. Also measured were monthly concentrations of the environmental tracers dichlorodifluoromethane, trichlorofluoromethane, trichlorotrifluoroethane, and sulfur hexafluoride. Major and trace elements, dissolved nitrogen, oxygen, argon, carbon dioxide, methane and the stable isotopic concentration in the water of the springs were measured. Mixing ratios of the environmental tracers dichlorodifluoromethane, trichlorofluoromethane, triclorotrifluoroethane, trifluorobromomethane, sulfur hexafluoride and trifluoromethyl sulfur pentafluoride were measured weekly in air at the Big Meadows Air Monitoring Station from September 1995 through March 2014. Between March 2001 and August 2003, temperature, concentrations of environmental tracers and major gases in the unsaturated-zone air were analyzed monthly in seven multi-level piezometers.

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