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GRAND CANYON NATIONAL PARK'S WATER CORRIDOR: WATER SUPPLY, WATER QUALITY, AND RECHARGE ALONG THE BRIGHT ANGEL FAULT

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ABSTRACT

Grand Canyon's 'water corridor' includes the Transcanyon Pipeline that conveys water from Roaring Springs near the North Rim to Grand Canyon Village on the South Rim to provide water for the park's 6.5 million annual visitors. Roaring Springs water has been used at the park and reclaimed at the South Rim Water Reclamation Plant since the 1970s. Our hypothesis is that the pipeline water infiltrates through faults and intermingles with the South Rim groundwater system. We use geochemical tracers to develop mixing models for these waters. Tracers considered are major ions, water isotopologues, radiogenic strontium, and pharmaceuticals. This study has implications for future changes in water quality and supply due to uranium mining and increased local pumping. Other implications are that current plans to change from Roaring Springs to Bright Angel Creek water will increase available water supply and only marginally decrease water quality, but will have adverse consequences of increased turbidity due to flash floods and forest fires.

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1.0 Introduction

Grand Canyon provides a cross sectional view of an aquifer system within a highly faulted arid-land region on the Colorado Plateau, 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 sub-provinces. In particular, the Kaibab Plateau is a high elevation region directly north of Grand Canyon, and the Coconino Plateau borders the canyon to the south extending to Flagstaff, AZ, including the San Francisco Peaks (Huntoon 1974). Grand Canyon Village's main water source is Roaring Springs, a large-volume (baseflow of ~170 l/sec) karst spring flowing from the regional Redwall-Muav aquifer near the North Rim of the canyon (Jones et al. 2018). 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 of value to the 11 Native American tribes that are traditionally associated with the park, as well as to the endemic species and ecosystems that rely on the springs within the park. Roaring Springs joins with other springs to form the baseflow of Bright Angel Creek that 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 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 versus 170 l/s; Jones et al. 2018; USGS 2020). For this reason as well as the aging 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.

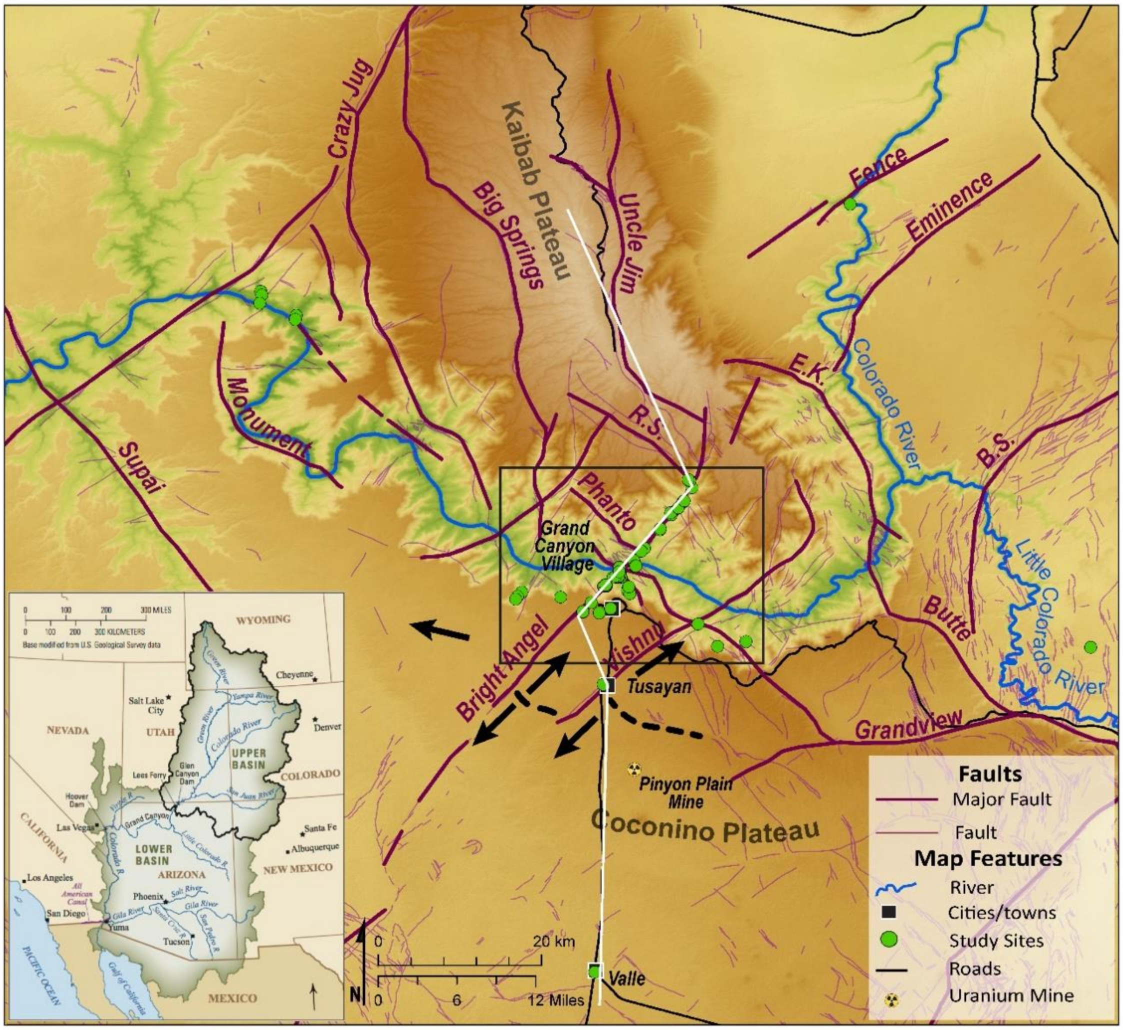

Figure 1. Regional setting of springs and faults in the eastern Grand Canyon. Box shows area of Figure 2 which is the critical water corridor for Grand Canyon National Park. White line shows the path of the hydrogeology cross section of Figure 5. Black dashed line shows a fault-influenced groundwater divide near Tusayan; black arrows are flow directions in the Redwall-Muav (RM) aquifer away from the divide (Crossey et al. 2009)

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 and 19 sample points from previously published work.

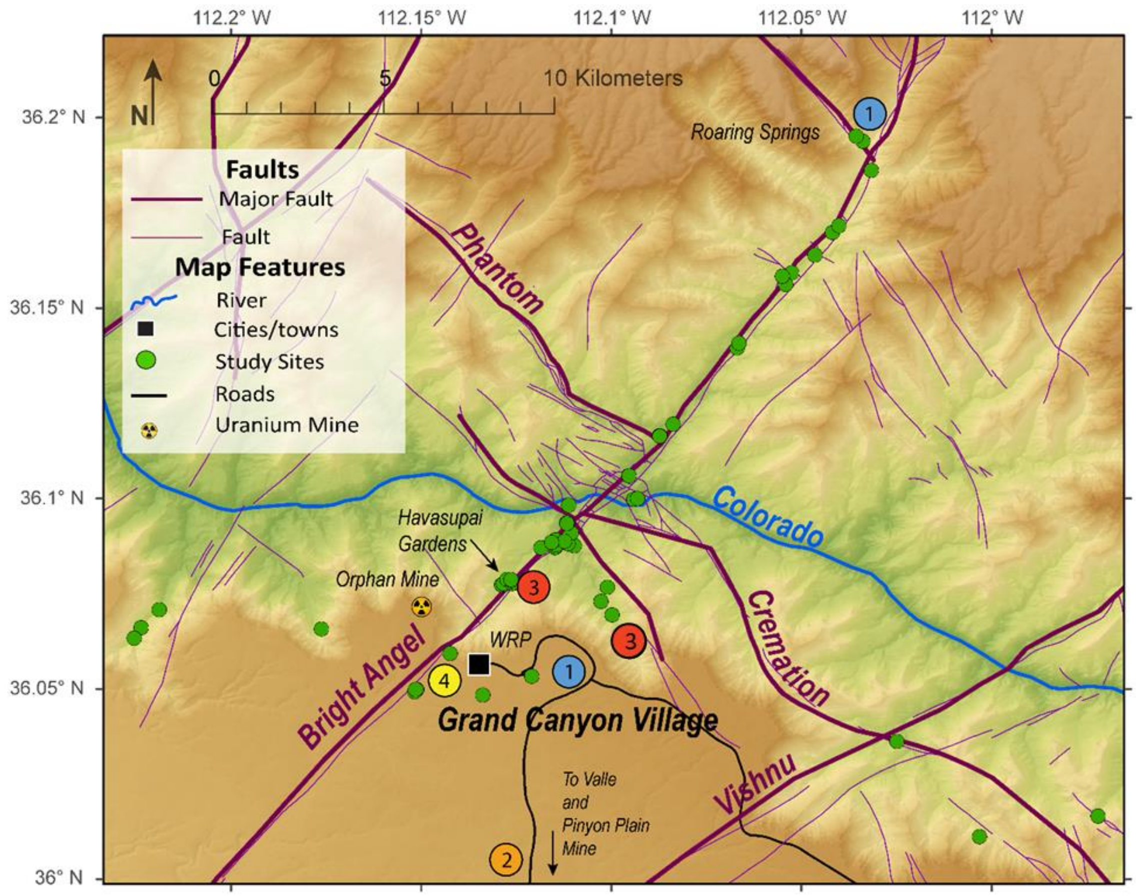

Figure 2. Map of springs and sample points for the water corridor. Four groups of waters to be studied include: 1- North Rim waters, especially Roaring Springs that supplies pipeline water to water tanks at Grand Canyon Village; 2- groundwater wells to the south, from Tusayan, Valle, and the Pinyon Plain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

We identify 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, especially Havasupai Garden Spring and Two Trees Spring which are hypothesized here to reflect mixing of pipeline (N-Rim) and S-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, and discharged along the Bright Angel fault.

Grand Canyon National Park has been performing an anthropogenic recharge experiment since 1970 that involves infiltration of North Rim pipeline water, including reclaimed water from the Water Reclamation Plant (WRP), in Grand Canyon Village (Ingraham et al. 2001) to mix with South Rim groundwater. Reclaimed water is utilized in many regions of the Southwest as demand for water increases and in the face of most climate change scenarios (USEPA 2012). Figure 3 schematically shows that water has been piped from Roaring Springs to the South Rim water tanks for distribution since 1970 (HAER 2015). The pipeline has a capacity of up to 42 l/s (conversion table 1) of Roaring Springs water to the South Rim (HAER 2015). The distribution of this water is multi-faceted, including piping water ~ 40 km east to Desert View (Fig. 3), while 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 to the Clearwell Overflow (Coconino Wash) 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).

