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REPORT

The Grand Canyon National Park (USA) water corridor: water supply, water quality, and recharge along the Bright Angel Fault

Brionna H. Curry[1] · Laura J. Crossey[1] · Karl E. Karlstrom[1]

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Abstract
The "water corridor" of Grand Canyon (Arizona, USA) includes the Transcanyon Pipeline, which conveys water from Roaring Springs (North Rim) to Grand Canyon Village (South Rim) to supply the park's 5–6 million annual visitors. The North Rim water has been reclaimed at the South Rim Water Reclamation Plant (WRP) since the 1960s. This report describes a hypothesis in which the returned pipeline water infiltrates along the Bright Angel Fault and intermingles with groundwater. Geochemical tracers (major ions, stable isotopes) are used to define end members and develop mixing models for South Rim groundwater. It was found that Havasupai Gardens Spring water, discharging below the South Rim along the Bright Angel Fault (~1 km below the WRP), is ~40% North Rim water. Other South Rim springs below the rim also have 10–60% anthropogenic North Rim contribution. Similarly, Coconino Plateau groundwater wells in the town of Tusayan and the Pinyon Plain uranium mine may contain tens of percent of North Rim water. Compatible with this hypothesis, pharmaceutical and personal-care products present in discharge from the WRP, and also in Havasupai Gardens Spring and Pipe Creek Spring below the rim, were found in trace amounts. This study explains the hydrochemical variability of South Rim springs and groundwater as primarily due to anthropogenic groundwater mixing and secondarily due to variations in local recharge, as proposed by others. The hypothesis suggests that uranium mining, local groundwater pumping, and management of the pipeline and WRP infrastructure are all part of an interconnected South Rim groundwater system.

Keywords Stable isotopes · Hydrochemistry · Environmental tracers · Groundwater development · USA

Introduction

Grand Canyon provides a cross-sectional view of an aquifer system within a highly faulted arid-land region on the Colorado Plateau, USA, with over 750 groundwater-fed springs that discharge below the North and South Rims (Tobin et al. 2018). The canyon and Colorado River divide the Colorado Plateau into several subprovinces. In particular, the Kaibab Plateau north of Grand Canyon is a high-elevation recharge region. The Coconino Plateau borders the canyon to the south extending to Flagstaff, Arizona, including the San Francisco Peaks (Huntoon 1974). Grand Canyon Village's main drinking-water source is Roaring Springs, a large-volume (baseflow of ~170 L/s) karst spring flowing from the regional Redwall-Muav (R-M) aquifer near the North Rim of the canyon (Jones et al. 2017). Figure 1 shows a regional map of the study area with special attention on Grand Canyon's 'water corridor', an area centered on Bright Angel and Pipe Creeks as well as the Transcanyon Pipeline that transports Roaring Springs water from the North Rim to the South Rim. Grand Canyon water is a vital resource to over 6.5 million park visitors per year and residents of Grand Canyon Village. The springs within the park are also important to sustain endemic species and ecosystems that rely on them, and to the numerous Native American tribes that are traditionally associated with the park. Roaring Springs joins with other springs to form the baseflow of Bright Angel Creek, which merges with the Colorado River just below Phantom Ranch. This water is of increased importance as the park plans to transition its water supply from Roaring Springs to a composite Bright Angel Creek surface-water source (NPS 2019). Bright Angel Creek has a number of springs that feed into it, including the high discharge springs of Roaring, Angel, and Emmett Springs and the creek flows at about three times the rate of Roaring Springs (510 L/s

✉ Brionna H. Curry
brionna.oconnor@gmail.com

[1] Department of Earth and Planetary Sciences, University of New Mexico, 1515 Eubank Blvd. SE, Albuquerque, NM 87131, USA

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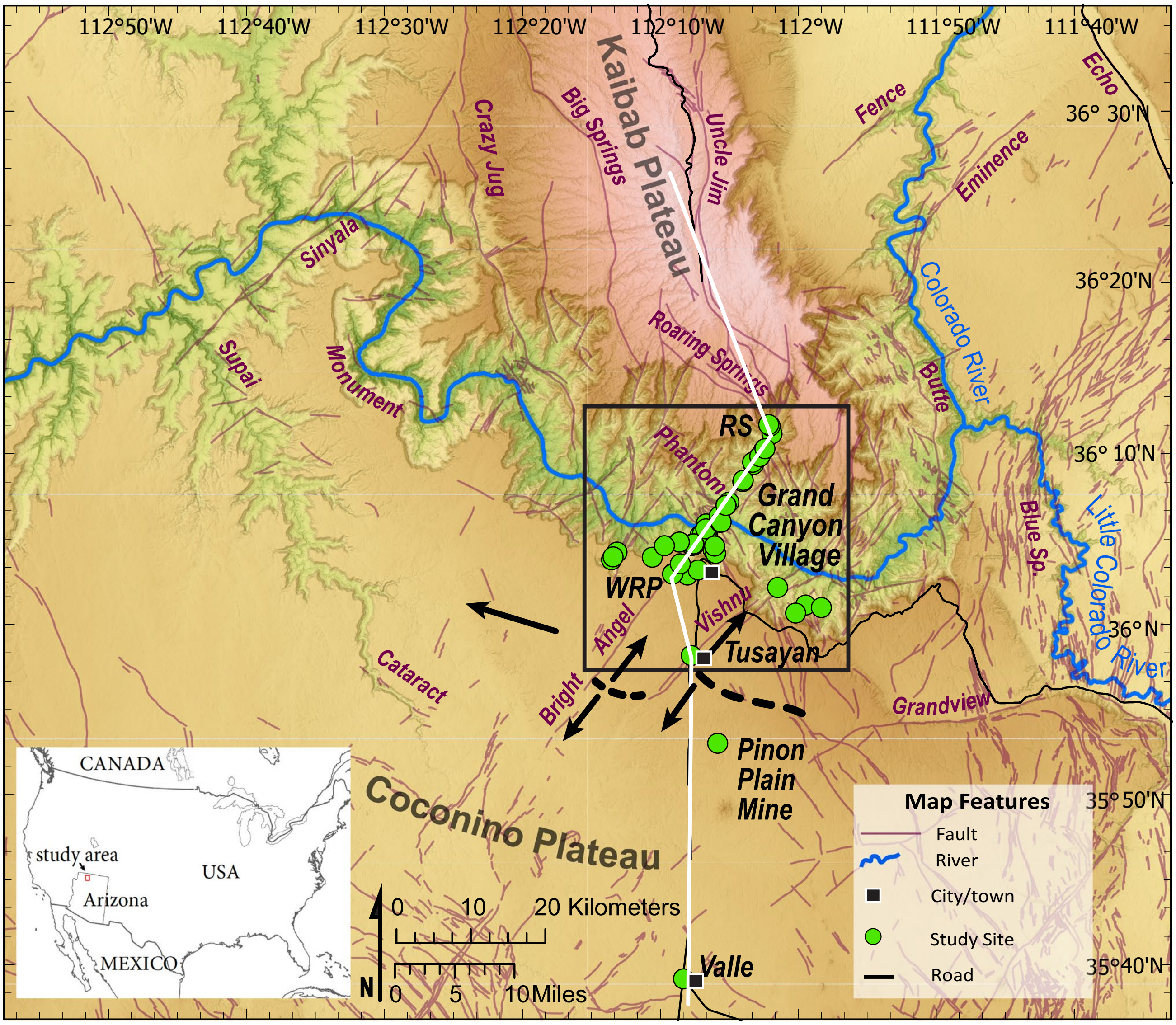


Fig. 1 Regional setting of springs and faults in the eastern Grand Canyon. Box indicates area that is the critical water corridor for Grand Canyon National Park. White line shows the path of the hydrogeology cross section depicted later with kinks at Roaring Springs (RS) and the Water Reclamation Plant (WRP). Heavy black-dashed line shows a fault-influenced groundwater divide near Tusayan; black arrows are flow directions in the R-M aquifer away from the divide (Crossey et al. 2009)

versus 170 L/s; Jones et al. 2017; USGS 2020). For this reason as well as the aging pipeline infrastructure that brings water across the canyon, Bright Angel Creek is an attractive option when considering future park water supply needs; however, in addition to quantity, water quality is also a factor of consideration.

This study uses geochemical tracers to build on previous work to help establish a water quality baseline for the water corridor. Figure 2 shows water sample locations from this study, including 66 new analyses of both new and previously analyzed sample locations. This study identified four types of water to be investigated: (1) Roaring Springs karst groundwater that is piped to Grand Canyon Village; (2) South Rim groundwater, as sampled from wells on the Coconino Plateau to the south; (3) South Rim springs below the rim, especially Havasupai Gardens Spring and Two Trees Spring, which are hypothesized here to reflect mixing of pipeline (North Rim) and South Rim water; and (4) Grand Canyon Village water delivered from the pipeline to Grand Canyon Village water tanks, used in the Village, treated at the Water Reclamation Plant (WRP), and discharged along the Bright Angel fault.

Grand Canyon National Park has been performing an anthropogenic recharge experiment since the 1960s that involves infiltration of North Rim pipeline water including reclaimed water from the WRP in Grand Canyon Village

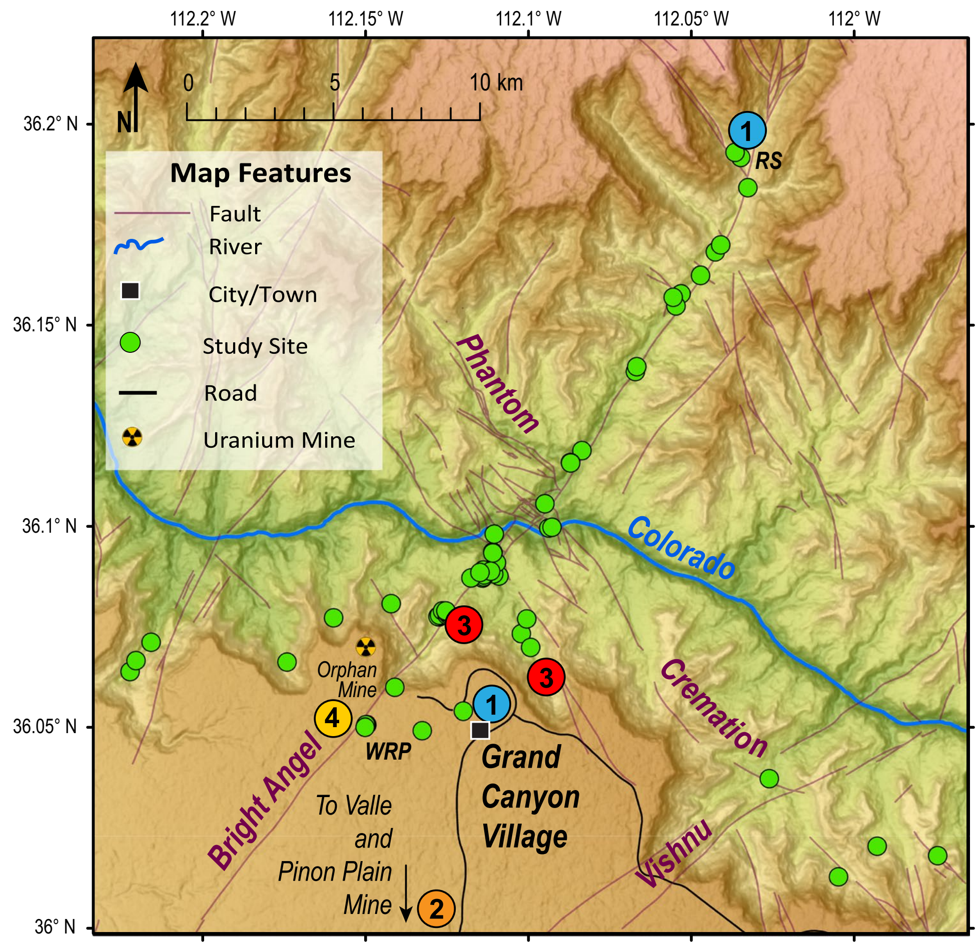


Fig. 2 Map of springs and sample points within the water corridor. Four groups of waters to be studied include: North Rim waters (1), especially Roaring Springs (RS) that supplies pipeline water to water tanks at Grand Canyon Village; groundwater south of the South Rim (2), including Tusayan, Valle, and the Pinyon Plain Mine wells (locations in Fig. 1); South Rim springs below the rim (3), especially Havasupai Gardens Spring and Two Trees, hypothesized to be a mix of 1 and 2; Grand Canyon Village water treated at the Water Reclamation Plant (WRP) and reinfiltrated along the Bright Angel fault (4) to mix with 2 and 3

(Ingraham et al. 2001) to mix with South Rim groundwater. Figure 3 shows that water is piped from Roaring Springs to the South Rim water tanks for distribution, with a pipeline capacity of up to 42 L/s (NPS 2015; see conversion Table 1). The distribution of this water is multifaceted, and has included piping water ~40 km east to Desert View (Fig. 3) and trucking water west to Hermit's Rest. Water from South Rim hotels, housing, businesses, and Village and Park installations is fed to the South Rim Water Reclamation Plant (WRP), first built in 1926. Effluent is discharged

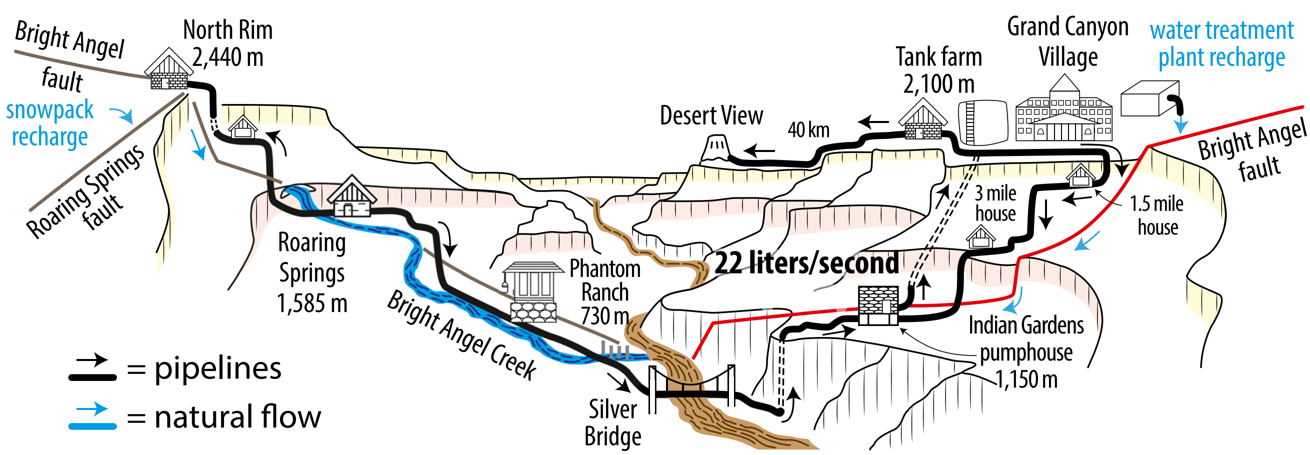


Fig. 3 Schematic drawing of Grand Canyon's water corridor from north to south showing natural and pipeline flow pathways. Key components include Roaring Springs, Bright Angel Creek, the Transcanyon Pipeline, Havasupai Gardens Spring (formerly Indian Garden Spring) and pumphouse, South Rim Tank farm, Water Reclamation Plant, and the Bright Angel fault

