

Prepared in cooperation with the Bureau of Land Management

# **Geochemical Characterization of Groundwater Discharging from Springs North of the Grand Canyon, Arizona, 2009–2016**



Scientific Investigations Report 2017–5068

**Cover.** Schmutz Spring as seen by helicopter in August 2009, photo by Donald J. Bills.

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By Kimberly R. Beisner, Fred D. Tillman, Jessica R. Anderson, Ronald C. Antweiler, and Donald J. Bills

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Scientific Investigations Report 2017–5068

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

**U.S. Department of the Interior**

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**U.S. Geological Survey**

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U.S. Geological Survey, Reston, Virginia: 2017

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Suggested citation:

Beisner, K.R., Tillman, F.D., Anderson, J.R., Antweiler, R.C., and Bills, D.J., 2017, Geochemical characterization of groundwater discharging from springs north of the Grand Canyon, Arizona, 2009–2016: U.S. Geological Survey Scientific Investigations Report 2017–5068, 58 p., <https://doi.org/10.3133/sir20175068>.

ISSN 2328-0328 (online)

## Acknowledgments

The geochemical investigation presented in this report was supported by the U.S. Geological Survey (USGS) Toxic Substances Hydrology Program and the Bureau of Land Management. The report benefitted greatly from input from James Paces and Nick Paretti.

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## Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
Volume		
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m <sup>3</sup> )
gallon (gal)	3.785	cubic decimeter (dm <sup>3</sup> )

International System of Units to U.S. customary units

Multiply	By	To obtain
Volume		
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
liter (L)	61.02	cubic inch (in <sup>3</sup> )

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

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

Tritium (<sup>3</sup>H) concentrations are given in units of picocuries per liter. The conversion of picocuries per liter to Tritium Units (TU), based upon a tritium half-life of 12.32 years (Lucas and Unterweger, 2000), is: 1 TU = 3.22 picocuries per liter.

## Datum

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).



# Geochemical Characterization of Groundwater Discharging from Springs North of the Grand Canyon, Arizona, 2009–2016

By Kimberly R. Beisner, Fred D. Tillman, Jessica R. Anderson, Ronald C. Antweiler, and Donald J. Bills

## Abstract

A geochemical study was conducted on 37 springs discharging from the Toroweap Formation, Coconino Sandstone, Hermit Formation, Supai Group, and Redwall Limestone north of the Grand Canyon near areas of breccia-pipe uranium mining. Baseline concentrations were established for the elements As, B, Li, Se, SiO<sub>2</sub>, Sr, Tl, U, and V. Three springs exceeded U.S. Environmental Protection Agency drinking water standards: Fence Spring for arsenic, Pigeon Spring for selenium and uranium, and Willow (Hack) Spring for selenium. The majority of the spring sites had uranium values of less than 10 micrograms per liter (µg/L), but six springs discharging from all of the geologic units studied that are located stratigraphically above the Redwall Limestone had uranium values greater than 10 µg/L (Cottonwood [Tuckup], Grama, Pigeon, Rock, and Willow [Hack and Snake Gulch] Springs). The geochemical characteristics of these six springs with elevated uranium include Ca-Mg-SO<sub>4</sub> water type, circumneutral pH, high specific conductance, correlation and multivariate associations between U, Mo, Sr, Se, Li, and Zn, low <sup>87</sup>Sr/<sup>86</sup>Sr, low <sup>234</sup>U/<sup>238</sup>U activity ratios (1.34–2.31), detectable tritium, and carbon isotopic interpretation indicating they may be a mixture of modern and pre-modern waters. Similar geochemical compositions of spring waters having elevated uranium concentrations are observed at sites located both near and away from sites of uranium-mining activities in the present study. Therefore, mining does not appear to explain the presence of elevated uranium concentrations in groundwater at the six springs noted above. The elevated uranium at the six previously mentioned springs may be influenced by iron mineralization associated with mineralized breccia pipe deposits. Six springs discharging from the Coconino Sandstone (Upper Jumpup, Little, Horse, and Slide Springs) and Redwall Limestone (Kanab and Side Canyon Springs) contained water with corrected radiocarbon ages as much as 9,300 years old. Of the springs discharging water with radiocarbon age, Kanab and Side Canyon Springs contain tritium of more than 1.3 picocuries per liter (pCi/L), indicating they may contain a component of modern water recharged

after 1952. Springs containing high values of tritium (greater than 5.1 pCi/L), which may suggest a significant component of modern water, include Willow (Hack), Saddle Horse, Cottonwood (Tuckup), Hotel, Bitter, Unknown, Hole in the Wall, and Hanging Springs. Fence and Rider Springs, located on the eastern end of the study area near the Colorado River, have distinctly different geochemical compositions compared to the other springs of the study. Additionally, water from Fence Spring has the highest <sup>87</sup>Sr/<sup>86</sup>Sr for samples analyzed from this study with a value greater than those known in sedimentary rocks from the region. Strontium isotope data likely indicate that water discharging at Fence Spring has interacted with Precambrian basement rocks. Rider Spring had the most depleted values of stable O and H isotopes indicating that recharge, if recent, occurred at higher elevations or was recharged during earlier, cooler-climate conditions.

## Introduction

Grand Canyon National Park in Arizona is a United Nations World Heritage Site (United Nations Educational, Scientific and Cultural Organization [UNESCO], 2016) and an international tourist destination. The Grand Canyon region is a home or sacred place of origin to many Native Americans and its cultural significance extends back thousands of years. The Colorado River, which runs through Grand Canyon, is a primary source of drinking and irrigation water for millions of people in the United States and Mexico. The Grand Canyon region is also believed to host some of the highest grade uranium ore in the United States (Alpine and Brown, 2010). In 1956, high-grade uranium ore was discovered in the Orphan Lode copper mine, just 3.2 kilometers (km) west of Grand Canyon Village (fig. 1), initiating the era of uranium exploration and mining in the area (Alpine and Brown, 2010). Uranium exploration and mining activity roughly tracked the price of uranium over time, with increasing prices and activity beginning in the late 1970s and declining prices and activity in

the early 1990s. A brief uranium price spike in 2007 prompted renewed interest in deposits in the area, and by 2009 over 10,000 mining claims had been located in the Grand Canyon region (U.S. Department of the Interior, 2012). In 2012, then-U.S. Secretary of the Interior Ken Salazar signed a Record of Decision (ROD) to withdraw over 1 million acres in three segregation areas of Federal land (north, east, and south) in the Grand Canyon region from new uranium mining activities for the next 20 years, subject to valid existing rights (fig. 1; U.S. Department of the Interior, 2012). A key factor in the decision for the withdrawal was the limited amount of scientific data and resulting uncertainties on the potential effects of uranium mining activities on cultural, biological, and water resources in the area.

Since 2012, the U.S. Geological Survey (USGS) has planned and conducted scientific investigations to address the uncertainties of potential uranium-mining impacts noted in the ROD. Investigations related to regional water resources include gaining a better understanding of the direction and rate of groundwater flow in the area, and understanding what constitutes background—or naturally occurring—concentrations of uranium and associated trace elements in groundwater (referred to as baseline data in this report). There are limited groundwater data available from the Grand Canyon area, owing to the remoteness of the area and depth to the regional groundwater system (more than 3,000 feet [ft] in some areas). Water-quality data collected from springs are the primary source of information for the Grand Canyon region groundwater studies because of the lack of groundwater wells.

## Purpose and Scope

Trace element concentrations in groundwater north of the Grand Canyon are not well understood. Springs were used to represent groundwater in this study as there are few groundwater wells to sample in the study area. Previous studies have investigated springs in the Snake Gulch and Jumpup Canyon areas, which includes Horse, Pigeon, Rock, Slide, Table Rock, Upper Jumpup, Willow (Snake Gulch), and Wildband Springs (fig. 1) where elevated uranium concentrations occur in some spring samples (Billingsley and others, 1983; Hopkins and others, 1984; Beisner and others, 2017). Knowledge gained from the spring studies in the Snake Gulch and Jumpup Canyon areas directed the approach to analyzing a larger data set for springs discharging north of the Grand Canyon, an area with mined and unmined mineralized breccia pipe deposits. Springs discharging from geologic units (Toroweap Formation, Coconino Sandstone, Supai Group, and Redwall Limestone) associated with breccia-pipe deposits north of the Grand Canyon were chosen to evaluate the geochemistry of the spring water in order to establish baseline values for trace element concentrations and to understand the recharge characteristics, geochemical reactions, and flowpaths as the groundwater circulates through these units.

The purpose of this report is to establish baseline trace element concentrations and geochemical characteristics for springs discharging from the Toroweap Formation, Coconino Sandstone, Supai Group, and Redwall Limestone north of the Grand Canyon and south of the Utah border. Spring sites with anomalous chemical characteristics are identified and characterized to understand possible sources. This report includes springs sampled by USGS between 2009 and 2016. Spring samples collected in 2009 are presented in Bills and others (2010) and are included in this study with more recent samples as part of a focused study scope in this report. Spring water geochemistry reflects past hydrologic and geochemical conditions, as groundwater moves from areas of recharge along geochemically reactive flowpaths. Spring geochemistry represents a snapshot based on the age of the water and the contribution of water of different ages, and it may take time for changes in the groundwater system to propagate to the spring.

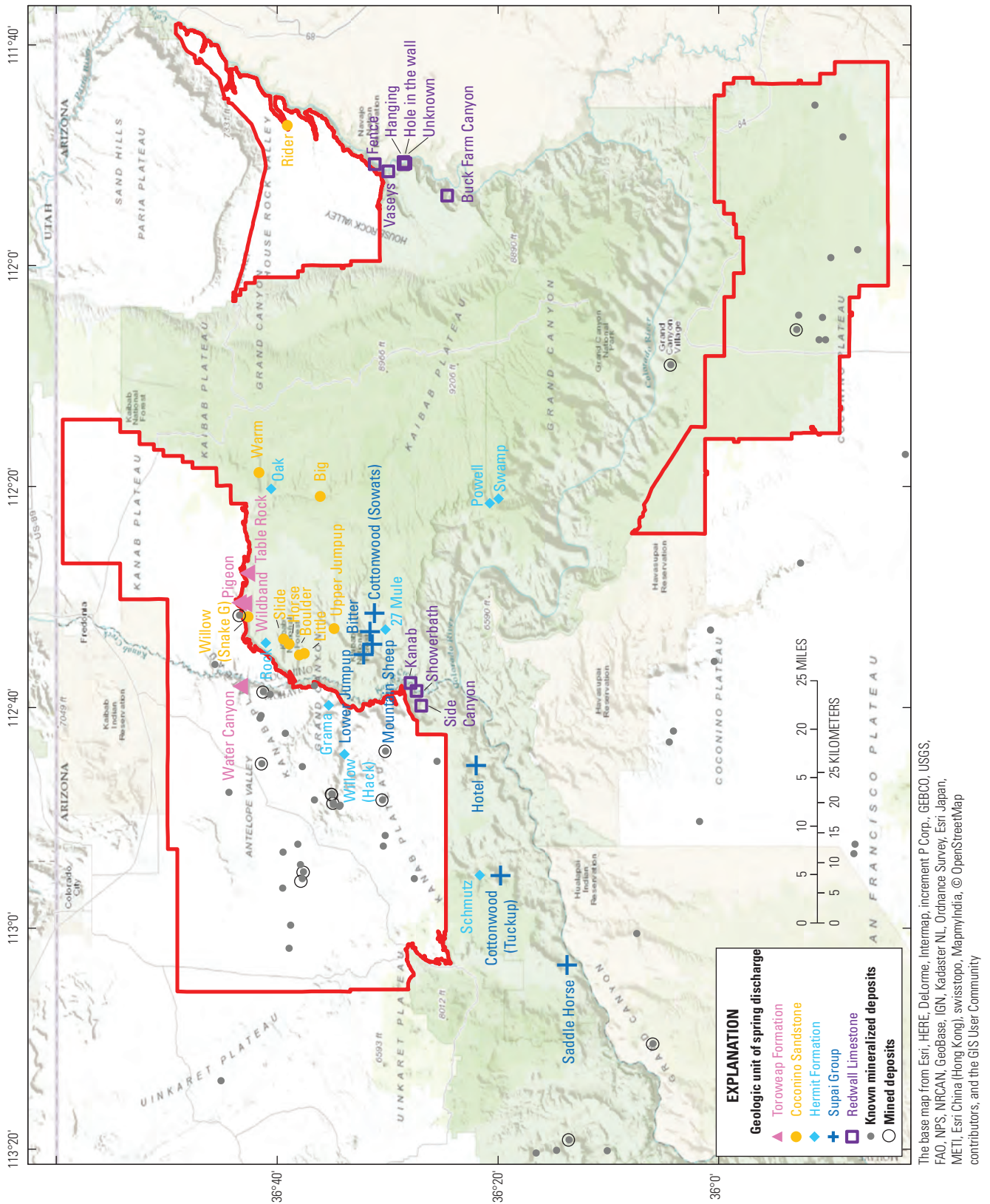
## Study Area

The study area is located north of the Grand Canyon and south of the border with Utah, near the north and east segregation withdrawal areas. The area contains known mineralized breccia pipe deposits, some of which have been mined (fig. 1).

## Geologic Setting

The study area is located within the southern part of the Colorado Plateau physiographic province. Geologic descriptions in this and the next paragraph are from Billingsley and others (2008) unless otherwise noted. Geologic units of interest for this report are Paleozoic sedimentary strata that have a regional dip of about 1° to 2° north-northeast on the west side of the study area. Geologic units are warped by anticlinal and synclinal folds, of which the Kaibab Anticline is a large scale north-trending and plunging anticline that elevates the Paleozoic strata as much as 2,000 ft higher than the surrounding plateaus east and west of the structure. The east side of the Kaibab Anticline is marked by the East Kaibab Monocline and the west side is marked by the Muav and Big Springs Faults, which have a general north-south strike and strata offset by as much as 1,200 ft down to the west. Monoclines developed in response to the Laramide orogeny along pre-existing Proterozoic fault zones (Huntoon, 2003). Extensional stresses from Miocene to the present time have resulted in normal faulting, which displaces strata down to the west, also along the pre-existing Proterozoic fault zones. There are several normal faults and minor folds in the study area that commonly parallel the northeast and northwest trending bedrock joints and fractures, which are vertically continuous through all Paleozoic strata exposed in the study area.

Paleozoic units discussed in this report include, in order from oldest to youngest: Redwall Limestone (Mississippian), Supai Group (Upper Mississippian, Pennsylvanian, and Lower Permian), Hermit Formation (Lower Permian), Coconino



**Figure 1.** Study area with uranium mining withdrawal areas (red outline) and spring sample locations identified by the geologic unit they discharge from. Location of mineralized breccia pipes can be found in the following references: Alpine, 2010; Brown and others, 1992; Brown and others, 1986, 1988; Verbeek and others, 1988; Wenrich and others, 1988, 1990, 1997; Sutphin and Weinrich, 1989; VanGosen and Weinrich, 1989, 1991; Finch and others, 1990; Wenrich, 1992; Wenrich and Aumente-Modreski, 1994; Gardner, 1998; Mazeika, 2002; Ross and Moreton, 2012.

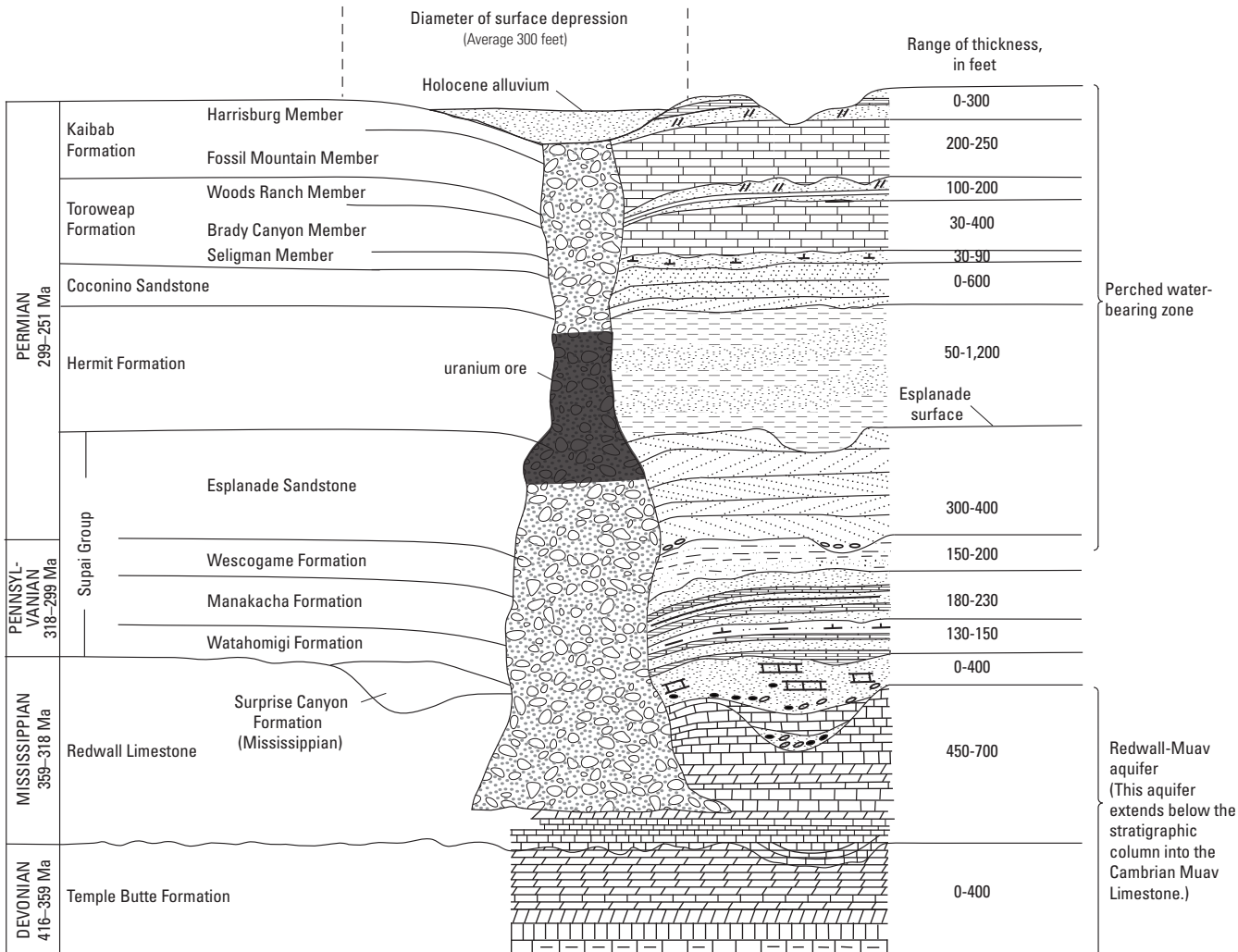


Sandstone (Lower Permian), Toroweap Formation (Lower Permian), and Kaibab Formation (Lower Permian). Several units are subdivided into distinct members presented here but not subdivided in this report. The Redwall Limestone includes the Whitmore Wash, Thunder Springs, Mooney Falls, and Horseshoe Mesa Members, and generally is composed of limestone with some chert and dolomite beds. The Supai Group includes the Watahomigi Formation (Upper Mississippian and Lower Pennsylvanian), Manakacha Formation (Middle Pennsylvanian), Wescogame Formation (Upper Pennsylvanian), and the Esplanade Sandstone (Lower Permian). The Supai Group is generally composed of sandstone, calcareous sandstone, dolomitic sandstone, siltstone, mudstone, conglomerate, dolomite, limestone, and chert. The Hermit Formation is composed of siltstone, sandstone, and calcareous sandstone; the unit gradually thickens westward and northward, and the sandstone beds gradually thin or pinch out from north to south. The Coconino Sandstone is a fine grained, well sorted quartz sandstone that pinches out to the north, the pinch out is visible in the upper reaches of Kanab Creek and north of Warm Spring. In some areas, where the Coconino Sandstone is

absent, the Toroweap Formation rocks unconformably overly the Hermit Formation. The Toroweap Formation includes the Seligman, Brady Canyon, and Woods Ranch Members. The Toroweap Formation is generally composed of gypsiferous siltstone, sandstone, gypsum, limestone, dolomite, and chert. The Kaibab Formation includes the Fossil Mountain and Harrisburg Members; the formation is generally composed of gypsiferous siltstone, gypsum, limestone, cherty limestone, and chert beds.

**Breccia Pipe Formation and Geochemistry**

Solution-collapse features known as breccia pipes are found throughout this region of Arizona. Breccia pipes are thought to form by dissolution and karst development in the underlying Redwall Limestone unit, with progressive collapse moving upwards through time into overlying rock units, forming a rubble (breccia) filled column that can be as much as 3,000 ft or more in height (Alpine and Brown, 2010; fig. 2). Breccia pipes are roughly circular in plan view, about 300 ft in



**Figure 2.** Schematic of breccia pipe. Modified from Van Gosen and Wenrich (1989) and Alpine and Brown (2010).

diameter, and are often characterized by inward dipping beds along the margins (Otton and VanGosen, 2010). Other collapse features found throughout the Grand Canyon region include sinkholes and localized shallow collapse caused by dissolution of gypsum in the Kaibab and Toroweap Formations (Billingsley and others, 2008). In the absence of breccia exposed at the surface, the most effective way to determine if a breccia pipe underlies a collapse feature is by obtaining geologic core from drilling.

Some breccia pipes contain concentrated deposits of uranium, copper, silver, lead, zinc, cobalt, and nickel minerals (Wenrich, 1985; Wenrich and others, 1989; Finch and others, 1992). Uranium mineralization in breccia pipes likely occurred after early mineralizing fluids moved through the pipe, creating reducing conditions within areas of the pipe that are amenable to reduction of oxidized uranium (U(VI)) and formation of lower solubility U(IV) minerals such as uraninite (Weinrich, 1985; Huntoon, 1996). Ore grade deposits are most commonly located in breccia adjacent to the Coconino Sandstone, Hermit Formation, and the upper members of the Supai Group (Otton and VanGosen, 2010). Mining of breccia pipe ore zones for copper, lead, zinc, and silver in the Grand Canyon region began in the 1860s, with uranium mining beginning in the 1950s.

## Radioisotope Geochemistry

The most common radionuclides in groundwater are  $^{222}\text{Rn}$ ,  $^{226}\text{Ra}$ ,  $^{238}\text{U}$ , and  $^{234}\text{U}$  of the  $^{238}\text{U}$  decay series, and  $^{228}\text{Ra}$  of the  $^{232}\text{Th}$  decay series (Zapecza and Szabo, 1987). The occurrence of radionuclides in groundwater depends on the presence and solubility of the parent element in the decay series of each daughter element (Focazio and others, 2001). Uranium is most soluble in bicarbonate-rich oxidizing groundwater with low total dissolved solids content, and solubility is enhanced by association with carbonate, phosphate, and fluoride ions, or with organic compounds (Langmuir, 1978; Zapecza and Szabo, 1987). Uranium is less mobile in reducing groundwater, while radium is most mobile in chloride-rich reducing groundwater with high total dissolved solids content (Tanner, 1964; Zapecza and Szabo, 1987). Gross alpha and gross beta activity measurements are used in drinking water regulations as a general screening tool to indicate the need for additional analysis of specific radionuclides. Radionuclides measured for this study include alpha emitters  $^{226}\text{Ra}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ , and beta emitter  $^{228}\text{Ra}$ .

Erosion and mining expose fresh uranium ore surfaces to the hydrosphere. When exposed to oxygen in the air or in water, dissolution of uranium is expected. Conditions that favor uranium mobility in groundwater are dissolved oxygen and dissolved carbonate, both present in northern Arizona aquifers. The isotopic composition of uranium can be used to help evaluate whether uranium in surface water and groundwater samples is derived from the natural dissolution processes from uranium-bearing rock units of the Grand Canyon region,

or from anthropogenic activities at active, on-standby, and abandoned uranium mines.

Natural uranium consists of three isotopes  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{234}\text{U}$  with relative abundances of approximately 99.27 percent, 0.72 percent, and 0.0057 percent, respectively. Unlike the  $^{235}\text{U}/^{238}\text{U}$  ratio, which exhibits an extremely small range of variation in nature,  $^{234}\text{U}/^{238}\text{U}$  can vary widely in natural waters. This variation is a result of processes related to the radioactive decay of daughter  $^{234}\text{U}$  from parent  $^{238}\text{U}$  such as alpha recoil, where during alpha decay of  $^{238}\text{U}$  the recoiling  $^{234}\text{Th}$  nuclei can be ejected from the solid to aqueous phase and then decay to  $^{234}\text{U}$ . These processes result in the preferential mobility of  $^{234}\text{U}$  relative to  $^{238}\text{U}$  during interactions between water and solid phases (Faure and Mensing, 2005). Uranium in undisturbed rocks and minerals older than approximately 1 million years reaches a state of radioactive equilibrium where the rate of decay of the short-lived  $^{234}\text{U}$  is limited by the rate of decay of the long-lived  $^{238}\text{U}$  parent. As a result, the  $^{234}\text{U}/^{238}\text{U}$  activity ratio (UAR) is expected to equal unity (defined as secular equilibrium or  $\text{UAR} = 1.0$ ). Solid phases subjected to water-rock interaction will be depleted in  $^{234}\text{U}$  relative to  $^{238}\text{U}$  and will have UAR values of equal to or less than 1.0. Bulk dissolution of the solid phase in a chemically aggressive environment (for example, fresh mill tailings or fresh exposures of ore) is likely to release uranium that has an isotopic composition similar to that of the rock (in other words, a UAR value close to 1.0). In contrast, water-rock interaction under less chemically aggressive conditions typical of natural flowpaths in aquifer rock that have been subjected to thousands of years of water/rock interaction allows preferential incorporation of  $^{234}\text{U}$  into groundwater resulting from various recoil processes associated with production of  $^{234}\text{U}$  through alpha decay. As a result, most near-surface waters have  $^{234}\text{U}/^{238}\text{U}$  AR values in excess of 1.0. Therefore, water in contact with high-grade uranium ore having a recent history of oxidation and leaching is likely to represent a mixture of material with UAR's both greater than and less than 1.0. Groundwater in aquifers with long residence times and long flow paths will typically have higher UAR than aquifers with shorter residence times and short flow paths. Most natural groundwater has UAR's greater than 1.0. Typical values fall in the 1–3 range but values in excess of 10 are possible (Kronfeld, 1974; Osmond and Cowart, 1976; Szabo, 1982).

## Groundwater Occurrence and Movement

Groundwater in the area occurs in locally perched aquifers of limited extent, which in this study includes spring discharge from the Toroweap and Hermit Formations, Coconino Sandstone, and Supai Group. Some springs discharge from Quaternary surficial deposits, which are limited in extent, and springs in this report are classified according to the adjacent stratigraphic unit from Billingsley and others (2008). The deeper regional Redwall-Muav aquifer is several hundred feet below the perched groundwater (fig. 2). Springs discharging from the Redwall Limestone were included as there were

enough for statistical analysis, whereas there were not enough springs sampled from the Muav Limestone for this study. Groundwater in perched aquifers discharges at several springs in the area or may migrate deeper into the subsurface (Bills and others, 2010).

Water in the Redwall Limestone is confined in some parts of the study area, as seen from pressure head encountered during well drilling, and is understood to be old water without a modern component (Bills and others, 2010). In some areas of the study, water may move quickly through the subsurface down to the Redwall Limestone. For example, dye tracers placed in a sinkhole on the Kaibab Plateau appeared after a year at Vasey's Paradise (Jones and others, 2016).

## Climate

The climate in the study area is semiarid to arid with temperature decreasing and precipitation increasing with increasing elevation. Average annual temperature at Page, Ariz. was 15.4 °C for January 1997 through December 2008 (Western Regional Climate Center, 2016). Freezing winter temperatures are common on the Kaibab Plateau and summer temperatures may exceed 38 °C in the inner canyons of the area. Average annual precipitation ranges from 500–800 millimeters (mm) on the Kaibab Plateau to less than 300 mm in the Kanab Creek canyon (PRISM Climate Group, 2015). The ratio of annual evaporation to precipitation is about 2:1 in the higher altitudes on the Kaibab Plateau and as much as 5:1 at lower elevations near Snake Gulch (Farnsworth and others, 1982; Alpine and Brown, 2010; PRISM Climate Group, 2015).