An important uncertainty of our study is the significance of the volume of infiltrated water compared to overall meteoric recharge on the South Rim. Because of the direct connection between the infiltration along the fault and the S-Rim groundwater our hypothesis is that >22 l/s over 50 years is an appreciable addition to the 0.0-0.10 inches per year of precipitation in this area as estimated by groundwater flow and recharge models (Pool et al. 2011, Knight and Huntoon 2022).

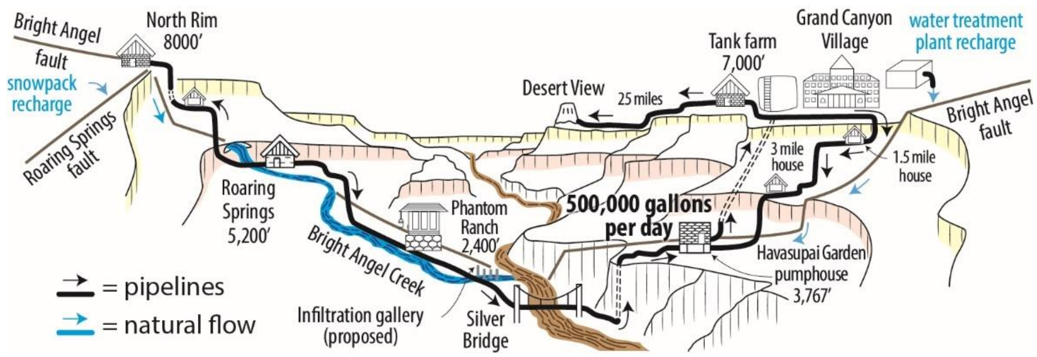

Figure 3. Schematic of Grand Canyon's water corridor from north to south showing natural and engineering flow pathways. Key components include Roaring Springs, Bright Angel Creek, the Transcanyon Pipeline, Havasupai Garden Spring (formerly Indian Garden Spring) pumphouse, South Rim Tank Farm, Water Reclamation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

Table 1. Units of Flow Measurement

location	reference	l/s	ft3/sec	milgal/ day	gal/min	ac-ft/yr
General Conversions		**10**	**0.35**	**0.23**	**159**	**256**
Havasupai Garden 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
GC w/ pipeline discharge	Dyer et al. 2016	59.5	2.1	1.4	943	1521
Roaring Springs (RS)	Jones et al. 2018	170	6.0	3.9	2695	4346
RS to South Rim	Steely 2015	22	0.8	0.5	342	552
Pipeline capacity	Steely 2015	42	1.5	1.0	666	1074
WRP Effluent Permit	ADEQ 2017	33	1.2	0.75	523	844
Bright Angel Ck baseflow	USGS 2020	510	18.0	11.6	8084	13039

This paper applies aqueous geochemistry as a powerful tool to understand hydrologic flow paths and to assess potential mixing between infiltrated North Rim pipeline water and indigenous South Rim groundwater within springs and groundwater near the South Rim and further to the south in groundwater at Tusayan, Valle, and the Pinyon Plain Mine (formerly the Canyon Mine) wells. We use multiple natural tracers including solutes and stable isotopes, 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 Garden spring (formerly Indian Garden Spring[1]) and other South Rim groundwaters.

[1]This spring name has not yet been changed formerly; however, we will use the likely future name change out of respect for native people.

2.0 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 aquitards of the Hermit Formation and Bright Angel Formation respectively. Shales of the Bright Angel Formation act as the region's most important aquitard 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 major joints and faults associated with regional structures (Huntoon 1974, 2000; Tobin et al. 2018). Water quality of both aquifers is influenced by relatively fast-traveled meteoric recharge (Schindel 2015), mixed karst and matrix flow in the C-aquifer (Brown 2011), resulting in both fast and slow pathways through the karst fracture network in the R-M aquifer (McGibbon et al. 2022). The major springs and perennial streams considered in this study are shown in green in Figure 5A 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 (Ledbetter et al. 2020).

Important aspects include the southward dip of strata off the Kaibab uplift that causes southerly surface drainage on both North and South rims. North Rim surface streams are large perennial streams and groundwater flow is the same direction as surface water flow. The 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 infiltrate the Kaibab Plateau through sinkholes, faults, and fractures (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. 2018).

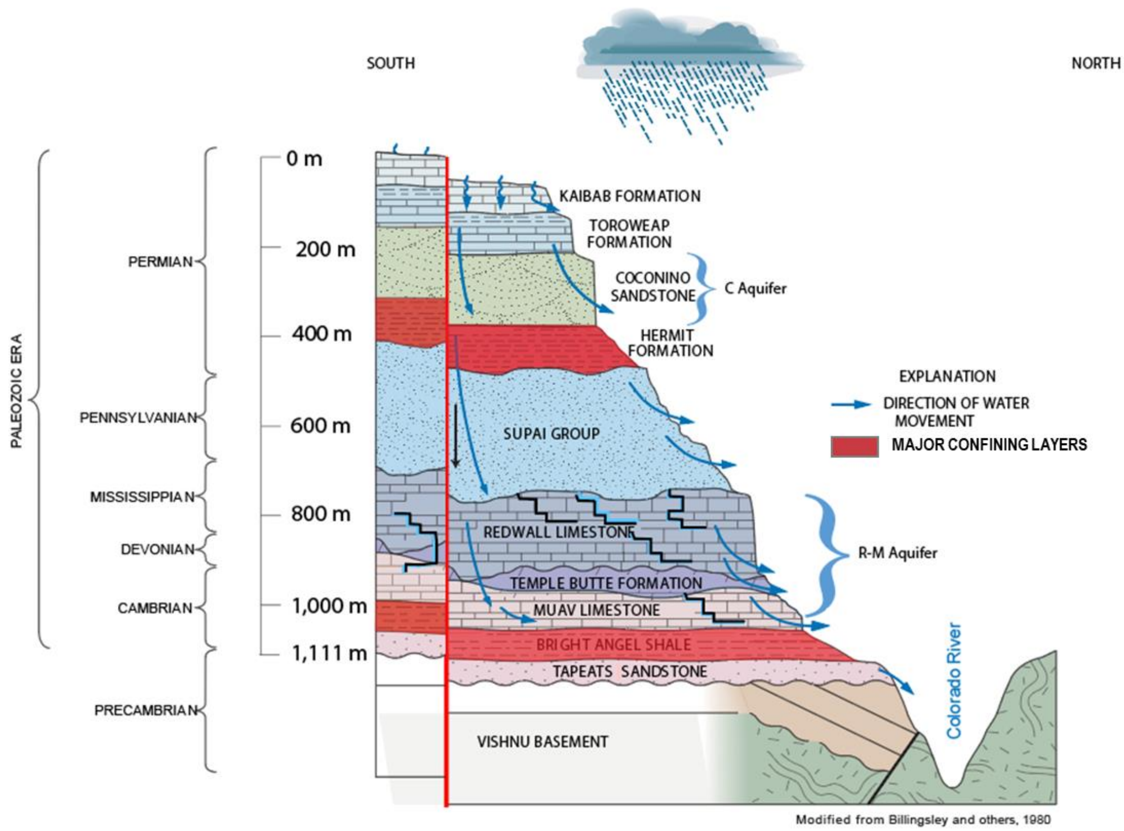

Figure 4. Stratigraphic section of eastern Grand Canyon adapted from Monroe et al. (2005). Figure shows approximately 1000 m of Paleozoic strata, major aquifer units, confining units (red), and direction of groundwater movement (arrows).

Ephemeral surface drainages above the South Rim flow south following the southerly dip of the Kaibab surface as shown in Figure 5, but the R-M groundwater flows north toward Grand Canyon from a divide near the town of Tusayan (Errol L. Montgomery and Associates 1999). Figure 1 shows R-M aquifer flow to be strongly influenced by faults as modeled in Crossey et al. (2009; from Kessler 2002). The present divide is not well constrained, but Figure 5B expresses the hypothesis to be tested in this paper—that North Rim pipeline water that is delivered to Grand Canyon Village, including effluent from the Grand Canyon Village Water Reclamation Plant (WRP), infiltrates down the Bright Angel fault and flows in both directions: north to recharge the highest volume South Rim spring at Havasupai Garden Spring and perhaps other springs; and south to interact with the regional R-M aquifer groundwater.

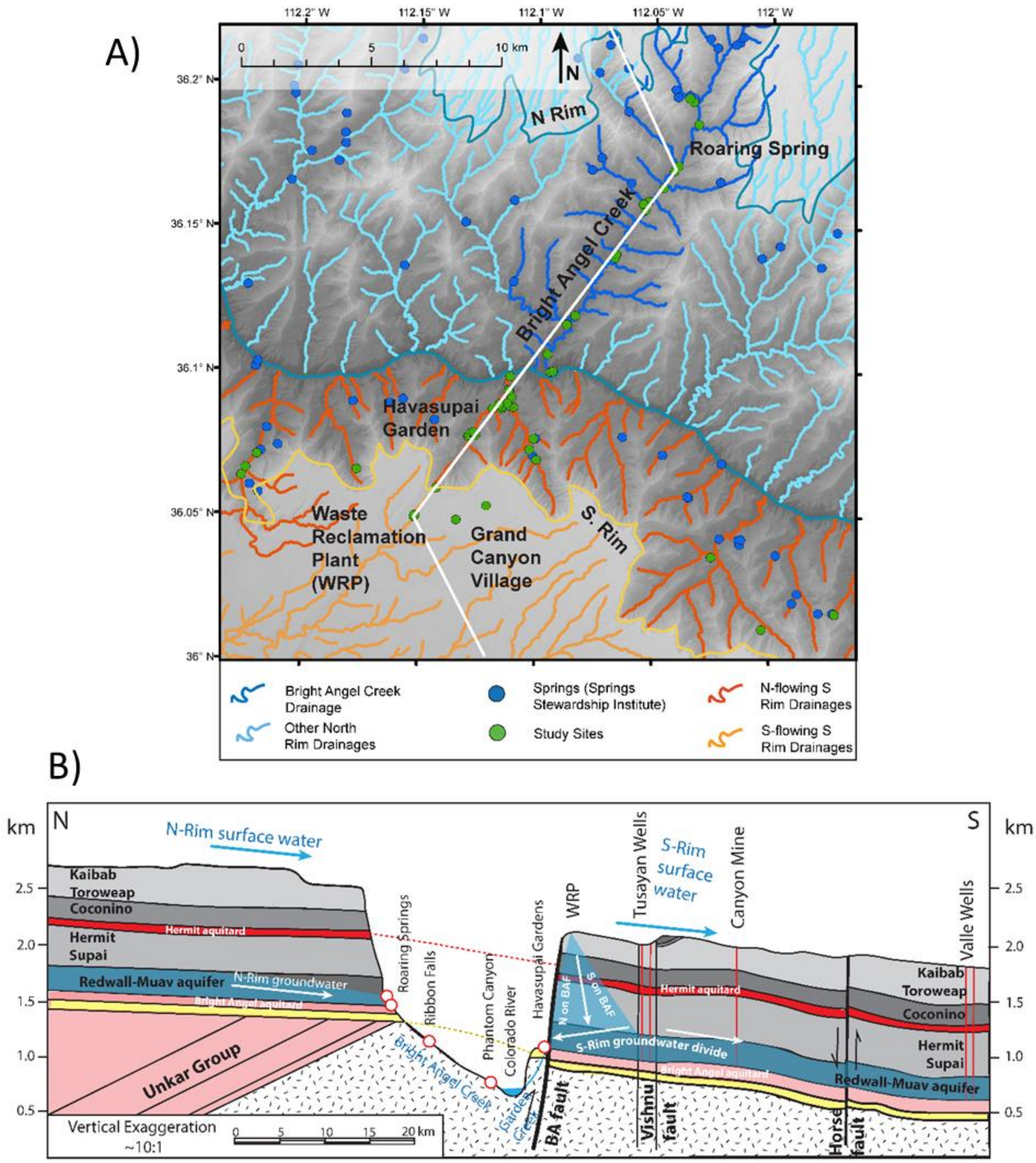

Figure 5. A) Surface water drainages shown for area of Figure 2, highlighting north and south rim drainages and flow direction. B) Hydrogeology profile of the N-S Grand Canyon water corridor (line and locations shown in Figure 1). On North Rim, both surface water and groundwater flow south. On South Rim, surface water flows south following the dip of the Kaibab surface, but groundwater flows north from a groundwater divide near Tusayan.