Table 1 Units of flow measurement

Location	Reference	L/s	ft^3/s	milligal/day	gal/min	ac-ft/year
General conversions		10	0.35	0.23	159	256
Havasupai Gardens Spring	Dyer et al. 2016	6	0.2	0.1	95	153
Garden Creek (GC)	Dyer et al. 2016	28	1.0	0.6	444	716
Garden Creek combined with pipeline discharge	Dyer et al. 2016	59.5	2.1	1.4	943	1,521
Roaring Springs (RS)	Jones et al. 2017	170	6.0	3.9	2,695	4,346
RS to South Rim	NPS 2015	22	0.8	0.5	342	552
Pipeline capacity	NPS 2015	42	1.5	1.0	666	1,074
WRP effluent permit	ADEQ 2017	33	1.2	0.75	523	844
Bright Angel Creek baseflow	USGS 2020	510	18.0	11.6	8,084	13,039

to the Clearwell Overflow (Ingraham et al. 2001) less than a mile from the edge of the canyon and directly on the trace of the Bright Angel fault. The WRP is permitted to discharge 33 L/s, although reportedly an average of ~22 L/s make it to the plant (as of ~2007) with ~15 L/s discharged to the Clearwell Overflow (Roberts et al. 2007). In addition to planned distribution and returns, pipeline leakage has taken place at numerous times and places, including a leak in the Transcanyon Pipeline in 2001 directly upgradient from Havasupai Gardens Spring (Ingraham et al. 2001), as well as major leaks at South Rim Village prior to the development of the directional pipeline drilled in the 1980s (Lattimore et al. 1987).

An important assumption of this study is that the volume of infiltrated North Rim water is a significant addition to local meteoric recharge on the South Rim. Seasonal variability of local recharge may have a significant influence on hydrochemcial signatures (Solder and Beisner 2020; Solder et al. 2020; Wood et al. 2020) but, accounting for evapotranspiration, the South Rim area has a very limited modeled potential recharge of 0–1 in/year (Knight and Huntoon 2022, their Figure 10). Thus, given the location of the WRP and its observed infiltration directly along the Bright Angel fault, the hypothesis presented in this report is that ~20 L/s over 50 years is an appreciable recharge amount that should be hydochemically detectable.

This report applies aqueous geochemistry as a tool for understanding hydrologic flow paths and for assessing the potential mixing of waters (Fig. 2). Multiple natural tracers including solutes and stable isotopes were used as well as anthropogenic tracers of pharmaceuticals and personal care products (PPCPs) to compare North Rim and South Rim water and test the sources of water at Havasupai Gardens spring and other South Rim springs and groundwaters.

Havasupai Gardens Spring is the proposed new name for Indian Garden Spring, acknowledging the Native American tribe for which it was named and who inhabited the area until 1928. The area has been used and inhabited by many tribes also including Ancestral Puebloan and Cohonina people prior to permanent white occupation. According to Lattimore et al. (1987), in the 1930s, it was an "unreliable spring" with a discharge of approximately 18 L/s and an "external pipeline" was built to permit the pumping of water to the distribution system on the South Rim. In the 1960s, Roaring Springs water was tapped and delivered to Indian Gardens via the Transcanyon Pipeline, then pumped through the external pipeline to the rim. In the 1980s, drilling of the directional pipeline (Fig. 3) changed the South Rim distribution system and was accompanied by the fixing of numerous open breaks in the distribution system. Other developments throughout the 1900s that affected the hydrology of the Havasupai Gardens area included permanent structures with a leaching field, the settling ponds at the Transcanyon Pipeline pumphouse, and the gauging of Pumphouse Spring (Two Trees Spring; JMA 2005).

Hydrogeologic setting

Figure 4 summarizes the hydrostratigraphy of the eastern Grand Canyon. The main aquifers are Kaibab-Coconino aquifer (C-aquifer) and the Redwall-Muav aquifer (R-M aquifer), each underlain by shale confining layers of the Hermit Formation and Bright Angel Formation, respectively. Shales of the Bright Angel Formation act as the region's most important confining layer that focuses spring discharge above the shale (Huntoon 1974). The C- and R-M aquifers are separated by a leaky aquitard (Supai Group) and connected via subvertical joints and faults (Huntoon 1974, 2000; Tobin et al. 2018). Water quality of both aquifers is influenced by a component of relatively fast-traveled meteoric recharge (Schindel 2015), mixed karst and matrix flow in the C-aquifer, and both fast and slow pathways through the karst fracture network in the R-M aquifer (Brown 2011; McGibbon et al. 2022). Deeply circulated groundwater in the crystalline basement is a geochemically potent fluid component that also mixes in the aquifers on the regional scale (Crossey et al. 2006; Kim et al. 2022). The major springs

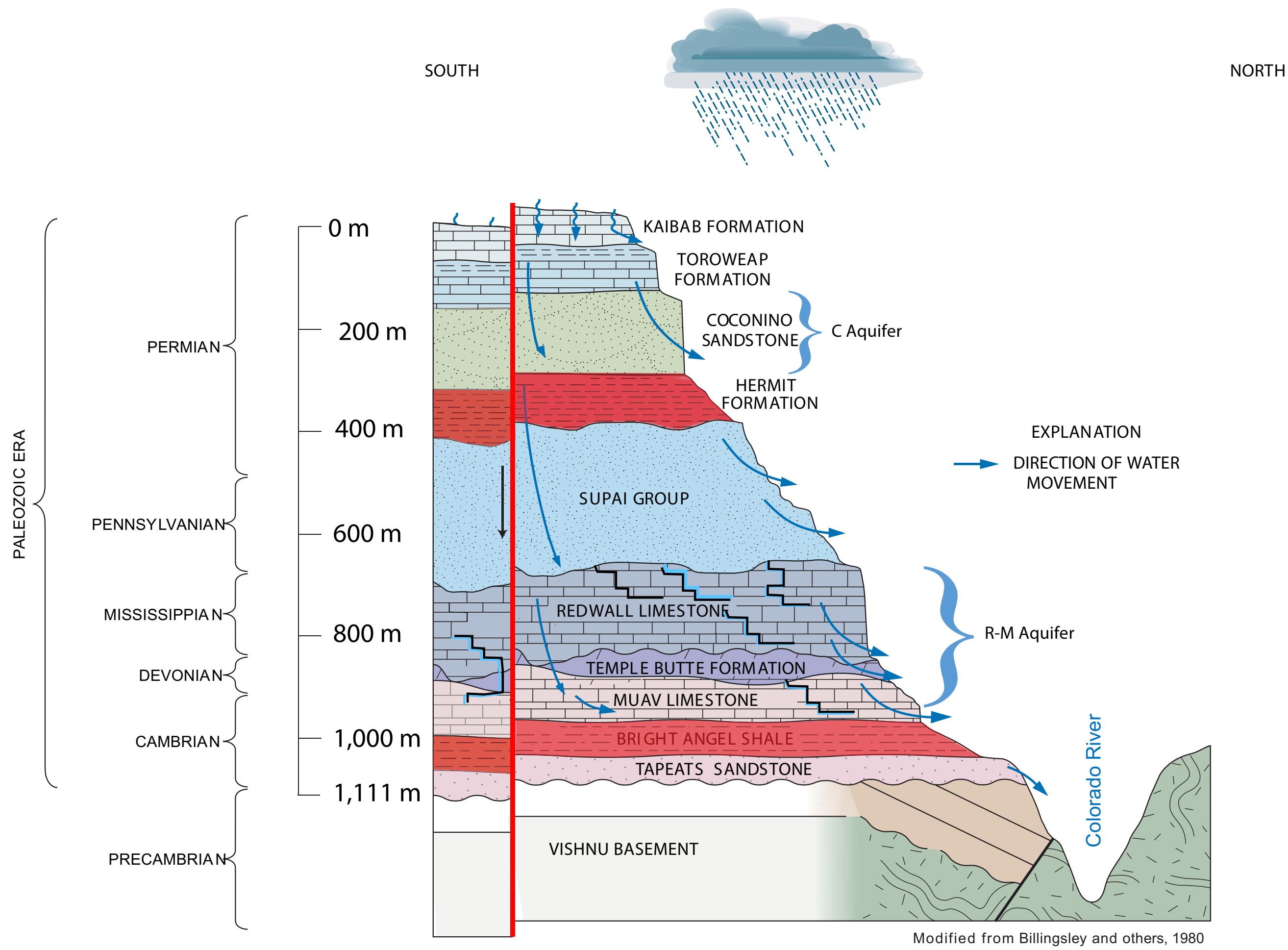


Fig. 4 Hydrostratigraphic section of eastern Grand Canyon, adapted from Monroe et al. (2005) and Billingsley et al. (1980), shows ~1 km of Paleozoic strata, major aquifers, confining units (red), and directions of groundwater movement (arrows). The NE-striking Bright Angel fault (red) is oblique to this cross section and has 46 m of NW-side-up displacement

and perennial streams considered in this study are shown in green in Fig. 2 along with hundreds of other small springs that flow from the R-M and C aquifers on both the North and South Rims in blue (Fig. 5a, Ledbetter et al. 2020).

The structural setting involves the southward dip of strata off the Kaibab uplift that causes southerly surface drainage on both the North Rim and South Rim (Fig. 5a). North Rim surface streams are large perennial streams and groundwater flows in the same direction as surface-water flow. The North Rim R-M aquifer is drained by high-volume Roaring, Angel, and Emmett springs that emerge from the base of the Muav Formation and come together to form Bright Angel Creek. Recharge on the North Rim occurs through surficial karst features as snowmelt and rainfall that infiltrate the Kaibab Plateau through sinkholes, faults, and fractures (Jones et al. 2019; Tobin et al. 2021). North Rim dye tracer studies have shown recharge on the Kaibab uplift traveling to springs up to 35 km away within just a few months (Jones et al. 2017).

Figure 5b expresses the hypothesis to be tested in this report that the North Rim pipeline water that is delivered to Grand Canyon Village, including effluent from the Grand Canyon Village WRP, infiltrates down the Bright Angel fault and flows in both directions—north to recharge Havasupai Gardens Spring, the highest volume South Rim spring, and other springs; and south to interact with the regional R-M aquifer groundwater.

Ephemeral surface drainages on the Coconino Plateau above the South Rim flow south following the southerly dip of the Kaibab surface as shown in Fig. 5. However, water well levels (red lines of Fig. 5b) suggest the R-M groundwater flows north toward the Grand Canyon from a divide near the town of Tusayan (Errol L. Montgomery and Associates 1999). Although this divide is shown in numerous flow models (Bills et al. 2007; Crossey et al. 2009; Knight and Huntoon 2022), the number of deep wells is small and the water level data are two decades old. Figure 1 shows R-M aquifer flow across the

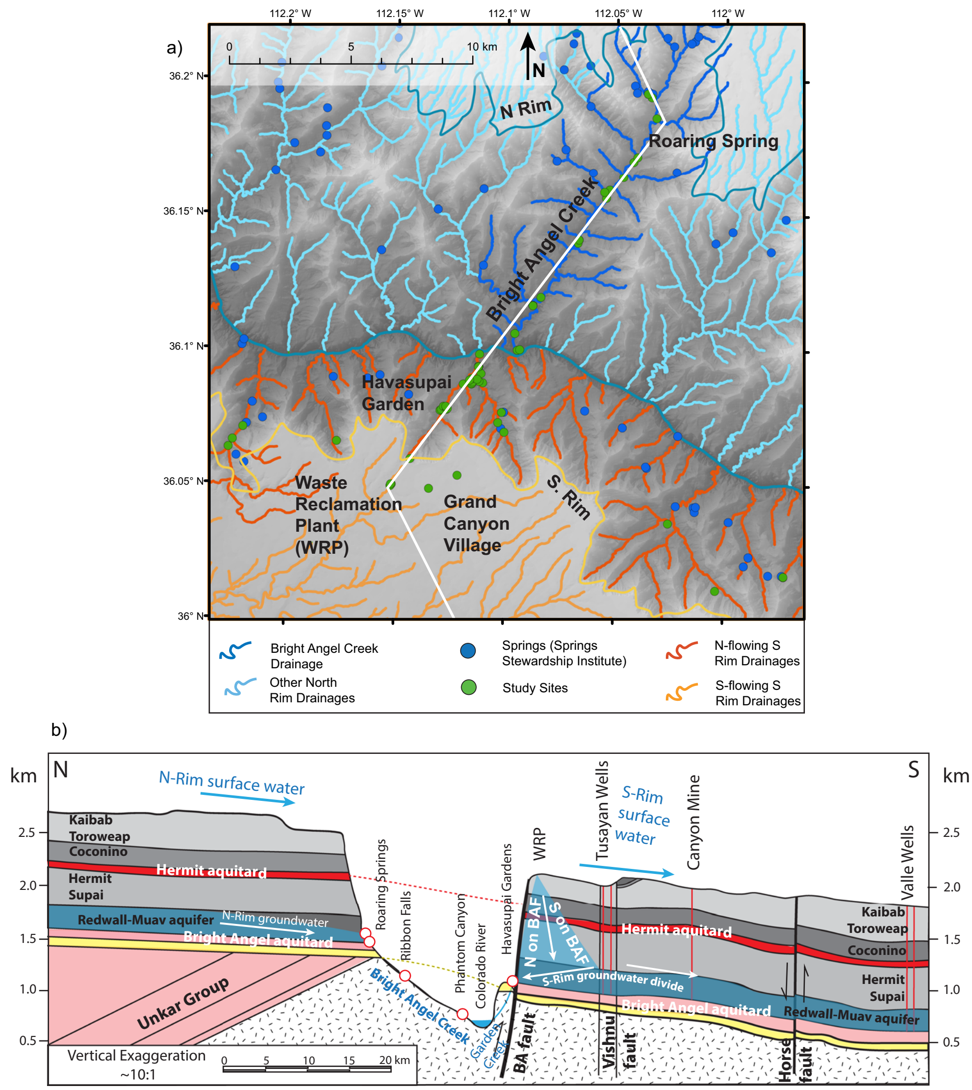


Fig. 5 **a** Surface-water drainages shown for an area of Fig. 2, highlighting north and south rim surface water flow direction. **b** Hydrogeology profile of the N–S Grand Canyon water corridor along white line in Fig. 5a. On the North Rim, both surface water and groundwater flow south. On South Rim, surface water flows south following the dip of the Kaibab surface, but groundwater flows north from a groundwater divide near Tusayan. Red lines show groundwater levels in R-M aquifer wells as of ~1999 (Errol L. Montgomery and Associates 1999)

groundwater divide to be strongly influenced by faults as modeled in Crossey et al. (2009; from Kessler 2002); however, the geometry of this divide is poorly resolved.