## Methodology

### Field

Water samples were collected from 37 spring sites between August 2009 and May 2016, and spring characteristics are included in appendix 1. Thirteen springs were sampled more than one time during the sampling period. Water samples were collected following standard U.S. Geological Survey protocols (U.S. Geological Survey, variously dated). Field parameters including pH, water temperature, specific conductance, dissolved oxygen, and barometric pressure were measured on site just before water samples were collected. Spring discharge was measured by using volumetric techniques. Water samples were filtered (0.45 micrometers [ $\mu\text{m}$ ]) for major cations; trace and rare earth elements; alkalinity; carbon-14; uranium, radium and strontium isotopes; and gross alpha and beta radioactivity. All samples, except for major anions, alkalinity, and carbon-14, were preserved to pH<2 by using ultrapure nitric acid. Unfiltered samples were collected for tritium and stable isotopes. Alkalinity titrations were performed in the field with the incremental equivalence method (U.S. Geological Survey, variously dated).

Three samples, Upper Jumpup (2009), Willow (Hack) (2012), and Kanab Spring (2009) were analyzed by a large volume method for radium isotopes, with detection limits less than 4 pCi/L, which involves passing at least 100 gallons through a series of filters including, in order, a 0.2  $\mu\text{m}$  polypropylene-medium filter, and two manganese-impregnated acrylic fiber cartridges. The first cartridge primarily extracts the radium, and the second is used to check the efficiency of the first (Kraemer, 2005).

### Analytical

Water samples were analyzed for major, trace, and rare-earth elements by the USGS National Research Program Laboratory in Boulder, Colo. (USGSTMCO) and at the USGS National Water Quality Laboratory (USGSNWQL). Analytical methods from the USGSTMCO included inductively coupled plasma-mass spectrometry (ICP-MS) to analyze for Al, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ho, La, Li, Lu, Mn, Mo, Nd, Ni, P, Pb, Pr, Rb, Re, Sb, Se, Sm, Sn, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr (Garbarino and Taylor, 1996; Taylor, 2001). An inductively-coupled plasma optical emission spectrophotometer (ICP-OES) was used to analyze for Ca, Fe, K, Mg, S, and  $\text{SiO}_2$  (Garbarino and Taylor, 1979). Anions Cl, F,  $\text{NO}_3$ , and  $\text{SO}_4$  were analyzed by ion chromatography. Samples were analyzed in triplicate and the average was used for the final value.

Water samples analyzed for major and trace elements at the USGSNWQL include Buck Farm Canyon, Fence, Hanging, Hole in the Wall, Rider, and Unknown Springs. Analytical methods from the USGSNWQL included ICP-MS to analyze for Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Li, Mo, Ni, Se, Ag, Sr, Tl, W, U, V, and Zn (Garbarino and others, 2006). ICP-AES was used to analyze for Ca, Fe, K, Mg, Mn, and Na (Fishman, 1993). Anions Cl, F, and  $\text{SO}_4$  were analyzed by ion chromatography, and  $\text{SiO}_2$  was evaluated by discrete analyzer colorimetry (Fishman and Friedman, 1989). Nitrate ( $\text{NO}_3$ ) + nitrite ( $\text{NO}_2$ ) was analyzed by colorimetry (Patton and Kryskalla, 2011). USGSNWQL reports values between their method detection level and laboratory reporting level as an estimated value, denoted with an E. Comparison of the USGSTMCO and USGSNWQL are described in the quality assurance section of this report.

Stable isotope ratios ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) were measured at the USGS Reston Stable Isotope Laboratory following methods by Révész and Coplen (2008a,b). Uncertainties reported at the 2-sigma level are 0.2 per mil (‰) for oxygen and 2‰ for hydrogen isotopic ratios relative to Vienna Standard Mean Ocean Water. Strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) were measured by the USGS National Research Program Laboratory in Menlo Park, Calif. using methods described in Bullen and others (1996) with precision of  $\pm 0.00002$  or better at the 95 percent confidence level.

The USGS National Research Program Laboratory in Reston, Va., analyzed UAR using quadrupole ICP-MS mass



spectrometric methods described in Kraemer and others (2002) for samples of Wildband, Pigeon, Rock, Slide, Willow (Snake Gulch), Upper Jumpup, Rider, Schmutz, Willow (Hack), Grama, Hotel, Mountain Sheep, Lower Jumpup, Buck Farm Canyon, Side Canyon, Showerbath, Kanab, Hole in the Wall, Hanging, Fence, and Unknown Spring near Hanging Springs collected between 2009 and 2012. Multiple laboratories were used to analyze the  $^{234}\text{U}/^{238}\text{U}$  activity ratio (UAR) owing to changes of the USGS contract laboratory. Uranium isotopes ( $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ ) were measured using alpha-counting methods (ASTM D 3972) by Eberline Services in Richmond, Calif. for samples from 2011 and 2012; by Test America in Richland, Wash. in 2014; and by ALS Environmental in Fort Collins, Colo. in 2015 and 2016. Details of laboratory comparisons and determination of final UAR values are presented in the Quality Assessment section.

Total gross alpha was analyzed by counting using the  $^{230}\text{Th}$  curve and total gross beta was analyzed by counting using the  $^{137}\text{Cs}$  curve following U.S. Environmental Protection Agency (EPA) method 900.0 (U.S. Environmental Protection Agency, 1980) at Eberline Services in Richmond, Calif. for samples from 2009 and 2012; by Test America in Richland, Wash. in 2014; and by ALS Environmental in Fort Collins, Colo. in 2015 and 2016.

Radium isotopes ( $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ) were analyzed by the USGS National Research Program Laboratory in Reston, Va. for samples collected in 2009 through 2012 using methods described in Bills and others (2010). Three samples, Upper Jumpup (2009), Willow (Hack) (2012) and Kanab Spring (2009), were analyzed by a large volume method described in the field section of this report and analytical details are documented in Kraemer (2005).

Carbon-14 and  $^{13}\text{C}$  were analyzed by the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) at Woods Hole Oceanographic Institution. Carbon-14 values reported by the NOSAMS as absolute percent modern (pM) were denormalized using equation 5 of Plummer and others (2012) to percent modern carbon (pMC). NetpathXL was used to calculate corrected groundwater ages using model (11), "Revised F&G solid ex" (Parkhurst and Charlton, 2008). Values used in the calculation of groundwater age were  $^{14}\text{C}$  values of 0 pMC for carbonate and 100 pMC for soil  $\text{CO}_2$ , and  $\delta^{13}\text{C}$  values of -1.1‰ for the Toroweap and Hermit Formations and Coconino Sandstone, -2‰ for the Supai Group, and -1.8‰ for the Redwall Limestone carbonate (Monroe and others, 2005; Bills and others, 2007) and -17‰ and -22‰ for soil  $\text{CO}_2$  (Hart and others, 2010).

Tritium ( $^3\text{H}$ ) is a useful tracer for determining if there is a component of water recharged during the period of nuclear bomb testing in the 1950s and 1960s when tritium values peaked and subsequently declined over the following decades. Tritium values have stopped decreasing in recent (after 1992) precipitation, and average values of tritium in precipitation range from 16.4 pCi/L in Camp Verde to 28.7 pCi/L in Flagstaff (Eastoe and others, 2012). Tritium was measured on the majority of samples, but was not collected for

samples in 2011. Tritium was measured at the USGS Menlo Park Tritium Lab using the electrolytic enrichment liquid scintillation counting method (Thatcher and others, 1977) with a detection limit of 0.5 pCi/L. Values below the laboratory detection level are reported including zero and negative values (McCurdy and others, 2008). The half-life of tritium is 12.32 years (Lucas and Unterwieser, 2000), so the age of the modern component of water can be quantified if the starting value is known. Tritium was assessed with a categorical age classification—as there is a large variation of tritium values in precipitation in northern Arizona—where less than 1.3 pCi/L is considered pre-modern (before 1952), greater than 12.8 pCi/L is modern (primarily after 1952), and values between the thresholds indicate a possible mixture of pre-modern and modern water. Additionally, a combination of measured tritium and geochemically corrected  $^{14}\text{C}$  were used to categorize springs based on age and calculate preliminary groundwater age estimates for select springs.

## Quality Assurance

Quality assurance samples included blank and replicate samples evaluated based on methods from Mueller and others (2015). Five field blank samples were analyzed for major ion and trace element analysis by the USGSNWQL, and four field blank samples were analyzed by the USGSTMCO between 2009 and 2015. Two equipment blanks were also collected for this project between 2010 and 2011. A threshold of 10 times the greatest blank concentration was used, where environmental sample concentrations above the threshold likely contain less than 10 percent influence from contamination and are not likely to be substantially affected by high bias, while concentrations below the threshold may contain more than 10 percent contamination and may be affected by high bias from sampling equipment and (or) field conditions.

There were 22 replicate water sample pairs analyzed for major ions and trace elements by the USGSTMCO. Replicate variability among all samples was determined for each element by calculating the standard deviation for each replicate pair and taking the average of the standard deviations and calculating a 90 percent confidence interval. Results from quality assurance samples are presented in the Quality Assessment section.

## Laboratory Selection

At the beginning of this project in 2009, four laboratories were chosen to analyze splits of water samples for major ions and trace elements (Bills and others, 2010). Labs used included the (1) USGS National Research Program Laboratory in Boulder, Colo. (USGSTMCO), (2) USGS National Water Quality Laboratory in Lakewood, Colo. (USGSNWQL), (3) USGS National Research Program Laboratory in Reston, Va., and (4) Northern Arizona University. A decision was made to choose only one laboratory for analysis of subsequent

samples collected after 2014 for this project. Laboratory selection was based on laboratory quality-control data.

The USGSTMCO and USGSNWQL participate in the USGS Office of Water Quality Branch of Quality Systems (BQS) Inter-laboratory standard reference sample (SRS) comparison study where numerous labs across the country complete a round robin standard reference sample analysis and comparison. The USGS National Research Program Laboratory and Northern Arizona University do not participate in the USGS BQS Inter-laboratory SRS comparison study, and were therefore excluded from selections for future analysis as part of this project. The SRS data are statistically analyzed using methods from Hoaglin and others (1983), where a most probable value (MPV) is calculated for each analyte that represents the median excluding less than values, F-pseudosigma (fps) that approximates the standard deviation when data has a Gaussian distribution, Z value which is calculated as the reported value minus the MPV divided by the fps and the percent difference of a given laboratory reported value relative to the MPV, and are presented in U.S. Geological Survey (2016a). Standard reference sample data are considered acceptable if they have Z values within  $\pm 2$ . The USGSTMCO was chosen as the sole laboratory for analysis of major ions and trace elements for samples collected by this project starting in 2014 based on performance in the SRS program, which gave acceptable values for all certified SRS for trace elements (U.S. Geological Survey, 2016a). Most major ion analysis from SRS at USGSTMCO were within the acceptable range except for the four samples analyzed between 2012 and 2015 presented in table 1 (U.S. Geological Survey, 2016a). No samples were analyzed in 2013 for this project and the other SRS reported values of potassium and sodium reported by the USGSTMCO with Z values outside the  $\pm 2$  threshold are within variability (calculated from environmental sample replicate pairs) of the MPV.

Seven samples collected in fall 2009 from Buck Farm Canyon, Fence, Hanging, Hole in the Wall, Rider, Unknown and Vaseys Springs were analyzed for major and trace elements by the USGSNWQL but not the USGSTMCO; the USGSNWQL data for these samples are used in this report. All major and trace element concentrations reported for fall 2009 standard reference samples by both the USGSNWQL

and USGSTMCO were within  $\pm 2$  Z-value and the percent difference between the two lab reported values were within  $\pm 15$  percent (appendix 2). Based on this laboratory quality-control data, it is acceptable to combine the USGSNWQL data for these samples with the USGSTMCO data.

**Data Analysis**

As the majority of trace elements had one or more values below a laboratory reporting level, with several elements containing multiple reporting levels, specific statistical methods (Helsel, 2012) for data with values below a threshold (laboratory reporting level) were used to analyze the majority of analytes presented in this study. Select trace elements (Si, As, Ba, B, Sr, Li, and U) did not have any data below the laboratory reporting level for the data set used in this paper.

Boxplots for elements with censored data (value reported as less or greater than a threshold) were made using the cenboxplot function from the NADA software package (Lee, 2015) in the R statistical computing environment (R Core Team, 2015). Outlier data points on boxplots were defined for this study as greater than 1.5 times the interquartile range (IQR). Chemical analysis from spring samples was analyzed for each element to determine the Kaplan-Meier model of the data using the cenfit function from the NADA package in R (Lee, 2015). A p-value threshold of 0.05 (95 percent confidence level) was used to indicate statistical significance for all mentioned statistical tests.

Robust regression on order statistics (ROS) using the cenros function from the NADA package in R (Lee, 2015) was used to calculate the median, mean, and standard deviation for trace elements for the first sample collected from each spring in the data set.

Spring samples were grouped by geologic unit of discharge and compared using the cendiff function from the NADA package in R (Lee, 2015). The cendiff function uses the Peto-Prentice test (Helsel and Lee, 2006) to determine whether there were significant differences between the groups for elements with censored data. An analysis of variance (ANOVA) was run for the elements without censored values and the TukeyHSD function was used to determine which groups were statistically different.

**Table 1.** Standard reference samples reported by the U.S. Geological Survey National Research Program Laboratory in Boulder, Colo. (USGSTMCO) outside of the  $\pm 2$  Z-value threshold.

[F-, indicates a less than value was reported for a standard reference sample; MPV, most probable value]

Standard reference sample number	Date	Elements and associated Z-value	Difference in concentration from MPV, in milligrams per liter
M-202	Spring 2012	Na (−2.99)	−1.11
M-208	Fall 2013	K (−3.29), Mg (−2.16), Na (F-)	K (0.86), Mg (−0.8)
M-212	Fall 2014	Na (−2.80)	−1.015
P-64	Spring 2015	K (−3.29)	−0.079



Non-metric multidimensional scaling (NMDS) was used to reduce the complex data structure (many samples and many elements) to represent the pairwise dissimilarity between objects in a low-dimensional space (Buttigieg and Ramette, 2014). The following elements, As, Cd, Cu, Li, Mn, Mo, Pb, Se, Sr, U, V, and Zn were used for multivariate comparison based on the distinction between breccia pipe uranium mining sediment leachate and spring chemistry from Beisner and others (2017). Uscres of the data were determined using the uscore function for R using the default to calculate the ranks of the scores (Helsel, 2012, 2016). The NMDS was performed on the uscores using the metaMDS function from the vegan package in R (Oksanen and others, 2016) using euclidean distance, zerodist = add and autotransform = false (Helsel, 2012). NMDS stress values less than or equal to 0.1 are considered fair, while values equal to or below 0.05 indicate good fit and values near or greater than 0.2 are deemed suspect (Buttigieg and Ramette, 2014).

The elements used in the NMDS analysis were then evaluated for correlation using the cenken function from the NADA package in R (Lee, 2015). Kendall's tau correlation coefficients were included in a correlogram using the corplot package in R (Wei and Simko, 2016). A cluster analysis was also used to identify similar groups in the spring samples by evaluating minimum differences within groups and maximum differences among groups using the hclust function for the elements used in the NMDS analysis. The Calinski criterion was used to determine the number of clusters that maximizes the difference between clusters, while minimizing the differences within clusters with the cascadeKM function of the vegan package in R (Oksanen and others, 2016). The anosim function was used to statistically evaluate whether or not groups of samples have significantly different concentration patterns (Helsel, 2012).

Water sample concentrations were compared to EPA drinking water standards presented in table 2 (U.S. Environmental Protection Agency, 2017). Springs are not utilized for public drinking water supply sources, but they are often located in remote locations where they may be the only source of water available to hikers.

## Results

### Quality Assessment

Spring sample quality assurance results are presented in appendixes 2–5, and are archived in the USGS National Water Information System database (U.S. Geological Survey, 2016b).

**Table 2.** U.S. Environmental Protection Agency (2017) water-quality standards for drinking water.

[Values presented in units used in this report. NA, not available; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level]

Element	Units	Primary drinking-water standard	Secondary drinking-water standard
		MCL	SMCL
Aluminum	µg/L	NA	50–200
Antimony	µg/L	6	NA
Arsenic	µg/L	10	NA
Barium	µg/L	2,000	NA
Beryllium	µg/L	4	NA
Cadmium	µg/L	5	NA
Chloride	mg/L	NA	250
Chromium	µg/L	100	NA
Copper	µg/L	1,300	1,000
Fluoride	mg/L	4	2
Iron	µg/L	NA	300
Lead	µg/L	15	NA
Manganese	µg/L	NA	50
Mercury	µg/L	2	NA
Nitrate (NO <sub>3</sub> )	mg/L	10	NA
pH		NA	6.5–8.5
Selenium	µg/L	50	NA
Silver	µg/L	NA	100
Sulfate (SO <sub>4</sub> )	mg/L	NA	250
Thallium	µg/L	2	NA
Total dissolved solids (TDS)	mg/L	NA	500
Uranium	µg/L	30	NA
Zinc	µg/L	NA	5,000
<sup>226</sup> and <sup>228</sup> Radium	pCi/L	5	NA
Alpha particles	pCi/L	15	NA
Beta particles	Millirems/year	4	NA

Constituents detected in field blank samples (value reported above laboratory detection level) are presented in table 3 and all blank results in appendix 3 along with a suggested threshold for contamination (concentration threshold for influence in table 3) based on a value 10 times the greatest blank concentration. Environmental sample concentrations above the threshold likely contain less than 10 percent contamination and are not likely to be substantially affected by high bias, while concentrations below the threshold may contain more than 10 percent contamination and may be affected by high bias from sampling equipment and conditions.

None of the environmental samples from this study had concentrations of major ion values less than the concentration threshold for influence for elements with blank detections. For trace elements, no environmental samples had values less than the concentration threshold for influence for B, Ba, and Sr. Environmental samples had greater than 50 percent of the samples with values less than the concentration threshold for influence for Al, Be, Cd, Co, Cr, Cu, Mn, Pb, Sb, and Zn (table 3). Blank detections for cobalt and chromium were only measured by samples submitted to the USGSNWQL, which accounts for 6 of the 52 environmental samples. The blank

sample data indicate that the potential influence from contamination bias is random and not systematic at either lab.

Two equipment blanks that were analyzed at the USGSNWQL had less constituents detected compared with the field blanks and consisted of detections of cobalt (0.046 and 0.12 µg/L) and manganese (E 0.14 and 0.23 µg/L) in each equipment blank, which were less than the highest field blank detection. Tungsten had a reported estimated value (E 0.019 µg/L) in one equipment blank. Tungsten was not used for analysis in this report as there were 15 samples with no reported value. Laboratory reporting levels are generally lower at the USGSTMCO than the USGSNWQL, and elements with blank detections from USGSTMCO were lower than the laboratory reporting level from the USGSNWQL with the exception of one sample from 2009 at Lower Jumpup Spring for calcium, where the blank detection at USGSTMCO was 0.11 and was <0.02 at USGSNWQL (appendix 3).

Replicate pair results are presented in appendix 4. Replicate variability among all samples was determined by calculating the standard deviation for each replicate pair and taking the average of the standard deviations of all replicate pairs. The 90 percent confidence intervals about a single sample are

**Table 3.** Results of field blank analysis.

[mg/L, milligrams per liter; µg/L, micrograms per liter; E, estimated value, greater than lab detection level and less than lab reporting level; USGSTMCO, USGS National Research Program Laboratory in Boulder, Colo.; USGSNWQL, USGS National Water Quality Laboratory in Lakewood, Colo.; four total blanks were analyzed by USGSTMCO and five by USGSNWQL; blank detection indicates a value reported greater than the laboratory detection level]

Constituent	Number of blanks with value greater than lab detection level		Concentration range of blank detections		Concentration threshold for influence	Units	Percent of environmental samples below threshold
	USGSTMCO	USGSNWQL	USGSTMCO	USGSNWQL			
Calcium	1	0	0.11		1.1	mg/L	0
Chloride	2	0	0.01–0.02		0.2	mg/L	0
Sodium	1	0	0.005		0.05	mg/L	0
Sulfate	1	0	0.034		0.34	mg/L	0
Silica	2	0	0.009–0.11		1.1	mg/L	0
Aluminum	2	0	0.16–0.45		4.5	ug/L	94
Boron	1	0	0.4		4	ug/L	0
Barium	2	0	0.01		0.1	ug/L	0
Beryllium	1	0	0.007		0.07	ug/L	100
Cadmium	2	0	0.001–0.005		0.05	ug/L	100
Cobalt	0	3		0.031–0.182	1.82	ug/L	100
Chromium	0	1		0.07	0.7	ug/L	60
Copper	3	0	0.015–0.12		1.2	ug/L	88
Manganese	1	1	0.07	0.32	3.2	ug/L	92
Lead	2	0	0.005		0.05	ug/L	77
Antimony	3	0	0.006–0.026		0.26	ug/L	96
Strontium	1	0	0.3		3	ug/L	0
Zinc	2	2	0.1–2	E1.4–E1.5	20	ug/L	96

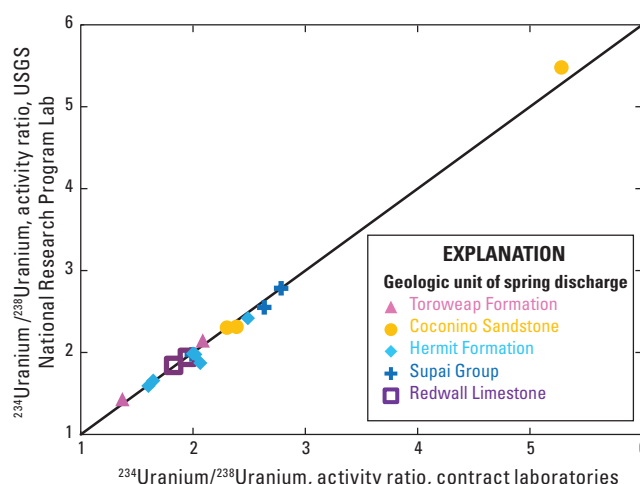
presented in table 4; there is a 90 percent confidence that the true value of any individual measurement for any constituent listed in table 2 will lie within the range given in table 4.

Values of UAR determined for 16 paired samples (appendix 5) analyzed by USGS and contract labs (Eberline Services, Test America, and ALS Environmental) were similar: differences ranged from 0 to 0.191 with an average deviation of 0.013 UAR values, over a range of UAR values from 0 to 10.2 with an average of 0.9 percent difference (fig. 3). If two UAR values were available for a single water sample, the value determined by the USGS National Research Program Laboratory was used.

**Table 4.** Results of water-sample replicate variability analysis.

[mg/L, milligrams per liter; µg/L, micrograms per liter; beryllium, bismuth, cobalt, and nickel did not have more than four replicate pairs with values above the laboratory reporting limit and therefore the variability was not quantified for these elements]

Element	Variability (90 percent confidence)	Variability units
Aluminum	± 0.27	µg/L
Arsenic	± 0.10	µg/L
Boron	± 3.84	µg/L
Barium	± 0.46	µg/L
Calcium	± 8.26	mg/L
Cadmium	± 0.01	µg/L
Chlorine	± 0.33	mg/L
Chromium	± 0.17	µg/L
Copper	± 0.09	µg/L
Fluorine	± 0.03	mg/L
Iron	± 7.50	µg/L
Potassium	± 0.16	mg/L
Lithium	± 1.52	µg/L
Magnesium	± 2.86	mg/L
Manganese	± 0.07	µg/L
Molybdenum	± 0.27	µg/L
Sodium	± 1.42	mg/L
Lead	± 0.003	µg/L
Sulfate (SO <sub>4</sub> )	± 6.19	mg/L
Antimony	± 0.003	µg/L
Selenium	± 0.72	µg/L
Silica (SiO <sub>2</sub> )	± 0.35	mg/L
Strontium	± 60.1	µg/L
Thallium	± 0.02	µg/L
Uranium	± 0.47	µg/L
Vanadium	± 0.15	µg/L
Zinc	± 0.76	µg/L



**Figure 3.** Uranium activity ratio (UAR) values from the U.S. Geological Survey (USGS) National Research Program Lab versus USGS contract labs.

## Environmental Samples

Spring sample environmental results are presented in appendix 6 and are archived in the USGS National Water Information System database (U.S. Geological Survey, 2016b).

## Parameters and Major Ions

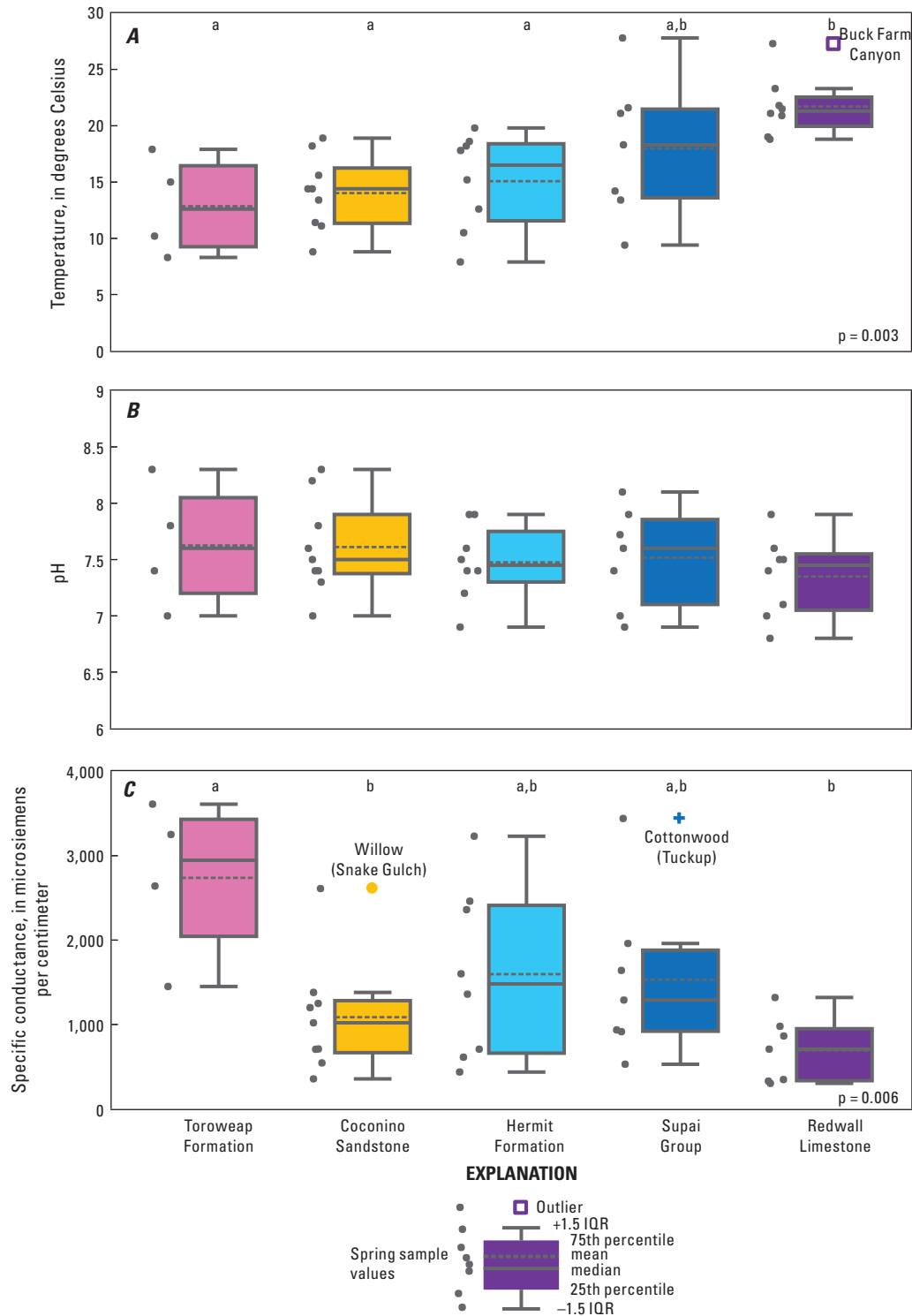
Water from springs sampled for this study had pH ranging from 6.6 to 8.6, moderately high specific conductance that varied over a wide range (300–3,610 microsiemens per centimeter [µS/cm]) (fig. 4), and measurable dissolved oxygen. Water temperatures generally were higher in springs discharging from lower stratigraphic units than in upper stratigraphic units. Water in springs discharging from the Toroweap Formation, Coconino Sandstone, and Hermit Formation was significantly different from springs discharging from the Redwall Limestone (fig. 4A). Hotel Spring hosted in Supai Group rocks had the greatest water temperature of 28 °C in July 2011. The median value for Supai Group springs (18.3 °C) was substantially lower than the median value obtained for springs discharging from the Redwall Limestone (21.5 °C; fig. 4A). For some springs measured more than once, temperatures varied depending on the time of year the sample was collected. For example, temperature in the Pigeon Spring pool ranged from 8.3 °C in March, to 20 °C in September, and 11.8 °C in November (Beisner and others, 2017). More temporal samples would be needed to determine which springs had seasonal temperature fluctuation.

