Prepared in Cooperation with the NATIONAL PARK SERVICE

Chemical Characteristics of Ground-Water Discharge along the South Rim of Grand Canyon in Grand Canyon National Park, Arizona, 2000–2001

Scientific Investigations Report 2004–5146

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

Hermit Creek near Hawaii Spring

Cover photograph: View of Palisades of the Desert from near Desert View, Grand Canyon, Arizona. Photograph by Colin McKay.

By Stephen A. Monroe, Ronald C. Antweiler, Robert J. Hart, Howard E. Taylor, Margot Truini, John R. Rihs, *and* Tracey J. Felger

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Conversion Factors and Datum

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: ${}^{\circ}$ F = (1.8 ${}^{\circ}$ C)+32

ABBREVIATED WATER-QUALITY UNITS

Chemical concentration and water temperature are given only in metric units. Chemical concentration in water is given in milligrams per liter (mg/L) or micrograms per liter (μg/L). Milligrams per liter is a unit expressing the solute mass (milligrams) per unit volume (liter) of water. One thousand micrograms per liter is equivalent to 1 milligram per liter. For concentrations less than 7,000 milligrams per liter, the numerical value is about the same as for concentrations in parts per million. Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μ S/cm at 25 °C). Radioactivity is expressed in picocuries per liter (pCi/L) or picocuries per gram (pCi/g), which is the amount of radioactive decay producing 2.2 disintegrations per minute in a unit volume (liter) of water or mass (gram) of sediment.

DATUMS

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929; horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27). Altitude, as used in this report, refers to distance above or below NGVD 29.

By Stephen A. Monroe, Ronald C. Antweiler, Robert J. Hart, Howard E. Taylor, Margot Truini, John R. Rihs, *and* Tracey J. Felger

Abstract

Springs flowing from the south rim of Grand Canyon are an important resource of Grand Canyon National Park, offering refuge to endemic and exotic terrestrial wildlife species and maintaining riparian areas. Population growth on the Coconino Plateau has increased the demand for additional development of ground-water resources, and such development could reduce spring discharge and affect the sustainability of riparian areas within the park. In addition, springs are an important source of drinking water for hikers and are culturally and economically important to Native Americans living in the region.

Water samples were collected from May 2000 to September 2001 from 20 spring and creek sites that discharge water from the Redwall-Muav Limestone aquifer along the south rim of Grand Canyon. Sample collection sites were described and samples were analyzed for major ions, nutrients, trace elements, radioactivity, and selected isotopes, and potential sources of ground-water flow to the springs. Rock samples representing the major stratigraphic units of Grand Canyon were collected near the Bright Angel Fault and analyzed for mineralogy, strontium-87/strontium-86, and carbon-13/carbon-12.

The chemical composition of water samples collected from a given spring did not vary appreciably over the course of the study. Although water at each spring

had a temporally constant composition, the composition was chemically distinct from that of every other spring sampled, indicating spatial variability in the groundwater composition. Most samples had a calcium magnesium bicarbonate composition; a few had a substantial sulfate component. Concentrations of arsenic, nitrate, selenium, uranium, and gross alpha approached or exceeded U.S. Environmental Protection Agency Maximum Contaminant Levels in water discharging from some springs. Oxygen and hydrogen isotopic compositions varied little among samples, and for most sites the isotopic data plot close to the global meteoric water line or below the local meteoric water line. Isotopic enrichment indicates fractionation due to evaporation occurs at some sites. The evaporative process may occur prior to recharge or post-discharge. Flow paths are differentiated between the eastern part of the study area where strontium-87/strontium-86 values for water from springs and creeks are more radiogenic than strontium-87/strontium-86 values for water that discharges from sites farther west. Tritium and carbon isotope analyses indicate that residence time of ground-water discharge from springs and creeks ranges from less than 50 years to about 3,400 years. Water with a residence time of less than 50 years is absent at several sites. Discharge of most springs and creeks is a mixture of younger and older waters.

INTRODUCTION

Spring flow from sedimentary rocks along the south rim of Grand Canyon is an important resource of Grand Canyon National Park (GRCA) and adjoining areas (**[fig. 1](#page-12-1)** and **[pl. 1](#page-70-0)**). Springs offer refuge to endemic and exotic terrestrial wildlife species of Grand Canyon and maintain associated riparian areas. Recent development and ground-water use near the south rim have made environmentalists, commercial developers, municipalities, and State and Federal resource managers increasingly aware of spring resources in the area. Native Americans who inhabit the Grand Canyon region, such as the Havasupai Tribe, are concerned about the effects of ground-water development on spring resources. Springs are economically important and culturally significant to Native Americans.

At the request of the GRCA, the U.S. Geological Survey (USGS) and GRCA began a cooperative study in 1999 to assess spring water quality and determine the sources of ground water discharged at the springs. This study was done under the auspices of the National Park Service (NPS)/USGS Water-Quality Assessment and Monitoring Program (WQAM).

Data collected for this study will provide GRCA resource managers an inventory of spring resources along the south rim of Grand Canyon. The springs result from ground-water discharge from aquifers that are being increasingly developed. As such, the springs are susceptible to increasing ground-water withdrawals on the Coconino Plateau.

Purpose and Scope

The purpose of this report is to present the results of a study of the chemical characteristics of ground-water discharge along the south rim of Grand Canyon in Grand Canyon National Park. The specific objectives of this study were to determine baseline water quality and the residence times and flow paths of water discharging from the Redwall-Muav Limestone aquifer along the south rim of Grand Canyon. Data included in this report were collected from May 2000 to September 2001.

This report describes the aquifers in the study area, the spring and creek sites selected for the study, the variation in water chemistry at the sites, the trends in chemical composition of water among the sites, and the sources and residence times for ground water that discharges at the springs.

Physical, chemical, and water-quality data are presented for 20 sites in the section of Grand Canyon from Red Canyon in the east to Boucher East Spring in the west at which ground water discharges from the Redwall-Muav Limestone aquifer (pl. 1). Sites included are in the core area of GRCA, close to

population centers and ground-water withdrawal sites. The 20 sites (**[table 1](#page-10-1)**) include 14 springs, 5 creeks, and 1 USGS streamflow-gaging station (station number 09403013). The streamflow-gaging station monitors flow from Pumphouse Spring. Two of the creek sites (Cottonwood No. 1 and Cottonwood No. 2) are in the same drainage, and one of the creek sites (Monument Creek No. 1) is in the same drainage as one of the spring sites (Monument Spring).

Data collected include physical descriptions, air and water temperature, pH, specific conductance, dissolvedoxygen concentration, field alkalinity, location, and altitude. Water samples were analyzed for concentrations of major ions, nutrients, and trace elements; for radioactivity; and for stable and radioactive isotope composition. Rock samples representing the major stratigraphic units of Grand Canyon near the Bright Angel Fault (pl. 1) were collected and analyzed for mineralogy and isotope composition.

Water Issues for Grand Canyon National Park

Grand Canyon National Park is recognized as a place of global importance, and the park contains surface and ground waters and associated habitats that are rare in arid environments. Water availability has been the greatest limitation to development in the south rim area, and historically, water has been expensive to acquire and water supplies have been the subject of contention (U.S. Department of Agriculture, Forest Service, 1999).

One of the highest priorities identified in the park's General and Resource Management Plans is to accurately document locations and water chemistry of springs issuing from within the park boundary. Addressing this issue would benefit GRCA by (1) providing documented water-resource information that can be used to develop a requisite resource management policy; (2) contributing to the understanding of ground-water movement and direction, and estimation of time since recharge of spring water; (3) identifying the presence or absence of effluent and landfill leakage to spring sources; (4) evaluating field logistics for potential long-term monitoring of south rim springs; (5) providing the general public with interpretive information regarding the spring resources of GRCA; (6) identifying future research and monitoring needs; and (7) providing supporting data for concurrent studies including Wild and Scenic River suitability studies, spring-flow monitoring, and biological studies being conducted on Colorado River tributaries in GRCA.

See footnotes at end of table.

Table 1. Locations of springs and creeks sampled in study—Continued

¹Measurements or samples collected during site visits: A, field parameters; B, chemical constituents; C, radiochemistry; D, oxygen and hydrogen isotopes; E, tritium; F, carbon isotopes; G, strontium isotopes.

 2 Pumphouse Wash gage is located in close proximity to Pumphouse Spring and monitors total spring discharge from the vicinity.

How existing and proposed ground-water development outside the park will affect the spring resources within the park is unknown. Ground-water flow paths in aquifers of the Coconino Plateau are poorly understood. In addition, little is known about the current and potential effects of human activities, such as wastewater treatment plants, landfills, and historic mining, on the ground-water systems.

Description of the South Rim of Grand Canyon

The south rim of Grand Canyon is a steep escarpment extending from the Coconino Plateau to the Colorado River. Vertical relief of the south rim is about 1,500 m. The Coconino Plateau is a physiographic feature of the Colorado Plateau that encompasses an area of about $13,000 \text{ km}^2$ in northern Arizona (**[fig. 1](#page-12-1)**). This study is focused on the part of Grand Canyon National Park centered on the Bright Angel Fault and extending as far east as Red Canyon and as far west as Boucher East Spring (**[pl. 1](#page-70-0)**). The south rim is characterized by numerous short, steep side canyons and differs from the north rim of Grand Canyon in that it has smaller tributary canyons and no extensively developed karst systems (Huntoon, 2000). Side canyon development is primarily controlled by regional dip of sedimentary rocks and folds and faults (Potochnick and Reynolds, 1990). The regional dip of south rim Paleozoic strata is south, away from Grand Canyon.

Grand Canyon Village, Tusayan, and Valle are small communities in and near Grand Canyon National Park near the south rim (fig. 1). No wells exist in the park; however, deep

wells have been developed in Tusayan and Valle. Wastewatertreatment plants and landfills are operated in Grand Canyon Village and Tusayan. Two abandoned mines are in the study area (pl. 1). The Last Chance mine was developed near a breccia pipe at Horseshoe Mesa and produced copper during the early 1900s (Kenny, 2001). The Orphan mine was developed in a breccia pipe in the Horn Creek drainage and produced copper in the early 1900s and uranium during the 1950s and 1960s (Amundson, 2001).

Climate

Climatic conditions of the Coconino Plateau vary in relation to altitude. Average precipitation varies from about 48 cm/yr at Grand Canyon Village on the south rim to about 23 cm/yr in the canyon at Phantom Ranch (Sellers and others, 1986). In the canyon, the climate is continental and arid. The greatest rainfall occurs during the warm season (June through October) as a result of the Southwestern monsoon. Snowfall on the rim of the canyon accounts for the greatest part of the total precipitation in the area. Along the canyon rim, vegetation is predominantly ponderosa pine. Altitude decreases to the south of Grand Canyon, and there is a corresponding decrease in precipitation and a transition to desert scrub vegetation. Deep in the canyon, where precipitation is also diminished, desert vegetation predominates.

Figure 1. Study area and south rim of Grand Canyon, Arizona.