Bright Angel fault along the Bright Angel Trail shows overall east-side-down throw of ~60 m. This fault zone has had multiple movements (Huntoon and Sears 1975) and both east-down and west-down conjugate faults are present and the overall subvertical breccia and fault network creates a permeable network of faults and joints capable of conveying water to the springs and groundwater below.

Our hypothesis that the 5-decades-long and ongoing discharge and infiltration of North Rim pipeline water on the South Rim, perhaps primarily down the Bright Angel fault, has resulted in a mix of North Rim- and South Rim- derived groundwater at Havasupai Garden Spring and other South Rim springs. The geometry of the sampling plan to help test this hypothesis is shown in Figure 6. Water in the pipeline is gravity-fed as far south as Havasupai Garden Spring, where it is pumped up to the South Rim. Havasupai Garden and Two Trees springs had pre-pipeline flows of ~20 l/s (Metzger 1961), compared to 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[2] discharges along the Bright Angel fault ~100 meters higher in elevation than Garden Creek. Garden Creek is the combined surface outflow from Havasupai Garden Spring, Two Trees Spring, and unused pipeline water returned to the creek (HAER 2015). Pipe Creek is fed by two other South Rim springs (Burro and Pipe springs) and these waters were sampled at several location above Pipe Creek's confluence with Garden Creek, and above where the Travertine Cone Spring 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 Garden Spring water, and Pipe Creek water. All creeks experience significant evaporation along their paths.

[2] Also known as Pumphouse Spring

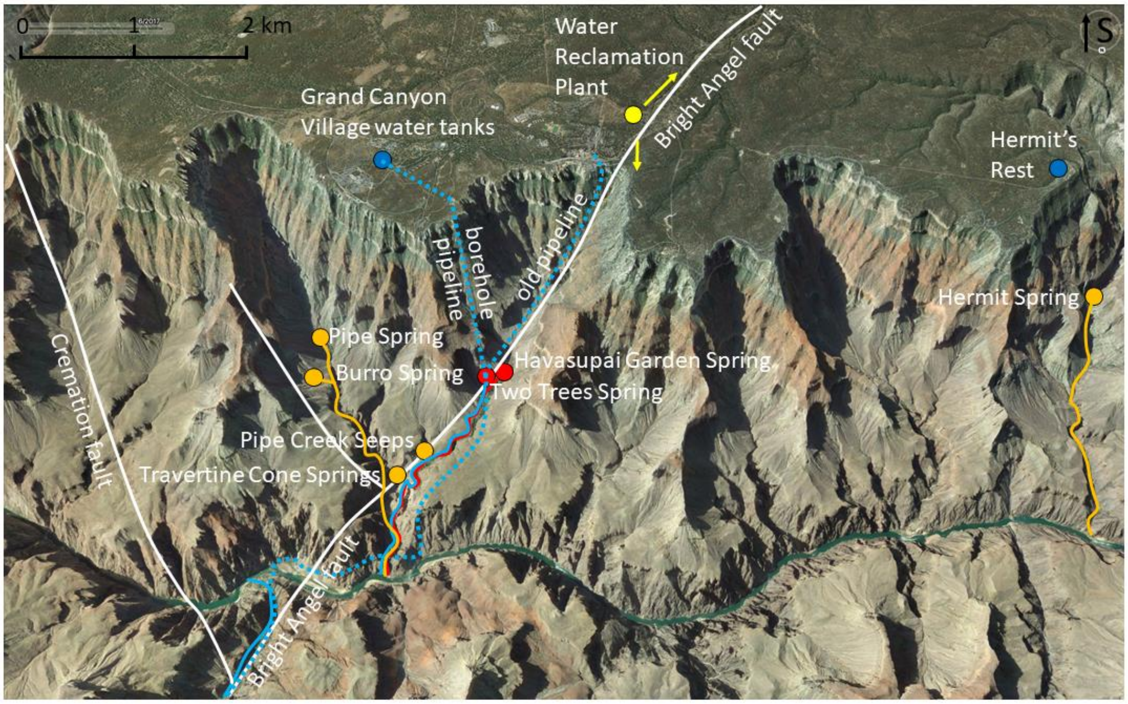

Figure 6. Perspective view from Google Earth looking south at the South Rim of Grand Canyon and showing the different waters that were sampled. 1) North Rim pipeline water reaches water tanks at Grand Canyon Village, then is reclaimed at the 2) Water Reclamation Plant and infiltrates along Bright Angel fault recharging springs such as 3) Havasupai Garden and Two Trees springs.

3.0 Methods

3.1 Water Sampling

Sampling was completed for select springs and surface water in the water corridor under a permitted agreement with GRCA. 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 spring (Havasupai Garden Spring), and Pipe Creek and its springs. Primary samples were collected in March, May, September, October, and December 2021. Additional samples were collected in 2017 and 2018. A priority was to sample in the fall 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 at 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 their stable isotopes plot within the overall South Rim groundwater array of previous workers (Solder and Beisner 2020) and appear to reflect their different groundwater compositions.

Sample locations were documented using GPS. Field parameters were measured for each location including pH, temperature (°C), specific conductance (μS/cm), and total dissolved solids (ppm) using an Oakton waterproof pH/CON 300 meter. All sampling equipment (bottles, syringes, and filters) were 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.

3.2 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 meter 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 et al. 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) that 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) in 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.

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

Each sample was analyzed 6 times, and then averaged. Results show each sample to be routinely within an error of 0.1‰ for $\delta^{18}O$ and 2.0‰ for δD. Duplicates were also run at a frequency of ten percent 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 in EPS at UNM. Standard methods include Eichrom Sr Resin in 200µL 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, CA. 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).

4.0 Results

Results are presented, by tracer, for North Rim then South Rim waters. 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 waters at nanograms/L concentrations. We also summarize results of dye tracers injection studies performed by previous workers on the North Rim.

4.1 Field Parameters and Ion Chemistry

Major ions such as calcium, magnesium, and sulfate can help explain whether waters are in equilibrium with the 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 2-5). We also compiled all available tracer data 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; Tables 2, 3, 4, and 6). Field parameters measured for all new samples include temperature (ranging from 7 to 24.5 ºC), pH (6.2-8.8), and conductance (284 to 3000 µS/cm) (Table 2). Alkalinities ranged from 43.9 to 756.6 mg/L HCO_3^- with the lowest values measured at the treated effluent from the WRP and the highest recorded at Pipe Seep at Bright Angel Fault (Table 3). Total dissolved inorganic carbon (DIC) ranged from 0.00127 to 0.0147 (Table 5). The following sections report results from each tracer analysis, first for North Rim, then for South Rim.

Stiff diagrams (Figure 7) show the general "shape" of the solute content for the different waters shown in Figures 2 and 6. 1) North Rim waters: Roaring Springs, Bright Angel Creek, tributaries to Bright Angel Creek, and pipeline water sampled in Grand Canyon Village, are all similar low-TDS calcium bicarbonate waters. 2) South Rim groundwaters from wells on the Coconino Plateau are saltier. 3) South Rim springs: Havasupai Garden Spring, Two Trees Spring, Pipe Spring, and Burro Spring share the shape of North Rim waters but with additional salts. 4) Water from the South Rim Water Reclamation Plant (WRP) is high in NaCl.

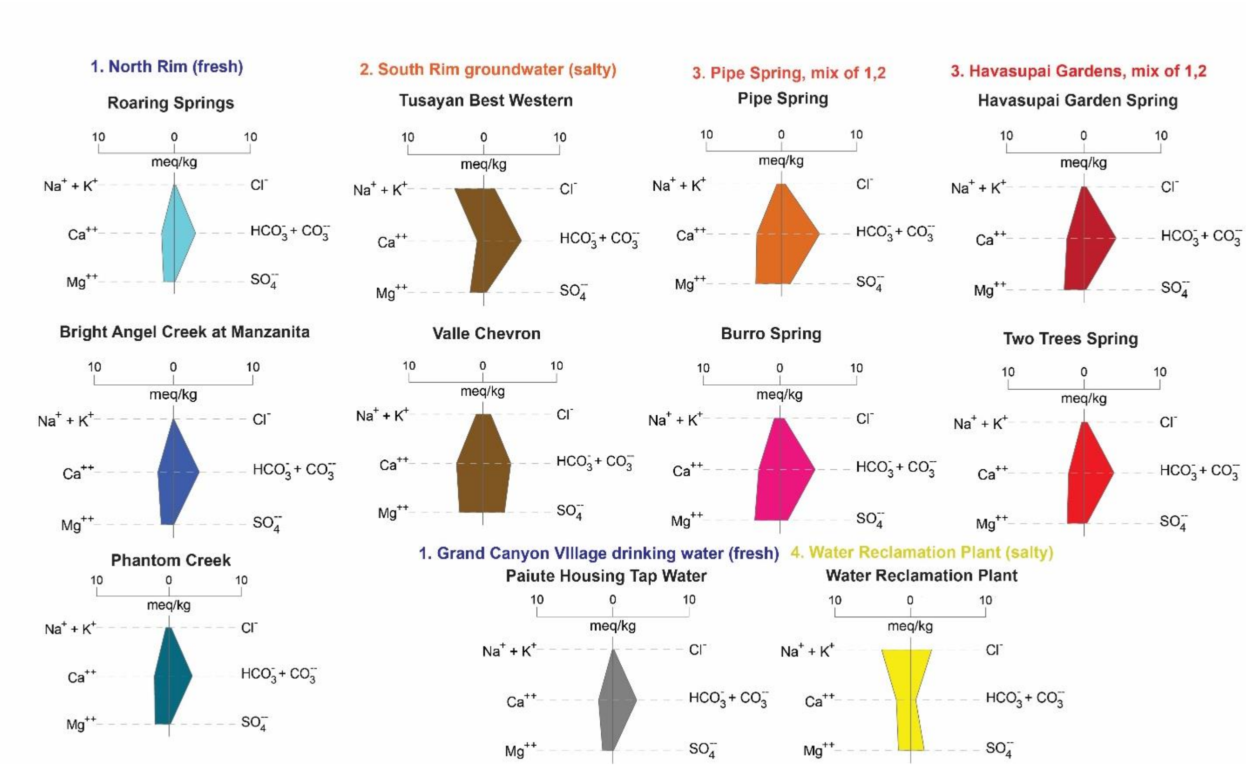

Figure 7. Stiff diagrams portray the shapes of waters from the groups shown in Figure 2. 1) Low TDS North Rim water is piped from Roaring Springs such that Grand Canyon Village drinking water is the same. 2) South Rim groundwater is higher in TDS and has different shape; 3) South Rim springs below the rim may be a mix of #1 & #2; 4) Water Reclamation Plant water is treated and reinfiltrated to mix with #2.