The pH values varied over a similar range at springs discharging from all geologic units (fig. 4B) and statistical differences between the groups were not determined as the data did not fit a lognormal distribution. Specific conductance was

greatest in springs discharging from the Toroweap Formation and significantly different from springs discharging from the Coconino Sandstone and Redwall Limestone, which had lower values (fig. 4C). Willow (Snake Gulch) and Cottonwood (Tuckup) Springs specific conductance values were outliers

(greater than 1.5 times the interquartile range) compared to the other springs discharging from the Coconino Sandstone and Supai Group respectively (fig. 4C).

Spring discharge varied across the study area. Several springs were slow seeping springs with flow rates ranging



**Figure 4.** Temperature (A), pH (B), and specific conductance (C). The interquartile range (IQR) is the 25th to 75th percentile. Letters a and b indicate significantly different groups and a,b are not distinct from either group where the p-value indicates the significance of the test for difference between groups.

from less than a gallon a minute to several gallons per minute. Springs with high flow rates ranging from 200 to 730 gallons per minute were primarily discharging from the Redwall Limestone.

Water discharging from the Toroweap Formation had significantly higher values of calcium, magnesium, and fluoride compared to springs discharging from other units (figs. 5 and 6) most notably the Coconino Sandstone (calcium, magnesium) and Redwall Limestone (calcium, magnesium, and fluoride). Willow (Snake Gulch) Spring had several elements (calcium, magnesium, sodium, and sulfate) which were outliers compared to the remaining springs discharging from the Coconino Sandstone (figs. 5A,B,D and 6D). Cottonwood (Tuckup) Spring had high outlier values for calcium, magnesium, and sulfate (fig. 5A,B,D). Rider and Fence Spring had high outlier values for potassium, sodium, and chloride (figs. 5C,D and 6B). Fence Spring had a high outlier value and Rider Spring had a low outlier value for bicarbonate (fig. 6A). Fluoride had a high outlier for Rider Spring (fig. 6C). Lower Jumpup and Saddle Horse Springs had high and low outlier values, respectively, for fluoride (fig. 6C).

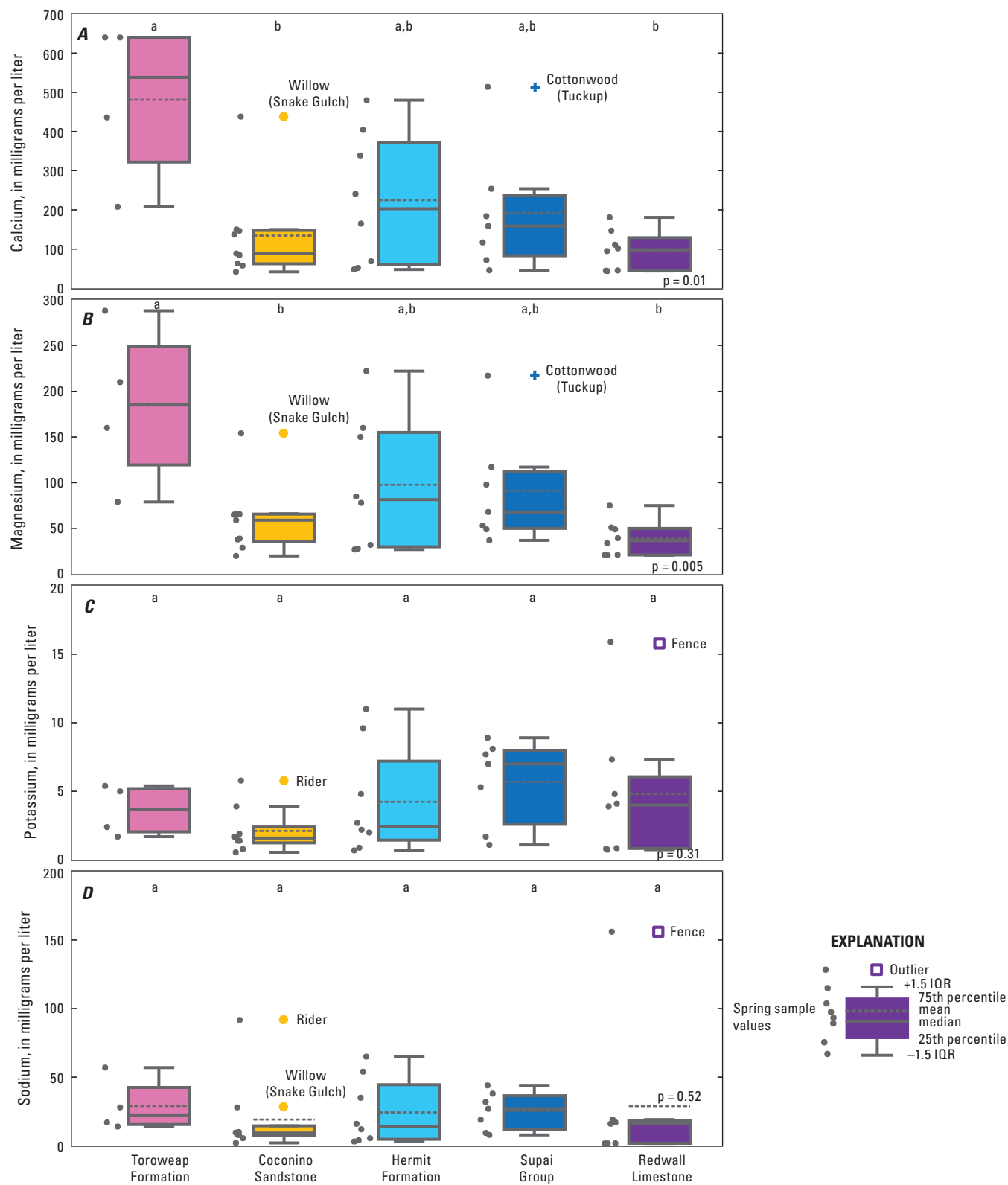
Most spring waters were characterized by calcium and magnesium as the dominant cations and sulfate and bicarbonate as the dominant anions (fig. 7). Rider and Fence Springs had distinctly different water type classifications compared with the other spring samples in this study, with a larger proportion of sodium and potassium and chloride. All springs discharging from the Toroweap Formation sampled for this study had a dominant sulfate anion, which may be due to gypsum dissolution from the host rocks (Beisner and others, 2017). Coconino Sandstone springs varied primarily with respect to the proportion of bicarbonate. In Big Springs the dominant anion was bicarbonate; in Upper Jumpup, Horse, Slide, Willow (Snake Gulch), and Rider Springs the dominant anion was sulfate; and Little, Boulder, and Warm Springs were a mixture of the two (fig. 7). Hermit Formation springs also

varied with respect to bicarbonate; in Swamp, Powell, and Oak Springs the dominant anion was bicarbonate and the other springs were dominated by sulfate (fig. 7). Two Supai Group springs (Hotel and Saddle Horse Springs) had a higher proportion of magnesium compared with other Supai Group springs. In Saddle Horse Spring the dominant anion was bicarbonate, whereas Hotel Spring contained a mixture of bicarbonate and sulfate anion waters and had a slightly higher proportion of chloride compared to the other springs. The rest of the Supai Group springs contained dominantly sulfate anion waters except for Cottonwood Spring (Sowats), which was a mixture of bicarbonate and sulfate (fig. 7). Redwall Limestone springs also varied with respect to bicarbonate proportion; in Hole in the Wall, Hanging, and Unknown near Hanging Springs the dominant anion was bicarbonate. The other springs were a mixture of bicarbonate and sulfate, except for Side Canyon Spring, in which the dominant anion was sulfate (fig. 7).

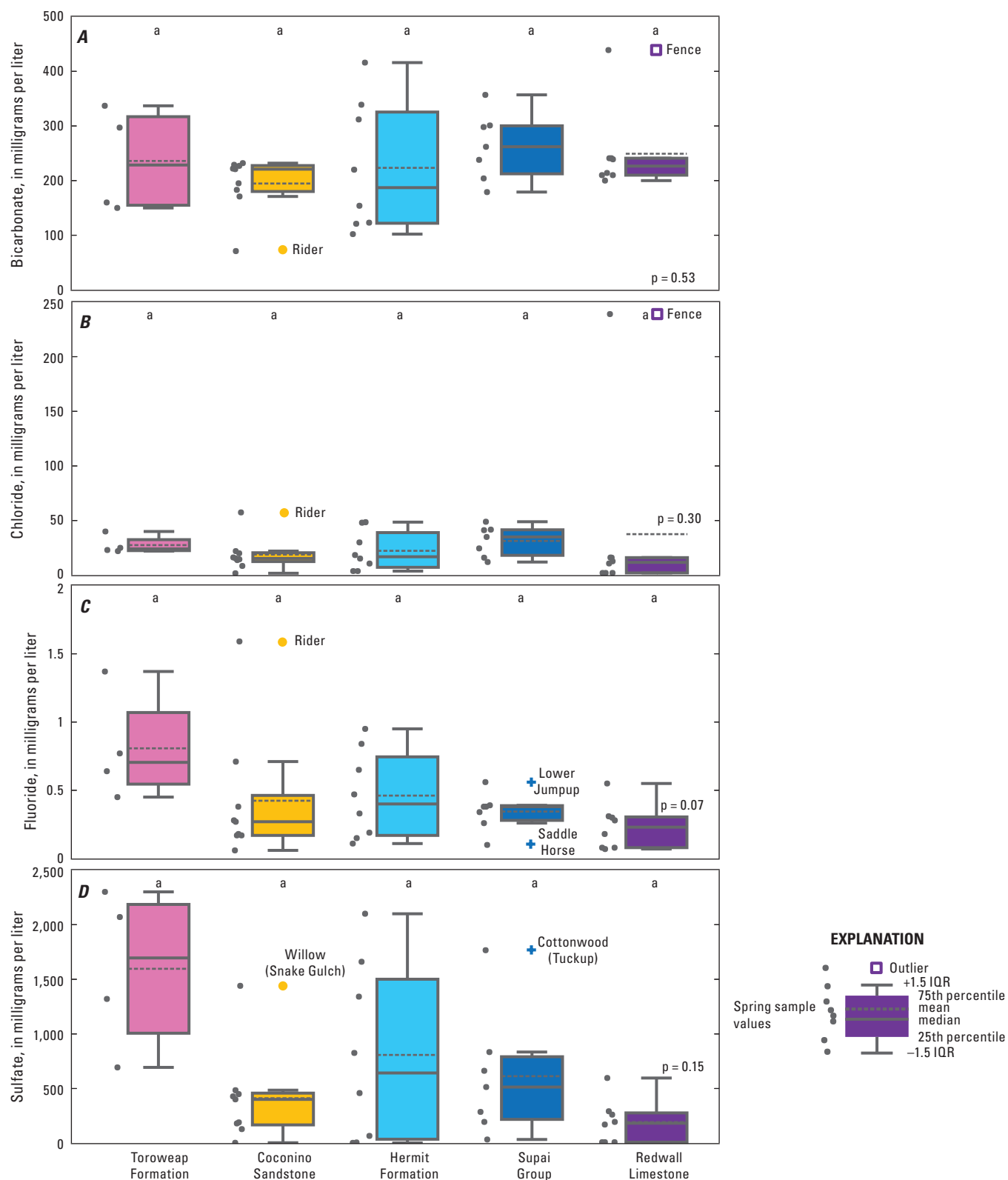
## Trace Elements

Three springs exceeded the EPA drinking water standard (table 2); Fence Spring for arsenic, Pigeon Spring for selenium and uranium, and Willow (Hack) Spring for selenium (figs. 8–10, table 5).

Median and mean values for all springs discharging north of the Grand Canyon from the Toroweap and Hermit Formations, Coconino Sandstone, Supai Group, and Redwall Limestone sampled for this study are listed in table 5. For all of the trace elements quantified in table 5 there are springs that are statistical outliers. Elements that were not statistically quantified had a majority (greater than 50 percent) of samples with values less than the threshold of influence from blank samples (Al, Be, Cd, Co, Cr, Cu, Mn, Pb, Sb, and Zn) or did not fit a lognormal distribution (Ba, Fe, Mo, and Ni).

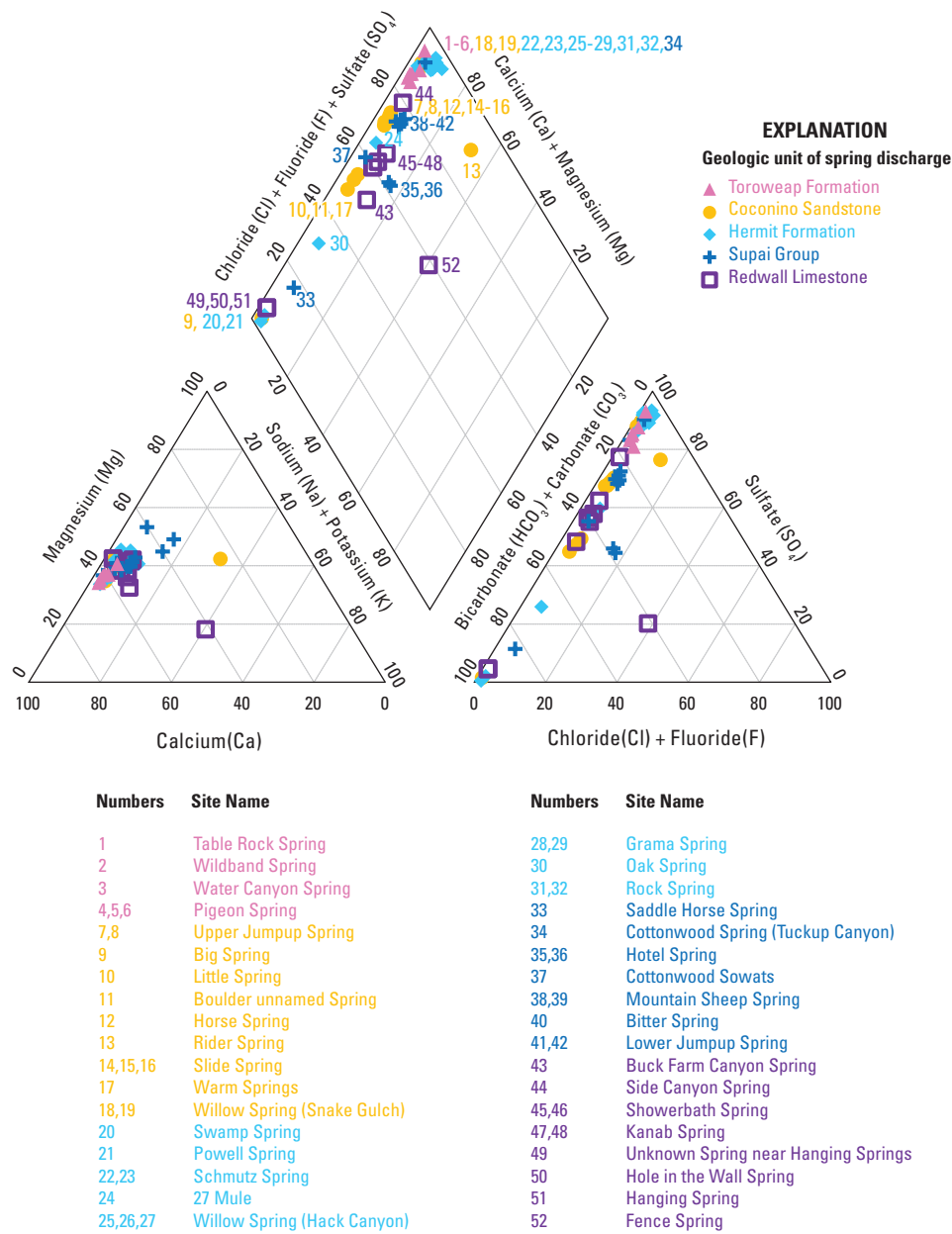


**Figure 5.** Major cation concentrations; calcium (A), magnesium (B), potassium (C), and sodium (D). The interquartile range (IQR) is the 25th to 75th percentile. Letters a and b indicate significantly different groups and a,b are not distinct from either group where the p-value indicates the significance of the test for difference between groups.



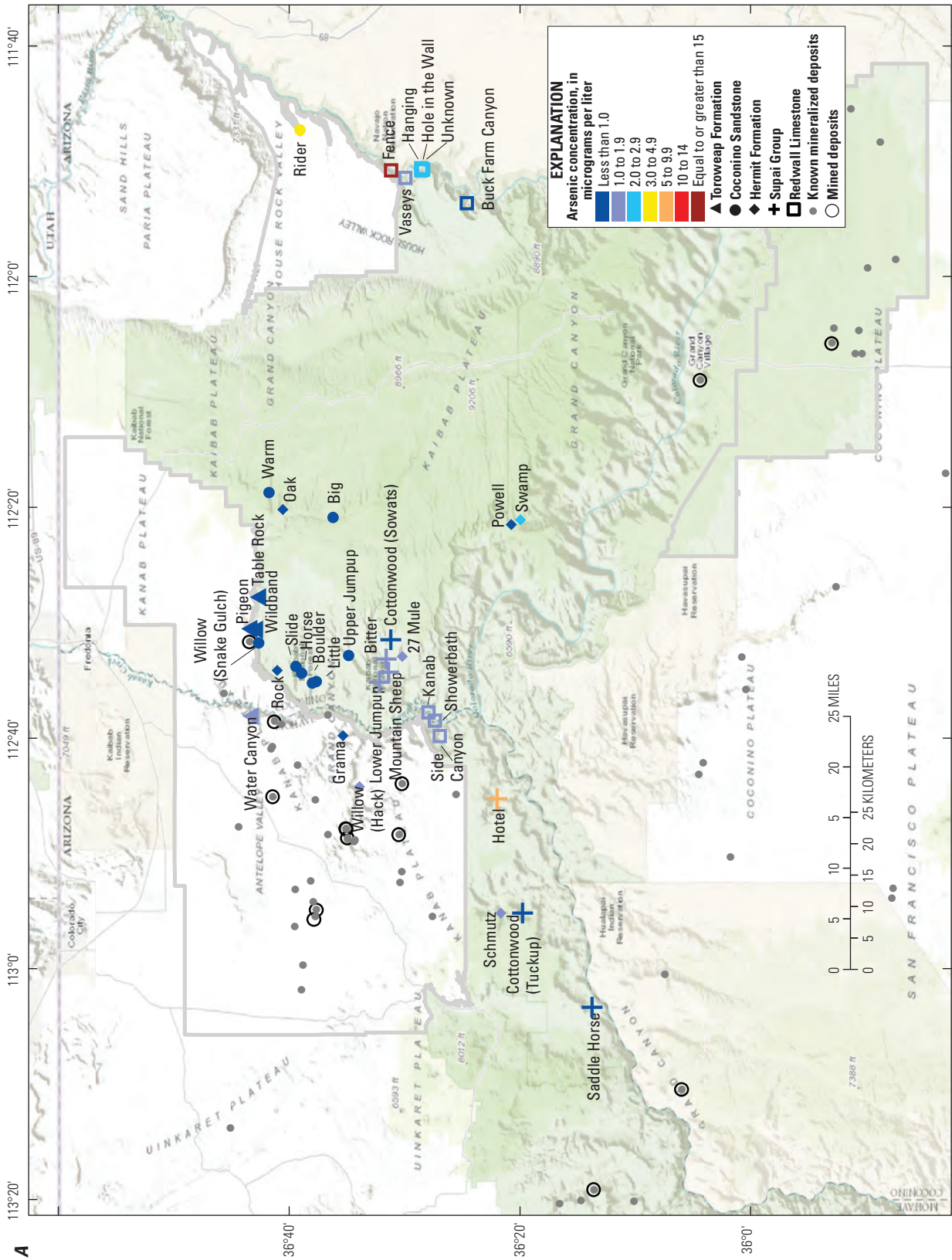
**Figure 6.** Major anion concentrations; bicarbonate (A), chloride (B), fluoride (C), and sulfate (D). The interquartile range (IQR) is the 25th to 75th percentile. Letters a and b indicate significantly different groups and a,b are not distinct from either group where the p-value indicates the significance of the test for difference between groups.





**Figure 7.** Major ion composition for spring samples.



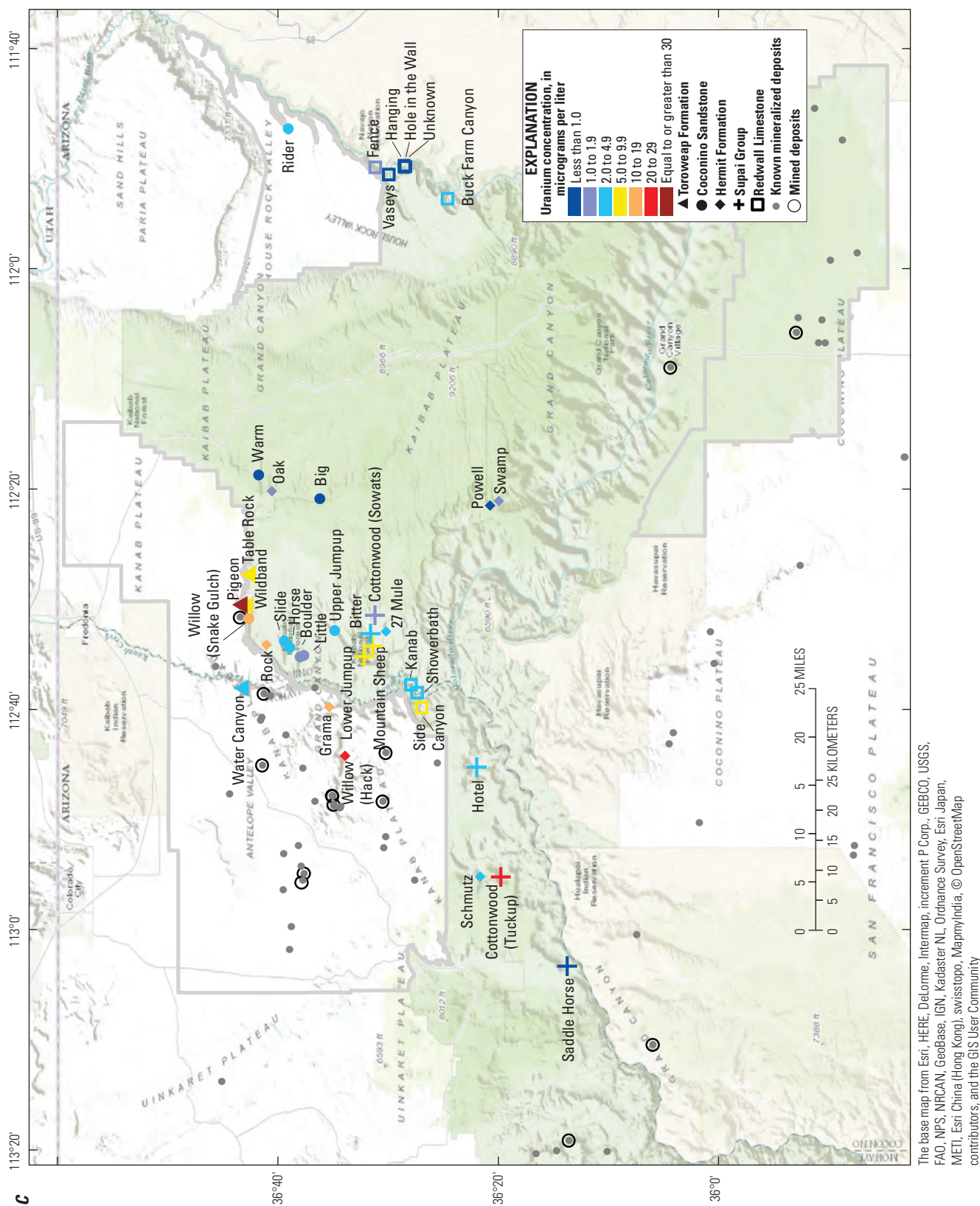


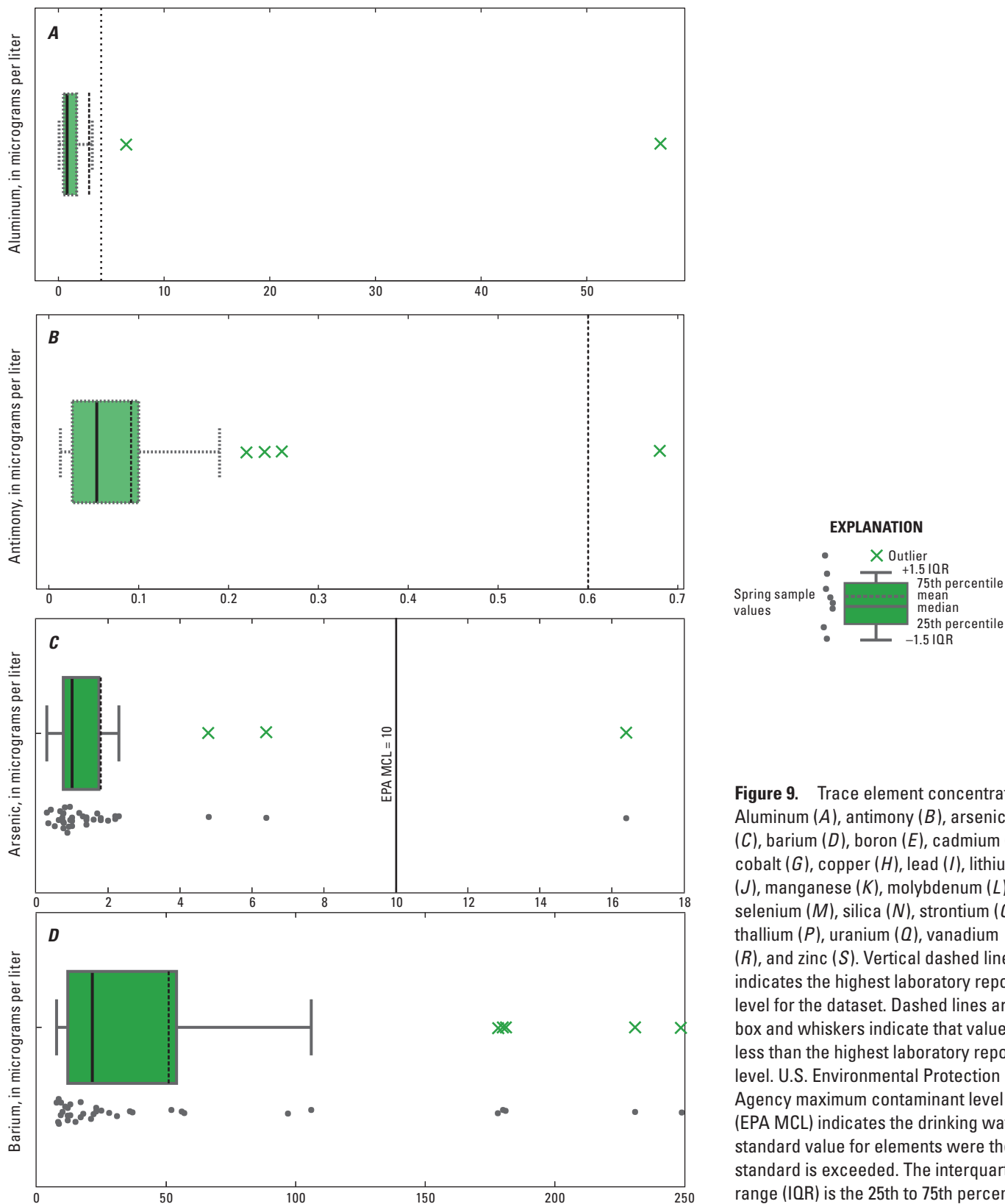
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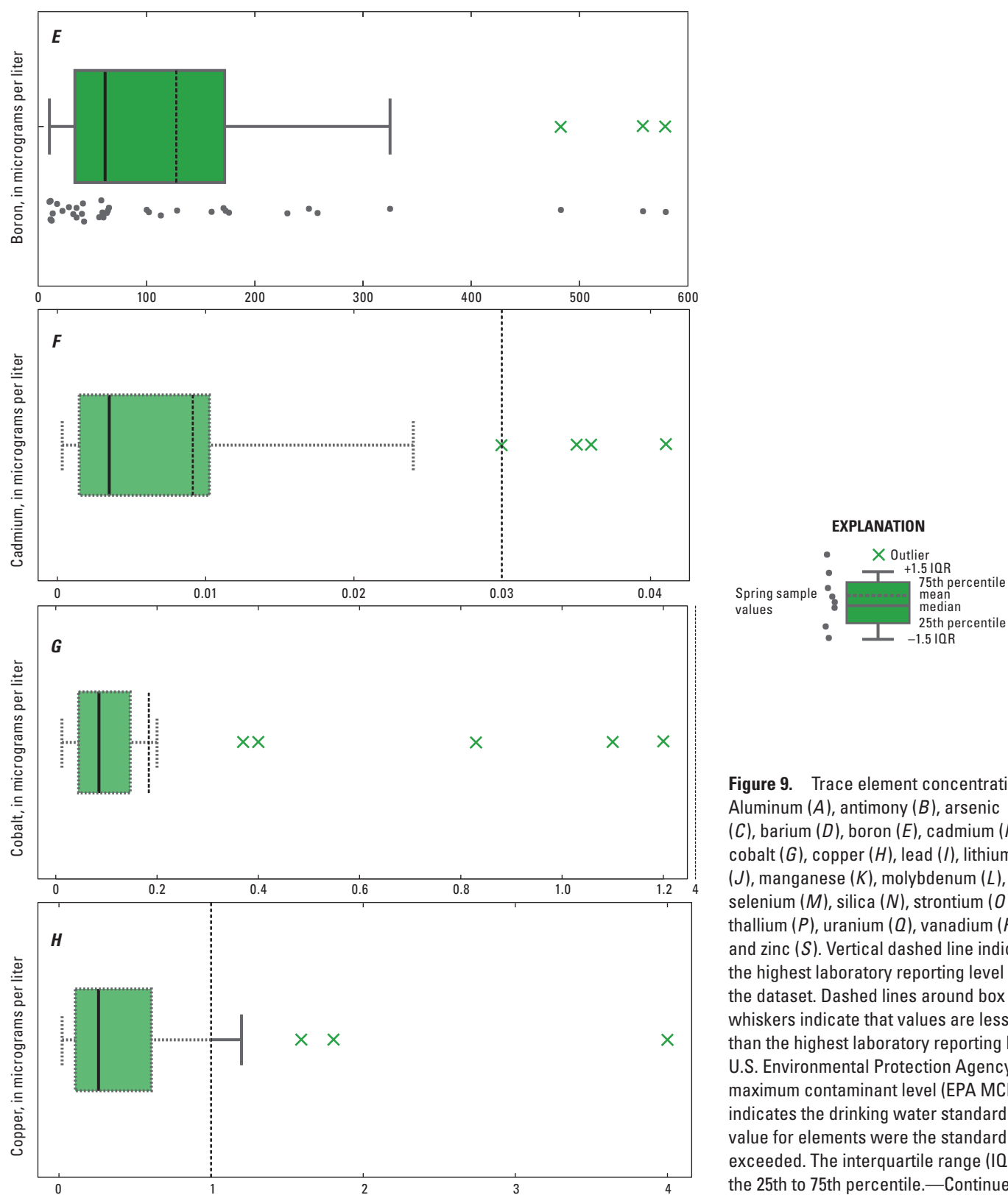
**Figure 8.** Trace element concentration for arsenic (A), selenium (B), and uranium (C) from spring samples. Location of mineralized breccia pipes can be found in the following references: Alpine, 2010; Brown and others, 1992; Chenoweth, 1986, 1988; Verbeek and others, 1988; Wenrich and others, 1988, 1990, 1997; Sutphin and Weinrich, 1989; VanGosen and Weinrich, 1989, 1991; Finch and others, 1990; Wenrich, 1992; Wenrich and Aumente-Modreski, 1994; Gardner, 1998; Mazeika, 2002; Ross and Moreton, 2012.