Hydrogeologic Characteristics

The primary water-bearing units of the Coconino Plateau near Grand Canyon are the lower Paleozoic carbonate rocks (Metzger, 1961). These rock units constitute the Redwall-Muav Limestone aquifer and are generally found 500 m to 700 m below the land surface of the plateau. Included in the aquifer are the Cambrian Bright Angel Shale, Cambrian Muav Limestone, Devonian Temple Butte Formation, and Mississippian Redwall Limestone (Metzger, 1961; Cooley and others, 1969). The Bright Angel Shale and Muav Limestone intertongue in the study area and thicken towards the west. The Temple Butte Formation is a discontinuous dolomitic limestone that thickens (30 m to 100 m) from east to west in Grand Canyon (Beus, 1990). The Redwall Limestone is a mostly dolomitic limestone that is continuous and massive throughout the study area. In the study area, the aquifer is bounded on the north by the Colorado River, on the west by structural controls near the Aubrey Cliffs, on the east by a

generally defined ground-water divide near the Little Colorado River (E.L. Montgomery and Associates, 1997), and on the south by a generally defined ground-water divide near Williams (Bills and Flynn, 2002).

Perched water-bearing zones also occur near Grand Canyon. Ground water discharges from these zones at springs and seeps in the Pennsylvanian and Permian Supai Group, the Permian Coconino Sandstone, and the Permian Kaibab Formation (Metzger, 1961). The Supai Group is a series of limestone, mudstone, and sandstone rock units and tends to be highly fractured. The Permian Hermit Formation, overlying the Supai Group, is a siliciclastic siltstone, mudstone, and sandstone (Blakey, 1990). The Coconino Sandstone is a homogeneous silicate sandstone. The Kaibab Limestone is a resistant rock unit that forms a cap throughout most of the Grand Canyon region (fig. 2). Flow at the springs and seeps is generally small and discontinuous, and wells developed in these zones typically have low production rates (McGavock and others, 1986).

Modified from Billingsley and others, 1980

Figure 2. Stratigraphic section of the south rim of Grand Canyon, Arizona.

Water-bearing units near the south rim of Grand Canyon are recharged primarily by precipitation that infiltrates volcanic rocks and the Kaibab Formation in the higher altitudes of the Coconino Plateau (Johnson and Sanderson, 1968). Faults and fractures, many widened by dissolution, create zones of secondary permeability that could be the primary controls of ground-water movement. Ground water in the northern parts of the Coconino Plateau generally flows toward the south rim and discharges at springs and seeps (Metzger, 1961). Springs and seeps in Grand Canyon typically occur at geologic contacts where water-bearing rocks are underlain by less permeable rocks. The larger springs in the canyon are associated with regional faults.

Most of the major springs along the south rim of Grand Canyon discharge from the Muav Limestone, the Temple Butte Formation, or the Redwall Limestone (**[fig. 2](#page-13-2)**) and are associated with faults, fractures, or solution cavities in these rock units (Metzger, 1961; Huntoon, 1974). Springs and seeps discharge along the south rim from the Cambrian Tapeats Sandstone in many tributary canyons. Above the Tapeats Sandstone, the Bright Angel Shale acts as a physical barrier limiting downward movement of ground water from overlying rocks (Metzger, 1961).

Numerous breccia pipes occur on the Coconino Plateau (Billingsley, 2000). The form of breccia pipes found in this region are the result of solution collapse in the Redwall Limestone and a stoping of overlying rock units. The presence of breccia pipes in the study area may be significant because secondary mineralization associated with breccia pipes can potentially influence water chemistry and because breccia pipes can act as conduits for ground-water flow (Wenrich and others, 1994). Breccia pipes are small features, and because they are so numerous in the study area, only those that are close to springs included in this report are shown on illustrations.

The hydrogeology of the Redwall-Muav Limestone aquifer and its hydraulic connection with water-bearing zones in overlying Pennsylvanian and Permian rocks near Grand Canyon is not well understood. Few wells have been developed on the Coconino Plateau, and knowledge of subsurface geology in the region is limited. Little is known about the movement of ground water through the rocks of the Coconino Plateau; therefore, travel times to points of discharge are unknown.

The hydraulic gradient of the potentiometric surface near the south rim is primarily controlled by secondary porosity and is downward towards the canyon (Metzger, 1961); most tributary canyons contain springs or seeps. Depth to ground water is about 900 m. Most springs along the south rim of Grand Canyon are small (discharge less than 15 L/min). There is little or no surface flow on the Coconino Plateau near the south rim, and flow in the side canyons derives from spring discharge or storm runoff.

Previous Investigations

Scientists have visited springs and measured spring flow along the Colorado River of Grand Canyon since the late 1800s; however, most springs have not been inventoried and measured at or near their source. John Wesley Powell, during 1869–72, was the first scientist to describe spring flow in Grand Canyon (Powell, 1874). Johnson and Sanderson (1968) wrote the most recent comprehensive report on spring flow in the Grand Canyon region and summarized previous investigations by LaRue (1925). Johnson and Sanderson (1968) visited major spring sites along the Colorado River in 1960, measured flow at 14 sites close to the river, and estimated flow at several other locations. Miscellaneous spring measurements have been made since 1950 by various investigators, and data for those sites are available in published reports or from the USGS National Water Information System database.

Huntoon (1974) described structurally controlled spring flow for the Kaibab Plateau north of Grand Canyon, and concluded that 65 to 97 percent of the plateau is drained through carbonate rocks 900 m below the north rim of Grand Canyon and Marble Canyon. Huntoon (1981) measured flow at several springs along the Colorado River in Marble Canyon between river miles 30 and 34.

Cooley (1976) described spring flow issuing from pre-Pennsylvanian rocks in Marble Canyon and in the lower 21 km of the Little Colorado River canyon. Cooley and other investigators (1969) visited more than 50 spring sites in the Marble and Little Colorado River canyons during 1966–67. Many of these sites were seeps or had flows estimated at less than 3.8 L/min.

E.L. Montgomery and Associates, Inc. (1997 and 1999) created a numerical model of the ground-water system of the Coconino Plateau as part of an environmental impact statement related to proposed development in the Tusayan area. Wilson (2000) constructed a geologic framework model for the region. This work was expanded by Kessler (2002).

Several researchers have conducted geochemical investigations of springs in Grand Canyon in recent years. Loughlin and Huntoon (1983) compiled water-quality data from various sources. Foust and Hoppe (1985) studied seasonal variability of water chemistry from tributaries of the Colorado River in Grand Canyon. From 1990 to 1995 the USGS (unpublished data) collected data primarily from sites close to the Colorado River and on the Hualapai Indian Reservation in the western part of Grand Canyon (Donald Bills, hydrologist, USGS, written commun., 2002). The University of Nevada-Las Vegas also collected samples from springs in Grand Canyon for chemical analysis (Goings, 1985; Zukosky, 1995; Fitzgerald, 1996). The USGS conducted synoptic water-quality studies of many tributaries of the Colorado River in Grand Canyon in 1990 and 1991 (Taylor and others, 1996) and

throughout the Colorado River corridor (Antweiler and Taylor, unpublished data, 1992–93). NPS scientists have compiled several databases on the water resources of GRCA (National Park Service, 1996). The USGS and NPS have monitored discharge from the Redwall-Muav Limestone aquifer of Indian Gardens, Hermit Creek, and Cottonwood Creek since 1994.

Data from springs, creeks, and wells along the south rim of Grand Canyon have been collected by the USGS and others under separate programs subsequent to the WQAM study presented in this report, but are not presented in this report.

Acknowledgments

The authors thank the many individuals who helped collect and carry water samples out of Grand Canyon for this project. Personnel from the USGS Arizona District and the USGS National Research Program in Boulder, Colorado, carried heavy backpacks during harsh environmental conditions. Many volunteers also helped carry equipment and samples from remote sites in Grand Canyon. Without the assistance of these individuals, this project would not have succeeded. We also appreciate the assistance of GRCA personnel who provided backcountry permits to our datacollection teams and helped determine the feasibility of accessing many of the spring and creek sites. In addition, we thank Dave Roth, Terry Plowman, and Dale Peart with the USGS National Research Program for laboratory assistance.

INVESTIGATION METHODS

Field Logistics

Many of the springs issuing along the south rim of Grand Canyon (**[fig. 2](#page-13-2)**) are more than 900 m below the canyon rim. Spring sources generally are far from established trails in the headwaters of tributary canyons. Because this area is remote and its terrain rugged, most sample collection trips were made using backpacks to carry equipment and supplies. Some sites were accessed by boat from the Colorado River. Unsafe conditions precluded visits to several potential sampling sites.

Hiking trips varied from 1 to 7 days and required 2 to 6 people depending upon individual site characteristics. Many of the springs were accessible from the Tonto Trail, which traverses the slopes of the Bright Angel Shale (fig. 2 and pl. 1) parallel to the Colorado River. Sampling trips were timed for favorable weather conditions and for discharge conditions that represented base spring flow.

Sample Collection and Processing

Water samples were collected from each spring at or as near as possible to the point of issuance from the water-bearing rock (**[fig. 3](#page-16-2)***A*). Ground-water discharge generally occurs along bedding planes or through fractures. Most water samples were collected from the area of greatest discharge. Where the point of issuance could not be accessed, water samples were collected at the first accessible location downstream from this point. Efforts were made to minimize contact of spring water with the atmosphere.

Measurements of spring discharge, specific conductance, pH, air and water temperature, dissolved-oxygen concentration, and alkalinity using standard USGS protocols (U.S. Geological Survey, 1997) were made at each site when samples were collected. Specific-conductance and pH meters were calibrated in the field using standard solutions. Alkalinity titrations were done in the field using a pH meter and alkalinity kit. Measurements were made onsite directly in flowing water or from a sample of water. Locations and altitudes of sample sites were determined using Differential Global Positioning System or topographic maps.

Spring discharge was measured volumetrically, with a portable Parshall flume, or with a current meter according to methods described by Rantz and others (1982). Volumetric methods were used when discharge was less than about 25 L/min or where depths were too shallow for use of a current meter.

A distinct sampling protocol, described in this section, was used to collect water samples for laboratory analyses. Because different analytical methods required different sample treatments, each spring sample was collected into 10 distinct bottles for analysis (**[table 2](#page-16-2)**).

Samples were handled in a proper and consistent manner to minimize contamination. All bottles were pre-cleaned before sample teams entered Grand Canyon. The metals, anions, nutrients, dissolved organic carbon (DOC), and oxygen-18 and hydrogen-2 (D or deuterium) bottles for each site were sequestered into a separate zippered plastic bag, which also contained two pairs of polypropylene gloves, a new 60-mL polystyrene syringe, and four Acrodisk 0.45-micron nominal pore-size Luer-Lock filters (contained in their own zippered plastic bag). Mercury bottles were predosed with 2.5 mL of potassium dichromate/nitric acid and were sealed in their own individual Whirl-pak bags and kept separate from the rest of the sampling equipment and bottles. The remaining four bottles were kept together, but separate from all the other sample bottles. Because the large-volume radiochemistry, carbon-isotope, and strontium-isotope samples also required filtration, a hand-vacuum pump, a filtration manifold, and 0.45-micron polysulfone filters were also packed, but kept separate from the other sampling equipment.

Figure 3. Water-sample collection and processing. *A*. Water-sample collection at Miners Spring; *B*, Water-sample processing at Monument Spring.