Piper diagrams (Fig. 8) are used to examine major ions and plot a larger number of samples than presented in Figure 7. 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).

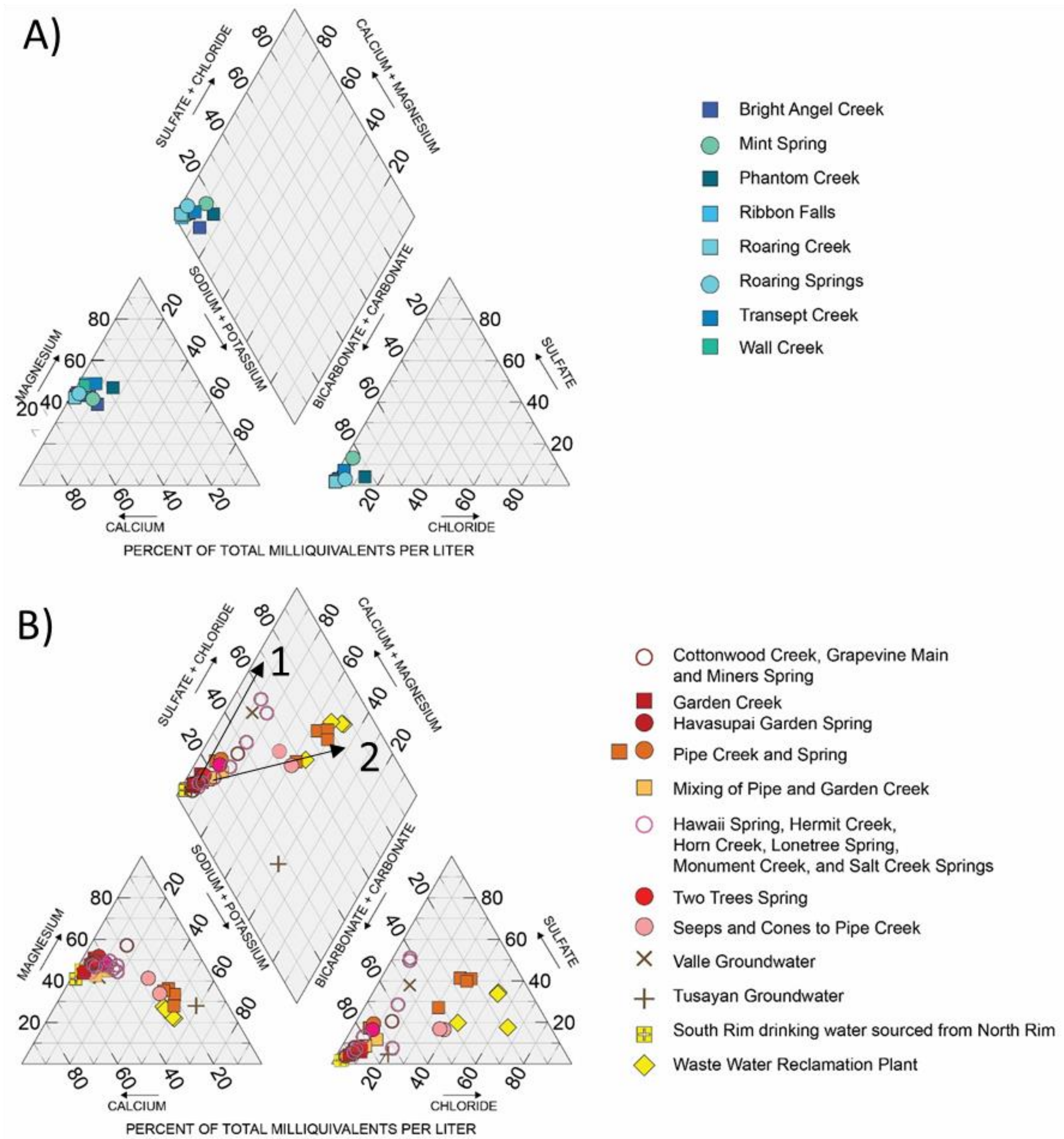

Figure 8. Piper diagram (Piper 1944) showing major ions. Filled symbols are new samples; open symbols are previously published samples (Monroe et al. 2005). Mixing trends are seen for N-Rim and S-Rim waters. A) North Rim waters show mixing between low TDS Roaring Springs water at left corner of parallelogram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

All of these samples have total dissolved solids less than 450 ppm with many samples at ~300 ppm, indicating that they are relatively fresh, near meteoric in composition. A few of the tributaries such as Phantom Creek and Mint Spring contribute slightly higher salts than Roaring Springs plotting further from the edge of the diagram.

Major ion chemistry for South Rim springs, creeks, and wells (Figure 8B) covers a larger range of water quality. For plotting purposes, a representative sample was selected for Havasupai Garden 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 percent relative standard deviation for major ions. The entire South Rim groundwater sample suite has total dissolved solids ranging from 172 to 3,244 ppm 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 variations 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 South Rim 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.

4.2 Stable Isotope Chemistry

Figures 9 shows the stable isotope geochemistry of all springs (circles), creeks (squares), and groundwaters from wells (+ and x) along the water corridor. As in other plots, new data are solid symbols and previously published data are open symbols. As also noted by Solder and Beisner (2020), the combined groundwater line has a lower slope than the Global Meteoric Water Line (GMWL). A complete summary of stable isotope data is included in Table 6.

Figure 10 shows the stable isotope data grouped into the four groups of waters of Figure 2. North Rim waters (blue colors) have values for oxygen and hydrogen that range between -14.3 to -12.8‰ for $\delta^{18}O$ and -100.5 to -84.8‰ for δD. The most depleted (negative) values are from Roaring, Angel, and Emmet springs. The most negative Bright Angel Creek waters are only slightly less negative (but outside the 2‰ analytical error in δD); these get slightly less negative downstream and were sampled on the same day, suggesting evaporation. Waters piped to Grand Canyon Village come from Roaring Springs; drinking water was sampled from the sink at Paiute Apartments/ Park Housing and the Village market; these have a mean value of $\delta^{18}O$ = -13.6‰ and δD= -95.0‰ (left yellow square with cross). The Water Reclamation Plant outflow has mean value of $\delta^{18}O$ = -13.3‰ and δD= -93.6‰ (left yellow diamond) 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 δD= -93.4‰ for samples taken in 1992-1993 (Ingraham et al. 2001; right yellow diamond).

South Rim waters are shown in orange (Fig. 10). South Rim springs and groundwater vary greatly. The most enriched (least negative) values include C-aquifer water from Canyon Mine Observation Well (-10.9‰, -82.3‰) and RM-aquifer groundwater from Valle wells that have $\delta^{18}O$ values of -11.8 to -11.5‰; Tusayan wells have $\delta^{18}O$ ~ -12‰. The Pipe Creek seep is even more enriched as a result of evaporation with $\delta^{18}O$ = -8.4‰ and δD= -78.2‰. The most depleted South Rim waters plotting closer to the North Rim waters are sampled from Cottonwood Creek, Grapevine Main, and Miners springs. The extreme of these South Rim data may be captured by Cottonwood Creek with $\delta^{18}O$ = -12.8‰ and δD= -94.6‰, although other springs and groundwaters are less negative.