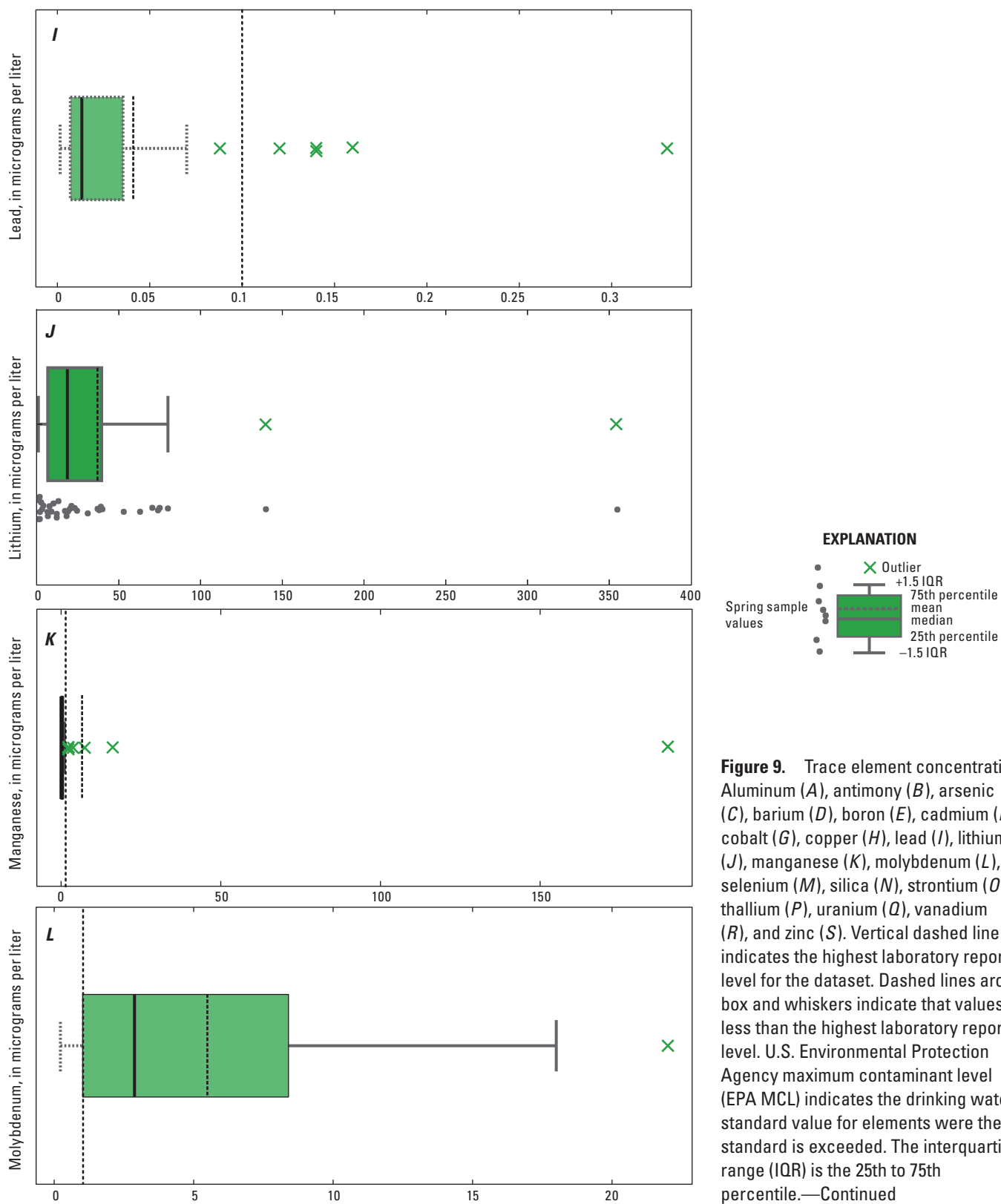


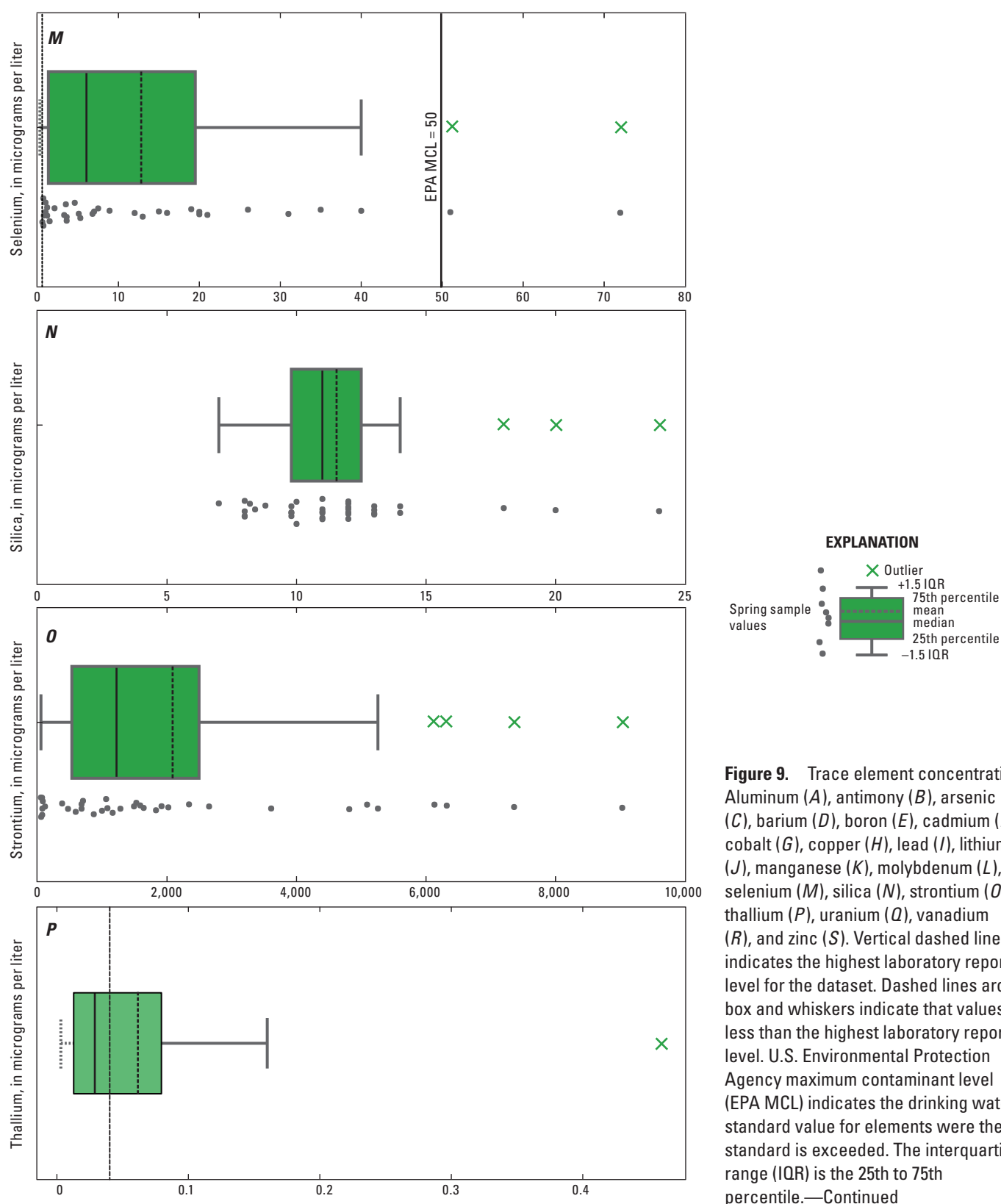


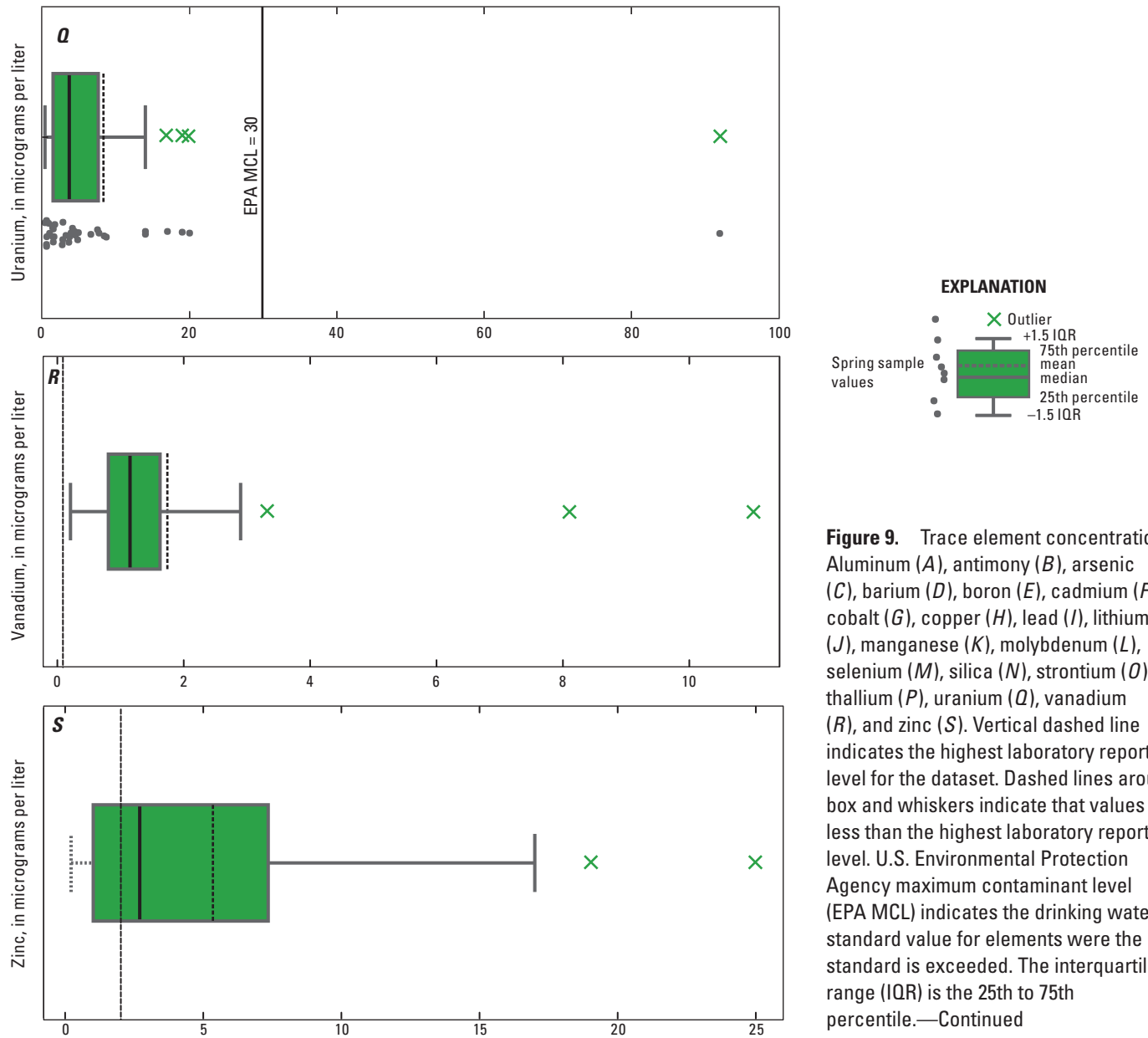




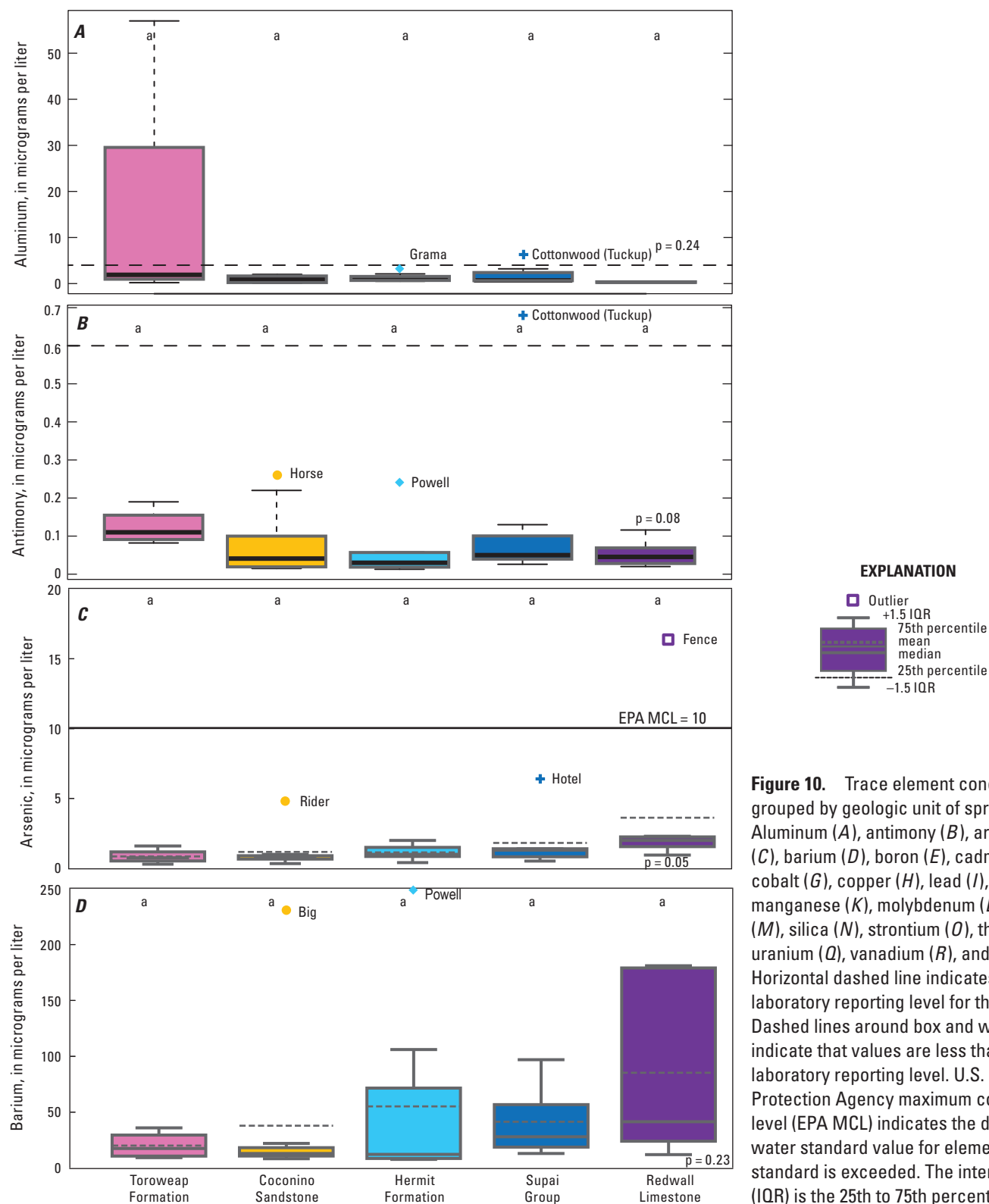




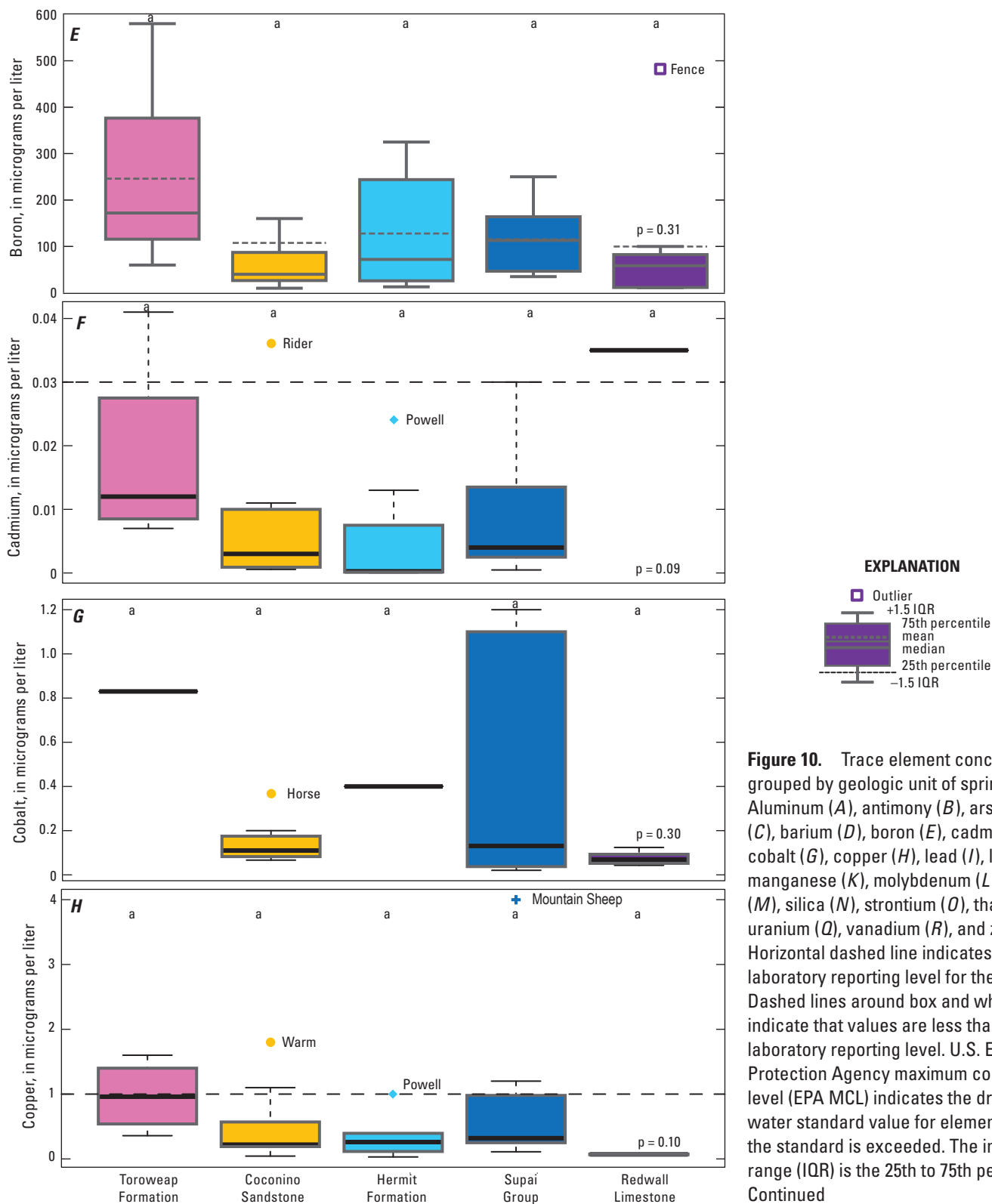


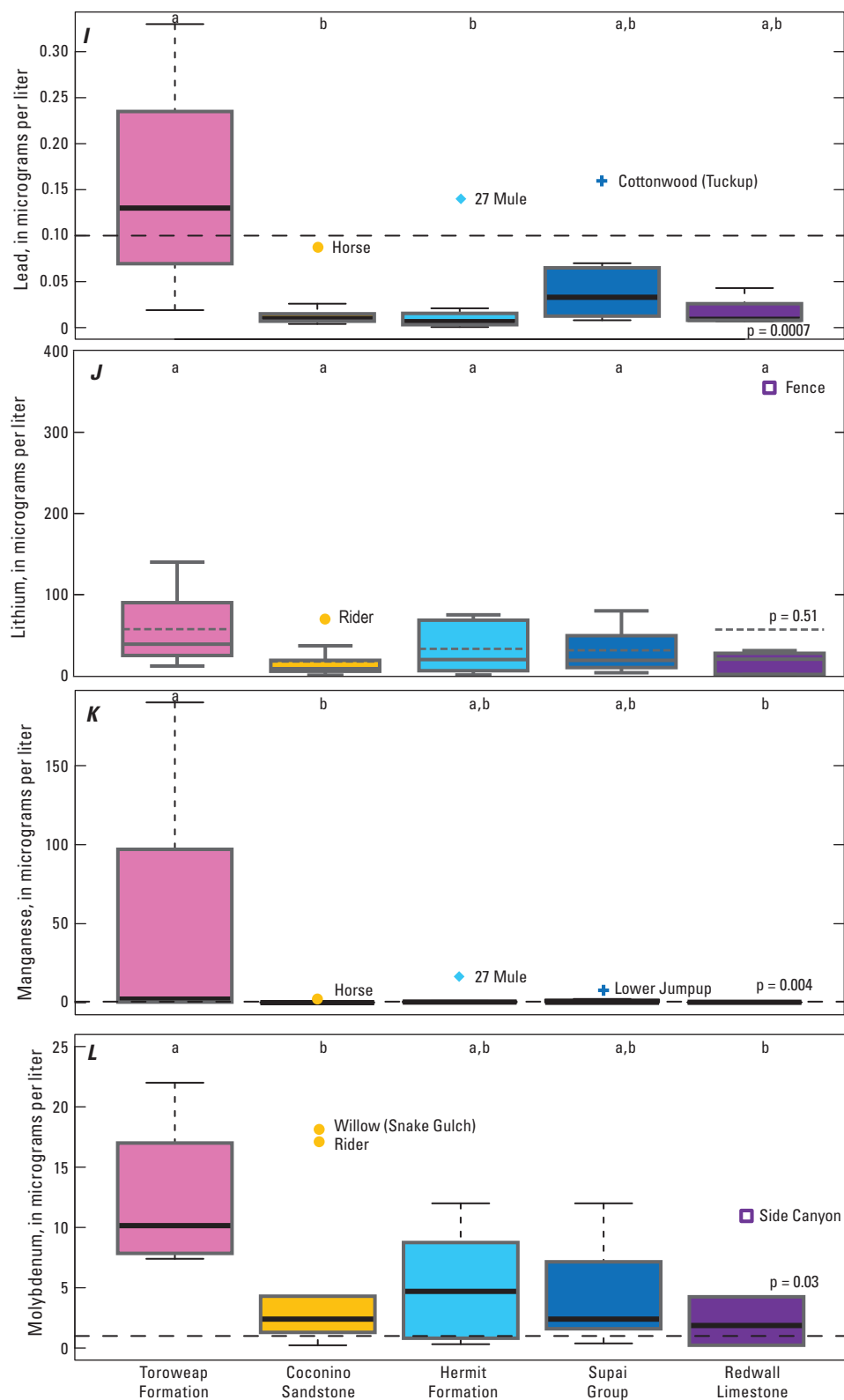




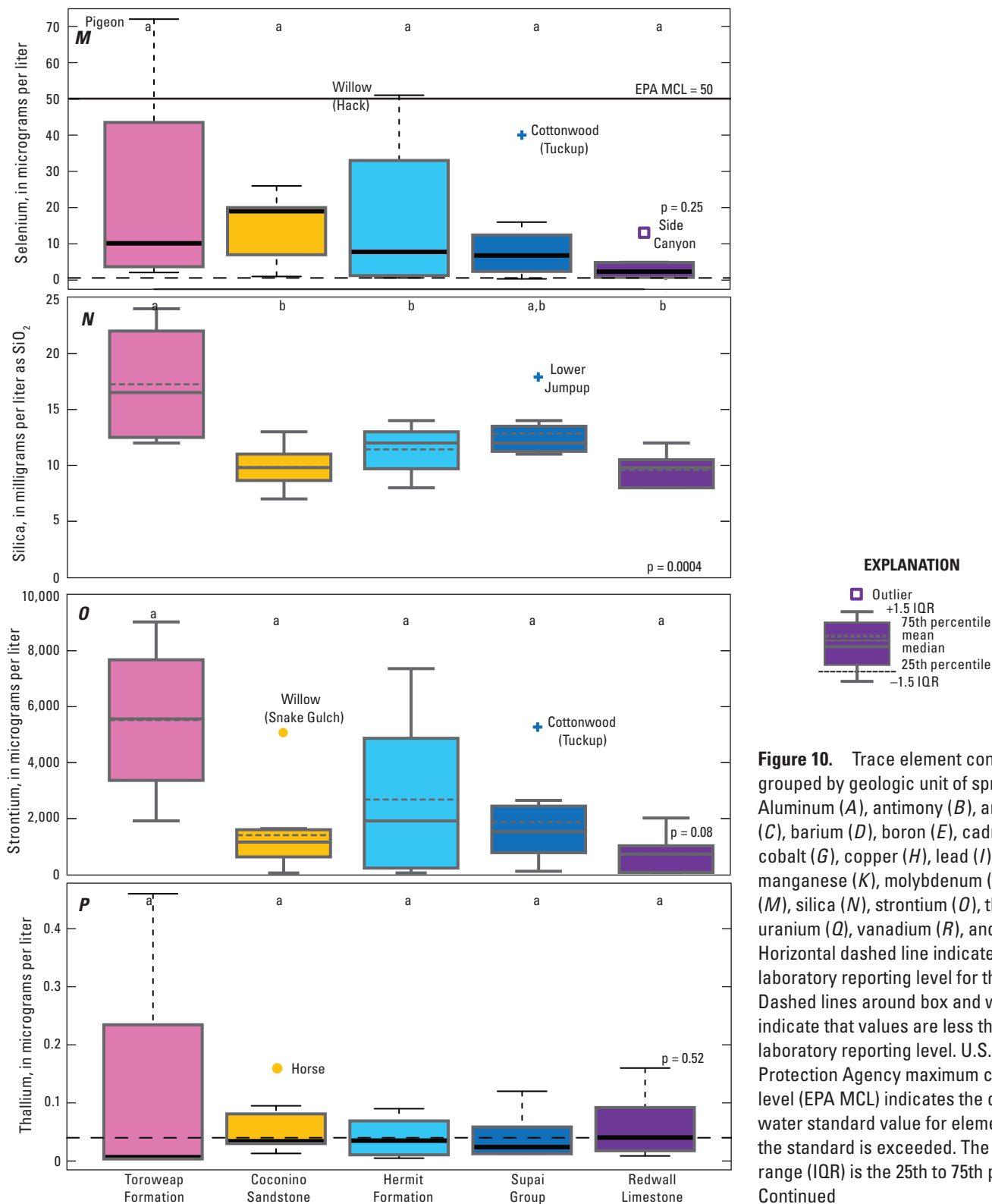


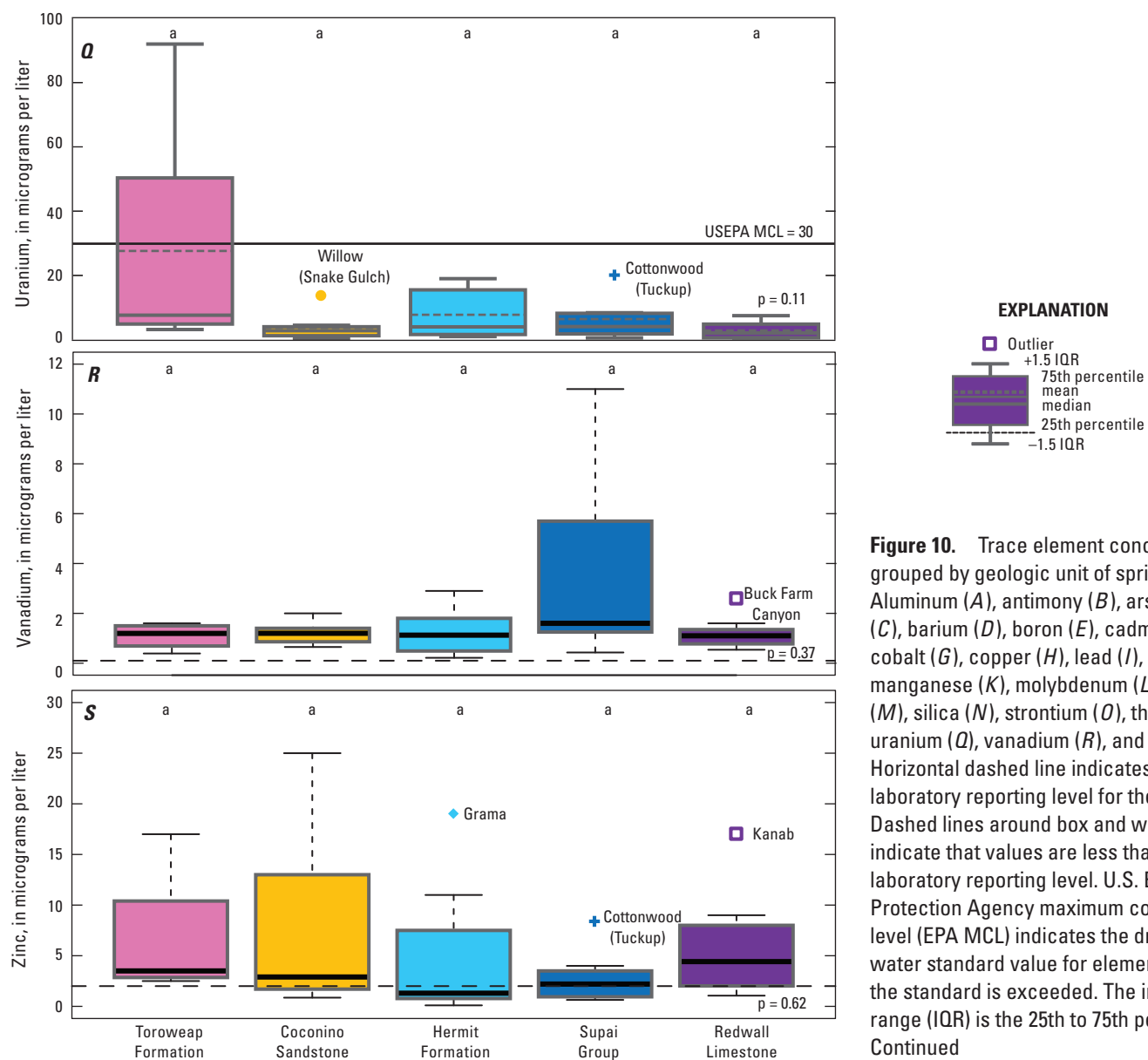
**Figure 10.** Trace element concentrations grouped by geologic unit of spring discharge. Aluminum (A), antimony (B), arsenic (C), barium (D), boron (E), cadmium (F), cobalt (G), copper (H), lead (I), lithium (J), manganese (K), molybdenum (L), selenium (M), silica (N), strontium (O), thalium (P), uranium (Q), vanadium (R), and zinc (S). Horizontal dashed line indicates the highest laboratory reporting level for the dataset. Dashed lines around box and whiskers indicate that values are less than the highest laboratory reporting level. U.S. Environmental Protection Agency maximum contaminant level (EPA MCL) indicates the drinking water standard value for elements were the standard is exceeded. The interquartile range (IQR) is the 25th to 75th percentile.





**Figure 10.** Trace element concentrations grouped by geologic unit of spring discharge. Aluminum (A), antimony (B), arsenic (C), barium (D), boron (E), cadmium (F), cobalt (G), copper (H), lead (I), lithium (J), manganese (K), molybdenum (L), selenium (M), silica (N), strontium (O), thallium (P), uranium (Q), vanadium (R), and zinc (S). Horizontal dashed line indicates the highest laboratory reporting level for the dataset. Dashed lines around box and whiskers indicate that values are less than the highest laboratory reporting level. U.S. Environmental Protection Agency maximum contaminant level (EPA MCL) indicates the drinking water standard value for elements were the standard is exceeded. The interquartile range (IQR) is the 25th to 75th percentile.— Continued





**Table 5.** Median and mean values for trace elements from 36 samples from springs discharging north of the Grand Canyon from the Toroweap and Hermit Formations, Coconino Sandstone, Supai Group, and Redwall Limestone sampled for this study. Springs exceeding the U.S. Environmental Protection Agency drinking water standard are shown in *italic*.

[–, not presented as data do not meet requirements for a robust statistical determination; µg/L, micrograms per liter; mg/L, milligrams per liter]

Element	Median	Mean	Standard deviation	Minimum	Maximum	Percent censored	Springs with outliers
Aluminum (µg/L)	–	–	–	<0.2	57	19	
Antimony (µg/L)	–	–	–	<0.04 and 0.013	0.68	17	
Arsenic (µg/L)	1	1.8	2.8	0.3	16.4	0	<i>Fence, Hotel, Rider</i>
Barium (µg/L)	–	–	–	7.7	249	0	
Beryllium (µg/L)	–	–	–	<0.0008	0.045	72	
Boron (µg/L)	61.5	127.3	150	10	580	0	Fence, Rider, Water Canyon
Cadmium (µg/L)	–	–	–	<0.001	0.041	50	
Chromium (µg/L)	–	–	–	<0.08	4	25	
Cobalt (µg/L)	–	–	–	<0.1	1.2 and <4	61	
Copper (µg/L)	–	–	–	<0.007	4	25	
Iron (µg/L)	–	–	–	<0.8	226	44	
Lead (µg/L)	–	–	–	<0.005	0.33	25	
Lithium (µg/L)	18.5	37	62	0.8	355	0	Fence, Water Canyon
Manganese (µg/L)	–	–	–	0.02	190	42	
Molybdenum (µg/L)	–	–	–	<1 and 0.223	22	3	
Nickel (µg/L)	–	–	–	<0.3 and 0.19	7	69	
Selenium (µg/L)	6.1	12.8	16.1	<0.6	72	3	<i>Pigeon, Willow (Hack)</i>
Silica (in mg/L as SiO <sub>2</sub> )	11	11.5	3.4	7	24	0	Lower Jumpup, Water Canyon, Wildband
Strontium (µg/L)	1,220	2,086	2,323	54	9,030	0	Rock, Water Canyon, Wildband, Willow (Hack)
Thallium (µg/L)	0.03	0.06	0.08	<0.01	0.46	19	Table Rock
Uranium (µg/L)	3.6	7.6	15.4	0.37	92	0	Cottonwood (Tuckup), Grama, <i>Pigeon</i> , Willow (Hack)
Vanadium (µg/L)	1.15	1.7	2.1	<0.1	11	3	Bitter, Hotel, Saddle Horse
Zinc (µg/L)	–	–	–	<0.09	25	19	

The results from this study were compared with the descriptive statistics for more than 2,100 groundwater samples from across the United States (Lee and Helsel, 2005), which present statistical values for the following elements, As, Ba, Co, Cr, Cu, Mo, Ni, Pb, Se, and Zn. Measured values for the same elements from our study were less than the maximum values in the Lee and Helsel (2005) study. The median and mean values of the elements from our study were generally within the IQR of the Lee and Helsel (2005) study with the following exceptions; chromium, copper, and lead median values were slightly lower than the 25th percentile, the mean of molybdenum was between the 75th and 90th percentile, and the median and mean of selenium were greater than the 95th percentile. Seiler and others (2003) analyzed groundwater samples from the National Irrigation Water Quality Program in the western United States for Al, As, B, Cd, Cr, Cu, Pb, Mo, Se, Ag, U, and Zn. Measured and median values of the select elements from this study were within the reported range and all medians were less than data from Seiler and others (2003).

Billingsley and others (1983) conducted a study in the Snake Gulch area, which sampled several springs included in this study and concentration comparisons are presented in Beisner and others (2017). Billingsley and others (1983) defined uranium concentrations based on concentration contrasts; between 1–9  $\mu\text{g/L}$  was considered background, 10–40  $\mu\text{g/L}$  was weakly anomalous, and greater than 40  $\mu\text{g/L}$  was strongly anomalous. Using the Billingsley and others (1983) criteria, most springs from this study have background uranium concentrations. Cottonwood (Tuckup), Grama, Rock, and Willow (Hack and Snake Gulch) Springs have weakly anomalous concentrations and Pigeon Spring has strongly anomalous concentrations. Data from this study indicate that uranium values greater than 14  $\mu\text{g/L}$  are statistical outliers ( $>1.5$  IQR) and may be a good determination of anomalous concentrations for future studies in the area. The Billingsley