Field teams wore polypropylene gloves for all sample processing and collected samples in a certain order to minimize the potential for contamination. The non-isotope samples were collected and filtered first. A new syringe and Acrodisk filter were used, after field rinsing with spring water, to collect samples at each site. The anions bottle was filled first, followed by the nutrients, metals, and DOC bottles. Because the mercury bottle already contained preservative, it was filled last, after all other non-isotope sample bottles were filled, to minimize the possibility of cross-contaminating the other samples with the potassium dichromate preservative. A second or third Acrodisk filter was used for some nonisotope samples because the original filter became clogged.

The oxygen-18 and deuterium sample was collected unfiltered and care was taken to eliminate head-space within the bottle. Tritium samples were also unfiltered. The radiochemistry, carbon-, and strontium-isotope samples were filtered using a filtration setup that consisted of a hand vacuum pump, which was connected to a polyethylene side-arm Erlenmeyer flask by plastic tubing (fig. 3*B)*. A magnetic filterholder on which was mounted a new 47-mm, 0.45-micron polysulfone filter was placed on the side-arm flask. The first 20 mL of the filtered sample was used to rinse the flask. Thereafter the sample was collected in the flask and distributed to either the radiochemistry bottle, the carbon-isotope bottle, or the strontium-isotope bottle.

All samples were kept as cool as possible in the absence of ice; these samples were refrigerated as soon as possible after leaving the field, and analyzed as quickly as possible thereafter. The metals and radiochemistry samples were acidified as soon as possible after leaving the field—metals bottles with 1 mL of doubly distilled concentrated nitric acid and the radiochemistry bottles with 5 mL of concentrated hydrochloric acid. The remaining samples did not require any additional preservation procedures.

Rock samples representing the major Paleozoic rock units in Grand Canyon were collected from outcrops near the Bright Angel Fault. These samples were analyzed for mineralogy and for strontium-87/strontium-86 and carbon-13/carbon-12 values.

Laboratory Methods

Three general categories of chemical analyses are described in the following section: (1) elemental and compound concentration analyses of water samples, (2) isotopic composition analyses of water samples, and (3) X-ray diffraction (XRD) and isotopic composition analyses of rock samples. Methods for these analyses are summarized below.

Elemental and Constituent Analyses of Water Samples

Elements present at concentration levels in the milligram per liter range, including calcium, potassium, magnesium, sodium, and silica, and some selected trace elements, such as iron, were determined in triplicate by inductively coupled plasma-atomic emission spectrometry (ICP-AES) utilizing a Perkin Elmer Optima 3300DV multichannel emission spectrometer. A general description of the analysis conditions and procedures are reported by Garbarino and Taylor (1979). Details of the operational conditions are described by Mitko and Bebek (1999, 2000).

Trace element determinations (excluding mercury) were performed in triplicate on undiluted field-preserved samples by inductively coupled plasma-mass spectrometer (ICP_MS) using a Perkin Elmer Elan Model 6000 inductively coupled plasma-mass spectrometer (ICP-MS). Analytes and their respective median detection limits are listed in table 3. These detection limits were computed by the method described by Skogerboe and Grant (1970) and may vary slightly between analysis runs owing to changes in instrument sensitivity or to required dilutions needed to minimize matrix interference effects. Details of the specific analysis techniques, procedures, and instrument settings are described in Garbarino and Taylor (1996) and Taylor (2001).

Table 3. Chemical and isotopic analytes and corresponding median detection limits

[µg/L, micrograms per liter; mg/L, milligrams per liter; mg N/L, milligrams nitrogen per liter; mg P/L, milligrams phosphorus per liter; mg C/L, milligrams carbon per liter; pCi/L, picocuries per liter; pmc, percent modern carbon; ‰, per mil]

See footnote at end of table.

Symbol	Detection limit	Units	Chemical constituent	Symbol	Detection limit	Units
Gd	0.001	$\mu\text{g}/\text{L}$	Terbium	Tb	0.0003	µg/L
Ho	0.0002	μ g/L	Thallium	Tl	0.005	µg/L
Fe	0.5	μ g/L	Thorium	Th	0.0006	µg/L
La	0.0007	μ g/L	Thulium	Tm	0.0003	µg/L
Pb	0.008	μ g/L	Tungsten	W	0.001	μ g/L
Li	0.07	μ g/L	Uranium	U	0.001	µg/L
Lu	0.0002	μ g/L	Vanadium	V	0.1	µg/L
Mn	0.06	μ g/L	Ytterbium	Yb	0.0007	µg/L
Hg	0.4	ng/L	Yttrium	Y	0.0008	μ g/L
Mo	0.03	μ g/L	Zinc	Zn	0.2	µg/L
Nd	0.001	μ g/L	Zirconium	Zr	0.003	µg/L
Ni	0.03	μ g/L	Gross beta	β	4	pCi/L
Pr	0.0004	μ g/L	Gross alpha	α	3	pCi/L
Re	0.001	μ g/L	$Oxygen-18/oxygen-16$	18O/16O	$1_{\pm 0.1}$	$\%o$
Rb	0.003	μ g/L	Hydrogen-2/hydrogen-1	$^2H/I$ H	$1_{\pm 1}$	$\%o$
Sm	0.002	$\mu g/L$	Strontium-87/strontium-86	${}^{87}Sr/{}^{86}Sr$	10.00002	none
Se	0.4	μ g/L	Carbon-14	^{14}C	$1_{\pm 3}$	pmc
Sr	0.1	μ g/L	Carbon-13/carbon-12	${}^{13}C/{}^{12}C$	$1_{\pm 1}$	$\%o$
Te	0.02	μ g/L	Tritium	$^3\mathrm{H}$		pCi/L

Table 3. Chemical and isotopic analytes and corresponding median detection limits—Continued

¹Reported precision.

Trace concentrations of dissolved mercury were measured in triplicate using an automated cold-vapor atomic fluorescence spectrometric method and a PS Analytical Millenium System mercury analyzer. Details of the method have been described by Roth (1994) and Roth and others (2001).

Chloride and sulfate were determined by ion exchange chromatography using a modified Dionex 2002i/SP series ion chromatograph. The details of the analytical procedure are described by Brinton and others (1996).

Dissolved nutrients including nitrate, nitrite, ammonium, and orthophosphate were determined in triplicate using methodology described by Antweiler and others (1996). Analyses were performed using an air-segmented continuous flow analyzer (Alpkem RFA-300).

Dissolved organic carbon was determined by oxidation of the organic carbon in the sample to carbon dioxide, which was subsequently measured by an infrared absorption spectrophotometric technique (Wershaw and others, 1983).

Gross-alpha/gross-beta counting is a semiquantitative technique for measuring overall radioactivity in water samples without extensive sample preparation. This method is most often applied for screening purposes. The method has the advantage of being sensitive to activity from a wide range of radionuclides, but does not inherently provide qualitative information about the identity of the radioactive isotopes

present. Samples are prepared by evaporation to dryness on a planchet. Gross alpha and beta emissions are measured on the dried residue using a gas-proportional counter by a method specified by the U.S. Environmental Protection Agency (1976). Count rates from the detector are converted to and reported as activities. More details of the methodology can be found in American Public Health Association (1985).

Isotopic Composition Analyses of Water and Rock Samples

Stable isotopes of oxygen, hydrogen, carbon, and strontium were measured relative to internationally agreed upon standards (International Union of Pure and Applied Chemistry, 1994). For oxygen, hydrogen, and carbon, the deviation of the sample from the standard mean is expressed by the delta (δ) notation, in parts per mil ($\%$), and is computed from equation 1 (appendix). Strontium values are shown as ratios.

Oxygen isotope ratio $({}^{18}O/{}^{16}O)$ analyses were performed using the carbon dioxide equilibration technique described by Epstein and Mayeda (1953). Hydrogen isotope ratios $(^{2}H/^{1}H)$ for water were determined using a hydrogen equilibration technique at 30 $\rm{°C}$ to measure ²H activity (Coplen and others, 1991). Oxygen and hydrogen isotopic results are reported in

per mil relative to Vienna Standard Mean Ocean Water (VSMOW) and normalized (Coplen, 1988, 1994; International Union of Pure and Applied Chemistry, 1994) on scales such that the $18O/16O$ and $2H/1H$ values of Standard Light Antarctic Precipitation (SLAP) are -55.5 ‰ and -428 ‰, respectively.

Water samples also were measured for tritium $({}^{3}H)$, the radioactive isotope of hydrogen, using a liquid scintillation counting technique (Kendall and Caldwell, 1998) after preconcentration by an electrolytic enrichment procedure. Results are reported in pCi/L with accompanying 2 sigma error in pCi/L, and tritium units (TU; 1 TU= $1³H$ per 1,018 hydrogen atoms; Fritz and Fontes, 1980; Clark and Fritz, 1997).

Strontium isotope $({}^{87}Sr/{}^{86}Sr)$ analyses of water and crushed rock samples were performed using solid source mass spectrometry (Taylor, 2000; Bullen and others, 1996). Rock samples were leached in a 0.1 N hydrochloric acid solution before analysis for strontium isotopes. This procedure normalized 87Sr/86Sr results (as ratios) for natural and analytical fractionation to 8.37521.

Carbon isotope $(^{13}C/^{12}C)$ analyses of water and crushed rock samples were measured by an isotope ratio mass spectrometric technique (Clark and Fritz, 1997) after conversion of inorganic carbon to carbon dioxide by addition of hydrochloric acid. All 13C results are reported in per mil relative to the Vienna Peedee belemnite standard (Coplen, 1994). These data are necessary to correct carbon-14 (^{14}C) results for ground-water dating applications.

Carbon-14 isotope analyses of water samples were measured by accelerator mass spectrometry according to methods described in Beukens (1992). All 14 C determinations are reported in percent modern carbon (pmc) normalized to the 1950 National Bureau of Standards (National Bureau of Standards, 1984) oxalic acid standard (Stuiver and Polach, 1977; Wigley and Muller, 1981), with accompanying 1 sigma error in pmc.

X-ray Diffraction Analyses of Rock Samples

Bulk mineralogy and the clay mineral fraction of rock samples representing the major stratigraphic units near the Bright Angel Fault in Grand Canyon were detemined using XRD techniques (Schultz, 1964; Moore and Reynolds, 1997). Physical grain-size techniques were used to determine particlesize distribution for the rock samples. Results of the XRD and grain-size analyses were compared with descriptions of similar rock units in the region (R. Parnell, professor, and T. Loseke, graduate student, Northern Arizona University, written commun., 2002).

Isotopic Analyses

Stable isotopes of oxygen and hydrogen are used in hydrologic studies to help determine sources of recharge for aquifers. During evaporation, the isotopes of hydrogen and oxygen in water fractionate. The lighter ${}^{16}O$ and ${}^{1}H$ molecules preferentially move from the liquid phase to the gas phase leaving behind 18 O and 2 H molecules. This action will affect the isotopic signature by making it more positive or enriched in the heavier water molecules. Ratios of these isotopes are unaffected by low-temperature geochemical processes in ground-water systems (Clark and Fritz, 1997).