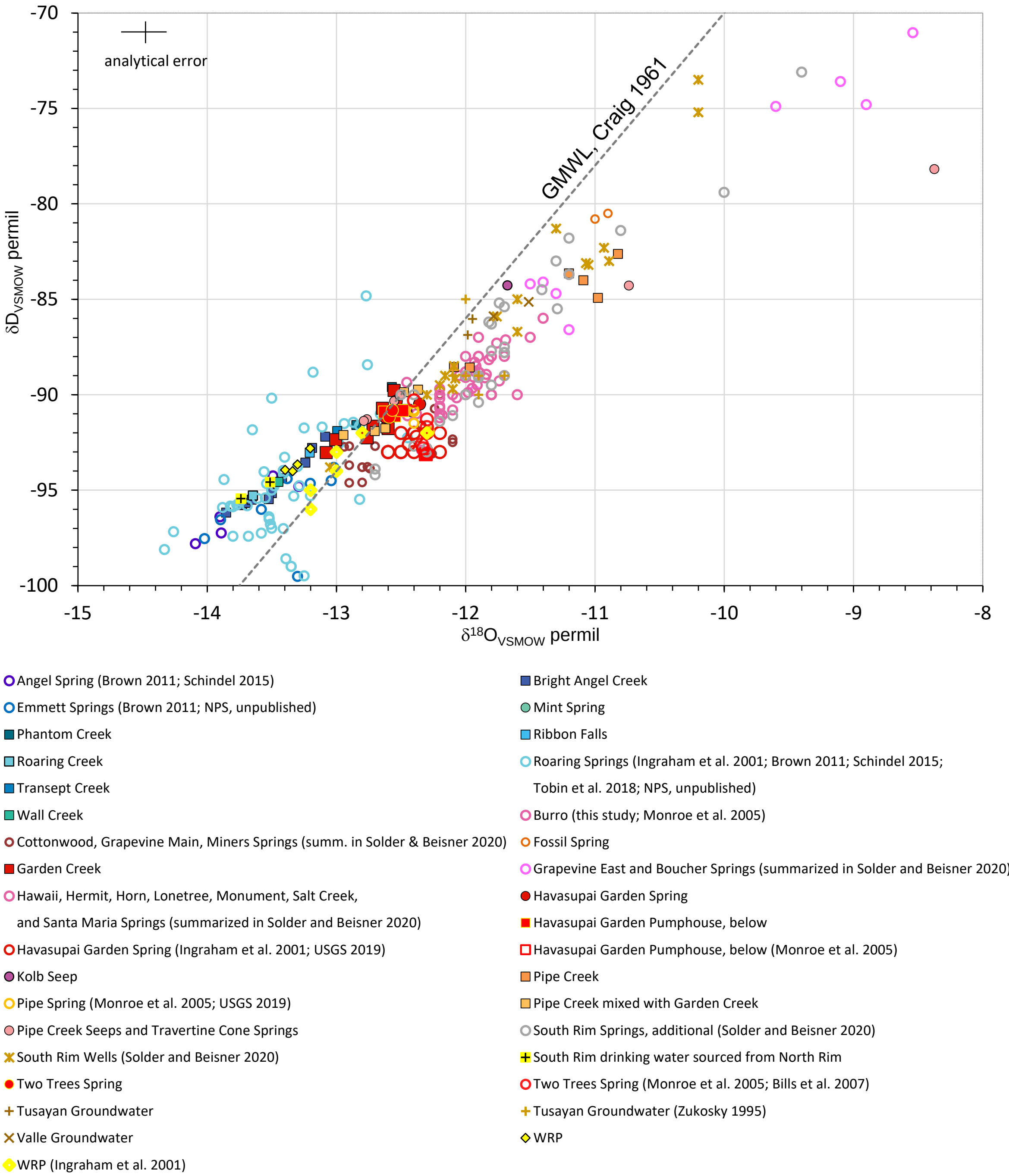

Figure 9. Stable isotopes for oxygen and hydrogen for all samples: springs (circles), creeks (squares), and wells (x and +). Unfilled symbols are from previously published analyses (Table 6). The global meteoric water line (GMWL) is $\delta D = 8*\delta 18O + 10$ (Craig 1961).

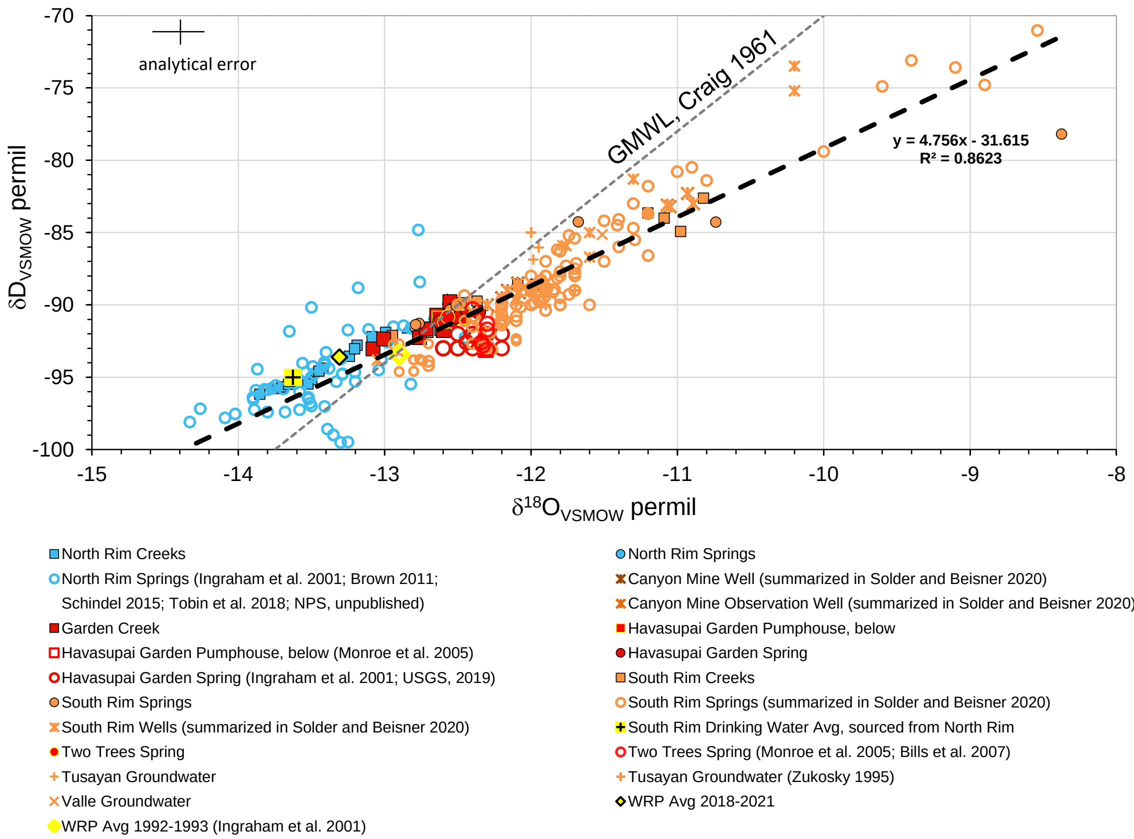

Figure 10. Stable isotopes for oxygen and hydrogen show four water groupings: Blue= North Rim waters, Yellow= Grand Canyon Village waters, Orange= South Rim springs and groundwater, Red= Havasupai Garden Spring and Two Trees springs. Regression line for all samples gives slope of 4.76 and R^2= 0.86.

A regression of all data (north and south) results in a slope of 4.76 and R^2 =0.86 (Figure 10). In comparison, Solder and Beisner (2020) reported a groundwater line (GWL) for just the South Rim springs and groundwaters with a slope of 6.46 and R^2 =0.92.

Havasupai Garden Spring waters are shown in red; these include springs at Havasupai Garden Spring and Two Trees Spring as well as outflow from these springs to Garden Creek and lower Pipe Creek (Fig. 6). Havasupai Garden 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‰. These values overlap with both North Rim and South Rim waters. Garden Creek has $\delta^{18}O$ between -13.1 and -12.5‰ becoming more negative downstream presumably because of

North Rim pipeline water that, at times, is discharged from the pipeline at the Havasupai Gardens pumphouse.

4.3 Chloride and Deuterium

Chloride behaves conservatively and can be used to evaluate mixing. Figure 11 plots two conservative tracers, δD against [Cl], to evaluate both water source and water solutes, respectively. North Rim waters plot in an array with low [Cl] and δD of about -95‰.

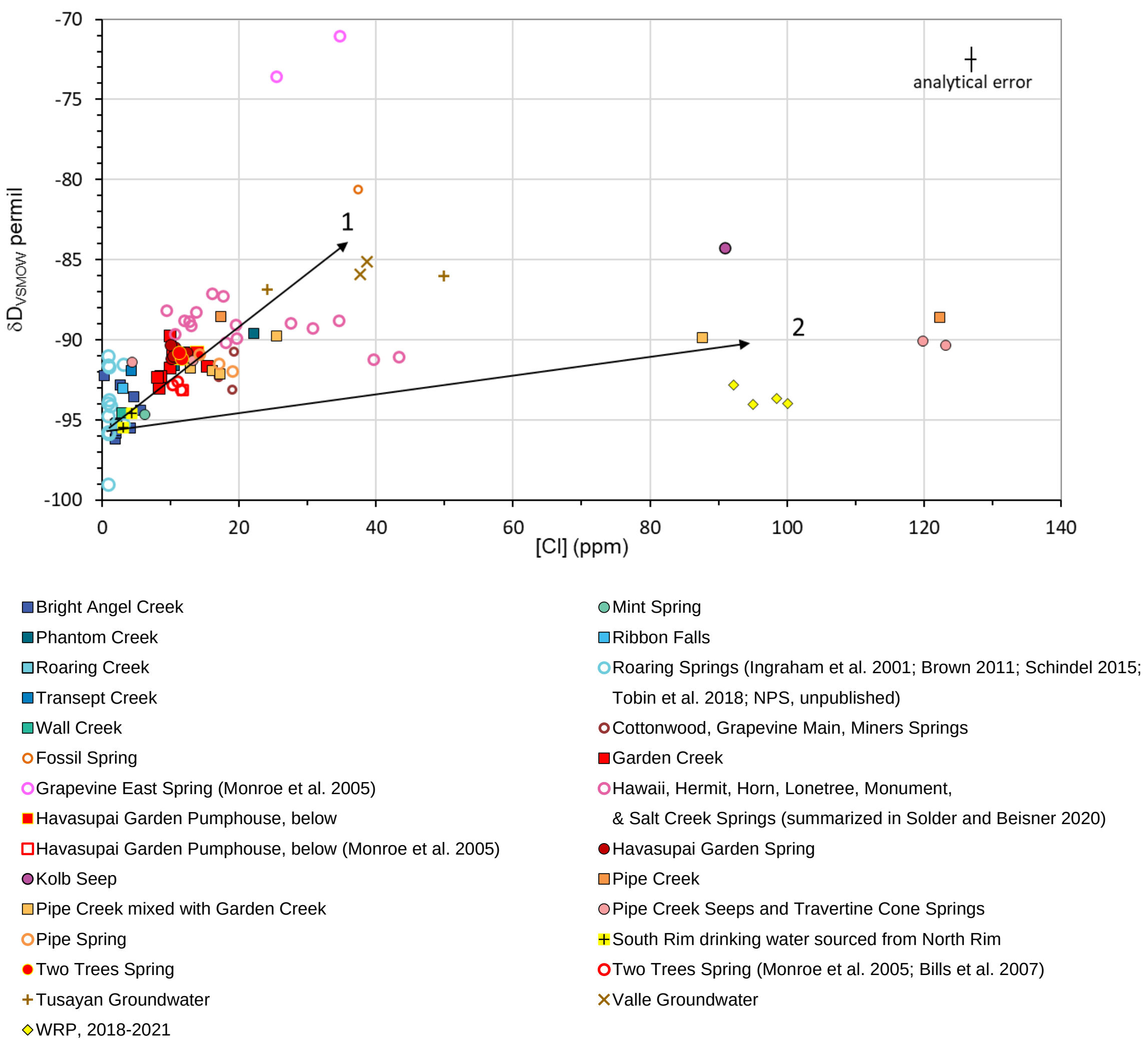

Figure 11. [Cl] versus δD for springs (circles), creeks (squares), wastewater (diamonds), and wells (x and +) of the water corridor. Unfilled symbols are from published samples (Table 6). Color groups are N-Rim (blues); S-Rim (oranges); Havasupai Garden (red), and Grand Canyon Village (yellow).

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 Garden and Two Trees springs plot in between the North- and South Rim waters. Similar to the Piper diagram, two variation trends are observed in the data that may reflect groundwater mixing (#1) and increasing chloride (#2).