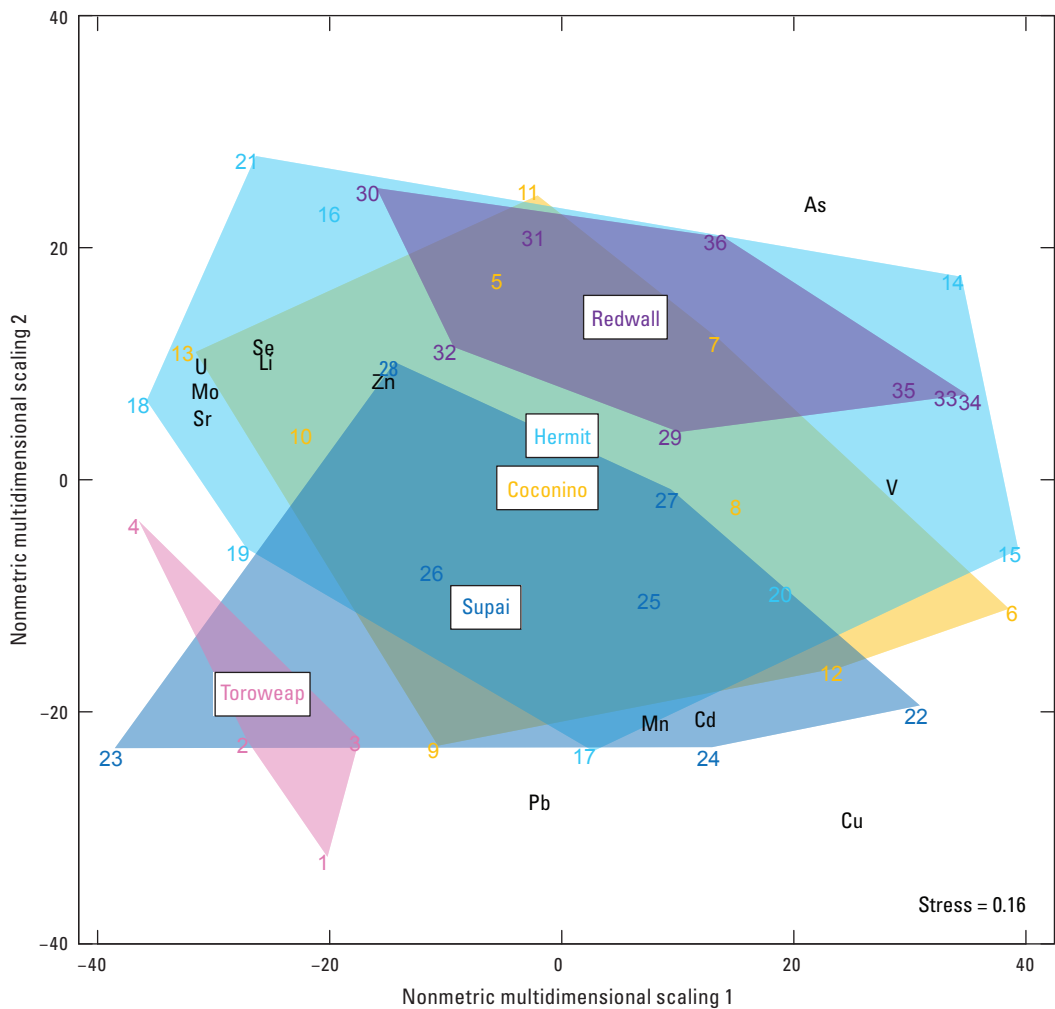
and others (1983) study also calculated ranges for zinc and all values from this study were within the 1.8–50  $\mu\text{g/L}$  background concentration range.

## Multivariate Analysis

A multivariate analysis was conducted on the data to understand dissimilarity between spring sites. The following elements, As, Cd, Cu, Li, Mn, Mo, Pb, Se, Sr, U, V, and Zn, were used for multivariate comparison based on separation within springs near Snake Gulch and between mining leachate and spring chemistry from principal component analysis analysis in Beisner and others (2017).

The NMDS analysis of the spring data resulted in 2 convergent solutions after 20 tries with a stress of 0.16 (fig. 11) which falls between a fair and suspect result (Buttigieg and Ramette, 2014). Elements associated near uranium were molybdenum, strontium, selenium and lithium, and springs with higher uranium loading were farther from springs influenced by arsenic, cadmium, copper, lead, and manganese (fig. 11). Elemental correlations were calculated using Kendall's tau and indicate that there are significant positive correlations between the following elements—lithium, molybdenum, selenium, strontium, uranium and zinc—as well as between lead and manganese, and cadmium, copper, and lead (fig. 12).

An ANOSIM analysis on the spring samples relative to the geologic unit of spring discharge group resulted in a test statistic value of 0.14 and a p-value of 0.017, indicating there is a difference between at least two of the groups. A cluster analysis was also run on the same elements used in the NMDS analysis (fig. 13). The Calinski criterion indicates that two is the correct number of distinct groups, and the difference between the groups is driven by higher values of Mo, Li, Se, Sr, U, and Zn for the group on the right side of the dendrogram in figure 13.



EXPLANATION

Numbers Site name

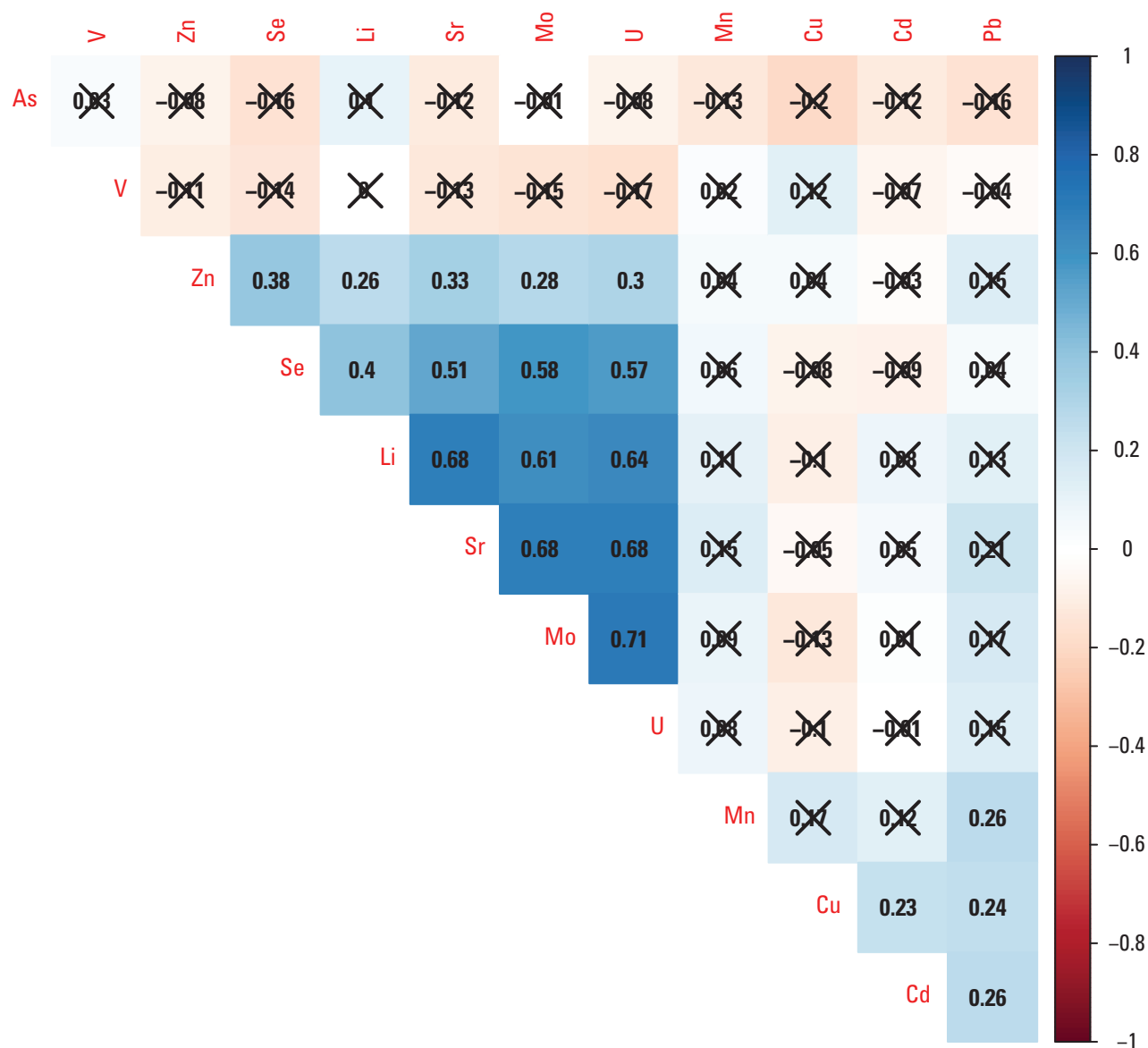
- 1 Table Rock Spring
- 2 Wildband Spring
- 3 Water Canyon Spring
- 4 Pigeon Spring
- 5 Upper Jumpup Spring
- 6 Big Spring
- 7 Little Spring
- 8 Boulder Spring
- 9 Horse Spring
- 10 Rider Spring
- 11 Slide Spring
- 12 Warm Springs
- 13 Willow Spring (Snake Gulch)
- 14 Swamp Spring
- 15 Powell Spring
- 16 Schmutz Spring
- 17 27 Mule Spring
- 18 Willow Spring (Hack Canyon)

Numbers Site name

- 19 Grama Spring
- 20 Oak Spring
- 21 Rock Spring
- 22 Saddle Horse Spring
- 23 Cottonwood Spring (Tuckup Canyon)
- 24 Hotel Spring
- 25 Cottonwood Spring (Sowats)
- 26 Mountain Sheep Spring
- 27 Bitter Spring
- 28 Lower Jumpup Spring
- 29 Buck Farm Canyon Spring
- 30 Side Canyon Spring
- 31 Showerbath Spring
- 32 Kanab Spring
- 33 Unknown Spring near Hanging Springs
- 34 Hole in the Wall Spring
- 35 Hanging Spring
- 36 Fence Spring

Figure 11. Spring samples with polygons outlining geologic unit of spring discharge. As, arsenic; Cd, cadmium; Cu, copper; Li, lithium; Mn, manganese; Mo, molybdenum; Pb, lead; Se, selenium; Sr, strontium; U, uranium; V, vanadium; Zn, zinc.





**Figure 12.** Correlogram including the Kendall's tau value for elemental pairs, where values with an X are not statistically significant with  $p > 0.05$ .

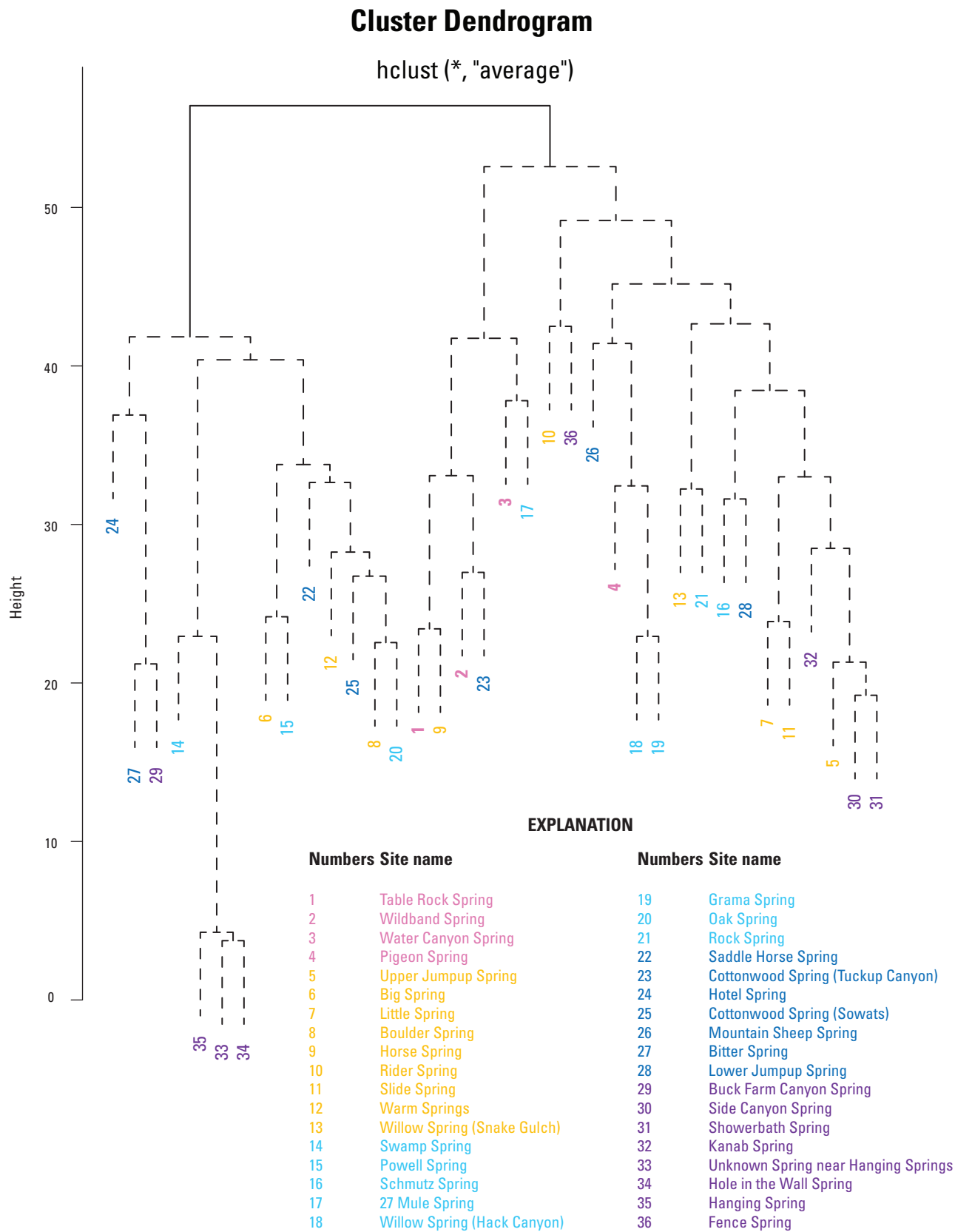


Figure 13. Cluster dendrogram for spring samples.

## Isotopic and Radioactivity Analysis

### Radiochemistry

Gross-alpha radioactivity in samples from seven springs—Pigeon, Willow (Snake Gulch), Willow (Hack), Grama, Rock, Mountain Sheep (2011), and Lower Jumpup (2009) Springs—equaled or exceeded the EPA drinking water standard of 15 pCi/L (figs. 14 and 15). Pigeon, Willow (Snake Gulch), and Rock Springs had samples with values that were statistical high outliers for all spring sites for gross alpha radioactivity (fig. 15A). Radioactivity was not measured at Water Canyon Spring, therefore, data from only three springs discharging from the Toroweap Formation were available and descriptive statistics could not be calculated for this rock unit. Water from Willow (Snake Gulch) Spring had an elevated concentration of gross-alpha radioactivity, which represents a high statistical outlier for springs discharging from the Coconino Sandstone (fig. 15B).

Measurements of gross-beta radioactivity in water samples are reported in terms of the  $^{137}\text{Cs}$  curve. Gross beta radioactivity was greater than 15 pCi/L, the activity at which the USEPA requires testing for drinking water suppliers for selected individual beta-emitting radionuclides (Lappenbusch and Cothorn, 1985), at four spring sites including Pigeon, Willow (Hack), Cottonwood (Tuckup), and Fence Springs. Pigeon and Cottonwood (Tuckup) Springs were statistical high outliers for all spring sites for gross beta radioactivity (fig. 16A). A sample from Fence Spring with a value of 15.4 pCi/L represents a statistical high outlier for springs discharging from the Redwall Limestone (fig. 16B).

Radium-226 and -228 concentrations were measured on samples from most springs and all had values less than the detection limit of 4 pCi/L. Three samples—Upper Jumpup (2009), Willow (Hack) (2012) and Kanab Spring (2009)—were sampled using a large-volume radium reduction method, which provides lower detection limits (Kraemer, 2005). These samples yielded  $^{226}\text{Ra}$  activities between 0.19 and 0.245 pCi/L, and  $^{228}\text{Ra}$  concentrations between 0.016 and 0.122 pCi/L.