Craig (1961) developed a relation between δ^{18} O and δ^2 H (or δD) for meteoric waters that is represented by equation 2 (**[appendix](#page-66-0)**) and is known as the global meteoric water line. Regional variations in δ^{18} O and δ D may be caused by differences in latitude, altitude, or temperature. For this study, a local meteoric water line was developed using $\delta^{18}O$ and δD data from precipitation samples collected by the NPS at the National Atmospheric Deposition Program National Trends Network Monitoring Location AZ03, Grand Canyon National Park, Coconino County, Arizona, between 1989 and 2002 (Pendall, 1997; Harvey, 2000; National Atmospheric Deposition Program, 2002). Water samples for $\delta^{18}O$ and δD analysis were collected at 14 springs and 4 creek sites along the south rim of Grand Canyon.

Tritium is commonly used as a tracer for studying groundwater residence time and ground-water mixing at time scales less than 50 years. Low activities of cosmogenic tritium occur as background in natural waters. Anthropogenic tritium was produced by atmospheric thermonuclear tests that began in 1952. Thermonuclear tritium activities peaked in about 1963 before thermonuclear testing was banned (Mazor, 1997).

Tritium has a half-life of 12.3 yr, and radioactive decay of tritium occurs according to equation 3 (appendix), allowing approximation of the date of ground-water recharge. Precipitation samples collected in Flagstaff between 1962 and 1971 were analyzed for tritium activities (International Atomic Energy Agency, 2001). Data range from 2.7 to 53 TU and generally show a decreasing trend over time. In continental regions, tritium activities of less than 0.5 TU indicate recharge prior to 1952. Activities of 0.5 TU to 10 TU indicate possible mixing of pre-1952 and post-bomb waters, and activities greater than 10 TU represent recharge less than 50 yr ago (Mazor, 1997). Water samples were collected for tritium analysis at 13 springs and 4 creek sites for this study.

Ground-water flow paths and water-rock interactions were identified using ${}^{87}Sr/{}^{86}Sr$ values. Strontium-87 is radiogenic and increases in concentration upon the beta-decay of rubidium-87. Geologic units have distinct ${}^{87}Sr/{}^{86}Sr$, and strontium enters water through dissolution of minerals from these units during chemical weathering. Dissolution rates are dependent on chemical processes and the minerals that are present. The ⁸⁷Sr/⁸⁶Sr in ground-water reflects the strontium ratios of the host rock, but may differ slightly if the groundwater flow path includes multiple rock units. This relation enables the use of strontium isotope composition as a tracer in many ground-water systems (Faure, 1986). Water samples collected from 13 springs and 4 creek sites and 16 rock samples collected near the Bright Angel Fault were analyzed for ${}^{87}Sr/{}^{86}Sr.$

Residence time of ground water can be estimated using the decay rate of naturally occurring 14C. During 2000–2001 water samples collected at 12 springs and 4 creek sites were analyzed for ${}^{13}C/{}^{12}C$ and ${}^{14}C$.

Carbon-14 data in pmc were converted (equation 4, **[appendix](#page-66-0)**) to time in years using a method known as Conventional Radiocarbon Age (Stuiver and Polach, 1977) to estimate ground-water residence times.

The Conventional Radiocarbon Age (years before present) term (Stuiver and Polach, 1977) implies

- 1. the use of the 5,568 yr half-life (mean life 8,033 yr);
- 2. the constancy of the ${}^{14}C$ atmospheric level during the past;
- 3. isotopic fractionation normalization of all sample activities to the base $\delta^{13}C = -25 \%$; and
- 4. the year 1950 is automatically the base year, or present, with ages given in years before present.

The Conventional Radiocarbon Age method converts ${}^{14}C$ in pmc to ages in years without considering either isotopic dilution or fractionation from water and carbonate rock interactions. This approach biases the adjusted ground-water age to be artificially older. A better estimate of ground-water residence time using ${}^{14}C$ data requires adjustment to account for the influence of isotopic dilution and fractionation from water and carbonate rock interactions along flow paths. Pearson and Hanshaw (1970) developed equation 5 (appendix), which accounts for isotopic dissolution when combined with the Conventional Radiocarbon Age method developed by Stuiver and Polach (1977). Corrected ground-water residence times were then developed using equation 6 (appendix). The ^{14}C (adjusted) is then plugged into equation 4 as the pmc value to adjust for isotopic dilution.

Data requirements for ¹⁴C adjustments include $\delta^{13}C$ from ground water and local carbonate rocks and carbon dioxide from the soil zone (soil gas). The δ^{13} C of the soil gas was not available for use in equation 5; therefore, this parameter was estimated. Values of -9 ‰, -11 ‰, -13 ‰, -15 ‰, and -17 ‰ were used, bracketing known values for soil gas in semiarid regions.

Springs and creeks along the south rim of Grand Canyon represent end points of the regional ground-water flow system. The lack of data from wells close to Grand Canyon, or from wells or springs at other points along the ground-water flow path, limits the ability to accurately estimate ground-water residence time from 14C data.

SITE DESCRIPTIONS

The 20 spring and creek sites sampled are in tributary drainages to the Colorado River, f[rom Red](#page-70-0) Canyon in the east to Boucher East Spring in the west (**pl. 1**). Some drainages contain more than one site. Sites where water discharged from bedrock or from above the flood plain were defined as springs. Sites where water discharged from channel alluvium were defined as creeks. In some drainages, debris had buried spring sources and water issued from alluvium. It is not known how

far the issuing water was from the source spring at these sites; however, interpretation of water chemistry data can provide information about this relation.

Site selection criteria developed by the USGS and GRCA were:

- 1. Accessibility. Remoteness of the site, access for sample collection, and safety of field personnel.
- 2. Spatial distribution. Because the study area is large and the boundaries of the Redwall-Muav Limestone aquifer are poorly defined, springs and creeks were selected to provide adequate coverage of the study area.
- 3. Source rock. Sample collection was limited to springs or creeks that discharge from the Redwall Limestone, the Temple Butte Formation, the Muav Limestone, or the Bright Angel Shale.
- 4. Spring discharge. Preference was given to springs having measurable discharges.
- 5. Location. Preference was given to springs and creeks closest to Grand Canyon Village and Tusayan. These are areas of present and likely future ground-water pumping, and the springs and creeks were selected because they could potentially show effects of ground-water pumping sooner than springs farther away from areas of pumping.
- 6. Point of issuance. Whenever possible, sample sites were selected where water emerged directly from bedrock. These springs were frequently several kilometers or more from the Tonto Trail and had not been previously inventoried.

Springs and creeks were categorized by geologic characteristics, which included (1) bedding planes, (2) fractures, (3) hillslopes, (4) stream alluvium, and (5) travertine deposits (**[fig. 4](#page-21-1)** and **[table 4](#page-22-1)**).

Springs that discharge from bedding planes are typically near the contacts between the Redwall Limestone and the Temple Butte Formation, where present; the Redwall Limestone and Muav Limestone; or the Muav Limestone and the Bright Angel Shale. Springs discharging from hillslopes emerge in alluvial deposits of tributaries immediately below bedrock outcrops. Sites where water discharges from stream alluvium differ from hillslope springs in that ground water discharges far below the head of the canyon or bedrock outcrop and from within the active stream channel. Springs issuing from travertine deposits are along canyon walls. Physical characteristics of each of the springs and creeks are described in the following section and are presented in order from east to west. Data describing physical location and dates of site visits are included in **[table 1](#page-10-1)**. Water samples were collected at all sites except where noted.

A. Bedding planes—water issues from bedding planes in the Muav Limestone at Salt Creek Spring

C. Hillslopes—Burro Spring issues from hillslope alluvium at the east side of the Pipe Creek drainage

B. Fractures—vertical fracture at Monument Spring

D. Channel alluvium— water issues from channel alluvium in the upper Horn Creek drainage

E. Travertine deposits—travertine deposits at Boucher East Spring

Figure 4. Spring types at sample sites. *A*, Bedding planes; *B*, Fractures; *C*, Hillslopes; *D*, Channel alluvium; *E*, Travertine deposits.

Table 4. Geologic characteristics of springs and creeks sampled in study [see plate 1]

Red Canyon Spring.—Red Canyon Spring discharges from bedding planes in the Muav Limestone in the main drainage of Red Canyon and consists of numerous small spring outlets close to one another. The site is at the head of the canyon and at the base of a 300-m-high, near vertical cliff of Redwall Limestone and Muav Limestone (**[fig. 2](#page-13-2)**). The springs lie along the north-striking Hance Fault (**[pl. 1](#page-70-0)**). Water samples were collected from the largest of the spring outlets at the east side of the canyon about 75 m downstream from the headwall. Discharge was measured about 300 m downstream where flow in the channel is constricted over a bedrock ledge. Water flowed in the channel of Red Canyon Creek for about 1 km downstream from the point of issuance during all visits. Farther downstream, flow becomes subterranean until it emerges near the mouth of Red Canyon. High cliffs shade the spring outlets much of the time, and maidenhair fern (*Adiantum capillusveneris*) and other riparian plant species are abundant at the site.

JT Spring.—JT Spring is in an alcove erosional feature that is a tributary to the east branch of Hance Creek. The spring has several outlets issuing from bedding planes in the Muav Limestone (fig. 2). The largest outlet at the time of sampling was at the north side of the amphitheater and was mostly covered by an alluvial slump block. The back wall of the amphitheater is a 300-m-high vertical cliff of Redwall Limestone. The Grandview-Phantom Monocline (pl. 1) trends parallel to the east arm of Hance Creek and is immediately southwest of JT Spring. Samples were collected where the water emerges directly from the slump block. Discharge was measured about 60 m from the spring outlet where all flow from the outlet is in a single channel. Immediately downstream from the confluence of the tributary containing JT Spring and the east branch of Hance Creek, flow becomes subterranean until it emerges near the contact between the Bright Angel Shale and Tapeats Sandstone close to the Tonto Trail (pl. 1).

Miners Spring.—Miners Spring (also known as Page Spring) is just south of Horseshoe Mesa near the head of a small unnamed tributary of Hance Creek (pl. 1). The perennial spring discharges from bedding planes at the cliff face near the contact between the Temple Butte Formation and the Muav Limestone (fig. 2). Spring water drips from beneath a small alcove into a pool in a bedrock depression created by miners in the early 1900s. The spring probably originates from localized faulting along the axis of the northwest-trending Grandview-Phantom Monocline (pl. 1). Water samples were collected by capturing drips coming from the wall of the small alcove. Discharge was measured volumetrically by constricting all flow discharging from the pool into a single conduit. Water leaving the small pool flows about 3 m across the bedrock outcrop and enters the alluvium, and does not reemerge downstream. Aquatic vegetation is extensive at the site, and frogs and water skates were observed in the pool and along its edge during sampling visits.

Cottonwood Creek No. 1.—Cottonwood Creek drains the western side of Horseshoe Mesa (pl. 1) and has three major branches in its upper reaches. The eastern branch, which abuts Horseshoe Mesa, is almost always dry. The central branch has perennial flow in places, and the USGS maintains a streamflow-gaging station (station number 09402450) on this branch about 150 m upstream from the confluence with the eastern branch. There is a small seep in the western branch near the base of the Bright Angel Shale. This seep was not included in this study. Water in the central branch discharges from channel alluvium about 80 m upstream from the streamflowgaging station during most of the year (see site description for Cottonwood Creek No. 2 in the following text). Several springs and seeps discharge from the Temple Butte Formation and Muav Limestone (fig. 2) near the head of this branch; however, these sites were not sampled. The water sample for Cottonwood Creek No. 1 was collected about 100 m

downstream from the gaging station. The discharge was measured near the sample site. Large Fremont cottonwood (*Populus fremontii*) trees and aquatic plant species are present.