Faults can be both barriers and conduits for flow and their permeability can change through time (e.g. Mozley and Goodwin 1995). Two faults of importance for this study are the Bright Angel and Vishnu faults (Fig. 1). Bright Angel fault strikes NE across the Coconino Plateau and has the South Rim's water treatment plant and sewage ponds along it. It is well exposed along the Bright Angel Trail, passes through Two Trees Spring near Havasupai Gardens, and is also well exposed in Pipe Creek and along the North Kaibab trail to Roaring Springs (Fig. 2). Its post-Paleozoic movement involves a net SE-side-down throw of ~46 m due to Miocene extensional reactivation of a Laramide fault that had Precambrian ancestry (Huntoon and Sears 1975). Both SE-down and NW-down minor faults are present along the Bright Angel Trail resulting in an overall subvertical network of faults, joints, and breccia that makes a permeable zone capable of conveying groundwater from South Rim groundwater to springs like Havasupai Gardens below the rim. Similarly, Vishnu fault parallels the Bright Angel fault and may connect groundwater near the town of Tusayan to inner canyon springs (Fig. 2).

There is also a family of NW-striking faults exposed in the inner canyon and along the Cremation-Grandview monocline (Fig. 2). These Laramide reverse faults reactivated Precambrian normal faults (Timmons et al. 2005) and provide some of the deepest-penetrating fluid pathways for circulation of fluids to great depth and ascent of geothermal "lower world" fluids (Crossey et al. 2006). Cenozoic E–W extension across this network of NE- and NW-striking faults creates an orthogonal grid of fluid pathways that allowed rapid groundwater water flow in many directions for the North Rim dye tracer experiment (Jones et al. 2017; Wood et al. 2020; Fig. 1). The South Rim fault network is likely to provide a similar network of fluid pathways.

This report proposes that the greater than six-decades-long and ongoing discharge and infiltration of North Rim pipeline water on the South Rim, primarily down the Bright Angel fault, has resulted in a mix of North Rim- and South Rim-derived groundwater at Havasupai Gardens Spring, other South Rim springs, and in groundwater wells at Tusayan and Pinyon Plain Mine. The geometry of the sampling plan to help test this hypothesis is shown in Fig. 6. Water in the pipeline is gravity-fed as far south as Havasupai Gardens, where it is pumped up to the South Rim. Havasupai Gardens and Two Trees springs had pre-pipeline flows of ~18–20 L/s (Metzger 1961), compared to the median discharge today of 28 L/s today or 59 L/s, when including North Rim rejected water (Dyer et al. 2016). Two Trees Spring (also known as Pumphouse Spring) discharges along the Bright Angel fault ~100 m higher in elevation than Garden Creek. Garden Creek is the combined surface outflow from Havasupai Gardens Spring, Two Trees Spring, and unused pipeline water returned to the creek (NPS 2015). Garden Creek flows into Pipe Creek, which is also fed by two other South Rim springs (Burro and Pipe springs) and Pipe Creek waters were sampled at several locations above Pipe Creek's confluence with Garden Creek, and above where the Pipe Creek travertine cone is located on the Bright Angel fault well above Garden Creek. Lower Pipe Creek is a mixture of Garden and upper Pipe creeks, and hence has North Rim pipeline rejected water, Havasupai Gardens Spring water, and Pipe Creek water (Fig. 6). All creeks experience significant evaporation along their paths.

Sources of groundwater variability and prior work

Natural geochemical tracer datasets have expanded in various publications (and in this report) such that this section outlines multiple working hypotheses that have been proposed to explain observed groundwater variability. These include (1) a multi-permeability R-M karst aquifer (Huntoon 2000); (2) mixing of "upper world" and lower world waters (Crossey et al. 2006, 2009); (3) spring composition determined by percentage of winter versus summer recharge in different springs (Solder and Beisner 2020), (4) variable C-aquifer contributions as meteoric waters descend to the regional R-M karst aquifer (Wood et al. 2020); (5) very fast-traveled (e.g. fault and karst conduits) interacting with baseflow pathways (Brown 2011; McGibbon et al. 2022; this report).

Springer et al. (2017) reported regional stable isotope results and concluded that springs of central and northern Arizona (including Grand Canyon) have only a weak elevation to $\delta^{18}O$ correlation across ~1.6 km of elevation. They concluded that the observed groundwater variation is dominated by high-elevation (winter) recharge and that variability results from the mixing of local and regional springs sources.

Jones et al. (2017) summarized a North Rim dye tracer study that documented fast pathways along faults. They also developed recession curves for springs that parse baseflow from more rapid flowpaths, which helps quantify the concept of multiple permeability flow (Huntoon 2000) and has been combined with stable isotope data (Ross 2005; Brown 2011; Schindel 2015) to link different flowpaths to better characterize baseflow versus the faster-travelling recharge components that make up the discharge at Roaring Springs, which feeds the Transcanyon Pipeline.

Wood et al. (2020) focused on recharge and infiltration processes between the upper C-aquifer and the R-M aquifer. The C-aquifer stable isotope data showed that meteoric recharge via sinkholes on the Kaibab uplift is dominated

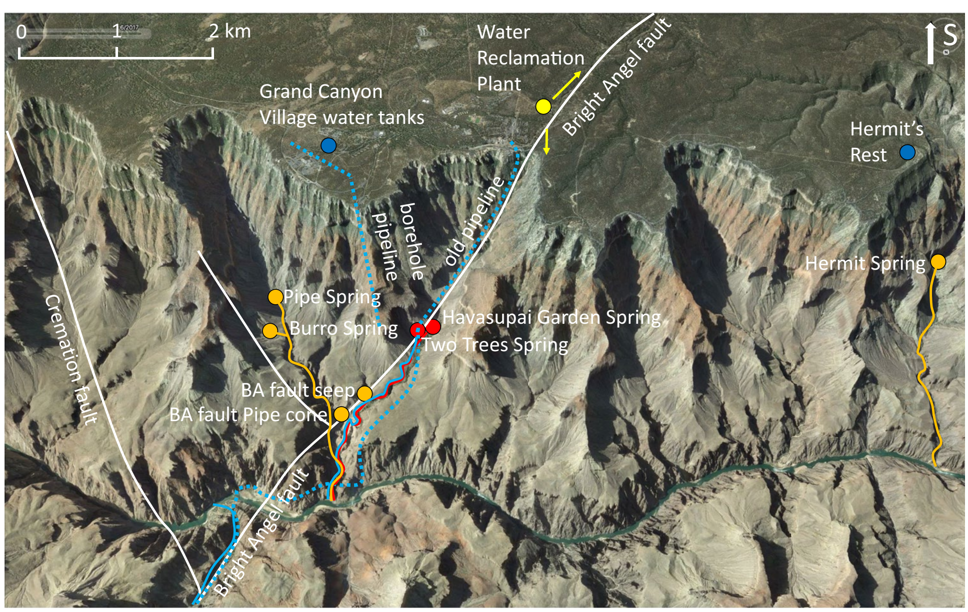


Fig. 6 Perspective view from Google Earth looking south at the South Rim of Grand Canyon and showing the different waters that were sampled. North Rim pipeline water reaches water tanks at Grand Canyon Village (blue dot), then is reclaimed at the Water Reclamation Plant (yellow dot), and infiltrates along Bright Angel fault recharging springs such as Havasupai Gardens and Two Trees springs (red dots) and other South Rim springs (orange dots). Note mingling of different water sources in Garden Creek and lower Pipe Creek below Havasupai Gardens

by winter recharge. C-aquifer springs are considerably less varied than Kaibab uplift meteoric recharge suggesting that spring water isotopes get seasonally homogenized in the groundwater system yet can preserve isotopic differences between North Rim recharge subbasins.

Solder and Beisner (2020) modeled observed groundwater stable isotopic variation of South Rim springs and groundwaters in terms of proportions of summer versus winter recharge reaching different springs. They suggested possible end-member isotopic values for winter versus summer recharge based on the means of observed and modeled precipitation values.

Solder et al. (2020) provided age models based on ^{14}C and tritium data that demonstrate the chemical mixing between older regional R-M groundwaters and a younger component. The study proposed the young waters were derived from modern groundwater or recharge from summer precipitation runoff. The age models are based on an assumption of closed system radioisotope decay, whereas Grand Canyon groundwater systems involve the mixing of "lower world" and different "upper world" waters (Crossey et al. 2006) traveling in a multipermeability (fast and slow pathway) layered aquifer (Huntoon 2000). For the proposed ^{14}C age model, the traditional "hard water correction" for dating assumes binary mixing between known $\delta^{13}C$ end members, which has been shown to be too simplistic (Crossey et al. 2009). This correction and the resulting ^{14}C age model have considerable uncertainty due to complex sources of dissolved inorganic carbon (Wang et al. 2020).

This report assimilates aspects of all these studies within a new hypothesis that mixing of a pipeline contribution of North Rim groundwater is a first-order explanation for South Rim groundwater hydrochemical variation, with recharge variability spring to spring of second-order importance.

Methods

Water sampling

Sampling was completed for select springs and surface water in the water corridor under a permitted agreement with Grand Canyon National Park. North Rim waters include Bright Angel Creek and numerous springs or creeks that flow into it. Spring waters on the south side below the rim include Garden Creek and its springs (Havasupai Gardens and Two Trees Spring), and Pipe Creek and its springs. Samples were collected in March, May, September, October, and December 2021. Earlier samples had been collected in 2017 and 2018, with a priority to sample in the fall and winter when baseflow conditions were expected. These data were compiled with previously published hydrochemical data for the area. Waters sampled at Grand Canyon Village were from the drinking water tap at Park Housing, the restroom sink at the market, and the outflow of the WRP. Away and south of the South Rim, water was sampled from bathrooms sourced by known deep wells in Tusayan (Best Western Hotel) and Valle (Chevron station). These samples may have had unknown treatments prior to sampling, but the stable isotopes plot within the overall South Rim groundwater array of previous researchers (Solder and Beisner 2020) and appear to reflect the different groundwater compositions.

Sample locations were documented using a global positioning system (GPS). Field parameters were measured for each location including pH, temperature (°C), and specific conductance (µS/cm) using an Oakton waterproof pH/CON 300 m—Table S1 in the electronic supplementary material (ESM1). All sampling equipment (bottles, syringes, and filters) was rinsed with sample water three times prior to collection. Two bottles were collected for each location including an unfiltered raw sample of 125 ml for alkalinity, anion, and stable isotope analysis and a filtered (0.45 µM) and acidified (HNO_3) sample of 60 ml for cation analysis. The 125 ml sample was collected with zero headspace to prevent degassing that could affect the alkalinity measurement in the lab.

Pharmaceutical and personal care products (PPCPs) were sampled in glass bottles following procedures provided by the analytical laboratory. These steps included wearing nitrile gloves, avoiding touching the sample, and filling the 4 × 40-ml amber vials with preservative up the bottle neck. Field blanks were collected using 18 mΩ of water brought into the field from the lab.

Water analysis

Alkalinity was determined using the *end point titration* method with 0.020 N sulfuric acid (H_2SO_4) and an Oakton pH/CON 300 m in the Diagenesis Laboratory at the University of New Mexico in the Department of Earth and Planetary Sciences in Albuquerque, New Mexico (UNM) (Baird et al. 2017). Samples are titrated from the zero-headspace bottle as soon as possible following sample collection and include analysis of 10% duplicates. Duplicate data showed an error of <2.0% for alkalinity. Anion samples are analyzed using ion chromatography (IC) and cation samples are analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) in the analytical geochemistry laboratory at UNM EPS. Standard methods were used for IC (Jackson 2000) and ICP-OES (Hou and Jones 2000) comparable to EPA 300.0 and EPA 200.7, respectively. Samples were run at dilutions of 1:10, 1:50, and 1:100 when concentrations exceeded the standard of 20 ppm for anions or 10 ppm for cations. Ten percent duplicates were routinely run in addition to the quality assurance lab standards and blanks during analysis. Ion charge balance from the chemical

ICP-OES and IC analyses of the preliminary samples were routinely within 5% error. Total dissolved inorganic carbon (DIC) was calculated using the speciation model PHREEQC (Parkhurst 1995), which uses pH, temperature, and measured alkalinity to estimate all components of the DIC (bicarbonate, carbonic acid, and carbonate).

Stable isotope analysis of hydrogen and oxygen was carried out using cavity ring down spectroscopy (Picarro L1102-I) at the Center for Stable Isotopes at UNM. Isotope values are reported based on the ratio of the heavy to the light isotope such as $^{18}O/^{16}O$ for oxygen or $^{2}H/H$ (D/H) for hydrogen. Both oxygen and hydrogen isotopes are reported with respect to the Vienna Standard Mean Ocean Water (VSMOW). Below is a standard calculation used to report the isotope composition in delta notation (Sharp 2017). The units for isotope composition are reported as parts per thousand (‰ or per mil) deviation from the standard.

$$\delta^{18}O = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1000; \text{where} \frac{R_{\text{sample}}}{R_{\text{standard}}} = \frac{^{18}O/^{16}O}{^{18}O/^{16}O}$$

Each sample was analyzed six times and then averaged. Results show each sample to routinely be within an error of 0.1‰ for $\delta^{18}O$ and 2.0‰ for δD. Duplicates were also run at a frequency of 10% and showed the same margins of error.

Radiogenic isotopes of strontium and the $^{87}Sr/^{86}Sr$ ratio were measured on a Neptune Multi-collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the Radiogenic Isotope Geochemistry Laboratory at UNM. Standard methods include Eichrom Sr Resin in 200-μL Teflon columns, loading and cleaning in 3N HNO_3 and eluting in ultrapure DI H_2O.

Pharmaceutical and personal care products were analyzed by Eurofins Eaton Analytical, Inc. (EEA) in Monrovia, California. A solid-phase extraction, high performance liquid chromatography, and spectrometry-mass spectrometry (SPE-LC/MS/MS) system was used to sample for the target list of over 90 analytes (Oppenheimer et al. 2011).