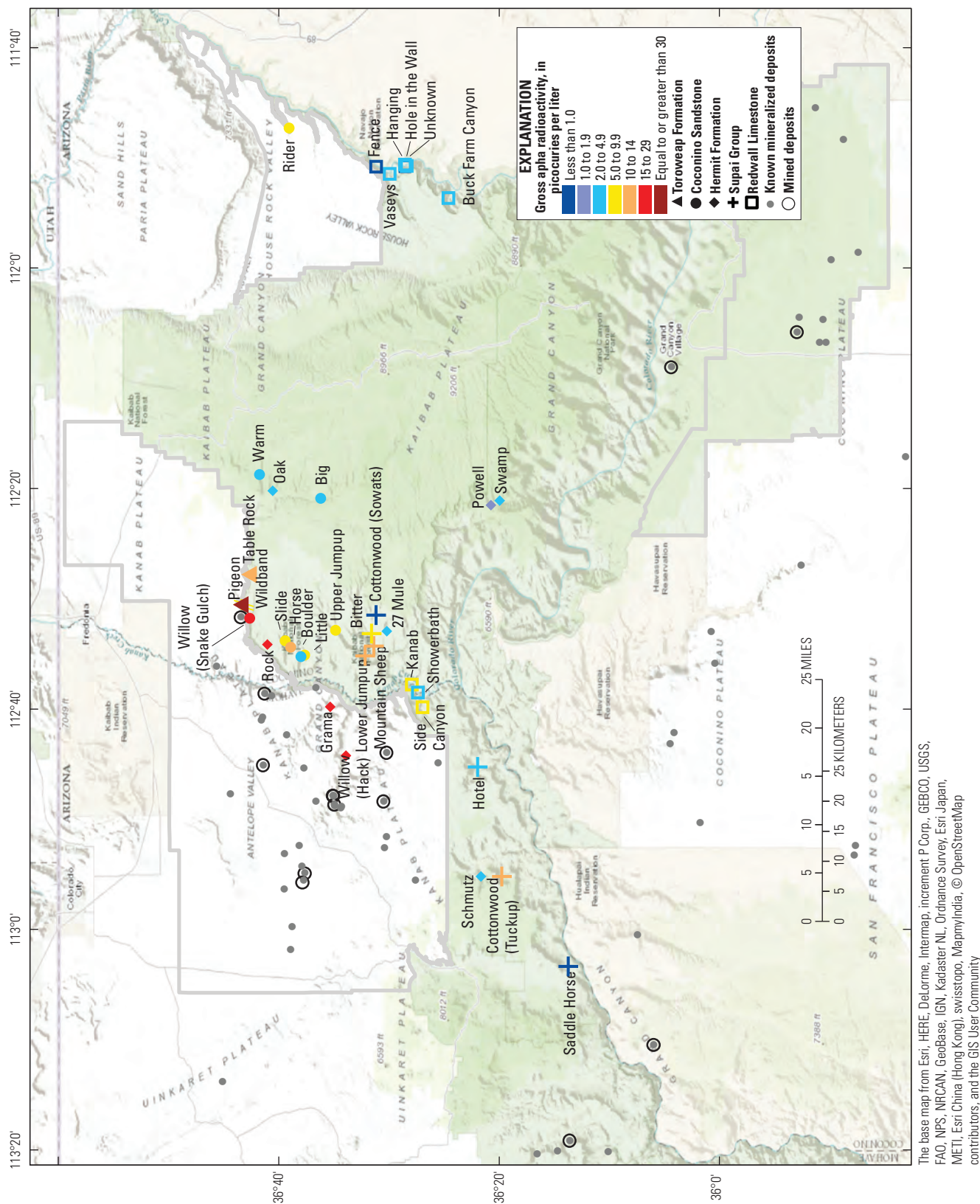
Fifty-one groundwater samples collected from 36 springs between 2009 and 2016 have UAR values ranging from 1.34 to 6.71. Figure 17 shows the UAR data plotted against reciprocal dissolved-uranium concentrations and an expanded plot

showing the range of higher uranium concentrations. Samples from the Toroweap Formation have low UAR values, whereas springs from the other units have a large range of UAR values. Some springs were sampled more than once and repeat samples are similar (fig. 17). The lowest UAR was from Cottonwood (Tuckup) Spring, although the concentration of uranium was greater at Pigeon and Willow (Hack) Springs. Generally, there is an inverse relation between uranium concentration and UAR, where UAR is lower for higher uranium concentrations (fig. 17).

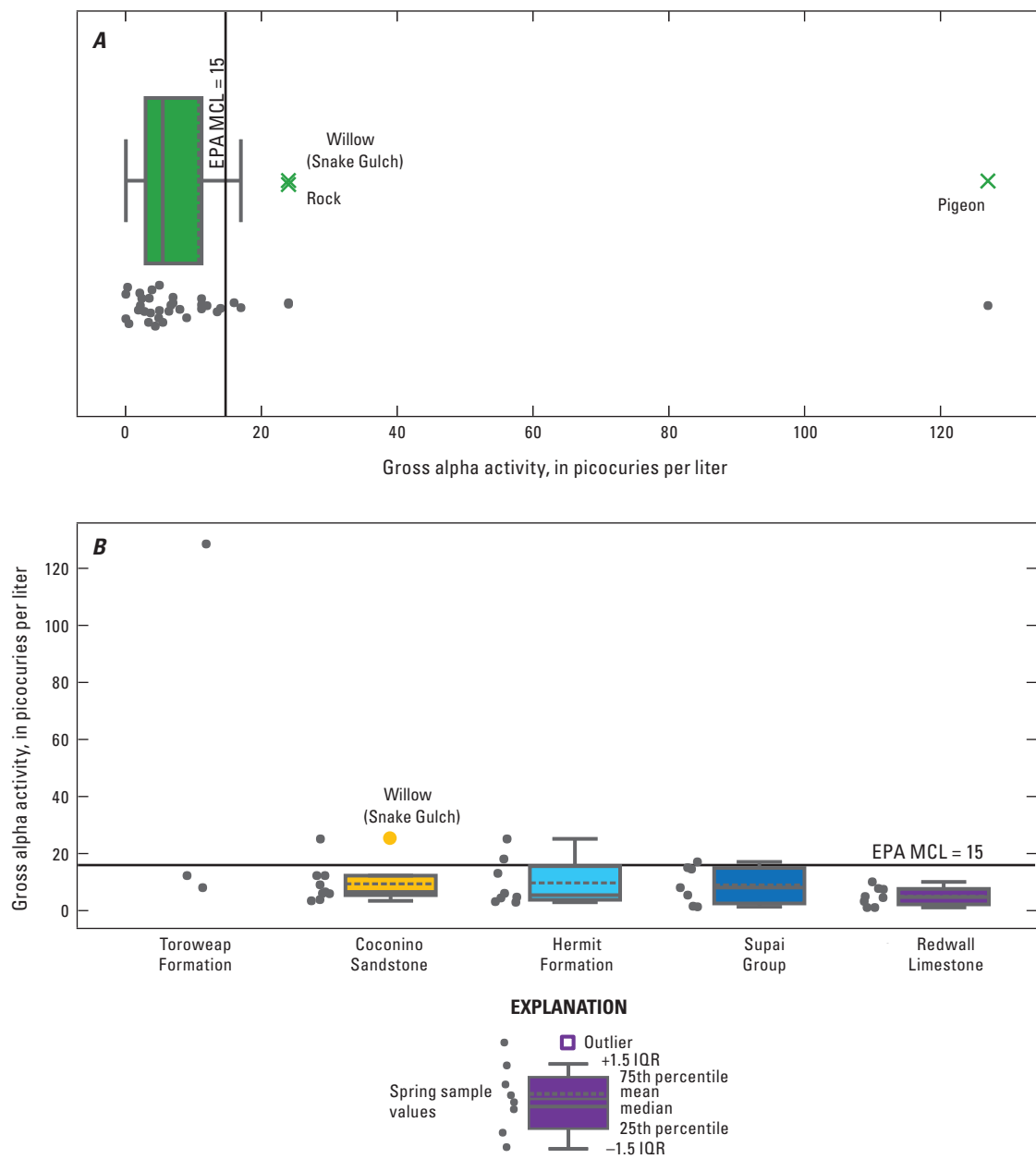
### Strontium Isotopes

Strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) provide a means for understanding the different rock types that groundwater may have interacted with along its flowpath. Values of  $^{87}\text{Sr}/^{86}\text{Sr}$  measured in spring water samples are within the range of values observed for sedimentary rocks in the region, from the Redwall Limestone to the Kaibab Formation (0.70756–0.71216; Monroe and others, 2005; Bills and others, 2007). The exception is water from Fence Spring, which had a substantially more radiogenic (higher proportion of  $^{87}\text{Sr}$ ) value of 0.71417 (fig. 18). Samples were not collected for strontium isotopic ratios from Saddle Horse and Water Canyon Springs.

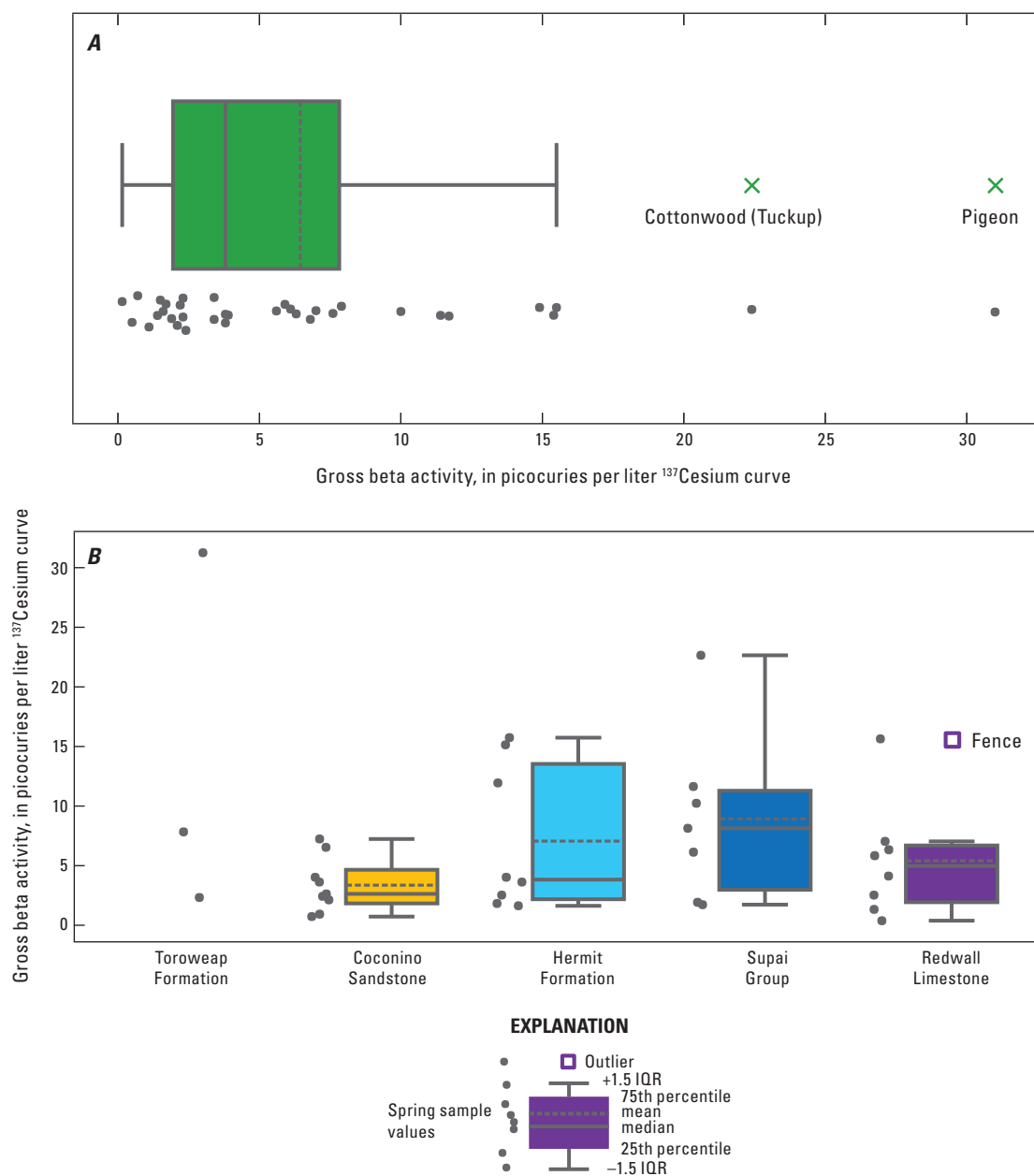
Values of  $^{87}\text{Sr}/^{86}\text{Sr}$  for most springs—excluding Fence Spring—fell into two general groups, those having higher strontium concentrations (greater than 350  $\mu\text{g}/\text{L}$ ) and lower  $^{87}\text{Sr}/^{86}\text{Sr}$  values (less than 0.7095) (group 1), or those with lower strontium concentrations (less than 90  $\mu\text{g}/\text{L}$ ) and higher  $^{87}\text{Sr}/^{86}\text{Sr}$  values (greater than 0.7095) (group 2) (fig. 18). Springs discharging from the Toroweap Formation and Supai Group all have characteristics of group 1. Springs discharging from the Coconino Sandstone, Hermit Formation, and Redwall Limestone rock units have samples that fall into both groups. The group 1 springs discharging from the Redwall Limestone include Buckfarm Canyon, Side Canyon, Showerbath, and Kanab Springs, and have strontium isotopic ratios similar to the average of the Redwall Limestone rocks (0.70875; Monroe and others, 2005; Bills and others, 2007). Group 2 includes two springs discharging from the Hermit Formation (Swamp and Powell Springs), one from the Coconino Sandstone (Big Spring), and four springs discharging from the Redwall Limestone (Unknown, Hole in the Wall, Hanging, and Vaseys Springs).



**Figure 14.** Gross alpha radioactivity from spring samples with different symbols by geologic unit of spring discharge. Location of mineralized breccia pipes can be found in the following references: Alpine, 2010; Brown and others, 1992; Chenoweth, 1986, 1988; Verbeek and others, 1988; Wenrich and others, 1988, 1990, 1997; Sutphin and Weinrich, 1989; VanGosen and Weinrich, 1989, 1991; Finch and others, 1990; Wenrich, 1992; Wenrich and Aumente-Modreski, 1994; Gardner, 1998; Mazeika, 2002; Ross and Moreton, 2012.

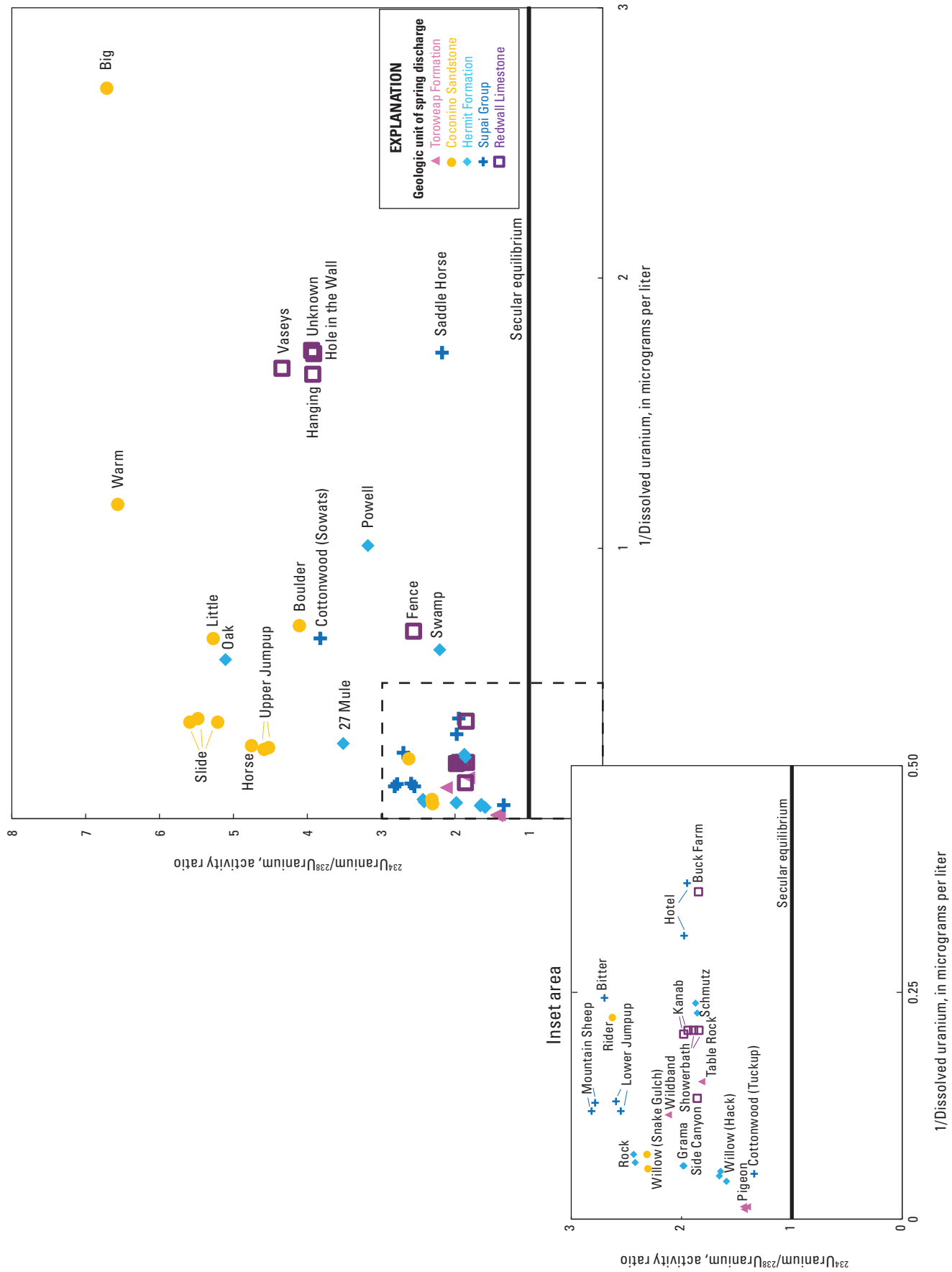


**Figure 15.** Distribution of gross alpha radioactivity for all spring sites (A) and divided by rock unit of spring discharge (B). EPA MCL, U.S. Environmental Protection Agency maximum contaminant level. The interquartile range (IQR) is the 25th to the 75th percentile.

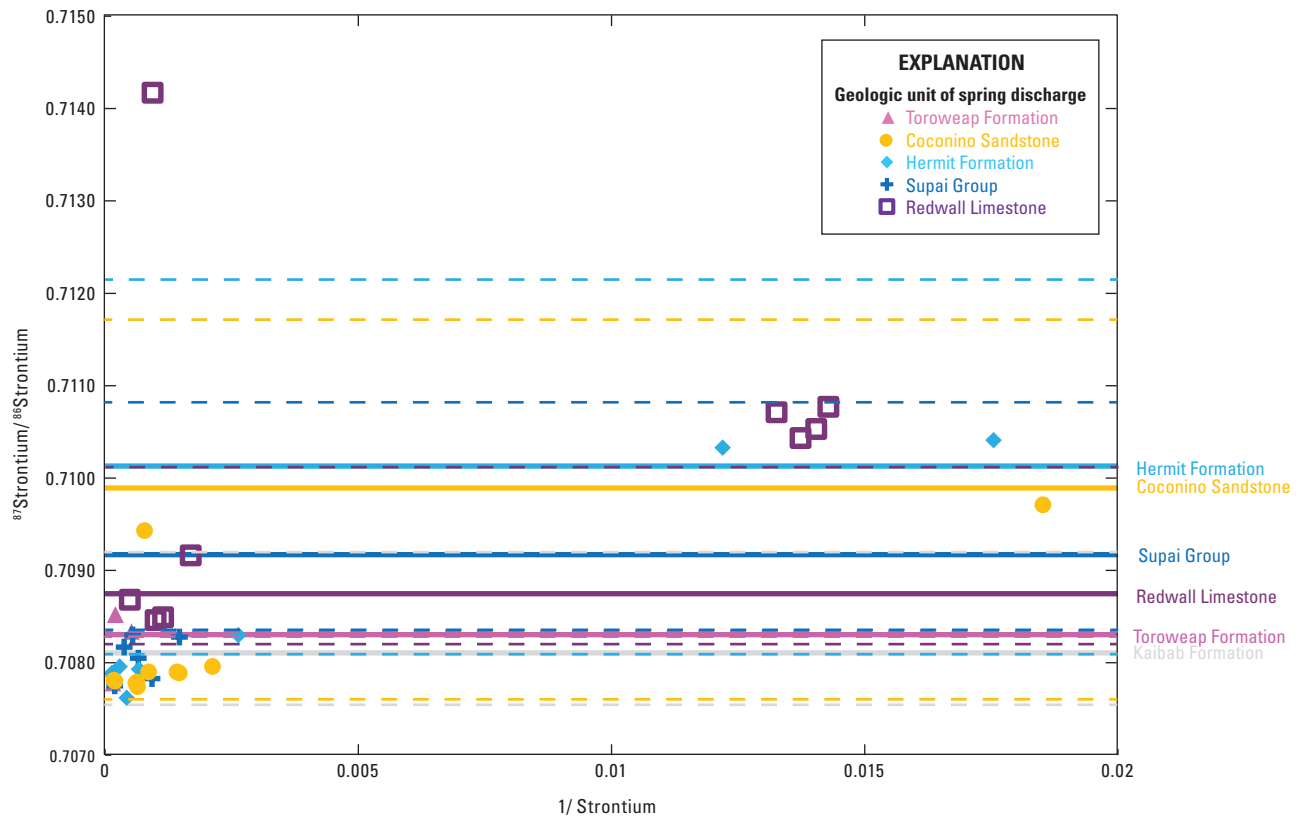


**Figure 16.** Distribution of gross beta radioactivity for all spring sites (A) and divided by rock unit of spring discharge (B). The interquartile range (IQR) is the 25th to the 75th percentile.





**Figure 17.** Uranium activity ratio data plotted against reciprocal uranium concentrations dissolved in spring samples collected from 2009 to 2016. Dashed area represents the area for the inset graph.



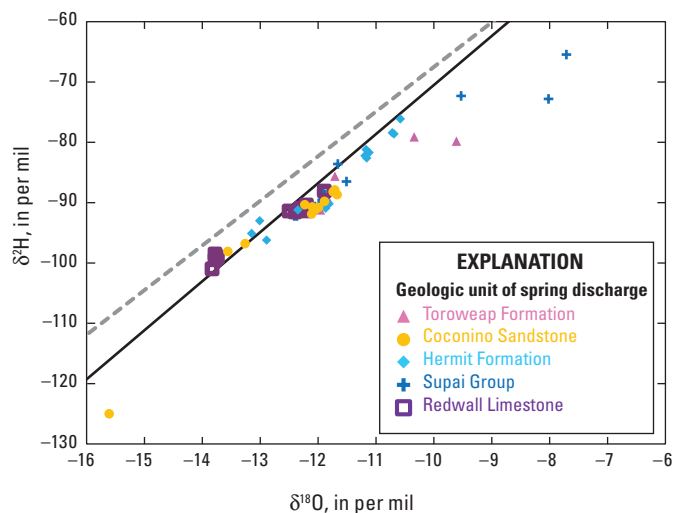
**Figure 18.** Strontium isotope ratio relative to the reciprocal strontium concentration for spring samples; values from rock samples in Bills and others (2007) and Monroe and others (2005). Solid lines represent rock, average value; dashed lines, minimum and maximum values.

### Oxygen and Hydrogen Stable Isotopes

The stable isotopes of oxygen and hydrogen can give a general indication of recharge elevation and evaporation. A local meteoric water line (LMWL) of  $\delta^2\text{H} = 7.4 \delta^{18}\text{O} + 6.5$  was developed for Grand Canyon National Park at Hopi Point (Pendall, 1997), which plots to the left of the global meteoric water line (GMWL; Craig, 1961) (fig. 19). All spring samples plot to the right of the LMWL and most plot to the right of the GMWL except Cottonwood (Tuckup), Swamp, Powell, Unknown, Hole in the Wall, Hanging, Fence, Warm, and Big Springs. Four springs (Water Canyon, Wildband, Bitter, and Hotel) plot farther to the right from the GMWL compared with other springs. Rider Spring is notable in that isotopic ratio is the most depleted of all the springs samples ( $\delta^{18}\text{O}$  of  $-15.61$  per mil,  $\delta^2\text{H}$  of  $-125$  per mil).

For springs discharging from the same rock unit groups, there are some general similarities and differences within each group. Toroweap Formation springs sampled for this study fell into two groups, one group (Table Rock and Pigeon Springs) had values in the middle range of all spring samples and one group had values farther to the right of the LMWL (Water Canyon and Wildband Springs). Coconino Sandstone springs generally have stable isotope values in the middle of the range of all spring samples ( $-12.23$  to  $-11.67$   $\delta^{18}\text{O}$  and  $-91.9$  to  $-87.9$   $\delta^2\text{H}$ ) except for springs with more depleted values;

Rider Spring, mentioned earlier, and Big and Warm Springs ( $-13.56$  to  $-13.26$   $\delta^{18}\text{O}$  and  $-98.1$  to  $-96.8$   $\delta^2\text{H}$ , respectively) which discharge on the Kaibab Plateau topographically above the surface expression of the Big Springs Fault. Hermit Formation springs span a large range of stable isotopic values



**Figure 19.** Stable isotope ratios ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) for spring samples. Global meteoric water line (solid line) from Craig (1961) and local meteoric water line (dashed line) from Pendall (1997).

with Swamp, Powell, and Oak Springs having more depleted stable isotopic values and Schmutz, Grama, and Willow (Hack) Springs having more enriched stable isotopic values. Supai Group springs generally plot near the middle range of spring values except for two sites (Bitter and Hotel Springs) that are more enriched and show strong evaporative signatures. Redwall Limestone springs plot in two general groups, one (Hanging, Unknown near Hanging, Hole in the Wall and Fence Springs) with a more depleted signature between the GMWL and LMWL, and one group in the middle range of the spring samples (Buck Farm Canyon, Side Canyon, Showerbath, and Kanab Springs). The depleted-isotopic group springs discharge in a similar geographic area (fig. 1) and may indicate a similar recharge elevation location.