Cottonwood Creek No. 2.—Cottonwood Creek No. 2 is on the western side of Horseshoe Mesa in the central branch of three branches in the headwaters of Cottonwood Creek (**[pl. 1](#page-70-0)**). The perennial site discharges from channel alluvium about 600 m upstream from the USGS streamflow-gaging station (station number 09402450). During site visits, water flowed from beneath a large boulder on the east side of the active channel. Flow continued in the channel 10 m before becoming subterranean and re-emerging about 80 m upstream from the streamflow-gaging station. Cottonwood Creek No. 2 is in the Bright Angel Shale (**[fig. 2](#page-13-2)**). This formation is not exposed near the site; however, outcrops are visible lower and higher in the drainage. The axis of the Grandview-Phantom Monocline trends northwest in this vicinity (pl. 1). Water samples were collected where water flows from a small pool adjacent to the point of issuance. Discharge was measured at the streamflowgaging station. A thick stand of woody riparian species and aquatic vegetation are present in and near the stream channel.

Grapevine Main Spring.—Grapevine Main Spring is in a small canyon that is tributary to the main southeast trending canyon of Grapevine Creek about 3 km upstream from the Tonto Trail (pl. 1). Water discharges from bedding planes at several places in the upper part of the Muav Limestone, just below the Redwall-Muav contact (fig. 2). The springs are at the base of a massive vertical cliff that is predominantly Redwall Limestone. An unnamed fault strikes parallel to the Grapevine Creek drainage near the spring, and the McKee Fault bisects the canyon near the Tonto Trail (pl. 1). The spring is south of the northwest-trending Grandview-Phantom Monocline. Water samples were collected where the water emerges from the bedding planes. Discharge was measured about 80 m downstream from the sample site where all flow is constricted over a bedrock ledge. Flow in Grapevine Creek was continuous from near the side drainage containing the spring to near where the Tonto Trail crosses the creek. Flow in Grapevine Creek is intermittent downstream from the Tonto Trail. The main canyon and the tributary where the spring is located are densely vegetated with woody xeric and riparian species.

Grapevine East Spring.—Grapevine East Spring is in a small drainage on the east side of the Grapevine Creek drainage, directly adjacent to the Tonto Trail (pl. 1). The Tonto Trail crosses the drainage near the lower end of a small wetlands. The wetlands are supported by a group of small springs and seeps, most of which are obscured by the vegetation. During the site visit in May 2000, the first appearance of water was in the midst of the wetlands, and water samples were collected at this point. During site visits in

December 2000 and April 2001, water was discharging from bedding planes in the lower part of the Bright Angel Shale (fig. 2) about 30 m upstream from the wetlands, and water samples were collected here. Discharge was measured at a small waterfall about 30 m downstream from the trail. The site is just to the north of the northwest-trending Grandview-Phantom Monocline. Riparian vegetation in the area consists of sawgrass (*Cladium californicum*), Fremont cottonwood, and willow (*Salix* spp.).

Lonetree Spring.—Lonetree Spring is at the upper end of a small steep tributary that trends south from the main Lonetree Canyon drainage about 2 km upstream from the Tonto Trail (pl. 1). A group of small springs discharge along bedding planes in the upper part of the Muav Limestone at the head of the drainage. The discharge points are near the Redwall-Muav contact below a massive vertical wall of Redwall Limestone (fig. 2). The spring group is south of the Grandview-Phantom Monocline (pl. 1). Flow at individual discharge points was too small to fill sample containers; therefore, water samples were collected about 30 m downstream where flow from all spring outlets was combined. Discharge was measured 3 m downstream from the sample site at a bedrock ledge constriction. Just downstream from the discharge-measurement site, spring flow becomes subterranean and re-emerges near the contact between the Bright Angel Shale and Tapeats Sandstone close to the Tonto Trail (pl. 1). During summer visits, however, spring flow did not occur near the trail crossing.

Sam Magee Spring.—Sam Magee Spring is a small spring that emerges from bedding planes at an outcrop of the Muav Limestone (fig. 2), about 500 m above the Tonto Trail, at the eastern side of the Cremation Creek drainage, and just west of Patti Butte (pl. 1). The water flows for about 5 m before it infiltrates the channel alluvium. Water samples were collected where flow emerges from the bedding planes, and discharge was measured about 3 m downstream. During this study, field parameters were measured and water samples were collected for $\delta^{18}O$, δD , and tritium analyses only. The spring is northeast of the Grandview-Phantom Monocline (pl. 1).

Pipe Creek.—Perennial flow in Pipe Creek discharges from alluvium in the main Pipe Creek channel about 250 m upstream from the Tonto Trail crossing (pl. 1). Water emerges from channel alluvium overlying the lower part of the Bright Angel Shale (fig. 2). The site is near the northwest-striking Pipe Fault (pl. 1). Water samples were collected where flowing water was first evident, and discharge was measured at a permanently installed weir that was originally part of a USGS streamflow-gaging station (Pipe Springs Creek above Tonto Trail, near Grand Canyon, Arizona, station number 09403010; discontinued in 1996). Water flows continuously at the surface of the Pipe Creek channel from the sample site to the Colorado

Burro Spring.—Burro Spring is along the Tonto Trail at [the east](#page-70-0) side of the Pipe Creek drainage below O'Neill Butte (**pl. 1**). This perennial spring discharges from hillslope alluvium overlying the lower part of the Bright Angel Shale (**[fig. 2](#page-13-2)**). The spring is southwest of an unnamed northweststriking fault (pl. 1) and lies beneath a breccia pipe on the west face of O'Neill Butte (pl. 1). Water discharges diffusely from the hillslope, and sustains an area of thick vegetation, obscuring the points of issuance. Thus, the water sample was collected at the Tonto Trail crossing. Discharge was measured below the trail crossing, just above a large waterfall into Pipe Creek canyon. The area surrounding the spring is covered with sawgrass and there are several large Fremont cottonwood trees.

Pumphouse Spring.—Pumphouse Spring (also known as Two Trees Spring) is about 100 m to the east and 50 m up the slope from the NPS Indian Gardens pump station (pl. 1). Spring water first emerges from beneath a large boulder that is about 3 m upslope from two prominent Fremont cottonwood trees. The spring discharges from hillslope alluvium overlying the Bright Angel Shale (fig. 2) and is in the northeast-striking Bright Angel Fault zone (pl. 1). Water samples were collected near the boulder, and discharge was measured volumetrically by constructing a temporary weir directly below that point. The water enters the alluvium immediately below the spring and re-emerges about 5 m above the USGS streamflow-gaging station Pumphouse Wash Spring near Grand Canyon, Arizona, station number 09403013.

Pumphouse Wash Gage.—The sample site is a USGS streamflow-gaging station (09403013) in the Garden Creek basin that monitors discharge from Pumphouse Spring. The station is about 40 m northeast and 8 m up the slope from the NPS Indian Gardens pump station and approximately 100 m down the slope from Pumphouse Spring (pl. 1) in a small stream channel developed in hillslope alluvium that overlies the Bright Angel Shale (fig. 2). The site is in the Bright Angel Fault zone (pl. 1). Water samples were collected from the small pool of flowing water at the streamflow-gaging station, and discharge was measured with a Parshall flume. Downstream from the gaging station, water flows continuously in a small channel for about 30 m and then enters Garden Creek, which flows continuously to the Colorado River.

Horn Creek.—Horn Creek consists of two primary branches. The west branch is usually dry, and the east branch has perennial flow in places. The sample site is in the east tributary about 500 m upstream from the Tonto Trail crossing (pl. 1) where water discharges from the channel alluvium that overlies the Bright Angel Shale (fig. 2). Water samples were collected at a small waterfall that was formed by boulders in the stream channel. Discharge was measured volumetrically at a small waterfall near the sample site. The spring flow emerges on the downthrown side of the northwest-striking Salt Fault (pl. 1) and flows intermittently to the Colorado River. At the head of the drainage is a breccia pipe and a historic uranium mine. Recent flooding has removed most of the vegetation at the site, leaving a few Fremont cottonwood trees in the nearby channel reach.

Salt Creek Spring.—Salt Creek Spring is at a headwall in the main Salt Creek drainage about 800 m upstream from the Tonto Trail crossing (pl. 1). Water discharges from bedding planes in the Muav Limestone and drips down an 8-m high cliff face of Muav Limestone onto a small talus slope on the west side of the canyon. The point of issuance of water is inaccessible; therefore, water samples were collected at the talus slope using a Visqueen sheet to funnel the flow into a Teflon holding bottle. All water enters the channel alluvium immediately downstream from the talus slope. During all site visits there was no evidence of flowing water in the stream channel from the talus slope to the Tonto Trail crossing. Discharge was measured where water flows over exposed Tapeats Sandstone (fig. 2) surfaces near the Tonto Trail (pl. 1). Water flows intermittently downstream from the Tonto Trail crossing to the Colorado River. No large-scale geologic structures have been identified near the spring. Recent flooding has removed large vegetation from the Salt Creek drainage.

Monument Spring.—Monument Spring is at the headwall of a small tributary on the east side of Monument Creek about 3 km upstream from the Tonto Trail. The head of the Monument Creek drainage is known as The Abyss, and the near-vertical cliffs rise about 1 km to the south rim of Grand Canyon (pl. 1). The spring is in an alcove above a series of waterfalls that support hanging gardens of ferns. There are numerous smaller springs and seeps in the alcove. The main spring discharges from a vertical fracture near the contact between the Redwall Limestone and the Temple Butte Formation (fig. 2). Water samples were collected at the point of issuance. Discharge measurements were made at the bedrock outcrop below the Tonto Trail. An unnamed fault strikes northwest near the spring. Monument Creek is intermittent between the small tributary where the spring is located and the Colorado River. The canyon wall has several hanging gardens that include maidenhair fern, golden columbine (*Aquilegia chrysantha*), and other aquatic plants.

Monument Creek No. 1.—At Monument Creek, water surfaces in the channel alluvium about 50 m upstream from the Tonto Trail crossing (pl. 1) and flows through a series of pools and riffles. A water sample was collected from Monument Creek about 30 m upstream from the trail. In this reach of Monument Creek, the channel alluvium overlies the Tapeats Sandstone (fig. 2). Discharge was measured about

300 m downstream near the NPS campground at a point where water emerges from the alluvium and flows in a small channel over an outcrop of Precambrian bedrock. Water flows intermittently in the stream channel from the discharge measurement site to the Colorado River. Several large debris flows removed vegetation from the stream channel during the 1980s and 1990s.

Hawaii Spring.—Hawaii Spring is about 1.8 km upstream from where the Tonto Trail crosses the Hermit Creek drainage (**[pl. 1](#page-70-0)**). The perennial spring discharges from bedding planes in the Muav Limestone (**[fig. 2](#page-13-2)**) in a small grotto to the west of Hermit Creek. There are numerous springs and seeps in the Hermit Creek drainage, and Hawaii Spring is among the largest of the springs. Water samples were collected from the largest of many seeps in the grotto. It was not possible to measure the discharge of Hawaii Spring. Instead, discharge was measured at the USGS streamflow-gaging station on Hermit Creek (Hermit Creek above Tonto Trail near Grand Canyon, Arizona, station number 09403043) approximately 325 m upstream from the Tonto Trail and the NPS campground. The station monitors total spring flow in Hermit Creek including flow from Hawaii and Hermit Springs. The north-striking Hermit Fault, adjacent to Hermit Creek (pl. 1), is a prominent structural feature in this part of Grand Canyon and probably influences ground-water movement. Hanging gardens near the spring include maidenhair fern and golden columbine; sawgrass grows in a dense stand outside the grotto.