Results

Stable isotopes of water, $\delta^{18}O$ and δD, are indicative of sources of recharge and are also conservative tracers that can be used with chloride to understand processes such as groundwater mixing, water–rock interaction, and evaporation (Glynn and Plummer 2005). Radiogenic isotopes of strontium were used to understand water–rock interactions and flow paths. Anthropogenic tracers used in this study include pharmaceuticals and personal care products (PPCPs) that indicate human impact on water at nanograms/L concentrations.

Field parameters and ion chemistry

Major ions such as calcium, magnesium, and sulfate can help explain whether waters are in equilibrium with limestone, dolomite, or gypsum, and minor ions such as chloride can serve as a conservative tracer. For this study 66 water samples were analyzed at 46 unique locations along the water corridor (Fig. 1; Tables S1–S4 in ESM1). Additionally, all available tracer data are from previous studies, plus data provided by Hannah Chambless at the National Park Service (Ingraham et al. 2001; Monroe et al. 2005; Bills et al. 2007; Brown 2011; Solder and Beisner 2020; Beisner et al. 2020; Tables S1–S5 in ESM1). Field parameters measured for all new samples include temperature (ranging from 7 to 24.5 °C), pH (6.2–8.8), and specific conductance (284–3,000 μS/cm; Table S1 in ESM1). Alkalinities ranged from 43.9 to 7 56.6 mg/L HCO_3^- with the lowest values measured at the treated effluent from the WRP and the highest recorded at Pipe Creek Seep along Bright Angel fault (Table S2 in ESM1). Total DIC ranged from 0.00127 to 0.0147 (Table S4 in ESM1).

Stiff diagrams (Fig. 7) show the general "shape" of the solute content for the different waters. North Rim waters: Roaring Springs, Bright Angel Creek, and tributaries to Bright Angel Creek are all similar with low-TDS (total dissolved solids) calcium bicarbonate waters. Pipeline water sampled in Grand Canyon Village is also similar, while South Rim groundwaters from wells on the Coconino Plateau are saltier. South Rim springs—Havasupai Gardens Spring, Two Trees Spring, Pipe Spring, and Burro Spring—share the shape of North Rim waters but with additional salts, whereas water from the South Rim Water Reclamation Plant (WRP) is high in NaCl.

Piper diagrams (Fig. 8) are used to examine major ions and plot the solutes from a larger number of samples (Piper 1944). North Rim waters (Fig. 8a) are calcium magnesium bicarbonate waters representative of a limestone or dolomitic aquifer (Bills et al. 2007; Crossey et al. 2009). All of these samples have TDS < 450 ppm with many samples at ~300 ppm, indicating that they are relatively fresh and near meteoric in composition. A few of the tributaries such as Phantom Creek and Mint Spring contribute slightly higher salts than Roaring Springs and plot further from the left edge of the parallelogram.

Major ion chemistry for South Rim springs, creeks, and wells (Fig. 8b) covers a large range of water quality. For plotting purposes, a representative sample was selected for Havasupai Gardens Spring, Two Trees Spring, and Pipe Spring, which were sampled multiple times. Data show that samples are consistent across seasons and years. Of the repeat samples, none varied by more than 10% relative standard deviation for major ions. The entire South Rim groundwater sample suite has TDS ranging from 172 to 3,244 ppm

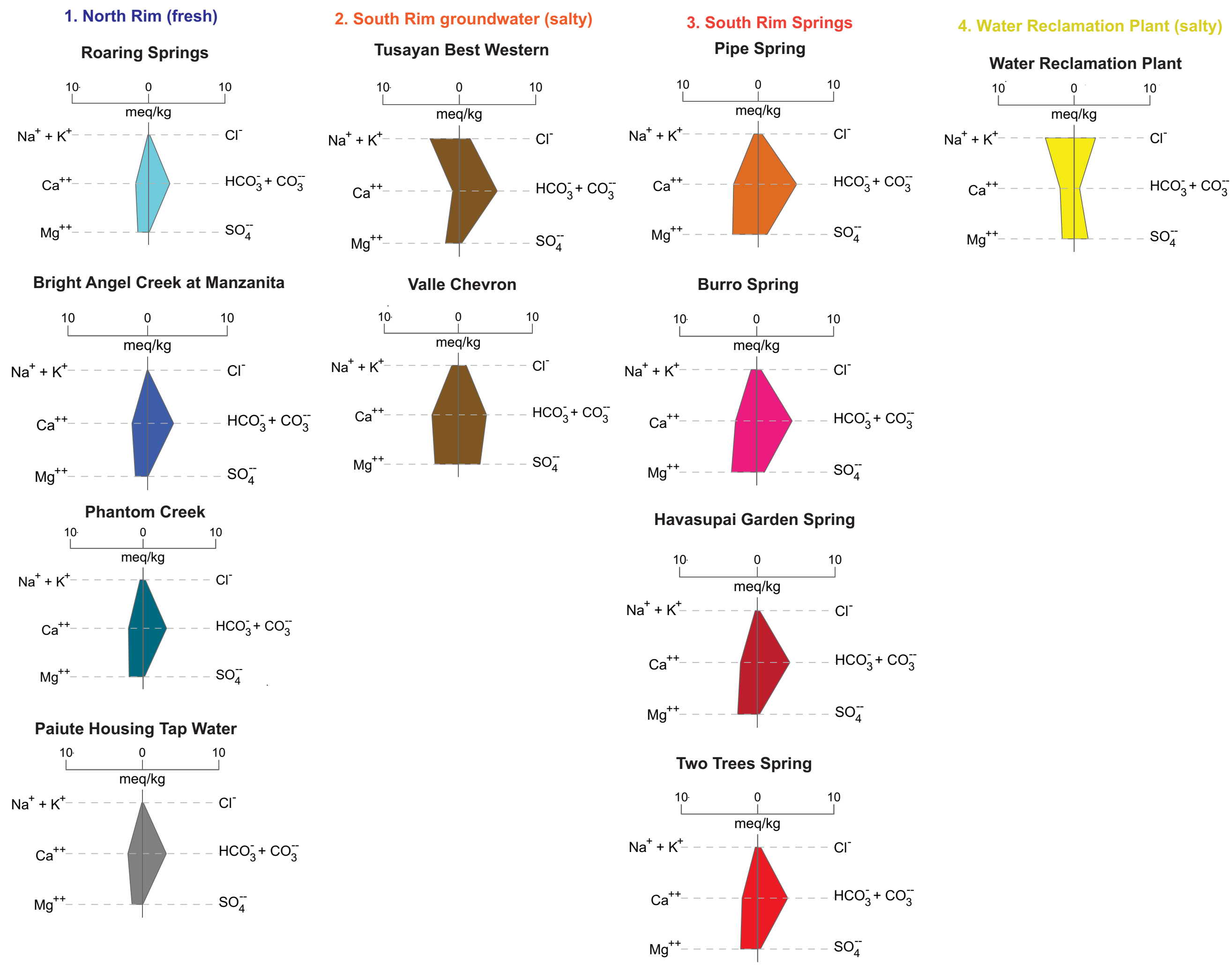


Fig. 7 Stiff diagrams portray the shapes of waters from the groups shown in Fig. 2. Low TDS North Rim water is piped from Roaring Springs such that Grand Canyon Village drinking water is the same (1). South Rim groundwater is higher in TDS and has different shapes (2); South Rim springs below the rim may be a mix of 1, 2, and 4 (3); and water reclamation plant (4)

along a mixing line between a meteoric end member similar to Roaring Springs and Pipe Creek seep, a high TDS spring along the Bright Angel fault. Published data from Monroe et al. (2005) were included for other South Rim springs to provide additional context for the water corridor South Rim springs and are plotted as open symbols. These samples include Hawaii, Horn, Hermit, Monument, and Salt Creek Springs to the west, and Cottonwood Creek, Grapevine Main, Lonetree, and Miners springs to the east. Two variation trends are (1) an apparent mixing trend between pipeline water (sampled at South Rim) and a more sulfate/chloride-rich water characterized by Valle groundwater wells and Salt Creek and Lonetree springs; and (2) higher chloride waters of the Water Reclamation Plant and springs/seeps along the Bright Angel fault in the Pipe Creek drainage (Fig. 6). Longitudinal sampling of creeks shows variation along both trends. Samples without a full list of cations and anions are not plotted on the Piper Diagram including the Pipe Creek Seep and Fern Seep.

Stable isotope hydrochemistry

Figure 9 shows the stable isotope geochemistry of springs and groundwaters from wells (+ and x) along the water corridor. North Rim springs (blue symbols), are most negative and range from –14.3 to –12.8‰ for $\delta^{18}O$ and –100.5 to –84.8‰ for δD. Pipeline waters sampled at South Rim Village (yellow symbols) overlap with the North Rim waters (blue symbols) and have a mean value of $\delta^{18}O = -13.6$‰ and $\delta D = -95.0$‰. The Water Reclamation Plant outflow has mean value of $\delta^{18}O = -13.3$‰ and $\delta D = -93.6$‰ which can be considered as an average of pipeline delivery water for the time of sampling (2018–2021), compared to mean values of $\delta^{18}O = -12.9$‰ and $\delta D = -93.4$‰ for samples taken in 1992–1993 (Ingraham et al. 2001).

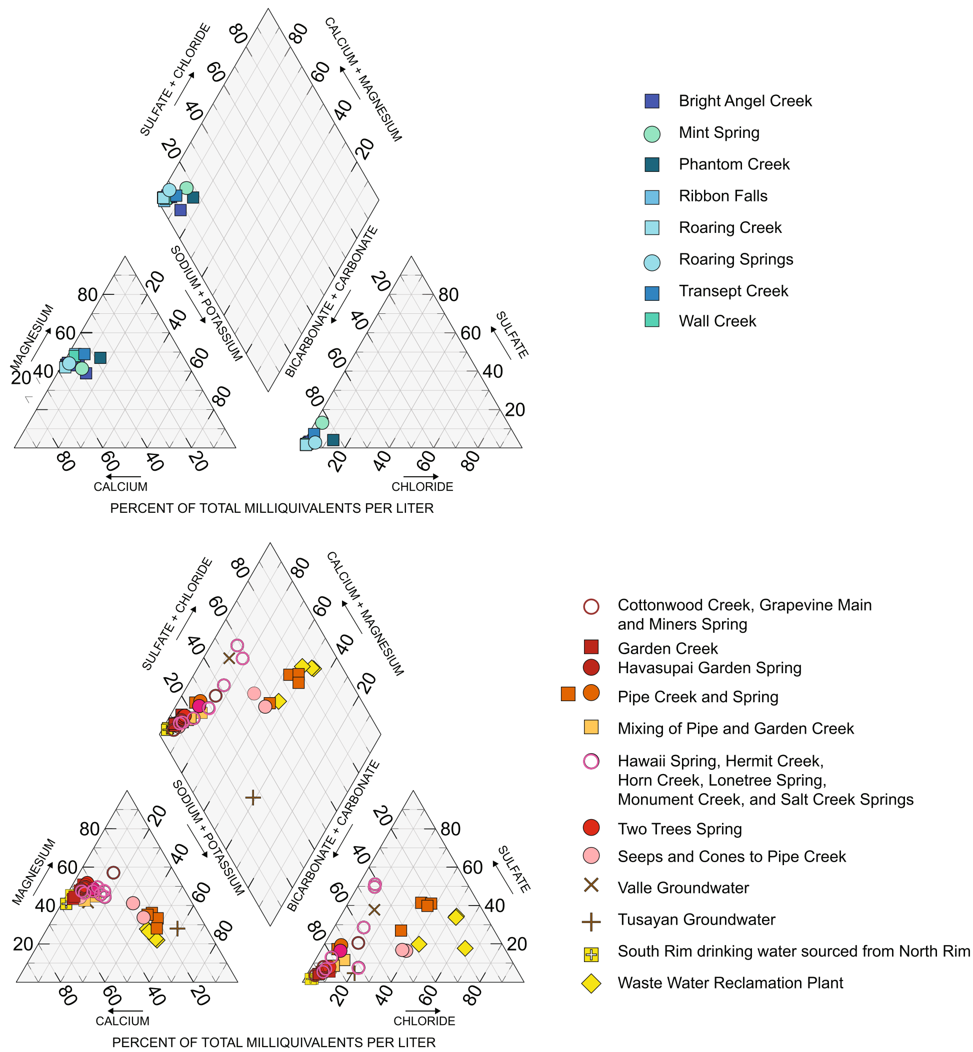


Fig. 8 Piper diagrams (Piper 1944) showing major ions. Filled symbols are new samples; open symbols are previously published samples (Monroe et al. 2005). Mixing trends are seen for North Rim and South Rim waters. **a** North Rim waters show mixing between low-TDS Roaring Springs water at left corner of parallelogram and higher-TDS side springs and side tributaries to Bright Angel Creek. **b** South Rim waters show two potential mixing trajectories: mixing of North Rim-derived low TDS waters with South Rim groundwater (1) (e.g. Tusayan groundwater), and higher chloride waters from evaporation in creeks or Water Reclamation Plant processes (2)

South Rim springs and groundwaters (orange symbols) have less negative values and means—C-aquifer water from Canyon Mine Observation Well has $\delta^{18}O = -10.9‰$, RM-aquifer groundwater from Valle wells has $\delta^{18}O$ of –11.8 to –11.5‰, and Tusayan wells have $\delta^{18}O$ ca. –12‰. Havasupai Gardens springs (red symbols) plot where North Rim and South Rim springs distributions overlap. Havasupai Gardens Spring at the campground has $\delta^{18}O$ between –12.6 and –12.4‰, indistinguishable from Two Trees Spring with $\delta^{18}O$ between –12.6 and –12.3‰. Garden Creek has $\delta^{18}O$ between –13.1 and –12.5‰ and reflects North Rim pipeline water that is discharged at the Havasupai Gardens pumphouse (Fig. 6). A complete summary of these stable isotope data is included in Table S5 in ESM1.

Chloride and deuterium

Chloride behaves conservatively and can also be used to evaluate mixing. Figure 10 plots two conservative tracers, δD against [Cl], to evaluate both water source and water solutes, respectively. The plot looks similar using $\delta^{18}O$ on the Y-axis because $\delta^{18}O$ and δD are linearly related with an R^2 of 0.9. North Rim waters plot in an array with low [Cl] and δD of about –95‰. Bright Angel Creek samples show a downstream change towards less negative δD. South Rim groundwaters have much higher [Cl] concentrating between 0 and 120 ppm over a range of δD values. Havasupai Gardens and Two Trees springs plot in between the North and South Rim waters. Similar to the Piper diagram, multiple variation trends are observed in the data that may reflect North Rim groundwater mixing, North and South groundwater mixing, and increasing chloride.