## Groundwater Ages

### Carbon-14

Groundwater age is inferred from  $^{14}\text{C}$  with corrections based on total dissolved inorganic carbon (the sum of inorganic carbon species; carbonic acid, bicarbonate, and carbonate) and  $\delta^{13}\text{C}$ . Graphs of carbon species were made according to Han and others (2012) and Han and Plummer (2016) to understand the potential processes influencing carbon water chemistry at the spring sample sites before interpretation of groundwater age (fig. 20, table 6). The colored lines on figure 20 represent the “zero age” lines, which are determined by the  $^{14}\text{C}$  and  $\delta^{13}\text{C}$  values of the soil gas and solid carbonate. Samples that plot within the zero age lines on figure 20A have a zero radiocarbon age, which may be explained by geochemical reaction with no radiocarbon decay; samples above the zero age area are likely mixtures containing some  $^{14}\text{C}$  recharge water, and samples below the zero age (radiocarbon age area) may have a radiocarbon age greater than zero, which indicates the presence of old water that has undergone radiocarbon decay (Han and Plummer, 2016). Results from NetpathXL are presented in table 6 for both values of  $\delta^{13}\text{C}$  in carbonate rock and soil gas for the uncorrected age (user-defined) and

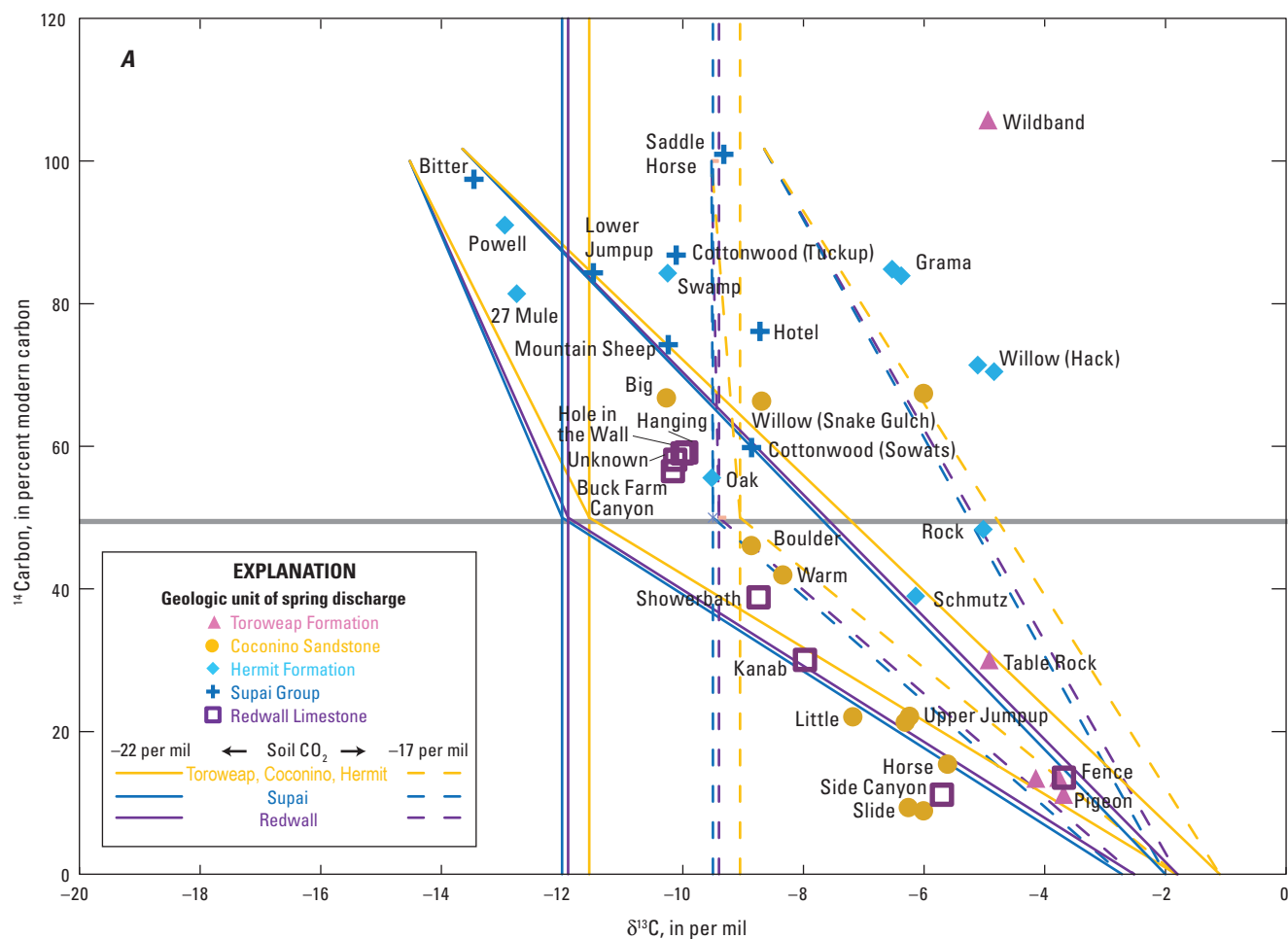
Revised Fontes and Garnier (solid exchange) (Han and Plummer, 2013).

Samples from several sites plot in the region below the zero age area, indicating that they may be old waters that could have undergone  $^{14}\text{C}$  decay (fig. 20A) (Han and others, 2012). Sites with a possible radiocarbon age using the values of  $\delta^{13}\text{C}$  in the soil gas  $\text{CO}_2$  and carbonate rock of  $-22$  and  $-1.1$  and  $-1.8$  per mil (Coconino and Redwall springs respectively) are Slide, Horse, Little, Upper Jumpup, and Kanab Springs. Sites with a possible radiocarbon age using  $-17$  for  $\delta^{13}\text{C}$  in the soil gas  $\text{CO}_2$  and  $-1.1$  (Toroweap Formation and Coconino Sandstone springs) and  $-1.8$  per mil (Redwall Limestone springs) include all of the sites listed previously as well as the following sites: Pigeon, Warm, and Fence Springs. Showerbath and Boulder Springs are near the radiocarbon zero-age area and may have a radiocarbon age depending on the soil and rock values used in the age correction (fig. 20, table 6).

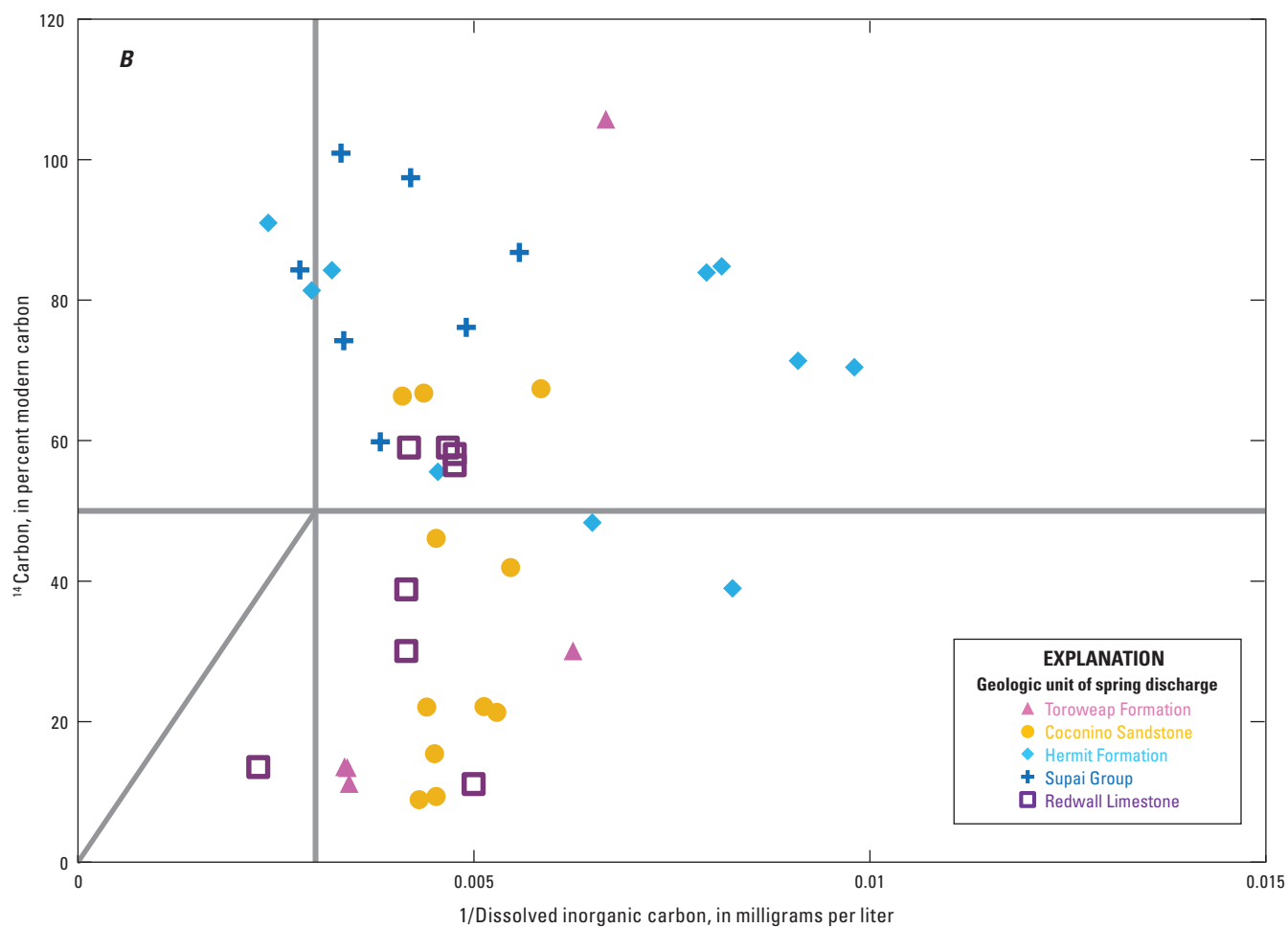
### Tritium

Tritium values ranged from  $-0.9$  pCi/L (which is below the reporting limit of  $0.5$  pCi/L) to  $11.5$  pCi/L. The tritium data indicate that the groundwater present at the spring sites was either primarily recharged prior to 1952 (pre-modern) or is a mixture of modern and pre-modern waters.

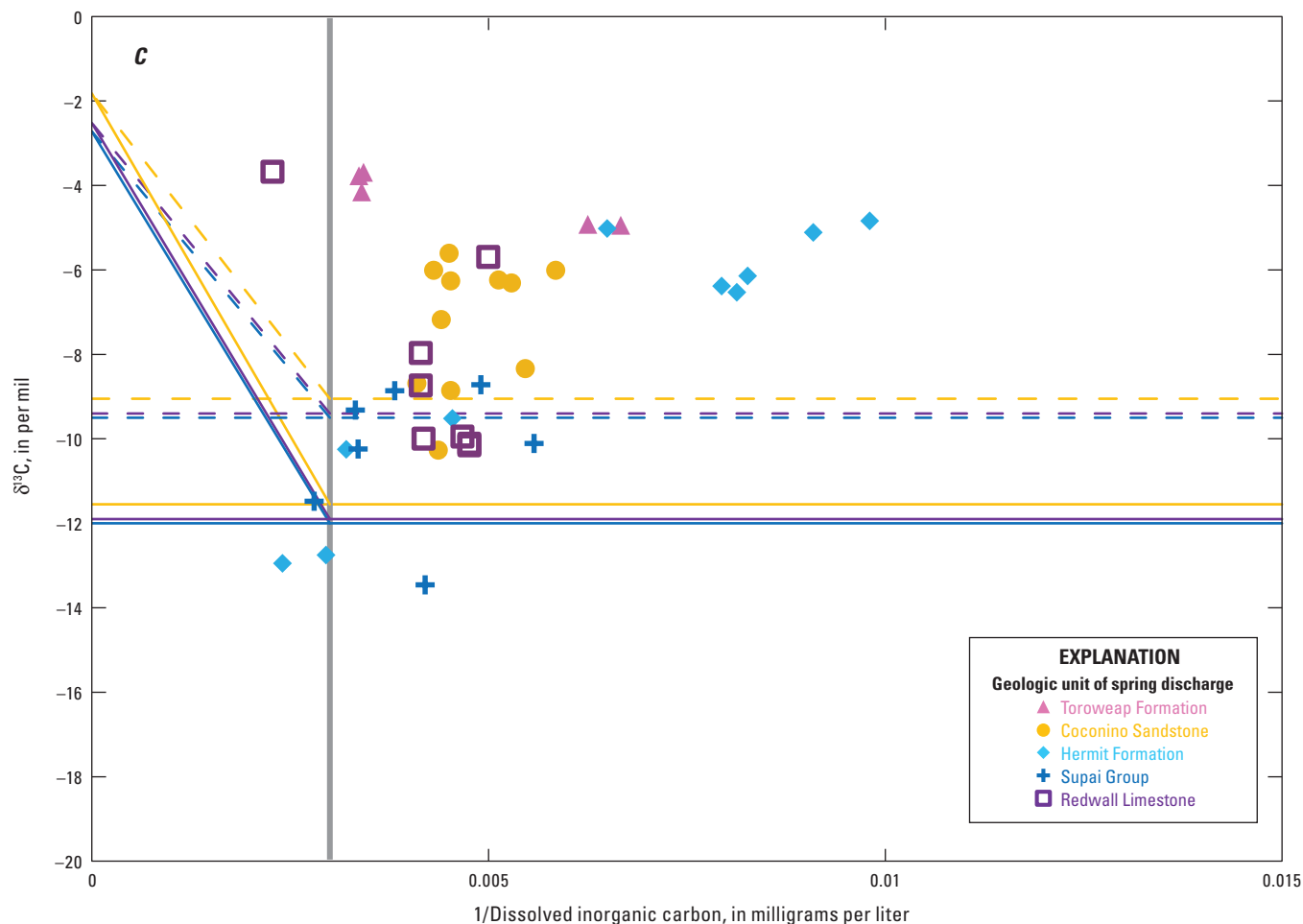
Bitter Spring had the highest tritium value of  $11.5$  pCi/L and is just below the threshold for being categorized as primarily modern water. None of the spring samples had tritium values that were statistical outliers from the entire dataset (fig. 21A). Tritium values were greater than the 75th percentile of the data ( $5.1$  pCi/L) for the following springs, Willow (Hack), Saddle Horse, Cottonwood (Tuckup), Hotel, Bitter, Unknown, Hole in the Wall, and Hanging. Willow (Hack) Spring was a high statistical outlier ( $6.38$  pCi/L) for springs discharging from the Hermit Formation (fig. 21B). The tritium values generally increased with deeper rock units, springs discharging from the Supai Group and Redwall Limestone had the highest median values.



**Figure 20.** Carbon data from spring water including <sup>14</sup>C versus δ<sup>13</sup>C (A), <sup>14</sup>C versus 1/dissolved inorganic carbon (B), and δ<sup>13</sup>C versus 1/dissolved inorganic carbon (C). The solid horizontal and vertical gray lines represent Tamers X and (or) Y. The colored angled lines represent the zero age lines, which are determined by the carbon-14 and δ<sup>13</sup>C values of the soil gas and solid carbonate.



**Figure 20.** Carbon data from spring water including  $^{14}\text{C}$  versus  $\delta^{13}\text{C}$  (A),  $^{14}\text{C}$  versus 1/dissolved inorganic carbon (B), and  $\delta^{13}\text{C}$  versus 1/dissolved inorganic carbon (C). The solid horizontal and vertical gray lines represent Tamers X and (or) Y. The colored angled lines represent the zero age lines, which are determined by the carbon-14 and  $\delta^{13}\text{C}$  values of the soil gas and solid carbonate. —Continued



**Figure 20.** Carbon data from spring water including  $^{14}\text{C}$  versus  $\delta^{13}\text{C}$  (A),  $^{14}\text{C}$  versus 1/dissolved inorganic carbon (B), and  $\delta^{13}\text{C}$  versus 1/dissolved inorganic carbon (C). The solid horizontal and vertical gray lines represent Tamers X and (or) Y. The colored angled lines represent the zero age lines, which are determined by the carbon-14 and  $\delta^{13}\text{C}$  values of the soil gas and solid carbonate. —Continued



**Table 6.** Groundwater corrected age values.

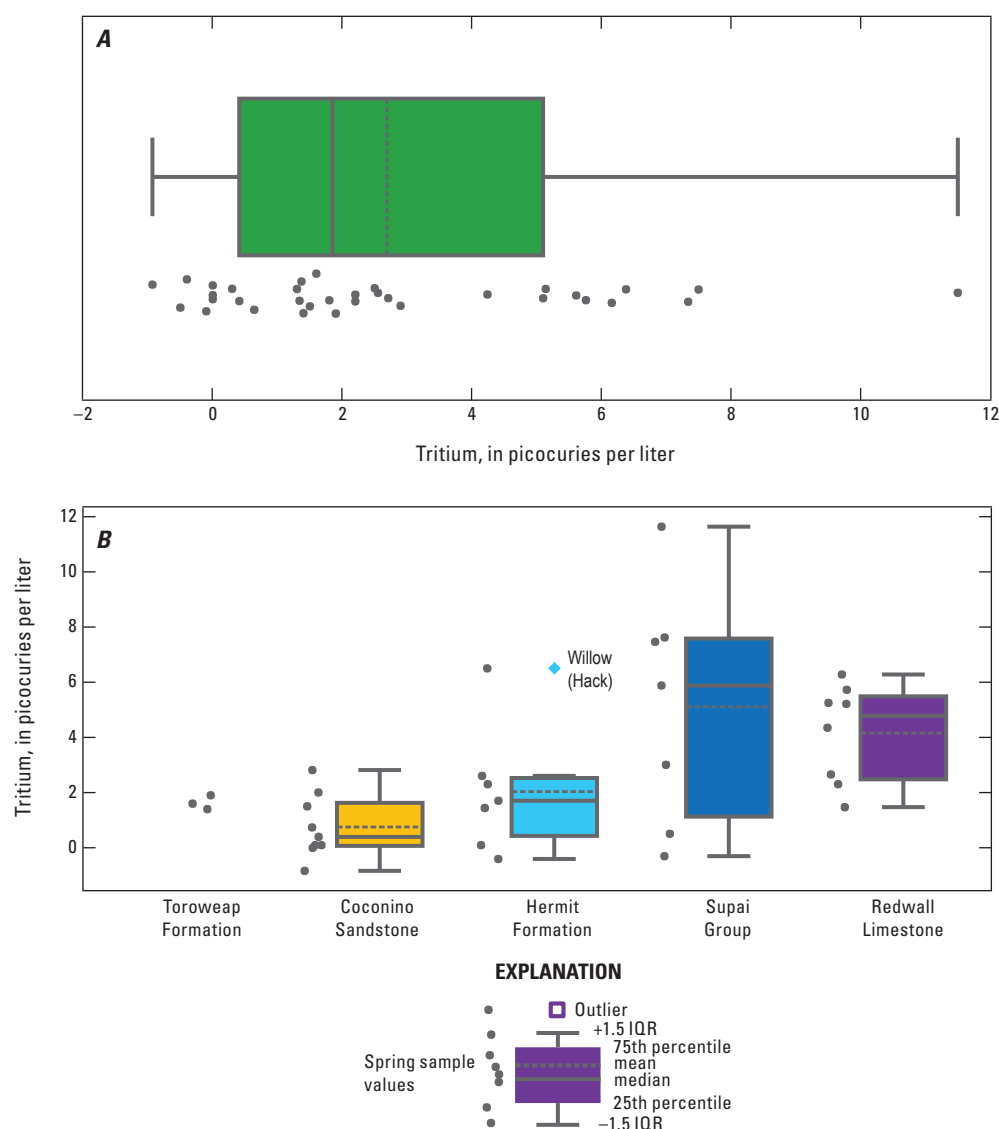
[pCi/L, picocuries per liter; pM, absolute percent modern (normalized); pmc, percent modern carbon (denormalized); R, radiochemistry non-detect; NA, not applicable; B. P., before present]

USGS site number	Common name	Sample date	Tritium (pCi/L)	Tritium error (pCi/L)	Denormalized <sup>14</sup> C (pmc)	Normalized <sup>14</sup> C (pM)	<sup>14</sup> C error (pM)	<sup>13</sup> C (per mil)	Uncorrected age	Minimum corrected age, in years B.P. (-22 per mil soil $\delta^{13}\text{C} - \text{CO}_2$ )	Maximum corrected age, in years B.P. (-17 per mil soil $\delta^{13}\text{C} - \text{CO}_2$ )	Average overlying rock unit $\delta^{13}\text{C}$ (per mil)	Categorical determination
364242112274701	Table Rock Spring	8/27/2015	1.5	0.27	30.06	29.09	0.16	-4.92	9,935	NA	NA	-1.1	Possible mixture
364259112303201	Wildband Spring	11/6/2012	1.8	0.42	105.76	102.3	0.27	-4.94	-463	NA	NA	-1.1	Possible mixture
364327112303101	Pigeon Spring	3/15/2012	1.3	0.41	13.60	13.12	0.11	-3.77	16,496	-1,175	969	-1.1	Possible mixture
364327112303101	Pigeon Spring	11/7/2012	0.9	0.26	11.20	10.81	0.14	-3.69	18,095	-420	1,776	-1.1	Pre-modern
364327112303101	Pigeon Spring	9/10/2014	0.8	0.29	13.45	12.99	0.07	-4.15	16,586	-1,904	418	-1.1	Pre-modern
363450112325001	Upper Jumpup Spring	8/27/2009	R -0.9	0.89	22.11	21.44	0.19	-6.24	12,474	67	2,279	-1.1	Pre-modern
363450112325001	Upper Jumpup Spring	7/7/2015	NA		21.30	20.67	0.08	-6.31	12,783	323	2,536	-1.1	
363607112205201	Big Spring	5/11/2016	2.71	0.41	66.76	65.31	0.15	-10.27	3,340	NA	NA	-1.1	Possible mixture
363741112350501	Little Spring	11/10/2015	R 0	0.28	22.07	21.45	0.09	-7.18	12,492	1,567	3,791	-1.1	Pre-modern
363756112350101	Boulder Spring	11/10/2015	R -0.1	0.32	46.08	44.94	0.14	-8.86	6,406	-2,400	-177	-1.1	Pre-modern
363901112341601	Horse Spring	8/25/2015	0.3	0.27	15.43	14.95	0.09	-5.61	15,450	1,537	3,818	-1.1	Pre-modern
363907111471701	Rider Spring	8/25/2009	0.6	0.96	NA	NA	NA	NA	NA	NA	NA	NA	Pre-modern
363922112334501	Slide Spring	8/27/2009	R 0	0.89	8.86	8.59	0.09	-6.01	20,031	7,058	9,302	-1.1	Pre-modern
363922112334501	Slide Spring	8/25/2015	0.4	0.31	9.34	9.06	0.07	-6.26	19,601	6,978	9,222	-1.1	Pre-modern
364143112184501	Warm Springs	8/26/2015	1.4	0.3	41.93	40.85	0.13	-8.34	7,186	-2,183	1	-1.1	Possible mixture
364210112310501	Willow Spring (Snake Gulch)	3/15/2012	1.9	0.43	67.38	65.32	0.2	-6.01	3,264	NA	NA	-1.1	Possible mixture
364210112310501	Willow Spring (Snake Gulch)	11/7/2012	1.7	0.39	66.32	64.64	0.16	-8.69	3,395	NA	NA	-1.1	Possible mixture
361959112210401	Swamp Spring	11/12/2015	2.2	0.42	84.26	82.41	0.21	-10.25	1,416	NA	NA	-1.1	Possible mixture
362045112212801	Powell Spring	11/12/2015	2.5	0.36	91.00	89.49	0.22	-12.95	780	NA	NA	-1.1	Possible mixture
362143112551201	Schmutz Spring	8/25/2009	1.6	0.96	38.99	37.79	0.2	-6.14	7,787	NA	NA	-1.1	Possible mixture
363014112325201	27 Mule Spring	4/22/2016	R -0.5	0.48	81.39	80.02	0.18	-12.75	1,702	NA	NA	-1.1	Pre-modern
363357112440801	Willow Spring (Hack Canyon)	8/26/2009	6.4	0.96	70.45	68.11	0.31	-4.84	2,895	NA	NA	-1.1	Possible mixture
363357112440801	Willow Spring (Hack Canyon)	11/8/2012	5	0.34	71.38	69.07	0.17	-5.11	2,787	NA	NA	-1.1	Possible mixture

Table 6. Groundwater corrected age values.—Continued

[pCi/L, picocuries per liter; pM, absolute percent modern (normalized); pmc, percent modern carbon (denormalized); R, radiochemistry non-detect; NA, not applicable; B.P., before present]

USGS site number	Common name	Sample date	Tritium (pCi/L)	Tritium error (pCi/L)	Denormalized <sup>14</sup> C (pmc)	Normalized <sup>14</sup> C (pM)	<sup>14</sup> C error (pM)	<sup>13</sup> C (per mil)	Uncorrected age	Minimum corrected age, in years B.P. (–22 per mil soil δ <sup>13</sup> C – CO <sub>2</sub> )	Maximum corrected age, in years B.P. (–17 per mil soil δ <sup>13</sup> C – CO <sub>2</sub> )	Average overlying rock unit δ <sup>13</sup> C (per mil)	Categorical determination
363521112394601	Grama Spring	8/10/2011	NA		84.82	82.3	0.29	–6.53	1361	NA	NA	–1.1	
363521112394601	Grama Spring	11/8/2012	3.4	0.3	83.92	81.41	0.2	–6.38	1449	NA	NA	–1.1	Possible mixture
364038112201001	Oak Spring	11/10/2015	R 0.0	0.29	55.58	54.28	0.16	–9.52	4856	NA	NA	–1.1	Pre-modern
364101112340601	Rock Spring	9/2/2009	1.3	0.93	48.35	46.76	0.3	–5.02	6007	NA	NA	–1.1	Possible mixture
361344113032001	Saddle Horse Spring	9/9/2014	7.5	0.53	100.93	98.52	0.2	–9.32	–77	NA	NA	–2	Possible mixture
361944112551001	Cottonwood Spring (Tuckup Canyon)	4/8/2016	5.8	0.66	86.81	84.89	0.22	–10.11	1170	NA	NA	–2	Possible mixture
362157112451601	Hotel Spring	8/25/2009	7.3	0.96	76.12	74.17	0.3	–8.72	2255	NA	NA	–2	Possible mixture
363110112314601	Cottonwood Spring (Sowats)	4/22/2016	R –0.4	0.54	59.83	58.36	0.17	–8.86	4246	NA	NA	–2	Pre-modern
363115112342601	Mountain Sheep Spring	9/1/2009	2.9	0.86	74.23	72.55	0.34	–10.24	2463	NA	NA	–2	Possible mixture
363135112330601	Bitter Spring	11/14/2015	11.5	1.4	97.45	95.93	0.22	–13.46	214	NA	NA	–2	Possible mixture
363209112350801	Lower Jumpup Spring	8/28/2009	0.4	0.89	84.31	82.61	0.3	–11.48	1411	NA	NA	–2	Pre-modern
362434111533601	Buck Farm Canyon Spring	8/23/2009	4.2	0.57	58.98	57.62	0.23	–10	4364	NA	NA	–1.8	Possible mixture
362702112394701	Side Canyon Spring	8/26/2009	1.4	0.89	11.10	10.75	0.1	–5.7	18172	2,595	5,052	–1.8	Possible mixture
362723112382801	Showerbath Spring	8/26/2009	5.1	0.96	38.79	37.8	0.18	–8.74	7828	–1,975	437	–1.8	Possible mixture
362802112374601	Kanab Spring	8/26/2009	2.2	0.93	30.02	29.21	0.21	–7.97	9946	–973	1,450	–1.8	Possible mixture
362827111504101	Unknown Spring near Hanging Springs	8/21/2009	6.2	0.64	56.48	55.19	0.25	–10.16	4723	NA	NA	–1.8	Possible mixture
362831111504401	Hole in the Wall Spring	8/22/2009	5.1	0.64	58.08	56.75	0.27	–10.12	4492	NA	NA	–1.8	Possible mixture
362837111504201	Hanging Spring	8/22/2009	5.6	0.61	58.99	57.62	0.26	–9.95	4363	NA	NA	–1.8	Possible mixture
363123111503101	Fence Spring	8/20/2009	2.6	1.6	13.50	13.02	0.12	–3.68	16,554	–8,851	–6,362	–1.8	Possible mixture



**Figure 21.** Tritium for all samples (A) and divided by rock unit of spring discharge (B). The interquartile range (IQR) is the 25th to the 75th percentile.

Tritium values are generally higher in samples with high  $^{14}\text{C}$  values, but there are tritium values as high as 5.1 pCi/L for spring samples with  $^{14}\text{C}$  carbon-14 values less than 50 percent modern carbon (fig. 22). Waters with tritium and low  $^{14}\text{C}$  carbon-14 values may represent a mixture of modern and pre-modern water. The following samples do not have tritium values above the reporting limit of 0.5 pCi/L and likely do not have a component of modern water (post-1952): Upper and Lower Jumpup, Little, Boulder, Horse, Slide, 27 Mule, Oak, and Cottonwood (Sowats) Springs (table 6). Of the aforementioned springs, 27 Mule, Oak, Cottonwood (Sowats), and Lower Jumpup have  $^{14}\text{C}$  values greater than 50 percent

modern carbon, ranging from 55.58 to 84.31 pmc. These springs may include water that was recharged prior to 1952, but is not old enough to be dated using radiocarbon techniques. The springs also fall within the zero age area of figure 20 for given soil gas and rock values, and may indicate some equilibrium condition with respect to carbon that precludes radiocarbon age determination. Two springs, Pigeon and Rider, have tritium values below 1.3 pCi/L, which are categorically determined to be pre-modern. These springs may have a very small component of modern water or may include water recharged in the decades prior to 1952.