Hermit Spring.—Hermit Spring is about 3.6 km upstream from where the Tonto Trail crosses the Hermit Creek drainage (pl. 1). Spring water discharges from bedding planes at the base of Redwall Limestone cliffs near the contact with the Temple Butte Formation (fig. 2). The north-striking Hermit Fault, adjacent to Hermit Creek (pl. 1) is a prominent structural feature in this part of Grand Canyon. The water sample was collected at the point of issuance. Flow in Hermit Creek is continuous from the spring to the Colorado River. The USGS streamflow-gaging station (station number 09403043) was used to determine discharge (pl. 1). The vegetation in the Hermit Creek drainage is dense and includes western redbud (*Cercis occidentalis*) and tamarisk (*Tamarix chinensis*).

Boucher East Spring.—Boucher East Spring is in the southeast branch of Boucher Creek (pl. 1). The perennial spring discharges from a large travertine deposit associated with a slump block in the upper part of the canyon. The travertine and the slump block overlie the Bright Angel Shale (fig. 2). The strike of the Crazy Jug Monocline (pl. 1) is northwest and parallel to the trend of the southeast branch of Boucher Creek. The actual point of spring issuance is obscured; however, water first appears in the Bright Angel Shale about midway up the slump block. The point of issuance is inaccessible; therefore, water samples were collected near

the base of the travertine deposit and discharge was measured in a small channel about 5 m downstream. The southeast branch of Boucher Creek is intermittent between the spring and the confluence with the main stem of Boucher Creek. The spring supports hanging gardens.

CHEMICAL CHARACTERISTICS OF GROUND-WATER DISCHARGE AT SPRINGS

Water sampled from springs during this study was generally a calcium magnesium bicarbonate type; a few samples had a substantial sulfate component (**[fig. 5](#page-26-1)** and pl. 1). To give a brief picture of the overall chemical characteristics of the springs, the concentration distribution of 18 different constituents is shown in three panels (**[fig. 6](#page-27-1)**). For example, sulfate ranged from 6 to 340 mg/L, and the median value was 37 mg/L; sodium ranged from 4 to 53 mg/L, and the median value was 11 mg/L (fig. 6*A*); zinc ranged from 0.4 to 57 µg/L, and the median value was 3.7 µg/L (fig. 6*B*); and lead ranged from near zero to 260 ng/L, and the median concentration was 15 ng/L (fig. 6*C*).

Comparison of Water-Chemistry Data from Springs with Data from Creeks

Although collection of samples from the point of issuance was emphasized, samples were collected both from the point of spring issuance and downstream from the point of issuance in the alluvial channel at Cottonwood and Monument Creeks. Water-chemistry data for samples collected from the point of issuance differ considerably from data for samples collected from the downstream sample site (**[table 5](#page-28-3)**).

The observed changes in chemistry in Cottonwood and Monument Creeks indicate that the chemical and physical processes occurring during the transmittal of water through the alluvium are dynamic and variable. The increase in concentration of some constituents can be attributed to dissolution of rock materials through interaction with water, and the decrease in concentration of some constituents is probably mostly due to adsorption or precipitation. The change in concentrations at Cottonwood and Monument Creeks reiterates the importance of collecting samples from the point of issuance in order to provide relevant information about the source of ground-water discharged at the spring.

Figure 5. Relative compositions of water from springs and creeks that discharge along the south rim of Grand Canyon, Arizona, 2000–2001.

Figure 6. Distribution of constituent concentrations of water that discharges from springs and creeks along the south rim of Grand Canyon, Arizona, 2000–2001. *A*, Major constituents: calcium, magnesium, sodium, bicarbonate, chloride, and sulfate; *B*, Trace elements (higher concentrations): arsenic, molybdenum, rubidium, selenium, uranium, and zinc; *C*, Trace elements (lower concentrations): neodymium, lead, rhenium, antimony, thallium, and yttrium.

Chemical Characteristics of Ground-Water Discharge at Springs 21

Table 5. Changes in constituent concentrations from the point of spring issuance sample location to the downstream sample location, Cottonwood and Monument Creeks, 2000–2001

Consistency of the Springs Data

The data indicate that there is a temporal consistency of results for individual springs. For those springs that were sampled more than once, the general rule is that concentrations were consistent over the duration of the study, regardless of seasonality, weather conditions, or any other factor. For example, Miners Spring was sampled three times, in May and November 2000 and in April 2001. In these samples, the calcium concentrations ranged between 21 and 22 mg/L and arsenic concentrations ranged between 17 and 19 μg/L. Similarly, Boucher East Spring was sampled in May and December 2000 and April 2001. Sodium concentrations in these samples ranged between 6.1 and 7.0 mg/L. Salt Creek Spring was sampled during the same months, and uranium concentrations in those samples ranged between 29 and 31 μg/L. The average variability (in percent relative standard deviation) in all chemical constituents sufficiently above their respective detection limits for all springs that were sampled more than once was less than 8 percent for all but two springs, JT Spring and Grapevine East Spring (table 6). The primary conclusion from these data is that spring-water chemistry appears to be consistent over short-term (year) periods. There are two major implications that follow from this conclusion. The first is that the ground water discharging from the sites sampled had a constant chemistry during this study that can be used to characterize it. The second is that the lack of agreement among constituent data for any given site suggests that at least some of the samples from that site probably do not represent spring water at the point of issuance. Data from Grapevine East and JT Springs had far greater variability than data from other springs and fall into this category. Conversely, data from Horn Creek, Cottonwood Creek No. 2, and Pipe Creek all demonstrated consistency and indicate that although the

samples may have been collected from the channel alluvium, they likely represent water issuing from bedrock close to the sample site.

Grapevine East Spring was sampled three times (May and November 2000 and April 2001), and constituent concentrations generally varied by 40 percent or more among samples. The spring is on the slopes of a large unnamed promontory that is connected to the regional land mass of the south rim only by a narrow strip of land. Pennsylvanian and Permian rock units are mostly absent from the promontory above the spring. This spring is unique in these characteristics among the springs sampled during this study. As noted in the site descriptions, the May 2000 sample was collected in the midst of a small wetlands, unlike the samples collected later. When the data from this wetlands sample are not included, the variability improves to about 11 percent relative standard deviation, but even this value is substantially greater than the variability in data for other springs. This suggests that samples from Grapevine East Spring probably do not represent spring waters sampled at the point of issuance, or that this spring has at least two source flow paths of water that do not contribute consistently the same proportions of water. Because of this, chemical data from Grapevine East Spring were excluded from discussion in the following sections titled ["Relations to Water-Quality Contaminant Standards"](#page-29-2) and "Chemistry of Selected Springs."

Table 6. Variability in chemical data for selected constituents for all springs sampled more than once during 2000–2001

[Selected constituents are arsenic, barium, bicarbonate, boron, bromide, calcium, chloride, lithium, magnesium, molybdenum, potassium, rhenium, rubidium, selenium, silica, sodium, strontium, sulfate, and uranium]

¹The second entry for Grapevine East Spring excludes the sample collected in the wetlands.

JT Spring was sampled in April and May 2001, and constituent concentrations varied by about 23 percent between samples. In general, the April 2001 sample had higher constituent concentrations than the May 2001 sample.

Immediately prior to collection of the sample in April 2001, the site received sustained rainfall. This sample, therefore, could have been affected by local surface-water runoff. Consequently, this sample was also excluded from the ensuing discussion.

These factors underscore the need to collect samples at more than one time from each spring. Good agreement of results suggests that samples represent the ground water at or near the point of issuance, whereas lack of agreement suggests either that one or more of the samples was compromised, or that the samples do not represent the ground water at the point of issuance.

Relations to Water-Quality Contaminant **Standards**

Concentrations of several constituents at some springs were higher with respect to the other springs in the study area and (or) exceeded U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Levels for drinking water (MCLs; table 7). MCLs are based on quantity of consumption and are intended for public drinking-water supply systems and not the occasional user (U.S. Environmental Protection Agency, 2003). Nevertheless, values above the MCLs represent a concern for water users.

Arsenic concentrations in samples from Red Canyon Spring, JT Spring, and Miners Spring exceeded the MCL of 10 µg/L (**[tables 7](#page-30-1)** and **8**[\), ave](#page-44-2)raging between 14 and 19 µg/L. Cottonwood Creek No. 2 and Grapevine Main Spring had concentrations of about 5 µg/L. All these springs are in the easternmost part of the study area (pl. 1). Other springs in the study area averaged about 2 µg/L of arsenic or less, with the exception of Monument Spring, which averaged 4 µg/L (**[fig.](#page-31-2) 7**). This pattern of the easternmost springs having the highest concentrations was also seen for cesium, thallium, tungsten, vanadium, and to a lesser extent, antimony and nitrate.

Concentrations of selenium ranged from 1.3 to about 11 µg/L; most springs had concentrations of approximately 4 µg/L (**[fig. 8](#page-31-2)**). Although these values are well below the MCL (50 µg/L), many other countries have adopted a standard of 10 µg/L (National Health and Medical Research Council, and Agriculture and Resource Management Council of Australia and New Zealand, 1996; Safe Drinking Water Foundation, 2003; Drinking Water Inspectorate, 2003). Concentrations of selenium were highest at Salt Creek Spring (9.4 to 11 μ g/L). With the exception of data from Salt Creek Spring, there is a decreasing trend in concentrations east to west from Lonetree Spring (6 μ g/L) to Boucher East Spring (about 3 μ g/L).

Concentrations of uranium did not show a regional pattern; however, v[alues at so](#page-32-2)me sites were significantly higher than at others (**fig. 9**). Uranium concentrations were about 30 µg/L (equal to the MCL) in all samples from Salt Creek Spring (table 7). Salt Creek Spring also had the highest dissolved gross alpha radioactivity (22 pCi/L, based on 230 Th). Only one sample from Horn Creek (April 2001) was near the MCL for uranium; the other two samples had values of about 9 µg/L. Uranium mining has occurred in the Horn Creek drainage, and unacceptably high levels of uranium were reported for samples collected previously (Fitzgerald, 1996). In Fitzgerald's study, samples were taken not at the point of spring issuance, but where the Tonto Trail crosses the drainage. The uranium in south rim springs may be related to the presence of nearby breccia pipes and faults.

Geochemistry of Barium and Sulfate

Concentrations of sulfate varied widely—between 6 and 190 mg/L when suspected compromised samples have been eliminate[d \(figs. 5](#page-26-1) [and 6\). T](#page-27-1)his variation is not seen for the other major ions. When sulfate data are plotted against barium data in molar concentrations (**[fig. 10](#page-32-2)**), an inverse relation is observed, indicating that barium and sulfate concentrations are controlling each other. Barium sulfate—barite (BaSO4) solubility is typically a control on sulfate concentration in natural waters (Hem, 1985). Figure 10 indicates that sulfate concentrations are limited by barite solubility for the samples in this study.