Strontium isotopes

Strontium concentration and $^{87}Sr/^{86}Sr$ were analyzed for 12 samples (Fig. 11). Sample locations were selected to cover a variety of water types in this study including

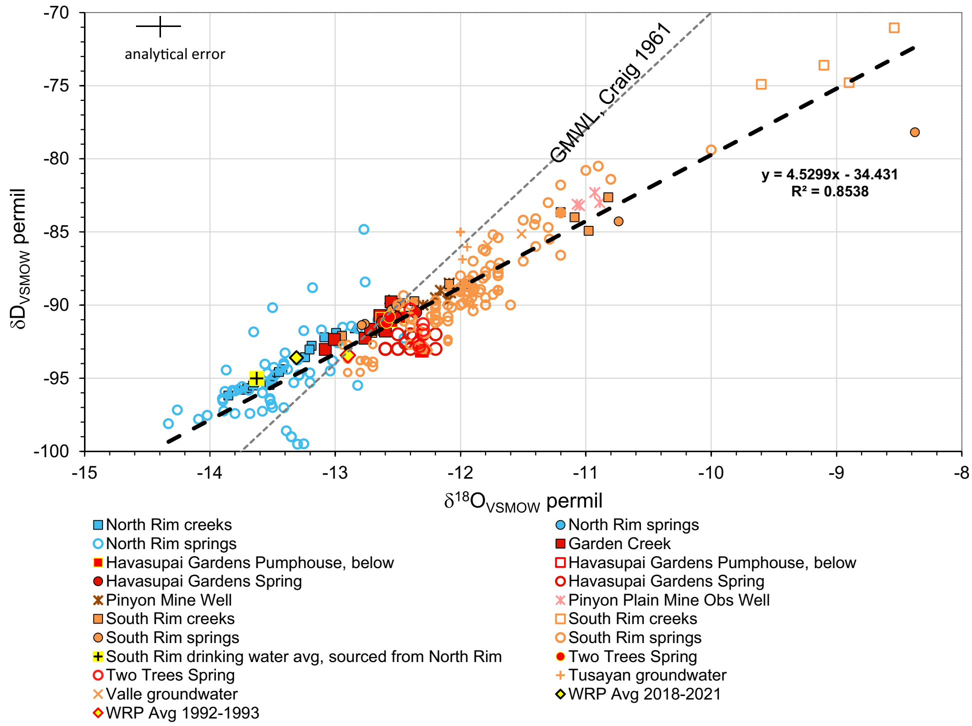


Fig. 9 Stable isotopes for oxygen and hydrogen show four water groupings: Blue = North Rim waters, Yellow = Grand Canyon Village waters, Orange = South Rim springs and groundwater, Red = Havasupai Gardens Spring and Two Trees springs. Unfilled symbols are from previously published samples (ESM1, Table S5). Regression line for these groundwater samples gives slope of 4.76 and $R^2 = 0.86$; this line is the groundwater line for the water corridor. Note that Havasupai Gardens plots at the transition from N-Rim to S-Rim distributions. GMWL (global meteoric water line) after Craig 1961

North Rim springs and creeks, South Rim springs, creeks and seeps, reclaimed effluent from the WRP, drinking water at South Rim Grand Canyon Village, and South Rim groundwater wells. For comparison, these samples are plotted along with published samples from western Grand Canyon from Crossey et al. (2006). Strontium concentrations ranged from 0.04 to 4.13 mg/L with the highest values observed at the Pipe Creek seep that feeds into Pipe Creek. $^{87}Sr/^{86}Sr$ values were between 0.710 and 0.734. Most of the samples have $^{87}Sr/^{86}Sr$ values between

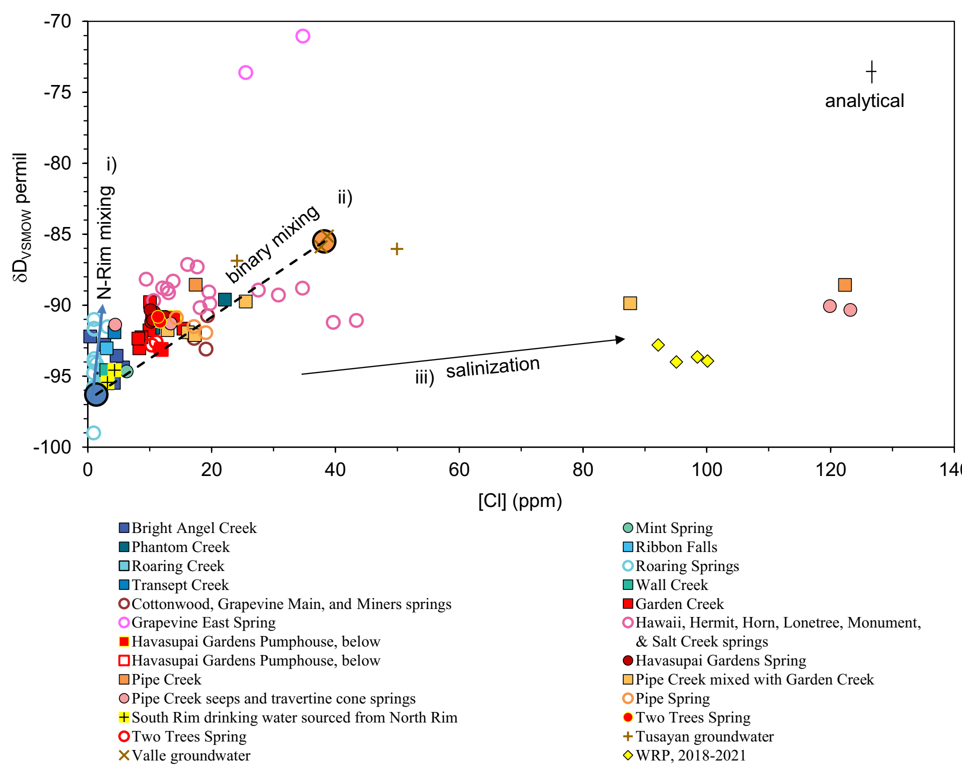


Fig. 10 Chloride [Cl] versus δD for springs (circles), creeks (squares), wastewater (diamonds), and wells (exes and crosses) of the water corridor. Unfilled symbols are from published samples (ESM1, Table S5). Color groups are North Rim (blues); South Rim (oranges); Havasupai Gardens (red), and Grand Canyon Village (yellow). Potential mixing trajectories: N-Rim mixing of Roaring Springs baseflow with recharge events (i), binary mixing of North Rim-derived low TDS waters with South Rim groundwater (ii) (e.g. Tusayan and Valle groundwater), and higher chloride waters from evaporation in creeks, water reclamation processes (Roberts et al. 2007), and/or addition of salts from deeply circulated geothermal fluids (iii)

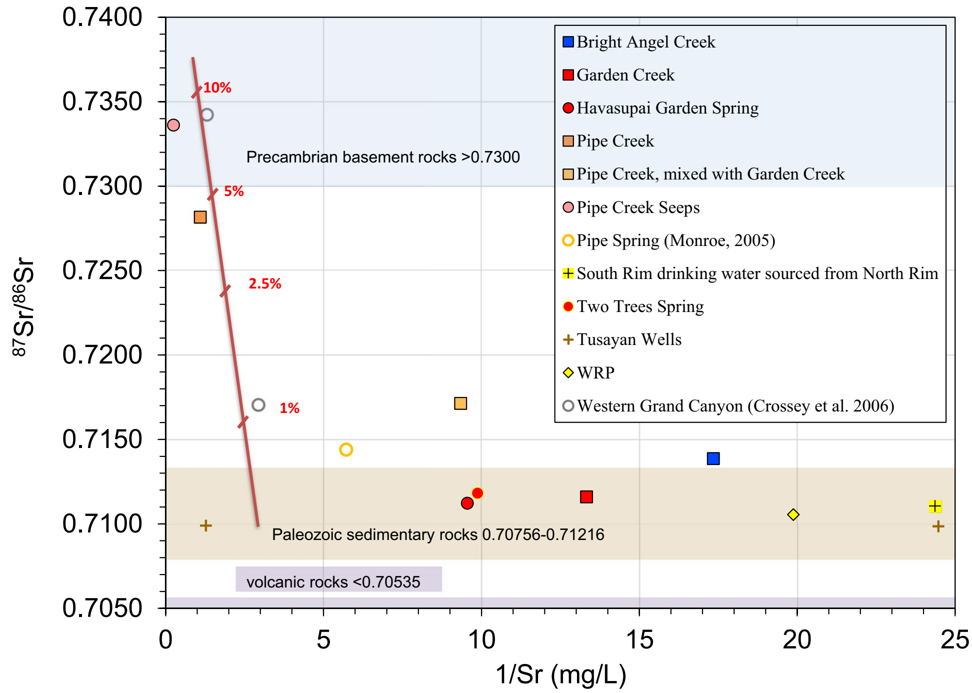


Fig. 11 Plot showing $^{87}Sr/^{86}Sr$ vs 1/Sr for selected water corridor samples (filled symbols) contrasted with published data (open symbols) and Grand Canyon rock values for $^{87}Sr/^{86}Sr$ from Monroe et al. (2005), Bills et al. (2007), and Crossey et al. (2006). Red line shows binary mixing model from Crossey et al. (2006) for western Grand Canyon geothermal water input

0.70756 and 0.71216, typical of Paleozoic marine carbonates of the R-M limestone karst aquifer (Bills et al. 2007). Somewhat higher values (0.714–0.718) are seen in Bright Angel and Pipe Creeks. High $^{87}Sr/^{86}Sr$ (>0.725) occurs in high [Sr] (low 1/[Sr]) waters in Pipe Creek seep along the Bright Angel fault. These values are similar to the most radiogenic samples in western Grand Canyon and are interpreted to be due to water–rock interaction within Precambrian basement granites (Crossey et al. 2006).

Pharmaceutical and personal care products

Pharmaceutical and personal care products were analyzed in the park's reclaimed effluent water and in select springs below the South Rim. Sampling took place in February, September, and December 2021. Data is summarized in Tables S6 and S7 in ESM1 and Fig. 12. All detections were above minimum reporting limits (MRL). Eurofins Laboratory reports are also included in the electronic supplementary material (ESM2). This report includes MRLs, surrogate spike recoveries for individual compounds, laboratory blank, duplicate, and matrix spike performance which generally performed well and are detailed throughout this discussion.

Field blanks were collected in February and December immediately following sampling at the Water Reclamation Plant. The reclaimed water sampled in both February and December showed 20 detections (blue columns, Fig. 12; Table S6 in ESM1). The analytical method can detect low-level concentrations of these anthropogenic compounds, even in treated water, and is not indicative of failed treatment. Sweeteners are commonly observed in reclaimed water, including Acesulfame-K and Sucralose which were found in the discharged water. Blanks were high (especially in the Feb sampling) for four compounds found in WRP (DEET, Salicylic Acid, TCEP, TCPP); hence, these results are more questionable as "detects". The salicylic acid detection in the field blank in February was also high in the matrix spike and matrix spike duplicate and may have been a false positive for this reason. The DEET detection in the field blank in December was also high in the matrix spike at 148% of the expected value (limits: 60–140%).

The South Rim springs analyzed include Havasupai Gardens Spring, Two Trees Spring, and Pipe Spring. During the winter sampling in February 2021, Havasupai Gardens Spring and Two Trees Spring had zero detections. When sampled again in October 2021, detections of PPCP included albuterol (used to treat asthma and other lung problems), caffeine, DEA (used in surfactants), phenazone (a pain reliever), propylparaben (a cosmetic preservative), sulfadiazine (an antibacterial drug), and theobromine (a caffeine derivative). Of these, only albuterol and caffeine were also detected in the WRP. In October albuterol was reported in the matrix spike duplicate at 155% of the expected value, exceeding the limit of 140%, suggesting that values in the samples may have also been slightly overestimated. However, the matrix spike and laboratory control spike performed within the expected range.

The third sampling event took place in December 2021 where repeat detections of theobromine and caffeine were found, in addition to new detections of 1,7-dimethylzannthine

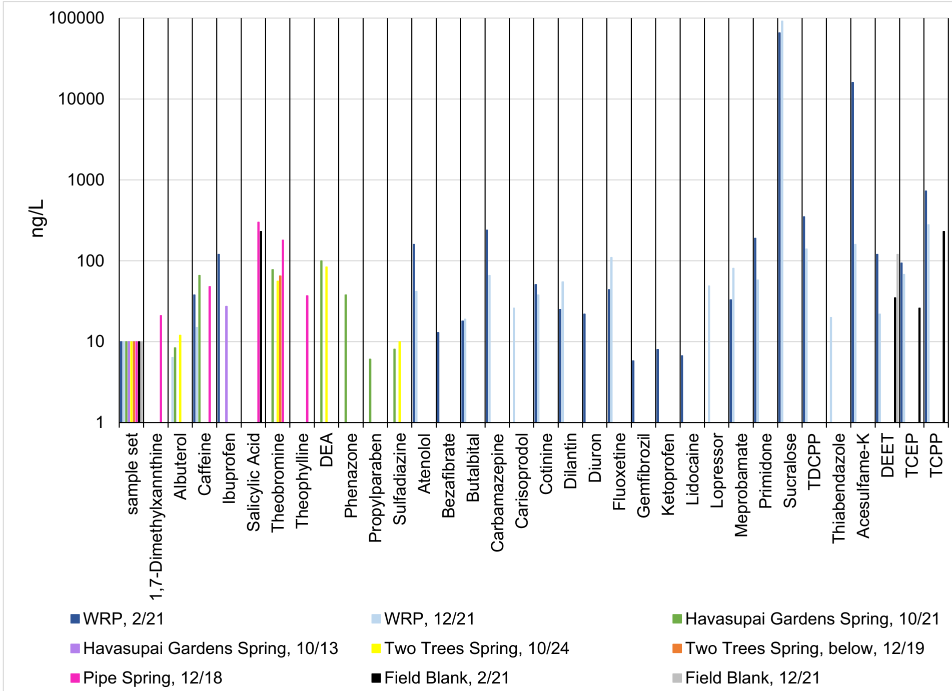


Fig. 12 Bar chart for PPCP detections at Havasupai Gardens Spring, Two Trees Spring, below Two Trees Spring, Pipe Spring, Water Reclamation Plant (WRP), and field blanks. Plots shows all detections at springs and equivalent detections for WRP. It does not include every detection in the WRP. Other reported data for Havasupai Gardens Spring is from Dyer et al. (2013). Salicylic acid was detected in both Pipe Spring and the blank, but during different sampling events

(caffeine derivative), theophylline, and salicylic acid all in Pipe Creek. Although salicylic acid was detected in a field blank, this was during the February sampling event. The matrix spike and matrix spike duplicate analyzed on 12/27/22 for 1,7-dimethylzannthine and theophylline were both below the expected yields of 60%, suggesting that the detections in Pipe Creek may be underreported (ESM2). In contrast, the matrix spike on 1/14/22 had a high yield of 149% of the expected value (upper limit: 140%).