4.4 Strontium Isotopes

Strontium concentration and $^{87}Sr/^{86}Sr$ were analyzed for 12 samples (Figure 12). Sample locations were selected to cover a variety of water types in this study including 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 mg/L to 4.13 mg/L with the highest values observed at the Bright Angel fault seep that feeds into Pipe Creek. Radiogenic strontium $^{87}Sr/^{86}Sr$ values were between 0.710 and 0.734. Most of the samples have $^{87}Sr/^{86}Sr$ values between 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 to 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 that are interpreted to be due to water-rock interaction within Precambrian basement granites (Crossey et al. 2006).

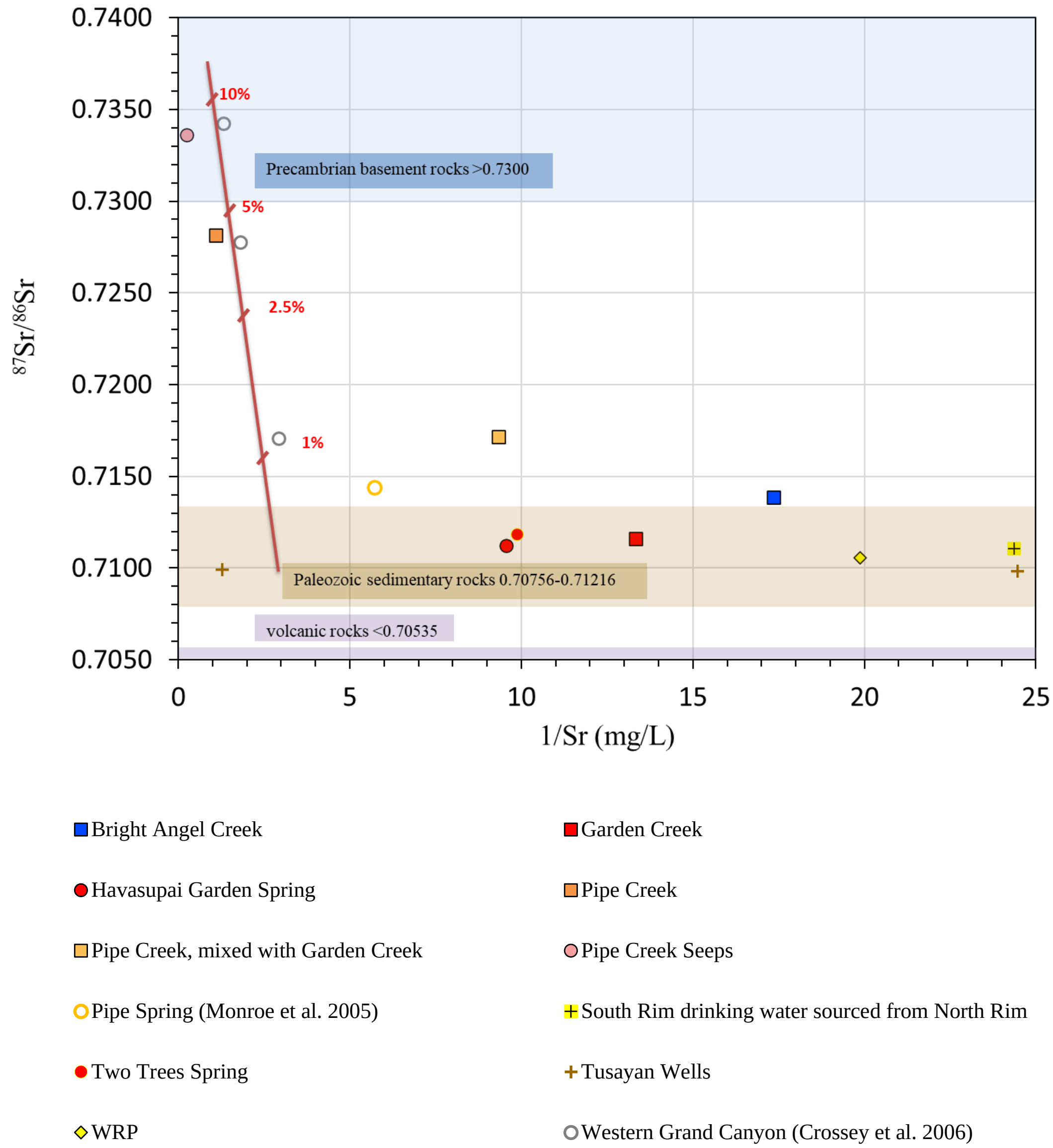

Figure 12. Plot showing $^{87}Sr/^{86}Sr$ vs 1/Sr for selected water corridor samples (filled symbols) contrasted with published data (open symbols) and Grand Canyon rock values for $^{87}Sr/^{86}Sr$ from Monroe et al. (2005), Bills et al. (2007), and Crossey et al. (2006). Red line shows binary mixing model from Crossey et al. (2006) for western Grand Canyon with percent of geothermal water input.

4.5 Pharmaceutical and Personal Care Products

PPCPs were analyzed in the park's reclaimed effluent water in addition to select springs below the South Rim. The reclaimed water was sampled in both February and December and showed 20 detections (Table 7). 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. South Rim springs analyzed include Havasupai Garden Spring, Two Trees Spring, and Pipe Spring. During the winter sampling in February 2021, Havasupai Garden 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).

A 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 (caffeine derivative) and theophylline. Salicylic acid was also detected during this event in both Pipe Creek and the field blank (Figure 13). A NPS Report for this region shows 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 non-detect (Dyer et al. 2016). Of the detections at South Rim springs, two of the same compounds were also detected in the reclaimed effluent. Concentrations of these compounds from the reclaimed water discharged in Coconino Wash overflow and the South

Rim springs in the water corridor are on the same order of magnitude such as caffeine, between 15 – 66 ng/L (Table 8).

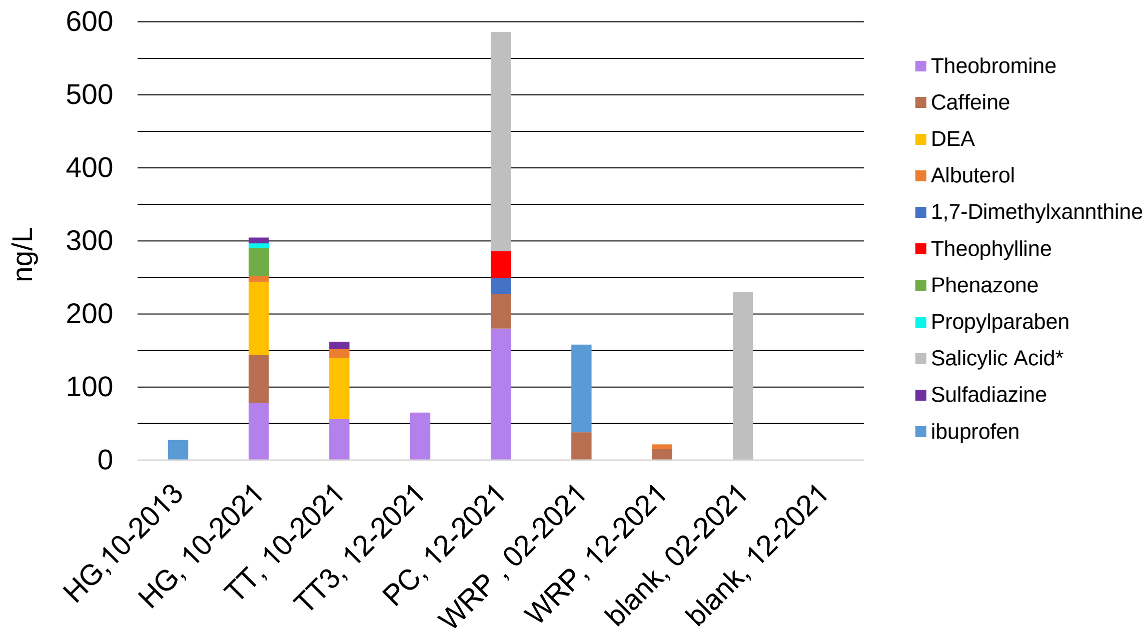

Figure 13. Bar chart for PPCP detections at Havasupai Garden Spring (HG), Two Trees Spring (TT), below Two Trees Spring (TT3), Pipe Creek (PC), Water Reclamation Plant (WRP), and field blanks (blank). Plots shows all detections at springs and equivalent detections for WRP. It does not include every detection in the WRP. Other reported data for HG from Dyer et al. (2013). *Salicylic acid was detected in both PC and the blank, but during different sampling events.

5.0 Interpretation, Combining Tracers

All of the hydrochemical plots reveal mixing of groundwater. This section interprets the combined multiple tracer data to understand different potential end members defined by the limits of our data, with the understanding that true end members may not have been be sampled. We follow water from the North Rim to the South Rim, and then its reinfiltration into the South Rim groundwater system.

Roaring Springs water has low and 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 good drinking water sources. Roaring Springs has significant variability in stable isotopes. The spread in Roaring Springs stable isotopic values shown in Figure 14 is based on Brown (2011) who identified a baseflow end member at $\delta^{18}O$ = -13.78‰, δD= -96.3‰ and a fast-traveled snowmelt recharge end member of $\delta^{18}O$ = -12.4‰, δD= -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 spring variation of our somewhat larger dataset that includes more negative values at Angel and Emmett springs that also feed Bright Angel Creek. Grand Canyon Village drinking water falls on Brown's (2011) Roaring Springs mixing model at an average value of $\delta^{18}O$ = -13.6‰, δD= -95‰, suggesting a predominance (about 80-90%) baseflow end member. The Water Reclamation Plant (WRP) waters averaged $\delta^{18}O$ = 13.3‰, δD= -93.6‰ during 2018-2021 sampling, also on the mixing line but with about 65% baseflow. This variation is reasonable because pipeline water reaching South Rim should vary along the mixing line depending on timing of fast-traveled snowmelt recharge events and result in an average at the WRP.