A plot of the spatial distribution of barium concentrations at sites in the study area reveals two populations that are spatially intermixed but can be distinguished from each other by concentrations (**[fig. 11](#page-33-5)**). One group contains concentrations lower than about 130 µg/L and consists of JT Spring, Miners Spring, Lonetree Spring, Burro Spring, Pipe Creek, Horn Creek, Salt Creek Spring, Hawaii Spring, and Boucher East Spring. The other population consists of those springs whose barium concentrations are higher than about 200 µg/L and contains Red Canyon Spring, Cottonwood Creek No. 2, Grapevine Main Spring, Pumphouse Spring, Monument Spring, and Hermit Spring. If the easternmost four sites (Red Canyon Spring, JT Spring, Miners Spring, and Cottonwood Creek No. 2) are separated from these two populations because of the arsenic, cesium, thallium, vanadium, and tungsten data (see previous discussion on arsenic) to create a third population, a set of clear intrapopulation relations becomes apparent. Population 1 consists of Lonetree Spring, Burro Spring, Pipe Creek, Horn Creek, Salt Creek Spring, Hawaii Spring, and Boucher East Spring, and shows a linear increase in barium to the west from about 40 µg/L at Lonetree Spring to about 110 µg/L at Boucher East Spring. Population 2 consists of Grapevine Main Spring, Pumphouse Spring, Monument Spring, and Hermit Spring, and shows a linear decrease in barium to the west from about 350 µg/L at Grapevine Main Spring to about 220 μ g/L at Hermit Spring. Population 3, consisting of Red Canyon Spring, JT Spring, Miners Spring, and Cottonwood Creek No. 2, shows no spatial barium relation, but shows a strong spatial arsenic relation (fig. 7).

Table 7. U.S. Environmental Protection Agency Maximum Contaminant Levels (MCLs) for selected constituents

[Values exceeding the Maximum Contaminant Level (MCL) are italicized. Source of MCLs: U.S. Environmental Protection Agency (2003)]

¹Action level. For public water systems, lead is regulated by a treatment technique that requires systems to control the corrosiveness of their water.

Figure 7. Concentrations of arsenic in relation to spring or creek locations along the south rim of Grand Canyon, Arizona, 2000–2001.

Figure 8. Concentrations of selenium in relation to spring or creek locations along the south rim of Grand Canyon, Arizona, 2000–2001.

Figure 9. Concentrations of uranium in relation to spring or creek locations along the south rim of Grand Canyon, Arizona, 2000–2001.

Figure 10. Relation between concentrations of barium and sulfate in water that discharges along the south rim of Grand Canyon, Arizona, 2000–2001.

Figure 11. Concentrations of barium in relation to spring or creek locations along the south rim of Grand Canyon, Arizona, 2000–2001.

The division of the springs into these three populations (based on barium and arsenic concentrations) is also observed, although less clearly, for calcium, magnesium, sulfate, and potassium. If Monument Spring is eliminated from this discussion, an action justified by the fact that it is anomalous with respect to the other springs in this study in many ways (see below), chloride and sodium also demonstrate the division.

Chemistry of Selected Springs

Monument Spring

Although much of the chemistry of Monument Spring is similar to that of surrounding springs, concentrations of several constituents are distinctly different. At the point of issuance, concentrations of nitrate ranged from 5.7 to 6.8 mg/L as nitrogen, which are less than the MCL of 10 mg/L (**[table 7](#page-30-1)**) but much higher than the concentrations at any other springs. The source of the nitrate in the spring is unknown. Monument Spring also had higher concentrations of chloride and several heavy metals, including copper, mercury, lead, arsenic, and thallium, than other springs. In addition, semiquantitative analyses of these samples indicated concentrations of dissolved gold that were an order of magnitude greater than concentrations at other springs. These patterns indicate that ground water discharging at Monument Spring is influenced

either by wastewater contamination on the south rim of Grand Canyon or by exposure to rocks and (or) geologic features in the subsurface (for example, breccia pipes or faults) not encountered by water discharging at the other springs.

Lonetree Spring

Water issuing from Lonetree Spring is unusual in that it has much higher concentrations of the rare earth elements (REE) than the other springs. The average concentration for lanthanum in all waters analyzed was about 0.004 μg/L, yet for Lonetree Spring it was 0.023 μg/L; similarly, the average concentration for holmium was about 0.0003 μg/L, yet for Lonetree Spring it was 0.0016 μg/L. In addition to the REE, Lonetree Spring was unusually high in sodium, calcium, lithium, rubidium, strontium, boron, and sulfate, and was unusually low in antimony and barium. There are no known sources of REE in the vicinity of Lonetree Spring.

Salt Creek Spring and Horn Creek

Salt Creek Spring had high concentrations of uranium and selenium, and had a high gross alpha radioactivity, and one of the Horn Creek samples had a high concentration of uranium. These springs also had anomalously high concentrations (relative to the other springs) of magnesium, potassium, sulfate, lithium, bromide, molybdenum, and

Chemical Characteristics of Ground-Water Discharge at Springs 27

rhenium. These sites are near mapped [breccia pip](#page-70-0)es and an abandoned copper and uranium mine (**pl. 1**), which may influence the chemistry of water that discharges at the two springs.

Grapevine Main, Pumphouse, Hawaii, Hermit, and Boucher East Springs

Grapevine Main Spring, Pumphouse Spring, Hawaii Spring, Hermit Spring, and Boucher East Spring tended to have low concentrations of a wide variety of major and trace elements and nutrients, including calcium, magnesium, sodium, potassium, strontium, lithium, rubidium, boron, selenium, uranium, antimony, and nitrate. To a lesser extent, this is also true of Pipe Creek, Burro Spring, and Cottonwood Creek No. 2. These springs, however, can be distinguished from one another on the basis of their chemistry. For example, a plot of barium and calcium concentrations (fig. 12) demonstrates a clear clustering of data for each spring. If more elements were added, the clustering would be even more exclusive: for example, if arsenic were plotted as a third dimension, the separation between Hermit Spring and

Cottonwood Creek No. 2 would be greater, because their respective arsenic concentrations are very different. Thus, although each of these springs has, in general, a similar chemistry—derived, no doubt, from the same aquifer—each also has its own particular chemistry that is dependent on its geological and spatial location.

Residence Times of Ground Water Discharging at Springs

A local meteoric water line for the south rim of Grand Canyon ([fig. 13](#page-35-1)*A*) was constructed using δ^{18} O and δ D analyses of precipitation samples collected between 1989 and 2002 from a site near the south rim of Grand Canyon (Pendall, 1997; Harvey, 2000; National Atmospheric Deposition Program, 2002). The δ^{18} O and δ D data for precipitation have a strong seasonal pattern: winter precipitation samples were isotopically lighter than summer precipitation samples. Delta oxygen-18 values range from -12.9 to -8.5 ‰, and δD values range from -95 to -71 ‰ for water samples collected from sites that discharge from the Redwall-Muav Limestone aquifer along the south rim of Grand Canyon (**[table 8](#page-44-2)**).

Figure 12. Relation between barium and calcium concentrations, demonstrating the clustering of data, for selected springs and creeks that discharge along the south rim of Grand Canyon, Arizona, 2000–2001.

δ18O, IN PER MIL, VIENNA STANDARD MEAN OCEAN WATER

B. Water from springs and creeks, 2000–2001

A. Precipitation, 1989–2002

Figure 13. Relation between oxygen-18 (δ¹⁸O) and deuterium (δD) in water along the south rim of Grand Canχon, Arizona. *A*, Precipitation 1989–2002; *B*, Water from springs and creeks, 2000–2001; *C*, Regional trend of oxygen-18 (δ18O) values for water from springs and creeks, 2000–2001.

Figure 13. Continued.

The local meteoric water line plots above the global meteoric water line, and data from the springs and creeks plot close to the global meteoric water line (fig. 13*B*). Possible reasons for this difference are the contribution of older water that was recharged during a different climate period or fractionation during secondary evaporation prior to recharge (Mazor, 1997).

Unlike precipitation, water samples from springs and creeks along the south rim of Grand Canyon do not show a clear seasonal pattern in isotopic compositions and are most similar to compositions in winter precipitation. Multiple water samples for δ^{18} O and δ D analyses were collected at most sites during multiple seasons, and data from repeat samples were generally consistent with data from the initial sampling. Values of δ^{18} O and δ D for a repeat sample at JT Spring, however, were substantially different from values for the initial sample. The δ^{18} O and δ D data can be divided into two groups. Group 1 δ^{18} O values range from -12.9 to -11.4 ‰ and show a trend of increasing 18O enrichment from east to west (fig. 13*C*). Group 1 includes Red Canyon Spring, JT Spring, Miners Spring, Cottonwood Creek No. 1, Cottonwood Creek No. 2, Grapevine Main Spring, Lonetree Spring, Burro Spring, Pipe Creek, Pumphouse Spring, Horn Creek, Salt Creek Spring, Monument Spring, Hawaii Spring, Hermit Spring, and Boucher East Spring. Group 2 includes JT Spring, Grapevine East Spring, and Sam Magee Spring. Group 2 sites are substantially enriched in 18 O and D and have δ^{18} O values that range from -10.0 to -8.5 ‰. The trend of isotopic enrichment

for group 2 sites is probably due to evaporative processes occurring prior to ground-water recharge or subsequent to spring discharge upgradient from sample collection points.

Strontium isotopes and concentrations can provide information about water-rock interactions in ground-water systems. Strontium-87/strontium-86 values (**[table 8](#page-44-2)**) for water samples from springs and creeks range from 0.70363 at Horn Creek to 0.71514 at Grapevine East Spring. Rock samples collected from the Bright Angel Fault area have $87\text{Sr}/86\text{Sr}$ values (**[table 9](#page-64-1)**) ranging from 0.70820 (Redwall Limestone) to 0.71216 (Hermit Formation). Values for springs and creeks east of the Bright Angel Fault (**[pl. 1](#page-70-0)**) are generally more radiogenic than values for sites to the west of the fault (**[fig. 14](#page-37-1)**). Values in water discharging from Red Canyon Spring, JT Spring, Miners Spring, Cottonwood Creek No. 1, Cottonwood Creek No. 2, Grapevine East Spring, Grapevine Main Spring, Lonetree Spring, Burro Spring, Pipe Creek, Pumphouse Spring, Salt Creek Spring, Hawaii Spring, and Boucher East Spring are more radiogenic than values in water that discharges at the other springs. The larger ratios may be due to interactions of ground water with the Coconino Sandstone or Hermit Formation, which are more radiogenic than the other rock units, to contact with secondary carbonates encountered in fractures or solution cavities along the flow path, or to interaction with rocks that were not analyzed during this study.

Figure 14. Strontium-87/strontium-86 in water from springs and creeks that discharge along the south rim of Grand Canyon, Arizona, and in rocks from near the Bright Angel Fault near the south rim, 2000–2001.

Water in Horn Creek had a $87Sr/86Sr$ value of 0.70363. None of the rocks sampled had a value similar to this value. It is possible that rock units present in the ground-water flow path near Horn Creek are different from those sampled and analyzed for 87Sr/86Sr values.