A NPS report for this region showed results from published PPCP sampling with a detection of ibuprofen in Garden Creek 10/23/2013. Other sampling events from the NPS report in June 2012, October 2012, April 2013, and July 2013 were labeled as "nondetect" (Dyer et al. 2016). Of the detections at South Rim springs, two of the same compounds (caffeine and albuterol) were also detected in the reclaimed effluent with the same order of magnitude concentrations (e.g. caffeine between 15–66 ng/L (Table S7 in ESM1).

Interpretation, combining tracers

All of the hydrochemical plots suggest mixing of groundwaters. This section interprets the combined multiple tracer data to understand different potential end members with the understanding that true end members may or may not have been sampled.

Roaring Springs water has low with only slightly variable TDS, making it an excellent drinking water source. Bright Angel Creek and side tributary inputs to Bright Angel Creek can have slightly higher TDS and salts, but average solute values are still very low and provide good drinking water sources. The variability in Roaring Springs stable isotopic values was reported by Brown (2011) who identified a baseflow end member ($\delta^{18}O = -13.78‰$, $\delta D = -96.3‰$), a fast-traveled snowmelt recharge end member ($\delta^{18}O = -12.4‰$, $\delta D = -90‰$), and a mixing line with a slope of 4.5. The baseflow value determined by Brown (2011) for Roaring Springs does not quite describe the entire variation of the somewhat larger North Rim dataset that includes more negative values at Angel and Emmett springs, which also feed Bright Angel Creek. Grand Canyon Village drinking water falls on Brown's (2011) Roaring Springs mixing model at an intermediate value ($\delta^{18}O = -13.6‰$, $\delta D = -95‰$) and suggests a predominant (~80%) baseflow. The Water Reclamation Plant (WRP) waters averaged $\delta^{18}O = -13.3‰$, $\delta D = -93.6‰$ during 2018–2021 sampling, suggesting ~65% baseflow. This variation is reasonable because pipeline water reaching South Rim varies along the mixing line, depending on the timing of fast-traveled snowmelt recharge events.

In 2021 longitudinal sampling, stable isotopes for water in Bright Angel Creek show a pattern of increasing enrichment of δD over 13 km from –96.2 to –93.5‰ at the Colorado River (Fig. 10). This pattern may represent both evaporation and mixing. Phantom Creek flows into Bright Angel Creek 1.5 miles upstream of the Colorado River and had δD between –91.6 and –89.6‰, an average of 5‰ heavier than Bright Angel Creek. The tributaries (springs and creeks) to Bright Angel Creek vary in δD from –95.3 to –89.6‰, which are all more enriched than the upstream value for

Bright Angel Creek. Average TDS levels are slightly higher from the springs and creeks that feed into Bright Angel Creek at 340 mg/L compared to the average TDS of Bright Angel Creek of 270 mg/L.

South Rim springs and groundwaters are more varied and range from Ca–HCO_3 waters similar to Roaring Spring, to SO_4^- and Na–Cl-rich waters. South Rim springs, seeps, and creeks show two mixing trends between Roaring Springs water with more Na–Cl rich waters as shown in Figs. 8 and 10. Trend No. 1 appears to be a mixing trend with an end member similar to Valle groundwater, which is also similar to several South Rim springs, suggesting complex mixing within South Rim springs and Coconino Plateau groundwater.

South Rim waters have a significant internal variation and a different fingerprint in solutes (Fig. 8), stable isotopes (Fig. 9), and $^{87}Sr/^{86}Sr$ (Fig. 11). Solutes and $^{87}Sr/^{86}Sr$ indicate variable water–rock interaction in some springs. South Rim stable isotopes are less negative than North Rim waters reflecting lower elevation and a likely component of local recharge (Solder and Beisner 2020). Figure 9 shows that there is an overlap in stable isotope composition between South Rim wells on Coconino Plateau and springs that discharge below the South Rim. Points that plot well to the right and at a lower slope than the overall groundwater trend are interpreted to be evaporation trends (Sharp 2017), as seen in Pipe Creek and Grapevine East springs.

Figure 13a shows mean and standard deviation values for repeat measurements of key springs and wells of the water corridor. The blue symbol is the proposed negative Roaring Springs baseflow end member of Brown (2011). The least negative (upper right) end member of this proposed mixing is poorly defined because of limited well data on the Coconino Plateau. A potential South Rim end member is Valle groundwater. Pinyon Plain Mine Observation Well is more negative, but is from the C-aquifer; thus, Valle groundwater is used as the endmember since it is near the limits of the data variability, providing a conservative end member for the mixing model. Note that Tusayan and Pinyon Plain Mine well stable isotopes fall between Valle and waters derived from the North Rim.

Figure 13a shows that Havasupai Gardens Spring plots at the intersection of the North Rim and South Rim stable isotope distributions. Using Valle as the choice of a S-Rim groundwater end member, Havasupai Gardens and Two Trees springs contains ~40% Roaring Springs baseflow mixed with Valle groundwater—Solder and Beisner (2020) and their equation 2, using $\delta^{18}O$; Table S9 in ESM1). Figure 10 shows that both solutes and δD for Havasupai Gardens spring are also compatible with a ~40% mixture of North Rim water with a Valle groundwater end member. This compares with an alternative estimate of 103% of mean modeled winter precipitation relative to mean summer runoff (Solder and Beisner 2020, their Table 3; also shown in ESM1 Table S9).

Mean values from other springs (Fig. 13a; Table S8 in ESM1) that emanate from the R-M aquifer below the South Rim also show a significant proportion of N-Rim component. Grapevine Main and Cottonwood Springs have the most negative isotopic values and most strongly overlap with Roaring Springs values. Hawaii, Hermit, Horn, Monument, and most of the other South Rim springs are spread out along the groundwater line between potential mixing end members. An estimate of the proportions of end members of individual springs along the linear mixing array of Fig. 13a suggests that most South Rim springs are sustained by 10–60% North Rim contributions (Fig. 13b; Table S9 in ESM1).

Figure 13b shows that the fault network of NE-striking and NW-striking faults and monoclines forms an orthogonal grid of basement-penetrating faults along the South Rim. This network is similar to the one on the North Rim that facilitated a long-distance fast transit during the dye tracer study (Jones et al. 2017). Hence pipeline water from the Water Reclamation Plant, plus general infiltration of North Rim groundwater to the R-M waters down the Bright Angel fault both south towards the Tusayan groundwater divide and north into Grand Canyon as shown in Fig. 5b may explain the variation in South Rim springs. This flow is driven both by the topographic head of the WRP infiltration site and by the head from the groundwater divide in the R-M aquifer near Tusayan.

In addition to this primary mixing story, solutes in the Piper diagram (Fig. 8) and the cross plot of [Cl] with δD (Fig. 10) suggest that the South Rim groundwater variation is not completely described by two-component mixing. In both diagrams, the Water Reclamation Plant, the Pipe Creek travertine cone along the Bright Angel fault, the Pipe Creek seep along the Bright Angel fault (Fig. 6), and some Pipe Creek samples, suggest that a salinization component needs to be added to the mixture. Possible salinization processes include evaporation, geothermal inputs, and reclamation processes (USEPA 1988; Roberts et al. 2007). Notably, as suggested in Fig. 6, the higher salts in Pipe Creek travertine cone and Pipe Creek seeps along the Bright Angel fault may be showing a direct pathway from the WRP. $^{87}Sr/^{86}Sr$ is far higher in the Pipe Creek seeps that emerge from Precambrian basement and this cannot be due to evaporation and therefore, the salts can also be explained in part by deeply circulated geothermal waters and water–rock interaction (Crossey et al. 2006, 2016). Coconino Plateau groundwater wells at Tusayan and Pinyon Plain Mine may have picked up salts from the WRP, among other processes.

Pharmaceutical and personal care products were used to test the hypothesis that there is a connection between the reclaimed effluent and the springs discharging along the Bright Angel

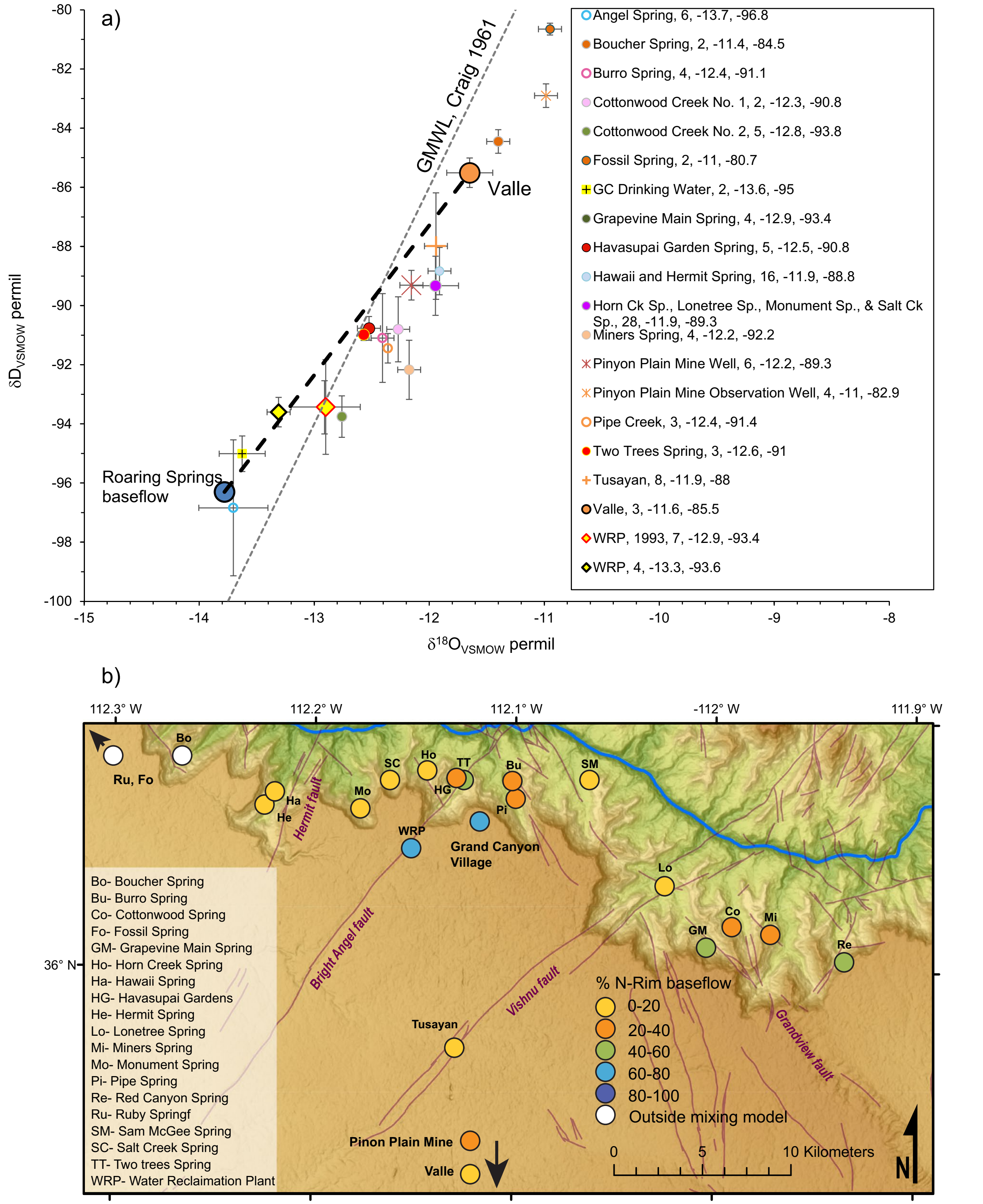


Fig. 13 Stable isotope variation in South Rim Springs and groundwaters. **a** Mean stable isotope water values fall on a variation trend between a North Rim end member (Roaring Springs base flow; blue dots) and Valle groundwater. **b** Map shows spring locations and estimate of mixing proportion in different springs due to infiltration of North Rim water at Grand Canyon Village (see ESM1 Table S9 for calculations). This supports the hypothesis of significant groundwater connectivity between springs and Coconino Plateau groundwater wells, including the Pinyon Pine Uranium Mine

fault. During both samplings of the WRP, relatively persistent compounds such as acesulfame-K, carbamazepine, and sucralose were detected that were not detected in the springs. Similarly, many detections at the springs were of compounds that were not in the WRP such as DEA, phenazone, propylparaben, sulfadiazine, and theobromine at Havasupai Gardens and Two Trees, and 1,7-dimethylzannthine, salicylic acid, theobromine, and theophylline at Pipe Spring. The only compounds found in both WRP and springs were albuterol, caffeine, and ibuprofen. One possible explanation for the lack of spring detects is that some PPCP degrade more readily in the environment than others. During the first of the three sampling events, no detections of PPCPs were found at the springs sampled. The first sampling event was conducted in February and may have been affected by snow at the spring sampling sites that may have diluted the spring water. The PPCPs at the springs if sourced from the reclaimed water show little dilution based on their concentrations. Thus, this pilot dataset may be compatible with the hypothesis that the reclaimed water has impacted the springs and suggest that these tracers may be a useful addition to natural tracers for understanding water pathways. However, questions about persistence of different compounds in the groundwater system and the timeframe for fluid transport are such that the PPCP results alone are inconclusive in terms of any transport of PPCPs from the WRP to springs. The high use of these locations by hikers and backpackers could also be a source for PPCPs in the springs, but sampling was done carefully directly at the spring vent, permitting the interpretation that PPCPs presence is due to recharge from WRP. Dyer et al. 2016 reported that up to 10 mule trips and up to 800 hikers may travel on Bright Angel Trail in a given day but, for example, Two Trees Spring is located along the Bright Angel fault and upslope from the hiking trail and relatively remote from hiking traffic. Similar work was conducted and reported on at the Goldschmidt conference by the US Geological Survey (USGS); however, no detections at Havasupai Gardens Spring were found (Beisner et al. 2022).

Discussion and implications

Many factors contribute to the need for better understanding of groundwater and springs in the Grand Canyon region including the increased groundwater extraction related to development (Solder and Beisner 2020), reduced recharge from climate change (Tillman et al. 2020; McGibbon et al. 2022), and the risk for environmental contamination and spring impact from nearby uranium mining (Bills et al. 2007; Solder et al. 2020; Beisner et al. 2017a, 2020). Further, the Park is changing the pipeline delivery system to better meet overall water needs. The data and interpretations presented here have provocative and testable implications for several aspects of Park and regional water management.