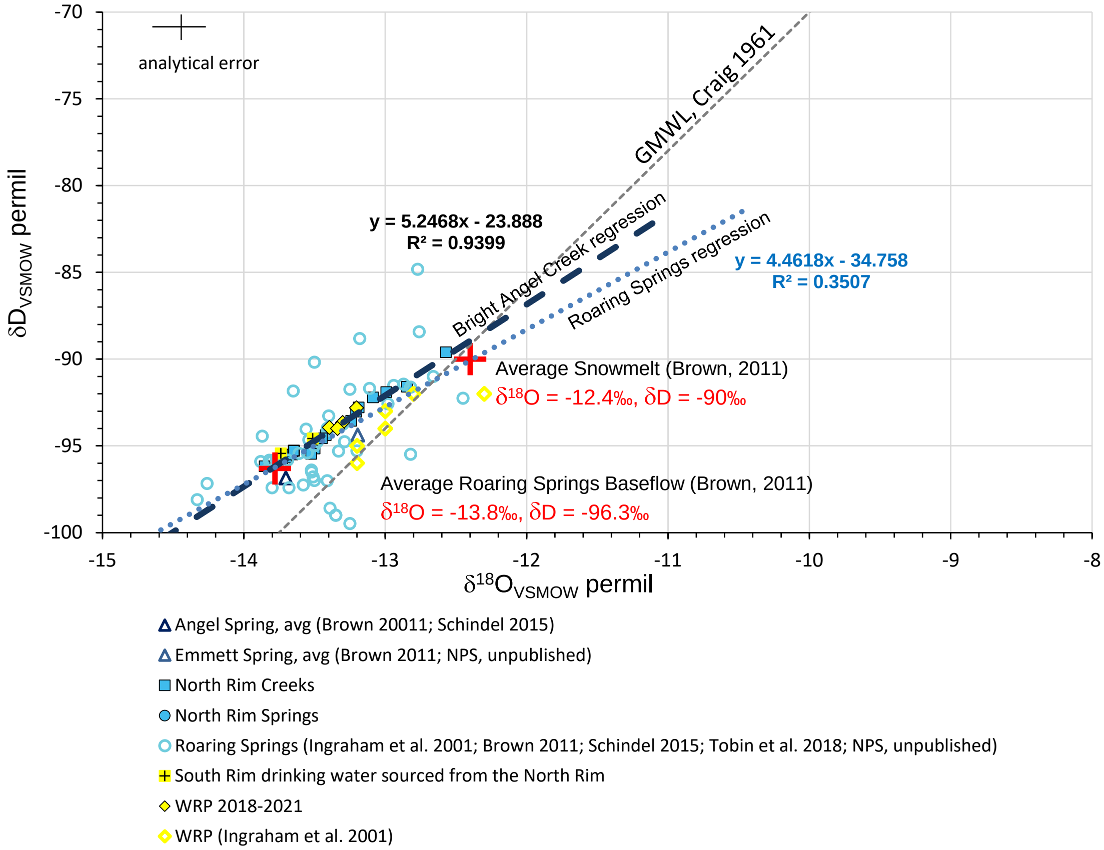

Figure 14. Interpretation of stable isotopes for North Rim water. Pluses show end members for Roaring Springs discharge proposed by Brown (2011) with baseflow at lower left, and fast-traveled snowmelt events at upper right. Our regression line (R2= 0.35) for a slightly larger dataset essentially matches Brown's (2011) end member mixing model. Bright Angel Creek waters show a regression line with a slope of 4.46.

Discharge data from Roaring Springs (Jones et al. 2018) shows that 80% of the discharge is at baseflow. Composition at a given time can vary as a result of snowmelt and monsoon excursions and a ~20% mix of rapid snowmelt recharge may represent average pipeline composition reaching South Rim, as suggested by the composition of WRP and South Rim drinking water (Fig. 14). As discussed below, WRP water has higher chloride, likely because of chlorination and other treatment processing (Roberts 2007).

In our 2021 longitudinal sampling, stable isotopes for water in Bright Angel Creek show a pattern of increasing enrichment of δD over 8 miles from -96.2 to -93.5‰ at the Colorado

River along a regression line with a slope of 4.46 (Fig. 14). This pattern may represent both evaporation and mixing, but the overall change is minimal.

Phantom Creek flows into Bright Angel Creek 1.5 miles upstream of the Colorado River 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 from -95.3 to -89.6‰ which are all more enriched than the upstream value for Bright Angel Creek. Average total dissolved solids are slightly higher from the springs and creeks that feed into Bright Angel Creek at 340 mg/L compared to 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 what we interpret to be two mixing trends between Roaring Springs water with more Na-Cl rich waters as shown in the Piper diagram (Fig. 8). Trend #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), $^{87}Sr/^{86}Sr$ (Fig. 12), and stable isotopes (Fig. 15). Solutes and $^{87}Sr/^{86}Sr$ indicate variable water-rock interaction in some springs. Stable isotopes are less negative than North Rim waters reflecting lower elevation and a likely component of local recharge (Solder and Beisner, 2020). Figure 15 shows that there is 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 of the overall groundwater trend are interpreted to be evaporation trends, as seen in Pipe Creek and Grapevine East springs (Sharp 2017). Potential stable isotope end members might be identified based on the extremes of the data, but the more negative end of South Rim groundwater trend overlaps with North Rim waters.

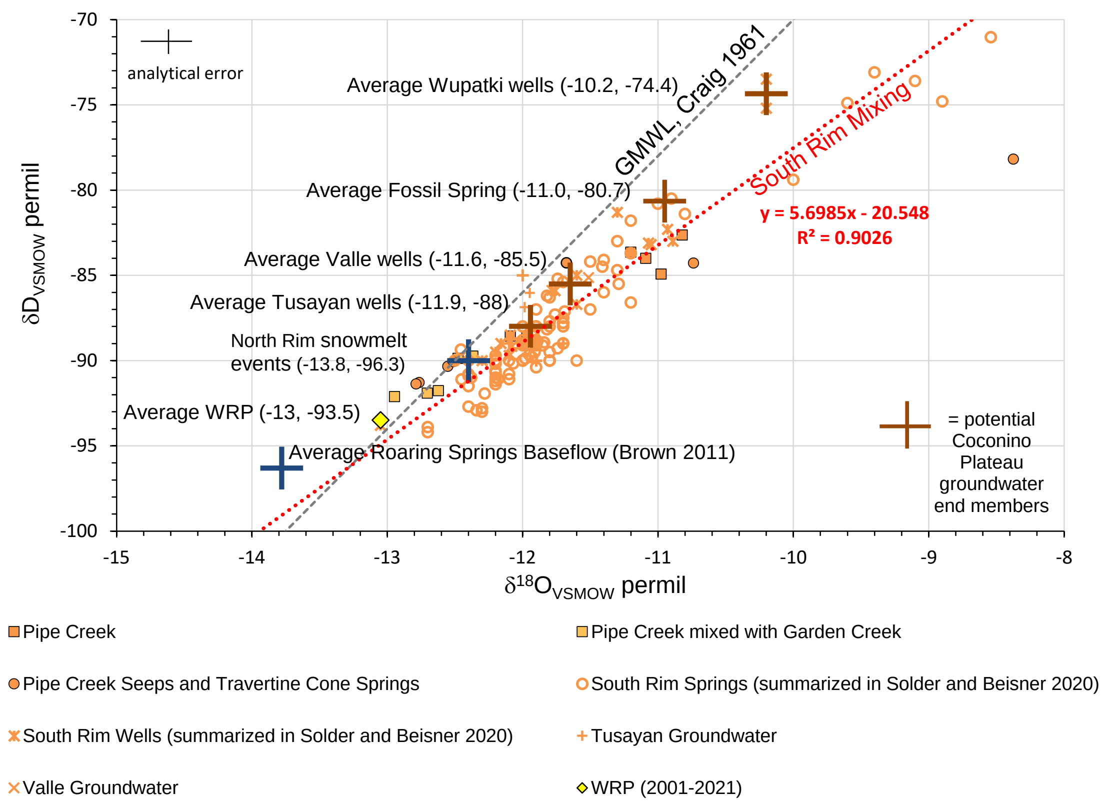

Figure 15. Interpretation of stable isotopes for South Rim springs and groundwater shows a mixing line regression (R^2= 0.90; excluding highly evaporated samples of $\delta^{18}0$ >-10). Roaring Spring base flow is shown for comparison; potential Coconino Plateau groundwater end members are shown.

The primary hypothesis of this paper is that observed South Rim groundwater variation of Figure 15 is best explained by mixing of North Rim pipeline water that infiltrates at Grand Canyon Village and mingles with South Rim groundwater. The depleted (more negative) end member (North Rim component) falls within the N-Rim mixing variation between the blue pluses of Figure 15 (Brown 2011). This end member is best represented by a point that is an ~80% mix of Roaring Springs baseflow and snowmelt events reflecting the average Roaring Springs discharge and validated by the average composition of the South Rim Water Treatment plant water that includes 2001 to 2021 data (Fig. 15). The enriched (less negative) end member of this proposed mixing is poorly defined because of limited well data on the Coconino Plateau and uncertainty of patterns of groundwater flow. Four potential end members are shown including Tusayan well, Valle well, Fossil Spring, and Wupatki Well. Of the potential end members shown (Fig. 15), Wupatki is likely too distant from the study area and discharges from the C-aquifer. In regards to the Tusayan well, Figure 5 shows northward flow of groundwater from the Tusayan area and fault connectivity with South Rim springs such that it is not a good choice as a South Rim mixing end member.

Greater than 50 years of infiltration of North Rim water at Grand Canyon Village seem likely to have interacted with the Tusayan divide groundwaters. Hence, our favored end members, based just on the stable isotopes, would be near the limits of our dataset (for example similar to Fossil Spring) or average well composition from Valle wells, south of the Tusayan groundwater divide. Figure 16 shows that Havasupai Garden Spring plots at the nexus of the North and South rim distributions and depending on choice of end members, for example could represent ~50% Roaring Springs baseflow mixed with Valle groundwater or ~70% Roaring Springs baseflow mixed with a Fossil Springs end member. However, both the solutes in Piper diagram (Fig 8) and the cross plot of [Cl] with δD in Figure 11 suggest that the South Rim groundwater variation may not be 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 a salinization component needs to be added to the mixture. Using the 80% Roaring baseflow end member and either average Valle groundwater, or a composition similar to Fossil Spring, Havasupai Gardens is sustained by ~50% to ~70% North Rim water, respectively.