Carbon-14 activities in water samples ranged from 38.3 pmc at Hawaii Spring to 103.4 pmc at Grapevine East Spring and for most sites was between about 40 and 75 pmc (**[table 8](#page-44-2)**). Ground-water residence times were estimated by Stuiver and Polach's (1977) method and by application of a combination of Stuiver and Polach's (1977) conventional radiocarbon-age method and Pearson and Hanshaw's (1970) dilution equation. Estimates of ground-water residence time using this method range from modern to 3,400 yr (table 8). Water-rock interaction in carbonate rock can cause a change of about 60 pmc from the recharged water (Mazor, 1997).

Tritium activities in water samples from sites in this study ranged from less than 0.3 TU (detection limit) to 4.1 TU (table 8). Water samples were collected for tritium analysis during more than one site visit at most sites. Tritium activities in samples collected during April 2001 were higher than activities in samples collected at other times at the same sites. A regional rainstorm during the April 2001 sample collection period could have caused this variability.

Three groups were identified on the basis of tritium and 14C data (**[fig. 15](#page-38-3)**). Sites in group 1, Pumphouse and Boucher East Springs, had tritium activities below the detection limit (0.3 TU) and estimated ground-water residence times ranging from modern to 1,900 yr. Low tritium activities indicate that ground-water discharge at the group 1 sites did not contain young water at the time samples were collected. The corrected residence time for Boucher East Spring was modern; however, extensive travertine deposits at this spring could be a source of unaccounted-for carbon in the ground-water flow path, which would result in a 14C value that is biased toward a shorter residence time.

Group 2 includes sites with tritium activities that ranged from 0.4 to 2.0 TU and ¹⁴C activities that ranged from 38.3 to 74.8 pmc. There is a general increase in TU with increasing pmc. Estimates of ground-water residence time for this group range from 500 to 3,400 yr. The 14 sites in this group discharge a mixture of young and old ground water. When a mixture of young and old water occurs, the actual residence time is greater than the calculated residence time (Mazor, 1997). Group 3 is composed of sites with predominantly post-bomb (after 1952; Mazor, 1997) carbon. Sites in this group are Grapevine East Spring (TU = 0.6 ; pmc = 103.4 and 98.7) and Cottonwood Creek No. 1 (TU = 0.7 ; pmc = 94.2). Carbon-14 activities higher than 100 pmc indicate the presence of predominantly post-bomb radiogenic carbon in ground water. A water sample collected at Grapevine East Spring (103.4 pmc) in May 2000 was the only sample with post-bomb carbon.

Figure 15. Relation between tritium and carbon-14 in water from springs and creeks that discharge along the south rim of Grand Canyon, Arizona, 2000–2001.

FUTURE STUDIES

The ongoing collection and evaluation of water-chemistry data will be a valuable component of GRCA's effort to document springs and other water sources in Grand Canyon. Continued operation of the three streamflow-gaging stations on Hermit Creek, Cottonwood Creek, and at Pumphouse Spring will provide long-term data on ground-water discharge. Additional gaging stations will improve the areal distribution of discharge data and provide long-term data that can be used to evaluate the effects of development and climate variability on ground-water resources.

The lack of water samples from wells on the Coconino Plateau has limited the data available for analysis of groundwater residence times and flow paths. Additional data from wells and from springs discharging from younger stratigraphic units are needed to adequately determine ground-water residence times and flow paths for the regional ground-water system on the Coconino Plateau. Collection and analysis of water samples from wells, repeat sampling and analysis at spring and creek sites included in this study, and expansion to include springs issuing from the Coconino Sandstone, Supai Group, and Precambrian rocks would help to provide additional understanding of the relations between the springs and local and regional ground-water flow systems. Collection of inner canyon precipitation samples would help improve

understanding of recharge and ground-water flow paths. Collection and analysis of rock samples from geologic units and areas of Grand Canyon not included in this study would help to refine existing knowledge of regional water-rock interactions.

Data describing springs along the south rim of Grand Canyon and wells on the Coconino Plateau have been collected by the USGS and other researchers as part of other projects and were not included in this report. A comprehensive analysis of all available data would be an important contribution to the understanding of the regional ground-water system.

SUMMARY AND CONCLUSIONS

Springs discharging along the south rim of Grand Canyon in Grand Canyon National Park, and the riparian areas that they support, are recognized as important resources by resource managers, Native Americans, and the general public. Development on the Coconino Plateau in the vicinity of the south rim has led to an increased demand for ground water. This study was designed to provide baseline data on springs and creeks issuing from the Redwall-Muav Limestone aquifer in the core-use area along the south rim, from Red Canyon Spring in the east to Boucher East Spring in the west. The data

in this report contain information on 20 springs and creeks including water chemistry, quantity, and quality, and the residence times of ground-water discharged at the springs.

Whenever possible, samples were collected at the point where water discharges directly from bedrock. Where this could not be done, samples were collected at the point where water first appeared. Each spring and creek is associated with one or more of five types of geologic characteristics: bedding planes, fractures, channel alluvium, hillslope alluvium, or travertine deposits. Most of the sites are associated with geologic structures such as faults or monoclines.

Major findings of this study:

- The water chemistry of a given spring did not appreciably vary over the course of the study. Samples had consistent compositions regardless of the season in which they were collected. This was in direct contrast to data presented in previous reports showing considerable seasonal variation in chemistry. Samples in previous studies may not have been collected near the point of the first issuance of water. Consequently, these data may not be representative of water discharging directly from the Redwall-Muav Limestone aquifer.
- The water chemistry of each spring was distinct from that of all other springs and creeks.
- The water discharging at most sites was a calcium magnesium bicarbonate type.
- Arsenic and uranium were higher than USEPA MCLs at some sites.
	- Arsenic concentrations were highest at springs near the Grandview-Phantom Monocline; Miners, JT, and Red Canyon Springs all contained concentrations above the MCL.
	- Uranium concentrations and gross alpha radioactivity were highest at Horn Creek and Salt Creek Spring. The average uranium concentration at Salt Creek Spring was equal to the MCL.
- Nitrate and selenium approached the MCLs or exceeded standards set in other countries at some sites.
	- Nitrate concentrations were highest in the Monument Creek drainage, and those samples collected at the spring were the highest in the drainage.
	- Selenium concentrations at Salt Creek Spring were the highest in the study. Whereas these concentrations do not approach the MCL, they exceed the drinking-water limit set by several other countries.
- The chemistry of Monument Spring was much different from that of the other springs in many respects. In addition to having the highest concentrations of nitrate, this spring also had high

concentrations of copper, mercury, lead, thallium, arsenic, chloride, and gold relative to other springs.

- The chemistry of Lonetree Spring was distinctively high in boron, calcium, lithium, rubidium, sodium, strontium, sulfate, and the REEs.
- The δ^{18} O and δ D data vary little among most sites and among multiple samples from individual sites, indicating that the water discharging from most sites is from a common aquifer.
- The δ^{18} O and δ D data for most sites indicate that recharge occurs on the Coconino Plateau; however, the presence of an evaporative signature for some sites suggests isotopic fractionation due to predischarge or postdischarge evaporation.
- The ⁸⁷Sr/⁸⁶Sr values for water samples collected at sites east of the Bright Angel Fault are more radiogenic than values for samples from sites west of the fault.
- Ground-water residence times estimated using radiocarbon dating techniques ranged from modern to about 3,400 yr.
- Tritium and 14 C results indicate that ground-water discharged from the Redwall-Muav Limestone aquifer at most springs and creeks is a mixture of young and old ground waters, suggesting that water discharging from the aquifer at these sites follows multiple flow paths and has multiple recharge areas.

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Physical and Chemical Data

Table 8. Physical and chemical properties, chemical-constituent concentrations, radioactivity, and isotopic data for water from springs and creeks that discharge along the south rim of Grand Canyon, Arizona, 2000–2001

[°C, degrees Celsius; μS/cm, microsiemens per centimeter at 25°C; mg/L, milligrams per liter, μg/L, micrograms per liter; gal/m, gallons per minute; L/m, liters per minute; nc, not collected; ICP-AES, Inductively Coupled Plasma-Atomic Emission Spectrometry; Avg, average; SD, standard deviation; IC, ion chromatography; MAD, median absolute deviation; na, not available; <, less than; ICP-MS, Inductively Coupled Plasma-Mass Spectrometry; CVAFS, Cold-Vapor Atomic Fluorescence Spectrometry; pCi/L, picocuries per liter; PE, two-sigma precision estimate; MDC, minimum detectable concentration; 137Cs, Cesium-137 curve; ²³⁰Th, Thorium-230 curve; mg C/L, milligrams of carbon per liter, IR infrared; δ, delta; per mil, per thousand; TU, tritium units; ≤, less than or equal to]

Table 8. Physical and chemical properties, chemical-constituent concentrations, radioactivity, and isotopic data for water from springs and creeks that discharge along the south rim of Grand Canyon, Arizona, 2000–2001—Continued

Table 8. Physical and chemical properties, chemical-constituent concentrations, radioactivity, and isotopic data for water from springs and creeks that discharge along the south rim of Grand Canyon, Arizona, 2000–2001—Continued

Table 8. Physical and chemical properties, chemical-constituent concentrations, radioactivity, and isotopic data for water from springs and creeks that discharge along the south rim of Grand Canyon, Arizona, 2000–2001—Continued

Table 8. Physical and chemical properties, chemical-constituent concentrations, radioactivity, and isotopic data for water from springs and creeks that discharge along the south rim of Grand Canyon, Arizona, 2000–2001—Continued

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Table 8. Physical and chemical properties, chemical-constituent concentrations, radioactivity, and isotopic data for water from springs and creeks that discharge along the south rim of Grand Canyon, Arizona, 2000–2001—Continued

¹Less than 50 years.

Table 9. X-ray diffraction mineralogy and isotope data for selected rock samples representing the major stratigraphic units present near the Bright Angel Fault in Grand Canyon, Arizona

¹Depth is calculated from the Bright Angel Fault at the south rim of Grand Canyon at an altitude of 1,945 meters above sea level.

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Appendix

Equation 1

δ= [(*Rsample-Rstd*)/*Rstd*] x 1,000

where:

 δ = delta notation,

Rsample = ratio of isotopes measured in sample, and

Rstd = ratio of same isotopes in the standard.

Equation 2

 2 H = 8¹⁸O + 10

Equation 3

 $t = -17.93 \ln(a_t{}^3H/a_o{}^3H)$

where:

Equation 4

t = (5,568/(ln2) x [ln (100/*pmc*)]-[(γ-1950)/1.029]

where:

Equation 5

Dilution factor = D = $(\delta^{13}C_{(RS)} - \delta^{13}C_{(soil-gas)}) / (\delta^{13}C_{(RS)} - \delta^{13}C_{(water)})$ where:

 $\delta^{13}C(\text{RS})$ = measured $\delta^{13}C$ from rock samples (_{RS}), $\delta^{13}C$ (soil-gas) = estimated value for $\delta^{13}C$ for soil-gas in the unsaturated zone, and $\delta^{13}C(\text{water})$ = measured $\delta^{13}C$ from the water sample.

Equation 6

$$
{}^{14}C(\text{adjusted}) = {}^{14}C(\text{pmc}) \times D
$$

where:

pmc = measured percent modern carbon and

D = dilution factor.

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