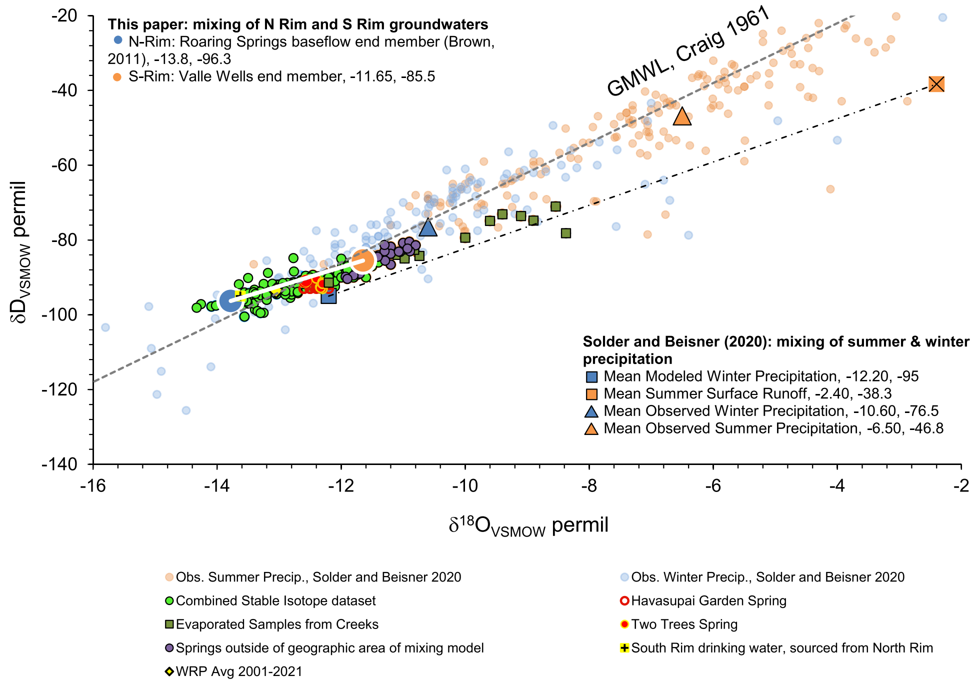
Distinct North Rim and South Rim groundwater hydrochemical fingerprints suggest that the >60-year anthropogenic recharge experiment has been a successful, if unintentional, use of pipeline water and WRP effluent to sustain springs and mitigate regional groundwater extraction in the South Rim groundwater system. Figure 13a summarizes this binary mixing hypothesis. Water at Grand Canyon Village is essentially 100% North Rim pipeline water (~80% Roaring Springs baseflow). Havasupai Gardens Spring is ~40% North Rim water using a Valle groundwater end member. Most other South Rim springs are also hypothesized to be sustained by 10–60% North Rim recharge. Any mixing model estimates are necessarily only semiquantitative because of the uncertainty about the most appropriate South Rim end member. Some South Rim springs are less negative than Valle groundwater and hence outside this specific mixing model; however, if additional studies show a wider range of South Rim hydrologic mixing, Valle groundwater itself may have a component of North Rim water.

As an alternative hypothesis to explain the observed stable isotope groundwater variation, Solder and Beisner (2020) proposed variations in the proportions of summer versus winter meteoric recharge that reaches different springs. Figure 14 shows that winter and summer precipitation data from the South Rim area vary more widely than the South Rim groundwater variation. Solder and Beisner's (2020) meteoric mixing models explored different precipitation end members: the most negative (lower left) end member was a precipitation-weighted mean of modeled winter precipitation ($\delta^{18}O = -12.2‰$; $\delta D = -95‰$). This value is more negative than the mean of observed winter precipitation ($\delta^{18}O = -11.1‰$; $\delta D = -82.6‰$). Their favored most positive (upper right) end member was the mean of the observed summer runoff ($\delta^{18}O = -2.4‰$; $\delta D = -38.‰$), which is more positive than the mean of the observed summer precipitation ($\delta^{18}O = -6.5‰$; $\delta D = -46.8‰$).

However, Solder and Beisner's (2020) proposed meteoric mixing lines do not pass through the groundwater values and the most negative proposed end member does not encompass the full range of South Rim groundwater data which is better described by groundwater mixing (Fig. 14). Thus, whereas South Rim groundwaters ultimately do reflect a mixture of winter and summer recharge, both local and regional (Springer et al. 2017), this recharge mixing model is once-removed from the aquifer processes that average out variations in precipitation recharge and exert first-order control on groundwater variability.

Havasupai Gardens springs plot (Fig. 13a) in the area of overlap of North Rim and South Rim stable isotope arrays, an observation that initially led to the hypothesis that pipeline water mixes with South Rim groundwaters (Crossey et al. 2019). The alternative, if Havasupai Gardens Spring composition were independent of North Rim (pipeline)

Fig. 14 Alternate mixing models to explain the observed stable isotope spring and groundwater variation of springs and wells of the water corridor. Solder and Beisner (2020), their Fig. 3, proposed that variation in the proportion of modeled mean winter precipitation and mean summer runoff end members (squares), or means of observed summer and winter precipitation (triangles) may explain the groundwater variation. Instead, mixing of North Rim springs (blue dot) and South Rim groundwater (orange dot) better describes the observed groundwater variation (this report)



input, is that Havasupai Gardens water is the most negative end member of South Rim springs, and even more negative than the proposed mean winter recharge end member of Solder and Beisner (2020). It seems unlikely that Havasupai Gardens springs would have a higher proportion of winter recharge than R-M groundwater wells from the higher elevation Coconino Plateau or than the nearby inner canyon springs such as Hermit Spring.

Other geochemical tracers are also compatible with North Rim (pipeline) water providing a young component to Havasupai Gardens and other South Rim springs. Tritium values measured at Roaring Springs in 2003 (Ross 2005) ranged from 2.3 TU in October (near baseflow) to 5.1 in May (larger snowmelt component). All these values represent mixing of a modern (post-1950s) recharge component characterized by > 12.8 TU (Beisner et al. 2017b) with entirely pre-1950s recharge characterized by < 0.5 TU (Solder et al. 2020) to < 1.3 TU (Beisner et al. 2017b). Water Treatment Plant water in 2021 was lower, 1.8 TU (USGS), but that also represents a mixture of post-1950s and older water arriving from the North Rim. Havasupai Gardens mainly has near-zero tritium values, but Two Trees in 2001 had up to 0.8 TU. Other South Rim springs also have significant but quite variable tritium indicating a component of post-1950s recharge: Pipe Creek is 0.9–1.1 TU; Hermit Spring is up to 0.6 TU; Horn Creek is 0.94–2.8 TU; Burro Spring is 0.53–1.91 TU (ESM1 S9). Solder et al. (2020) attributed this young component to local summer recharge, but these are all springs that may have > 10% North Rim water (Fig. 13b), which is the explanation preferred here. These springs have ^{14}C values that are 17–130% of modern values, also supporting the mixing of a significant modern water component. Evidence for groundwater mixing and the presence of this young component greatly complicates the "age model" from Solder et al. (2020) that South Rim groundwaters are thousands to tens of thousands of years old.

A key but relatively poorly resolved aspect of the interpretation for connectivity and mixing of North Rim, South Rim, and Coconino Plateau groundwaters within the greater South Rim area relies on the geometry of the Tusayan groundwater divide depicted in Fig. 5b. Scarcity of wells and poor public documentation of water level and historical data is such that additional data about geochemical and water level variation of key wells at Tusayan, Pinyon Plain Mine, and Valle are needed. Prior to the early 1990s, Tusayan's water supply was trucked from the South Rim water tanks, hence North Rim water. After deep drilling and pumping commenced, groundwater pumping was reported to have little effect on South Rim springs (Errol L. Montgomery and Associates 1999; Bills et al. 2007). Tusayan has historically pumped about 8 L/s, but development proposals suggest this value could increase to 18–65 L/s (Toll et al. 2020). The decadal-scale evolution of the Tusayan divide is unknown and has especially important implications for regional water use, future drilling and water extraction at Tusayan and Valle, and mining at Pinyon Plain Mine. Given the potential for fault-influenced flow combined with karst complexities, any change in the head in groundwater wells near the divide and especially along faults will likely affect South Rim springs.

Water quality as well as sustainability are concerns for South Rim springs. Two local uranium mines are of past and future concern (Beisner et al. 2020). The Orphan Lode

Mine, directly at the South Rim, had heavy mining from 1956–1969 and is now inactive. The Pinyon Plain Mine (formerly Canyon Mine) is about 16 km south of Tusayan (Fig. 1) and has yet to be actively mined but is resuming development activities (Beisner et al. 2020). The Pinyon Plain Mine has pumped over 49 million gallons (average of ~0.67 L/s) over the last 9 years from the mine shaft (Reimondo 2022), mostly from the R-M aquifer. The Pinyon Plain Observation Well was drilled to the C-aquifer for monitoring in 2017; its stable isotope chemistry is less negative than the Valle end member (Fig. 13a) and just outside the proposed mixing model (Fig. 13a). However, a direct connection between the perched C-aquifer and R-M aquifer and mining operations is likely.

A USGS report published in 2021 presents uranium data for greater than 200 groundwater sites sampled between 1981–2020. The study reports that 95% of the sites have uranium concentrations less than the USEPA MCL of 30 μg/L (Tillman et al. 2021) and concludes that the effects of mining on uranium in groundwater are inconclusive. However, among the highest uranium concentration values in groundwater in the study area were observed at Horn Creek (8.6–29 mg/L U), Monument Spring (7.1–7.3 mg/L U), and Salt Creek springs downslope from the Orphan Mine in waters that are calculated in this report to contain 10–20% infiltrated groundwater. Given the large spread of sample locations included in the study covering nearly 300 km east–west, and the lack of a groundwater monitoring network in close proximity to the mines, the extent to which uranium mining may have affected groundwater uranium concentrations remains poorly known (Tillman et al. 2021). This report proposes that the uranium mine wells are well connected with Grand Canyon springs and R-M groundwater of the Coconino Plateau, including Havasupai Gardens Spring and groundwater farther west.

The Bright Angel fault as a fast pathway for recharge to Havasupai Gardens Spring is provocative and testable in terms of understanding the rate of water transit. Additional tritium, PPCPs work, and other tracers should be used to test this fault connection in combination with a dye tracer study using biodegradable anthropogenic tracers similar to Jones et al. (2017). Different injection experiments at the WRP, Tusayan, and Pinyon Plain mine, and receptors located at Havasupai Gardens, Two Trees, Pipe Creek travertine cone, Burro, Horn, Monument, Hermit, Tusayan, Pinyon Plain Mine, and Valle (among others) would test the fault network model for the South Rim and better quantify connectivity between springs and rates of fast-traveled water movement. Such dye tracer data combined with natural tracers and a program of monitoring temperature, conductance, and water level at groundwater wells in the region can test their hypothesized interconnectivity and better define the potentially changing location and geometry of the groundwater water divide. The available data suggest that the South Rim fault network is like the North Rim network and will convey waters in days to months in many directions.

There are also implications of this study for the planned change in the pipeline system. The present plan is to intake water from Bright Angel Creek in addition to Roaring Springs. This will increase the available North Rim water supply by several fold. The geochemical data for Bright Angel Creek suggest this will cause only a very minor degradation of water quality (from 160 to 270 TDS and 0.0032–0.0036 DIC). However, a probable serious negative consequence of a change from Roaring Springs groundwater to Bright Angel Creek surface water will be the interruption of continuity of the water supply system because of expected increase in turbidity as a result of annual and perhaps increasing frequency of flash flood events and increasing fire impacts on the large drainage basin area of Bright Angel Creek (Fig. 5a).

Application of a multi-tracer approach using both natural and anthropogenic tracers and monitoring of both discharge and composition of springs and groundwater is needed to establish a better water baseline for the Grand Canyon water corridor. A recent analysis of snow telemetry data by the USEPA shows that many watersheds in the western US have experienced an average decrease in snowpack of 20% between 1955 and 2020 (USEPA 2021). Local precipitation data for Grand Canyon from 1893–2009 shows that drought conditions have been ongoing since the 1990s (Hereford et al. 2014; Tillman et al. 2020). Establishing a water baseline for the water corridor should have begun decades ago, but is needed now in order to be able to evaluate potential future water changes and appropriate management responses.

Conclusions

The overall goal of this study has been to evaluate an ongoing anthropogenic hydrologic experiment that the Park has been conducting over the past >60 years in order to help develop a present baseline that can be used to better understand the water corridor of Grand Canyon. Ingraham et al. (2001) made the observation that Havasupai Gardens Spring has more depleted stable isotope composition than other South Rim springs and was likely influenced by a North Rim water component from either pipeline leakage or recharge from reclaimed effluent. In this study, natural and anthropogenic hydrochemical tracers are used to show that North Rim and South Rim waters have distinct fingerprints and that mixing is occurring not only in springs near Havasupai Gardens Spring but also in many South Rim springs and Coconino Plateau groundwaters. The specific findings of this study are as follows.

1. North Rim water emerging from Roaring Springs varies in composition between a baseflow endmember plus faster-traveled snowmelt and monsoonal recharge. The average composition of the pipeline water reaching the South Rim is estimated here to be ~80% base flow (Brown 2011). This report presents a mixing model with 100% baseflow as the North Rim endmember with values of $\delta^{18}O = -13.78‰$ and $\delta D = -96.3‰$.
2. South Rim spring and groundwater geochemistry is highly variable, reflecting groundwater mixing. A conservative least negative (upper right) stable isotope end member is identified from the mean of Valle groundwater of $\delta^{18}O = -11.65‰$, $\delta D = -85.5‰$; this groundwater mixes with North Rim pipeline end member water that infiltrates at Grand Canyon Village, including reclaimed water.
3. In this mixing model, Havasupai Gardens Spring is sustained by ~40% from a North Rim end member.
4. A direct pathway from the WRP is proposed for Pipe Creek seeps and travertine cones along the Bright Angel fault based on high salts in these springs as well as the WRP. Havasupai Gardens Spring does not see these high salts and its composition reflects the mixing of North Rim with South Rim waters that are apparently mixed within the larger R-M aquifer system below the South Rim.
5. The fault-connected hydrologic system provides an explanation for the mixing of Roaring Springs (pipeline) water with groundwater wells in a wide region of the South Rim aquifer. Pumping at Tusayan and Pinyon Plain Mine may affect South Rim springs, but this may be mitigated by a southward flow of groundwater from below Grand Canyon Village along the Bright Angel fault towards Tusayan.
6. Dye tracer studies on the South Rim are needed to better identify fluid pathways and quantify groundwater transit times and connectivity. These should be conducted in tandem with continued tracer studies.
7. Under baseflow conditions, North Rim springs and surface water in Bright Angel Creek have similar water quality so the proposed change in Grand Canyon drinking water source should be minimal from a water quality viewpoint during baseflow conditions of Bright Angel Creek. However, this change has potential adverse consequences in terms of increased downtime needed to settle turbidity after flash floods and fire impacts that are likely to be increasingly frequent due to climate change.