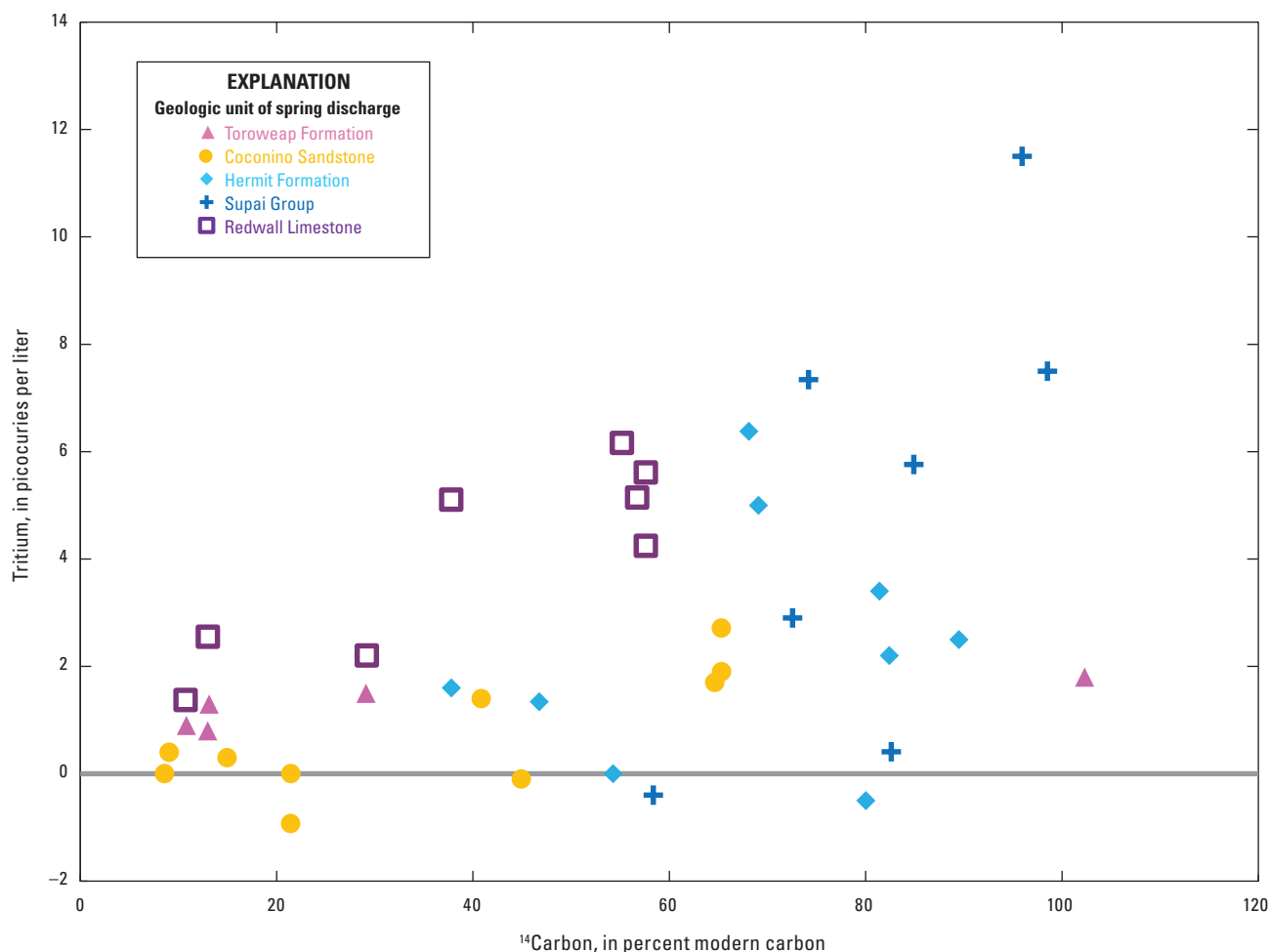


Figure 22. Tritium versus uncorrected carbon-14 values.

## Discussion

### Evidence for Water Rock Interaction with Implication for Flowpaths

The hydrologic system in the area is generally understood to consist of a series of perched aquifers of limited extent situated above unsaturated rock, with the regional Redwall-Muav aquifer below (Bills and others, 2010). This study evaluated the chemistry of water collected by the USGS between 2009 and 2016 discharging from perched springs in the Toroweap and Hermit Formations, Coconino Sandstone, and Supai Group, and regional springs in the Redwall Limestone.

A conceptual model of the flowpath to each spring is important to understand differences in chemistry compared to general trends of spring groups. General chemical characteristics for this data set are explored and specific springs with unique chemistry are discussed. More information is needed to be able to model the evolution of water through the subsurface for each individual spring, but the analysis in this report can provide a basis for that understanding, which is beyond the scope of this report.

Lower values of specific conductance in water discharging from springs in the Coconino Sandstone compared to water discharging from the overlying Toroweap Formation (fig. 4C) are likely caused by lower calcium, magnesium, and sulfate concentrations (figs. 5A,B and 6D). Fresher groundwater (lower specific conductance) in Coconino Sandstone springs may indicate that flow has not been affected greatly by water-rock interactions with gypsum present in the Kaibab and Toroweap Formations, and may indicate that water may move through the overlying units fairly quickly. Willow (Snake Gulch) Spring is an exception for Coconino Sandstone springs, and has a geochemical composition more similar to waters discharging from the Toroweap Formation (see fig. 7).

Strontium concentrations were low (less than 90  $\mu\text{g/L}$ ) and strontium isotope ratios were high (greater than 0.7095) for Big, Swamp, Powell, Unknown, Hole in the Wall, Hanging, and Vaseys Springs discharging from Coconino Sandstone, Hermit Formation, and Redwall Limestone. This may indicate that the water discharging at these springs is not interacting with Kaibab or Toroweap Formation rocks for very long, as springs discharging from the Toroweap Formation have high strontium concentrations (greater than 1,900  $\mu\text{g/L}$ ) and low

strontium isotopic ratios (less than 0.70852). Saddle Horse Spring, which discharges from the Supai Group, had a low strontium concentration of 117  $\mu\text{g/L}$ , but the strontium isotope ratio was not measured. The low strontium concentration may indicate that Saddle Horse Spring has similar characteristics to the aforementioned springs, and resampling may clarify the connections. There was some variation in the strontium isotopic values within rocks collected from the same geologic unit (Monroe and others, 2005; Bills and others, 2007), so additional analysis of strontium isotopic values in rock units from this study area would help with the interpretation of groundwater interaction.

All spring samples plot to the right of the LMWL and most also plot to the right of the GMWL suggesting that the water has undergone evaporation or that the springs were recharged by different moisture sources (fig. 19). Soil water near Red Butte, Ariz. (just south of the Grand Canyon) collected as part of another study plotted to the right of the LMWL—indicating evaporation influence (Pendall, 1997)—which suggests that the evaporation signature of the spring groundwater samples might result from groundwater infiltration. Localized water cycling, such as groundwater discharge that infiltrates and later emerges at another spring, could also contribute to the evaporative signature observed at the springs in this study. Springs that plot to the left or near the GMWL include Cottonwood (Tuckup), Swamp, Powell, Unknown, Hole in the Wall, Hanging, Fence, Warm and Big Springs. With the exception of Cottonwood (Tuckup) Spring, the aforementioned springs also have more depleted stable isotope values (less than  $-13$  per mil  $\delta^{18}\text{O}$ ). These springs are located on the margin of the Kaibab Plateau uplift and may indicate that the water discharging at these springs was recharged at a higher elevation. The isotopic ratio of Rider Spring is the most depleted of all of the spring samples ( $-15.61$ ,  $-125$  per mil), indicating that the water discharging at Rider Spring recharged at a distinctly higher elevation or from a colder climate compared to the other springs and that the water has undergone some evaporation, as it plots to the right of the GMWL.

Elevated tritium values (greater than 1.3 pCi/L) in groundwater discharging from stratigraphically lower rock units (Supai Group and Redwall Limestone springs; fig. 21) may indicate that a component of modern recharge can quickly (on the order of decades) move through the upper stratigraphic units to lower stratigraphic units. Rapid recharge would likely require flow through fractures or other preferential pathways. A general trend of increasing tritium concentrations with stratigraphic depth (fig. 21) indicates that some component of modern recharge ( $>28.4$  pCi/L) is present in the system and might suggest that high tritium associated with the bomb-peak is discernable in groundwater and gradually infiltrating to greater depth in the study area.

Corrected  $^{14}\text{C}$  activities and interpreted ages indicate that most springs discharging from the Hermit Formation, Supai Group, and Redwall Limestone do not have waters with radiocarbon age. Side Canyon, Showerbath, and Kanab Springs suggest a mixture of water with a radiocarbon age and modern water (table 6). Springs with a possible component of water with a radiocarbon age from this study discharge

from the Toroweap Formation and Coconino Sandstone. The calculated corrected groundwater ages are sensitive to the value of  $\delta^{13}\text{C}$  in the soil gas  $\text{CO}_2$  and carbonate rock, with the oldest ages using a soil gas value of  $-17$  per mil. Using a soil gas value of  $-22$  per mil decreases the corrected age for the springs and also results in negative ages for some of the samples, indicating that the correction methods are not appropriate for calculating the groundwater age or that the sample plots near the zero age line. There was some variation in the  $\delta^{13}\text{C}$  data from Monroe and others (2005) and Bills and others (2007), so analysis of  $\delta^{13}\text{C}$  in rock units from this study area would help with the interpretation of the age dating of the groundwater. A soil gas  $\text{CO}_2$  value of  $-22$  per mil for  $\delta^{13}\text{C}$  was used based on the values from Hart and others (2010) for C3-plant-dominated areas in Utah and  $-17$  per mil for a more arid area of the study. The biome for the majority of the study area is Great Basin Conifer, which is dominated by C3 plants; the Great Basin Desert Scrub biome is present in lower elevations on the west side of the study area (Arizona Game and Fish Department, 2015). The plant communities have been consistent for the last 14,040 yr B.P. in the area to the north of the Grand Canyon (Anderson and others, 2000), which includes springs with the range of corrected groundwater ages. Appelo and Postma (2005) report  $-27$  per mil for  $\delta^{13}\text{C}$  of C3 plants and some arid-zone C4 plants have a heavier  $\delta^{13}\text{C}$  value of  $-13$  per mil (Farquhar and others, 1989; Vogel, 1993). The  $-17$  and  $-22$  per mil values may represent a mixture of C3 and C4 plants, and provides a good estimation for the age of the groundwater in this study. Soil gas  $\delta^{13}\text{C}$  values for the study area would help better constrain the age of the groundwater at the sampled sites. A more detailed understanding of water-rock interactions along flowpaths contributing to discharge at the springs described in this study would result in better age constraints, and would likely need to be conducted separately for each spring.

## Springs with Elevated Uranium and Selenium Concentrations

Groundwater discharge from springs including Cottonwood (Tuckup), Grama, Pigeon, Rock, and Willow (Hack and Snake Gulch) Springs had uranium concentrations greater than 10  $\mu\text{g/L}$  (fig. 8C), which was considered to be above the threshold for anomalous uranium concentrations for the Snake Gulch area by Billingsley and others (1983). Groundwater from these springs were dominated by  $\text{Ca-Mg-SO}_4$ , and the specific conductance of these springs ranged from 2,350 to 3,440  $\mu\text{S/cm}$ . These springs were more closely associated with each other compared with other springs in this study on the basis of U, Mo, Sr, Se, and Li in a multivariate analysis (fig. 11), and U was significantly positively correlated with Li, Mo, Se, Sr, and Zn (fig. 12). The  $^{87}\text{Sr}/^{86}\text{Sr}$  values in these springs ranged from 0.70775 to 0.70852 and UAR values in these springs ranged from 1.34 to 2.31. Groundwater from all of these springs had detectable tritium ranging from 0.8 to 6.38 pCi/L, and interpretation of carbon data (fig. 20) from these springs indicate they may contain mixtures of modern

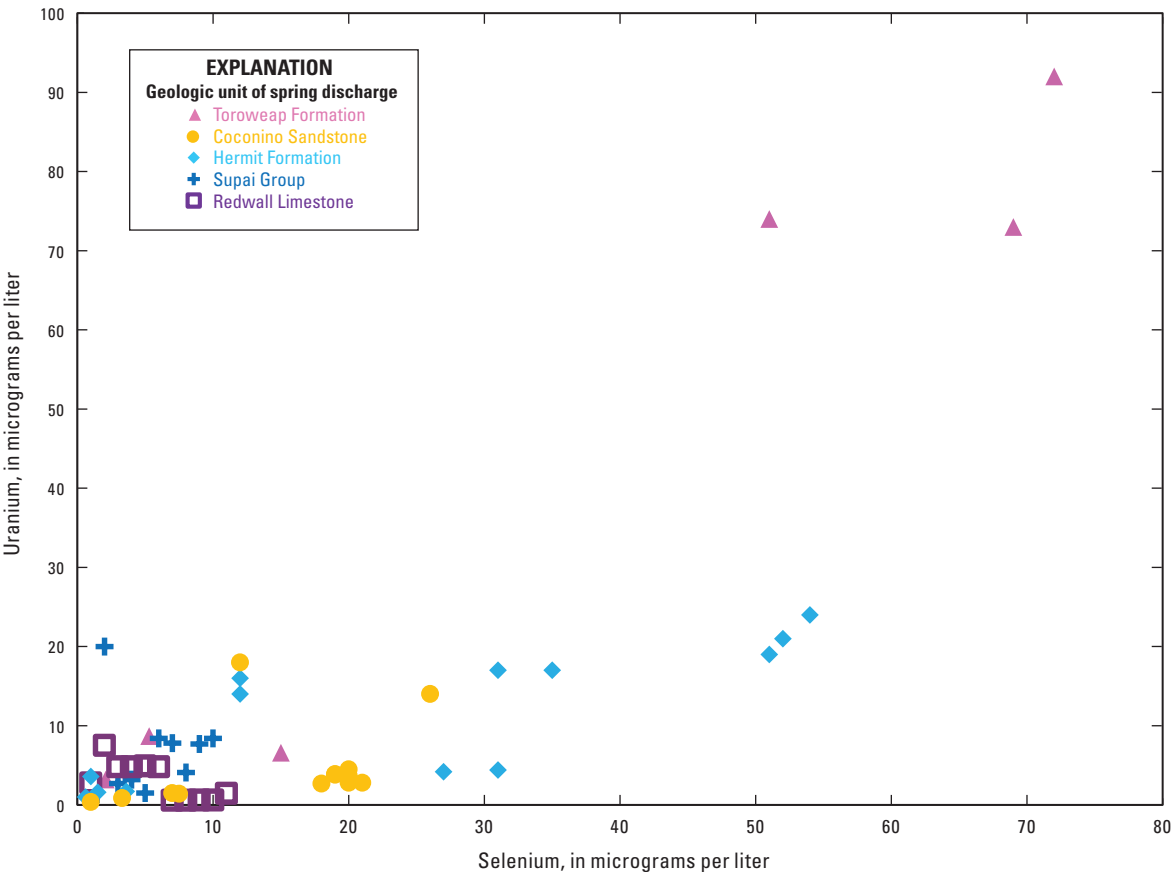
and pre-modern waters. Pigeon Spring may contain water with a radiocarbon age, depending on the parameters (soil gas CO<sub>2</sub> and rock δ<sup>13</sup>C) used to calculate groundwater age. The tritium values from multiple samples at the site fall within the pre-modern and possible mixture classification (table 6).

Springs with elevated uranium concentrations also tend to have elevated selenium concentrations (figs. 8 and 23). Selenium and uranium are positively correlated with a Kendall's Tau value of 0.57 that is significant at the <0.05 p-value threshold (fig. 12). Selenium is known to be concentrated in fine-grained marine sedimentary rocks of Late Cretaceous age (Seiler and others, 2003). Although there are no rocks of Cretaceous age present in the study area, Seiler and others (2003) suggest that any marine deposit formed in a shallow, biologically productive environment may be seleniferous. Selenium is commonly associated with Ca, Mg, SO<sub>4</sub>, Na, and U in waters from the western United States (Seiler and others, 2003).

Mazeika (2002) analyzed the geochemistry associated with mineralization in the Sage breccia pipe south of Grand Canyon. Selenium was associated with iron mineralization of the breccia pipe. The highest selenium concentrations were present in the Coconino Sandstone from core near the Sage breccia pipe and just below the Toroweap Formation/Coconino Sandstone contact as disseminated pyrite changes to iron oxide sandstone (Mazeika, 2002). Other high selenium concentrations were found in some high-uranium samples at

stratigraphic levels in the pipe equivalent to rocks of the Hermit Formation and Esplanade Sandstone (Mazeika, 2002).

Similar geochemical compositions of spring waters having elevated uranium concentrations are observed at sites located both near, and away from, sites of uranium-mining activities in the present study. In a principal component analysis of leachates of uranium-mining associated material from Pigeon Mine and groundwater springs (Horse, Pigeon, Rock, Slide, Table Rock, Upper Jumpup, Warm, Wildband, and Willow [Snake Gulch] Springs) near the Pigeon Mine, selenium was more associated with the groundwater spring samples than the mining waste material (Beisner and others, 2017). In that study, there was no evidence for physical movement of water from the nearby Pigeon Mine towards Pigeon Spring, which has elevated uranium and selenium concentrations. Additionally, uranium concentrations in the mine associated material leachates were orders of magnitude greater than values in spring water, whereas selenium concentrations in the two components were of similar magnitude. Therefore, simple dilution was not considered to be a plausible explanation. Mining does not appear to explain the presence of elevated uranium concentrations in groundwater at springs noted here. However, there is the possibility that changes in groundwater chemistry associated with uranium mining activity had not arrived at spring discharge locations at the time of sampling for this study.



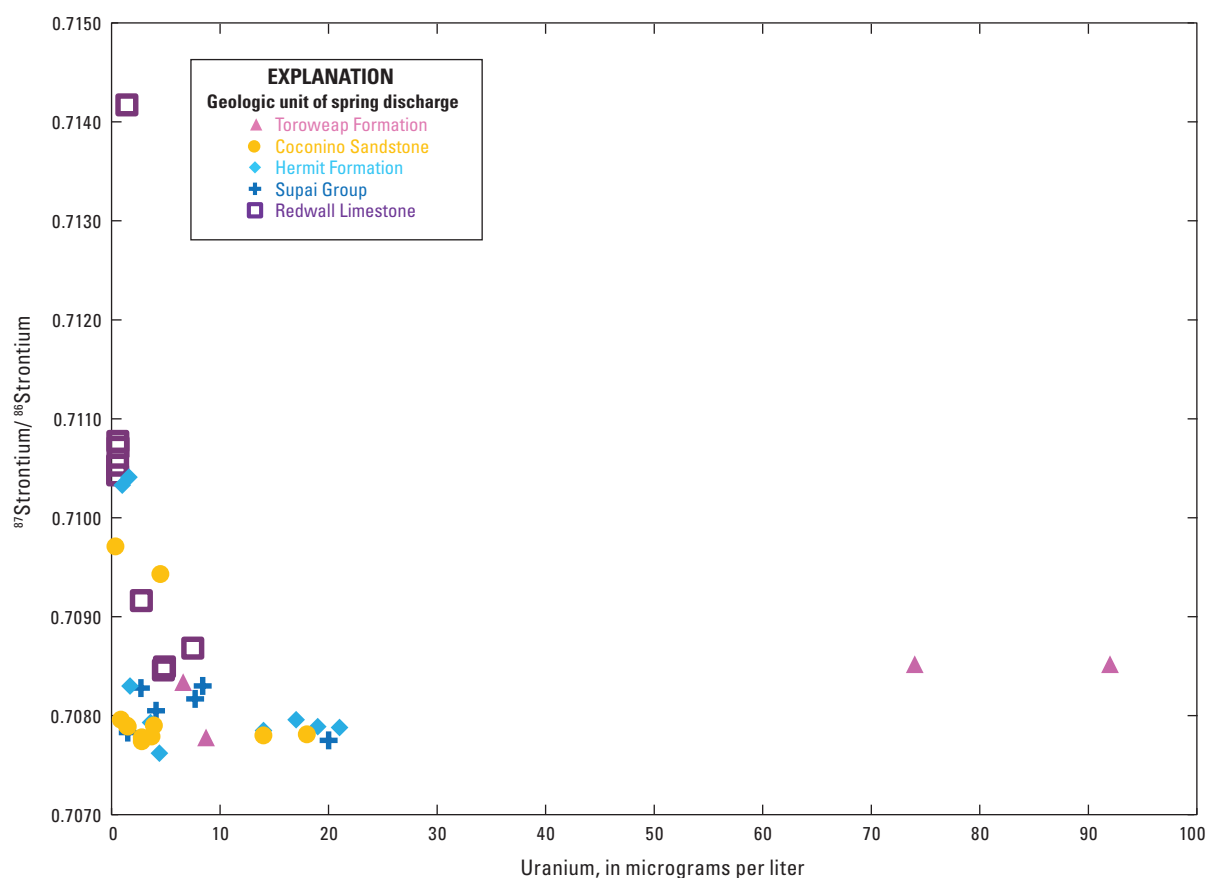
**Figure 23.** Selenium versus uranium from spring samples.



Values of  $^{87}\text{Sr}/^{86}\text{Sr}$  in uranium ore of the Orphan Mine are substantially more radiogenic (0.76288; Balboni and others, 2016) than any of the unmineralized Paleozoic sedimentary rocks (0.70756–0.71216; Monroe and others, 2005; Bills and others, 2007) from the region, as is waste rock associated with the uranium ore (Balboni and others, 2016). The elevated  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures of the uranium ore likely reflect a component of fluids that have interacted with Precambrian basement rocks as part of the ore forming process. Ludwig and Simmons (1992) came to a similar conclusion using lead isotopes from galena within uranium-mineralized breccia pipes. None of the groundwater samples with high uranium concentrations ( $>10\text{ }\mu\text{g/L}$ ) from this study have  $^{87}\text{Sr}/^{86}\text{Sr}$  values much greater than those observed in the Paleozoic host rocks (fig. 24). On the contrary, groundwater samples with elevated uranium concentrations tend to have  $^{87}\text{Sr}/^{86}\text{Sr}$  values lower than the mean value for rock units. Therefore, there is no clear indication from  $^{87}\text{Sr}/^{86}\text{Sr}$  data that water having interacted with uranium ore or waste rock similar to material from the Orphan Mine forms a significant contribution to current spring discharge sampled in this study. However, the results do not preclude a small component of water interacting with mining material to be present at the sampled springs. A previous study of Pigeon and associated

springs found no physical or geochemical evidence indicating that elevated uranium concentrations were related to processing at the nearby Pigeon Mine (Beisner and others, 2017). Strontium isotopes may serve as an important indicator of contribution from water interacting with uranium mine material for future samples from other springs or resampling of springs over time in the study area.

Conceptually, groundwater in the Grand Canyon region can be subdivided into (1) nonmineralized natural groundwater, unaffected by mining; (2) mineralized groundwater in areas where paleo-passage of hydrothermal fluids has deposited residual sulfides and metal sulfates, which on dissolution result in higher solute concentrations of uranium and other trace elements than in nonmineralized natural groundwater; and (3) anthropogenically altered groundwater, where disturbance of the natural system has influenced the chemistry of either mineralized or nonmineralized receiving waters. Differentiating between mineralized and nonmineralized groundwater chemistry at a mine site can be challenging if there is an overprint of past and (or) current mining on naturally mineralized conditions. Other considerations that aid in the evaluation are spatial distributions, sample types, and other chemical compositions of the water at the sites.



**Figure 24.** Strontium isotope ratio relative to uranium concentration for spring samples.

## Springs with a Possible Component of Geothermal Fluids

Fence and Rider Springs have elevated concentrations of As, B, Cl, Li, K, and Na that statistically outlie the ranges exhibited by other springs discharging from the Redwall Limestone and Coconino Sandstone, respectively (fig. 10). Crossey and others (2009) demonstrated that Ba, Li, F, B, and As are consistently higher in CO<sub>2</sub>-charged springs, and that those characteristics are consistent with contributions from a component of more deeply circulating geothermal fluid. Fence Spring also has the highest <sup>87</sup>Sr/<sup>86</sup>Sr value of all samples in this study. The observed value of 0.71417 is significantly greater than the highest strontium isotopic ratio for any of the Paleozoic sedimentary rocks of the Grand Canyon. Crossey and others (2006) and Patchett and Spencer (2001) indicate that Proterozoic basement rocks contain radiogenic strontium isotopic ratios greater than 0.714. Basement rocks from the Verde Valley in Arizona have <sup>87</sup>Sr/<sup>86</sup>Sr values that range from 0.7300 to 0.7800 (Johnson and others, 2011). Crossey and others (2006) suggest that springs with elevated <sup>87</sup>Sr/<sup>86</sup>Sr, such as Fence Spring, may include a component of deeply circulating groundwater that has interacted with Precambrian basement rocks.

## Conclusions

Baseline water chemistry was established for springs discharging north of the Grand Canyon from the Toroweap Formation, Coconino Sandstone, Hermit Formation, Supai Group, and Redwall Limestone in an area that includes uranium mining from breccia pipes. Of the 37 total springs sampled in this study, 3 springs had trace element concentrations that exceeded the USEPA drinking water standards: Fence Spring (arsenic), Pigeon Spring (selenium and uranium), and Willow (Hack) Spring (selenium). The majority of the spring sites had groundwater uranium concentrations less than 10 µg/L, but six springs discharging from all geologic units except the Redwall Limestone had uranium values greater than 10 µg/L (Cottonwood [Tuckup], Grama, Pigeon, Rock, and Willow [Hack and Snake Gulch] Springs). Geochemical characteristics of those springs include a Ca-Mg-SO<sub>4</sub> water type, circumneutral pH, high specific conductance, correlation and multivariate associations between U, Mo, Sr, Se, Li, and Zn, low <sup>87</sup>Sr/<sup>86</sup>Sr, low <sup>234</sup>U/<sup>238</sup>U activity ratios (1.34–2.31), detectable tritium, and carbon isotope interpretation indicating they may be mixtures of modern and pre-modern waters. Similar geochemical compositions of spring waters having elevated uranium concentrations are observed at sites located both near, and away from, sites of uranium-mining activities in the present study. Therefore, mining does not appear to explain the presence of elevated uranium concentrations in groundwater at

the six springs noted previously. The elevated uranium at the six previously mentioned springs may be related to iron mineralization associated with mineralized breccia pipe deposits.

Springs containing old water datable by radiocarbon methods discharge from the Coconino Sandstone (Upper Jumpup, Little, Horse, and Slide Springs) and Redwall Limestone (Kanab and Side Canyon Springs) and have corrected <sup>14</sup>C ages as much as 9,300 years old. Select springs with old apparent groundwater ages (Kanab and Side Canyon Springs) that also contain tritium above 1.3 pCi/L may possibly indicate that some component of modern water recharged after 1952 is present in spring discharge, but could also indicate all pre-modern water. In contrast, springs containing high tritium concentrations (greater than 5.1 pCi/L) indicate the presence of a significant component of modern water and include Willow (Hack), Saddle Horse, Cottonwood (Tuckup) Hotel, Bitter, Unknown, Hole in the Wall, Hanging and Bitter Springs.

Fence and Rider Springs are located on the eastern end of the study area near the Colorado River and have a distinct geochemistry compared to the other springs of the study. These springs have elevated values of As, B, Cl, Li, K, and Na, which may indicate a component of geothermal fluids. Additionally, Fence Spring has the most radiogenic strontium isotopic composition (<sup>87</sup>Sr/<sup>86</sup>Sr) of all samples analyzed from this study. Similarly, elevated <sup>87</sup>Sr/<sup>86</sup>Sr values have not been identified in any of the Paleozoic sedimentary rocks exposed in the area. The high <sup>87</sup>Sr/<sup>86</sup>Sr is most likely derived from a groundwater component that has interacted with Precambrian crystalline basement rocks. Rider Spring has the most depleted values for stable O and H isotopes, indicating that recharge water originated at higher elevations or from a previous, cooler climate relative to other analyzed springs.

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## **Appendixes 1–6**

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Appendixes 1–6 are presented as Excel table files, and are available for download at <https://doi.org/10.3133/sir20175068>.

- Appendix 1. Spring sample site characteristics.
- Appendix 2. Standard reference sample performance for USGS National Water Quality Laboratory (USGSNWQL) and USGS National Research Program Laboratory in Boulder, Colo. (USGSTMCO) for Fall 2009.
- Appendix 3. Blank data from USGS National Water Quality Laboratory (USGSNWQL) and USGS National Research Program Laboratory in Boulder, Colo. (USGSTMCO).
- Appendix 4. Replicate sample data from USGS National Research Program Laboratory in Boulder, Colo. (USGSTMCO).
- Appendix 5. Replicate sample data from USGS National Research Program Laboratory in Reston, Va. and contract labs for uranium activity ratio.
- Appendix 6. Spring sample results.

Menlo Park and Lafayette Publishing Service Centers  
Manuscript approved June 20, 2017  
Edited by Katherine Jacques  
Design and layout by James E. Banton