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Declarations

Conflict of interests On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

ADEQ (2017) Public Notice: Proposed Arizona Pollutant Discharge Elimination System (AZPDES) New Permit. In: Arizona Bus. Gaz. http://www.azdeq.gov/public-notice-proposed-azpdes-permit-renewal-south-rim-wastewater-treatment-plant. Accessed 9 Dec 2020

Baird RB, Eaton AD, Rice EW (2017) Standard methods for the examination of water and wastewater, 23rd edn. American Public Health Association, Washington, DC

Beisner KR, Tillman FD, Anderson JR, Antweiler RC, Bills DJ (2017a) Geochemical characterization of groundwater discharging from Springs North of the Grand Canyon, Arizona, 2009–2016. US Geol Surv Sci Invest Rep 2017–5068

Beisner KR, Paretti NV, Tillman FD, Naftz DL, Bills DJ, Walton-Day K, Gallegos TJ (2017b) Geochemistry and hydrology of perched groundwater springs: assessing elevated uranium concentrations at Pigeon Spring relative to nearby Pigeon Mine, Arizona (USA). Hydrogeol J 25:539–556. https://doi.org/10.1007/s10040-016-1494-8

Beisner KR, Solder JE, Tillman FD, Anderson JR, Antweiler RC (2020) Geochemical characterization of groundwater evolution south of Grand Canyon, Arizona (USA). Hydrogeol J 28:1615–1633. https://doi.org/10.1007/s10040-020-02192-0

Beisner KR, Paretti NV, Jasmann JR, Barber LB (2022) Anthropogenic compounds associated with groundwater near an abandoned copper and uranium mine, Grand Canyon, AZ, USA. Goldschmidt Geochem Conf Abstract USGS Natl Water Inf Syst. https://doi.org/10.5066/F7P55KJN

Billingsley GH, Breed WJ, Beasley D (1980) Geologic cross section along Interstate 41—Kingman to Flagstaff, Arizona. Petrified Forest Museum Association in cooperation with Museum of Northern Arizona, map sheet, Pagosa, Chandler, AZ

Bills D, Flynn M, Monroe S (2007) Hydrogeology of the Coconino Plateau and adjacent areas, Coconino and Yavapai counties, Arizona. US Geol Surv Sci Invest Rep 2005–5222

Brown CR (2011) Physical, geochemical, and isotopic analyses of R-aquifer Springs, North Rim, Grand Canyon, Arizona. MSc Thesis, Northern Arizona University, Flagstaff, AZ

Craig H (1961) Isotopic variations in meteoric waters. Am Assoc Adv Sci 133:1702–1703. https://doi.org/10.1126/science.133.3465.1702

Crossey LJ, Fischer TP, Patchett PJ, Karlstrom KE, Hilton DR, Newell DL, Huntoon P, Reynolds AC, de Leeuw GAM (2006) Dissected hydrologic system at the Grand Canyon: interaction between deeply derived fluids and plateau aquifer waters in modern springs and travertine. Geology 34:25–28. https://doi.org/10.1130/G22057.1

Crossey LJ, Karlstrom KE, Springer AE, Newell D, Hilton DR, Fischer T (2009) Degassing of mantle-derived CO2 and He from springs in the southern Colorado Plateau region: neotectonic connections and implications for groundwater systems. GSA Bull 121:1034–1053. https://doi.org/10.1130/B26394.1

Crossey LJ, Karlstrom KE, Schmandt B, Crow RR, Colman DR, Cron B, Takacs-Vesbach CD, Dahm CN, Northup DE, Hilton DR, Ricketts JW, Lowry AR (2016) Continental smokers couple mantle degassing and distinctive microbiology within continents. Earth Planet Sci Lett 435:22–30. https://doi.org/10.1016/j.epsl.2015.11.039

Crossey L, Karlstrom KE, Springer AE, Tobin B, Huntoon P (2019) Hydrochemistry at Grand Canyon: who knew groundwater hydrology could be so complicated? Geological Society of America Abstracts with Programs. Vol. 51, No. 5. https://doi.org/10.1130/abs/2019AM-335264

Dyer M, Monroe SA, Stumpf SE (2016) Water quality monitoring for Bright Angel, Garden, Pipe, and Hermit Creeks in Grand Canyon National Park: 2011–2013 summary report. National Park Service, Fort Collins, CO

Errol L. Montgomery and Associates (1999) Supplemental assessment of hydrogeologic conditions and potential effects of proposed groundwater withdrawal Coconino Plateau Groundwater Subbasin, Coconino County, Arizona. Montgomery, Scottsdale, AZ

Glynn PD, Plummer LN (2005) Geochemistry and the understanding of ground-water systems. Hydrogeol J 13:263–287. https://doi.org/10.1007/s10040-004-0429-y

Hereford R, Bennett GE, Fairley HC (2014) Precipitation variability of the Grand Canyon region, 1893 through 2009, and its implications for studying effects of gullying of Holocene terraces and associated archeological sites in Grand Canyon, Arizona. US Geol Surv Open-File Rep 2014-1006. https://doi.org/10.3133/ofr20141006

Hou X, Jones BT (2000) Inductively coupled plasma/optical emission spectroscopy. Encyclopedia of Analytical Chemistry: 9468–9485. https://doi.org/10.1002/9780470027318.a5110.pub3

Huntoon PW (1974) The karstic groundwater basins of the Kaibab Plateau, Arizona. Water Resour Res 10:579–590. https://doi.org/10.1029/WR010i003p00579

Huntoon PW (2000) Variability of karstic permeability between unconfined and confined aquifers, Grand Canyon Region, Arizona. Environ Eng Geosci 6:155–170. https://doi.org/10.2113/gseegeosci.6.2.155

Huntoon PW, Sears JW (1975) Bright angel and eminence faults, eastern Grand Canyon, Arizona. GSA Bull 86:465–472. https://doi.org/10.1130/0016-7606(1975)86%3c465:BAAEFE%3e2.0.CO;2

Ingraham NL, Zukosky K, Kreamer DK (2001) Application of stable isotopes to identify problems in large-scale water transfer in Grand Canyon National Park. Environ Sci Technol 35:1299–1302. https://doi.org/10.1021/es0015186

Jackson PE (2000) Ion chromatography in environmental analysis. Encyclopedia of analytical chemistry: 2779–2801. https://doi.org/10.1002/9780470027318.a0835

John Milner and Associates (JMA) (2005) Indian garden cultural landscape report, Grand Canyon National Park, Arizona

Jones CJ, Springer AE, Tobin BW, Zappitello SJ, Jones NA (2017) Characterization and hydraulic behaviour of the complex karst of the Kaibab plateau and Grand Canyon National Park, USA. Geol Soc Spec Pub 466(1). https://doi.org/10.1144/SP466.5

Jones NA, Hansen J, Springer AE, Valle C, Tobin BW (2019) Modeling intrinsic vulnerability of complex karst aquifers: modifying the COP method to account for sinkhole density and fault location. Hydrogeol J 27:2857–2868. https://doi.org/10.1007/s10040-019-02056-2

Kessler JA (2002) Grand Canyon Springs and the Redwall-Muav aquifer: comparison of geologic framework and groundwater flow models. MSc Thesis, Northern Arizona University, Flagstaff, AZ

Kim J, Bailey L, Noyes C, Tyne RL, Ballentine CJ, Person M, Ma L, Barton M, Barton I, Reiners PW, Ferguson G (2022) Hydrogeochemical evolution of formation waters responsible for sandstone bleaching and ore mineralization in the Paradox Basin, Colorado Plateau, USA. GSA Bull 134(910):2589–2610

Knight JE, Huntoon PW (2022) Conceptual models of groundwater flow in the Grand Canyon Region, Arizona. US Geol Surv Sci Invest Rep 2022-5037. https://doi.org/10.3133/sir20225037

Lattimore GM, Carden RS, Fischer T (1987) Grand Canyon directional drilling and waterline project. SPE/IADC Drill. Conf. SPE-16169-MS. https://doi.org/10.2118/16169-MS

Ledbetter J, Stevens L, Brandt B (2020) Springs online. Springs Stewardship Institute of the Museum of Northern Arizona. http://springsdata.org/. Accessed 12 September 2020

McGibbon C, Crossey LJ, Karlstrom KE (2022) Fence springs system of Grand Canyon: insight into the karst aquifer system of the Colorado Plateau Region. Hydrogeol J. https://doi.org/10.1007/s10040-022-02541-1

Metzger DG (1961) Geology in relation to availability of water along the South Rim Grand Canyon National Park Arizona. US Geol Surv Water Suppl Pap 1475–C, pp 105–135

Monroe SA, Antweiler RC, Hart RJ, Taylor HE, Truini M, Rihs JR, Felger TJ (2005) Chemical characteristics of ground-water discharge along the South Rim of Grand Canyon in Grand Canyon National Park, Arizona, 2000–2001. US Geol Surv Sci Invest Rep 2004-5146

Mozley PS, Goodwin LB (1995) Patterns of cementation along a Cenozoic normal fault: a record of paleoflow orientations. Geology 23(6):539–542. https://doi.org/10.1130/0091-7613(1995)023%3c0539:POCAAC%3e2.3.CO;2

National Park Service (2015) Transcanyon Water Line HAER No. AZ-95. Historic American Engineering Record, HAER No. AZ-95

NPS (2019) Grand Canyon news release: finding of no significant impact signed for the Transcanyon water distribution pipeline project in Grand Canyon National Park. NPS, Grand Canyon, AZ

Oppenheimer J, Eaton A, Badruzzaman M, Haghani AW, Jacangelo JG (2011) Occurrence and suitability of sucralose as an indicator compound of wastewater loading to surface waters in urbanized regions. Water Res 45:4019–4027. https://doi.org/10.1016/j.watres.2011.05.014

Parkhurst D (1995) Users guide to PHREEQC: a computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. USGS, Reston, VA

Piper AM (1944) A graphic procedure in the geochemical interpretation of water-analyses. Eos, Trans Am Geophys Union 25:914–928. https://doi.org/10.1029/TR025i006p00914

Reimondo A (2022) Update: flooding at uranium mine near Grand Canyon. https://www.grandcanyontrust.org/blog/update-flooding-uranium-mine-near-grand-canyon. Accessed April 2023

Roberts M, Schlinger C, Mead S (2007) An investigation of energy use, water supply and wastewater treatment at Grand Canyon National Park, Arizona. http://www.waterenergy.nau.edu/gcnp.html. Accessed April 2023

Ross LEV (2005) Interpretive three-dimensional numerical groundwater flow modeling, Roaring Springs, Grand Canyon, Arizona. Northern Arizona University, Flagstaff, AZ, 199 pp

Schindel GM (2015) Determining groundwater residence times of the Kaibab Plateau, R-Aquifer using temperature. Grand Canyon National Park, Arizona. MSc Thesis, Northern Arizona University, Flagstaff, AZ

Sharp Z (2017) Principles of Stable Isotope Geochemistry, 2nd Edition. https://doi.org/10.25844/h9q1-0p82

Solder JE, Beisner KR (2020) Critical evaluation of stable isotope mixing end-members for estimating groundwater recharge sources: case study from the South Rim of the Grand Canyon, Arizona, USA. Hydrogeol J 28:1575–1591. https://doi.org/10.1007/s10040-020-02194-y

Solder JE, Beisner KR, Anderson J, Bills DJ (2020) Rethinking groundwater flow on the South Rim of the Grand Canyon, USA: characterizing recharge sources and flow paths with environmental tracers. Hydrogeol J 28:1593–1613. https://doi.org/10.1007/s10040-020-02193-z

Springer AE, Boldt EM, Junghans KM (2017) Local vs. regional groundwater flow delineation from stable isotopes at Western North America Springs. Groundwater 55:100–109. https://doi.org/10.1111/gwat.12442

Tillman FD, Gangopadhyay S, Pruitt T (2020) Recent and projected precipitation and temperature changes in the Grand Canyon area with implications for groundwater resources. Sci Rep 10:1–11. https://doi.org/10.1038/s41598-020-76743-6

Tillman FD, Beisner KR, Anderson JR, Unema JA (2021) An assessment of uranium in groundwater in the Grand Canyon region. Sci Rep 11, 22157: 1–15 https://doi.org/10.1038/s41598-021-01621-8

Timmons JM, Karlstrom KE, Heizler M, Bowring SA, Crossey LC (2005) Tectonic inferences from the 1255-1100 Ma Unkar Group and Nankoweap Formation, Grand Canyon: Intracratonic deformation and basin formation during protracted Grenville orogenesis. GSA Bull 117:1573–1595

Tobin BW, Springer AE, Kreamer DK, Schenk E (2018) Review: The distribution, flow, and quality of Grand Canyon Springs, Arizona (USA). Hydrogeol J 26:721–732. https://doi.org/10.1007/s10040-017-1688-8

Tobin BW, Springer AE, Ballensky J, Armstrong A (2021) Cave and karst of the Grand Canyon World Heritage Site. Zeitschr Geomorphol 62:125–144. https://doi.org/10.1127/zfg

Toll M, Silver R, Bahr S, Dahl K (2020) Letter Re: forest service should reject Stilo and Tusayan's special use proposal. 2:1–9 https://www.grandcanyontrust.org/letter-forest-service-re-stilo-and-tusayans-special-use-proposal. Accessed April 2023

USEPA (1988) Ambient water quality criteria for chloride: 1988. United States Environ Prot Agency 440:1–39

USEPA (2021) Climate change indicators: snowpack. In: EPA. https://www.epa.gov/climate-indicators/climate-change-indicators-snowpack#ref5. Accessed 16 May 2022

USGS (2020) Grand canyon monitoring and research center: bright angel creek near Grand Canyon, AZ. USGS, Reston, VA

Wang T, Chen J, Zhang C, Zhan L, Li L (2020) 14C-Dating model for groundwater affected by CO2 inputs from deep underground formations. Water Resour Res 56:2–12. https://doi.org/10.1029/2019WR025155

Wood AJ, Springer AE, Tobin BW (2020) Geochemical variability in karst-siliciclastic aquifer spring discharge, Kaibab Plateau, Grand Canyon. Environ Eng Geosci 26:367–381. https://doi.org/10.2113/EEG-2345

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