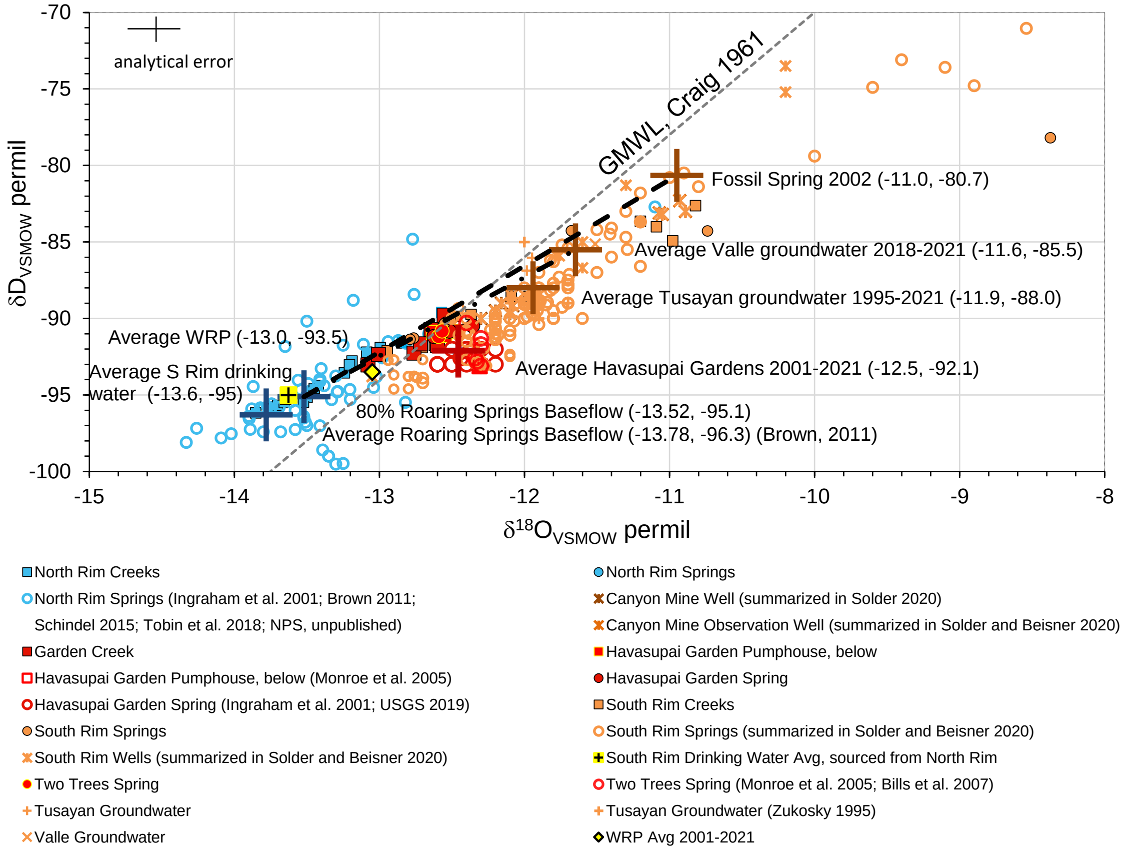

Figure 16- Stable isotopes for Havasupai Garden Spring and Two Trees Spring samples (red) shows that they plot between and overlap the North Rim and South Rim groundwater mixing arrays. Grand Canyon Village samples shown in yellow. Preferred mixing hypotheses use the 80% Roaring Springs base flow (Brown, 2011) as representative of pipeline waters reaching Grand Canyon Village that mixes with A) average Valle groundwater, or B) Fossil Spring end member. By these mixing end members, average Havasupai Garden spring is approximately: A) 50% to B) 70% North Rim water; Canyon Mine and Tusayan well waters are about A) 20% to B) 40% North Rim water.

Figure 17 combines solutes and stable isotopes and shows that Havasupai Garden Spring samples can be explained by a ~70% mixture of North Rim water with a hypothetical South Rim end member (near Fossil Spring) but this mixing trend cannot be explained by direct discharge down Bright Angel fault from the WRP due to the high [Cl] in the latter. Alternatively, all of the data is encompassed in a 3-mixing component model in which salts are added to the South Rim groundwater mix. Possible salinization processes include evaporation, geothermal inputs, and water treatment inputs and processes (USEPA 1988). All could have played a role. Some longitudinal creek sampling efforts (Pipe Creek, Grapevine East) suggest evaporation trajectories (Fig. 10) where points plot to the lower right of the GMWL (Sharp 2017).

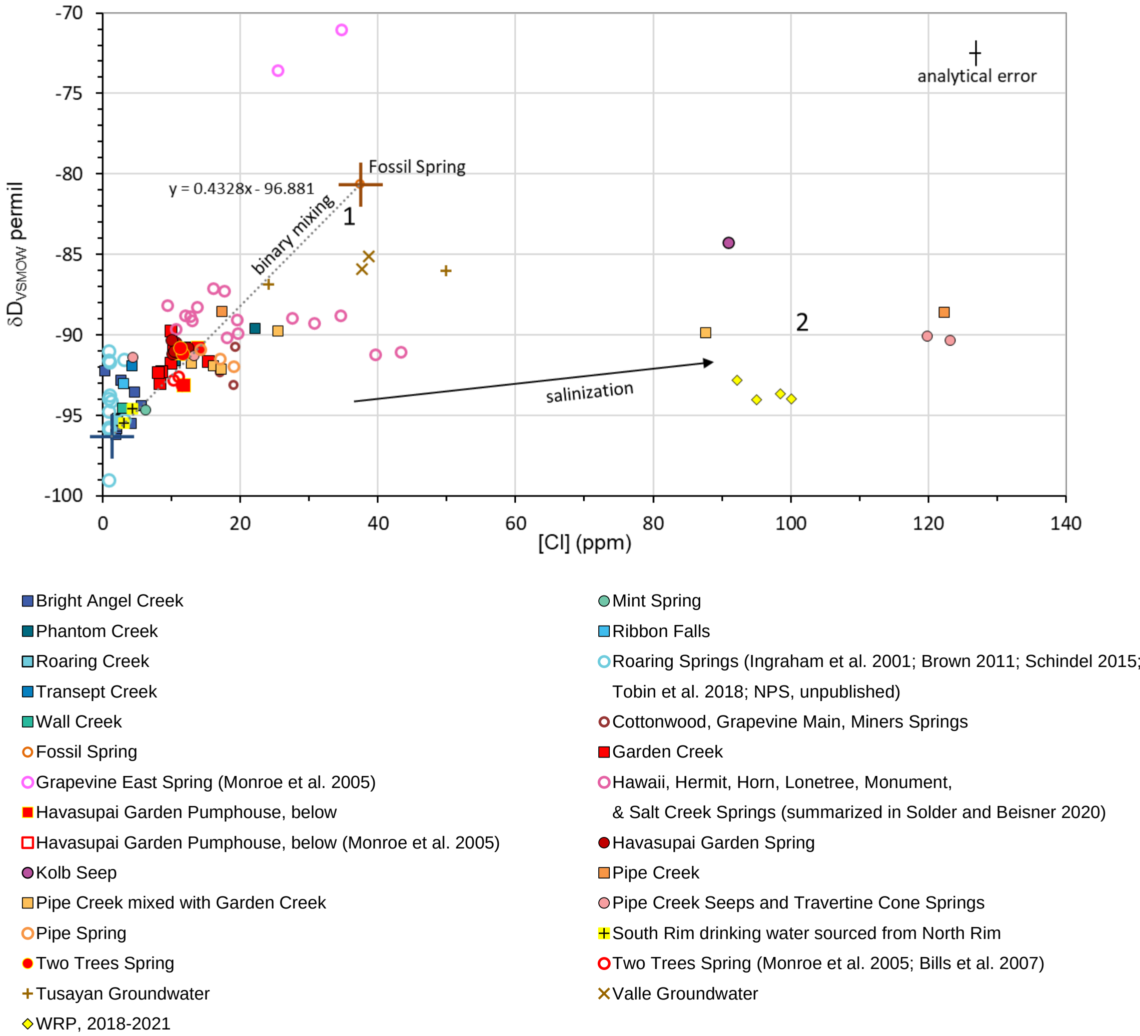

Figure 17. [Cl] versus δD for springs (circles), creeks (squares), wastewater (diamonds), and wells (exes and crosses) of the water corridor. Unfilled symbols are from previously published samples (Table DR-2). Color groups are N-Rim (blues); S-Rim (oranges); Havasupai Garden (red). This 2-tracer approach suggests that binary mixing may explain much, but not all of the water variation. Another process may involve: A) addition of sodium carbonate and salts during water reclamation (Roberts et al. 2007); and/or B) addition of salts from deeply circulated geothermal fluids.

Highly evaporated seeps like the Pipe Creek seep show highest chloride, perhaps as expected. On the Piper (Fig. 8), the same points plot on a different variation line. However,

$^{87}Sr/^{86}Sr$ is far higher in the Pipe Creek seeps that emerge from Precambian basement and this cannot be due to evaporation and therefore, the salts may also be explained in part by deeply circulated geothermal waters and water-rock interaction (Crossey et al. 2006; 2016). The high [Cl] of the WRP waters may be due to reclamation processes. Our preferred interpretation involves mixing of N-rim and S-rim groundwaters combined with one or more of the salinization processes.

The presence of PPCPs at Havasupai Garden Spring, Two Trees Spring, and Pipe Spring is compatible with the hypothesis that WRP and S-Rim groundwater has been impacted by human use, as also proposed by Monroe et al. (2005). This tracer was used to find a possible connection between the reclaimed effluent and the springs discharging along the Bright Angel fault. The results actually showed that all the South Rim springs sampled had detections of PPCPs without discrimination and that the concentrations for compounds detected were very similar. The PPCPs at the springs if sourced from the reclaimed water show little dilution. 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 a spring upslope from the hiking trail and relatively remote from hiking traffic.

Figure 18 examines mean stable isotopic values for other springs that emanate from the R-M aquifer below the South Rim (data summarized in Table 9). 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, 80% Roaring Springs baseflow and Fossil Spring. This suggests the provocative conclusion that, like Havasupai Garden Spring, all or most of the South Rim springs are sustained by 30-70% North Rim contributions. Figure 18b shows that the fault network of NE-trending and NW-trending 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 large distance fast transit during the dye tracer study (Jones et al. 2018). Hence pipeline water from the Water Reclamation Plant, plus general infiltration of N-Rim groundwater to the R-M waters down the Bright Angel fault both towards the Tusayan groundwater divide and ultimately into Grand Canyon may explain the variation in South Rim springs. If so, most or all South Rim springs are sustained by N-Rim-derived waters as infiltration and effluent driven by the topographic head of the WRP infiltration site and the head from the groundwater divide in the R-M aquifer near Tusayan. Notably, as suggested in Figure 17, the higher salts in travertine cone spring and Pipe Creek seeps along the Bright Angel fault may be showing a direct pathway from the WRP, and Coconino Plateau groundwater wells at Tusayan and Valle may have picked up salts from the WRP, among other processes.

6.0 Discussion and Implications

Many factors contribute to the need for better understandings 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), and the risk for environmental contamination and spring impact from nearby uranium mining activities (Bills et al. 2007; Solder et al. 2020, Beisner et al. 2017, 2020). Further, the Park is changing the pipeline delivery system to better meet overall water needs. Our data and interpretations have provocative and testable implications for several aspects of Park management.

Our analysis of distinct North Rim and South Rim groundwater hydrochemical fingerprints highlights that the 50-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 18 summarizes our binary mixing hypothesis using means of spring and groundwater measurements. Water at Grand Canyon Village is essentially 100% N-Rim pipeline water. Havasupai Garden Spring is ~50% N-Rim water using a Valle groundwater end member and ~70% using a composition similar to Fossil Spring, near the extreme of our data (see also Fig. 17). Most other S-Rim springs are also hypothesized to be sustained by >40% North Rim recharge. Our mixing model estimates are necessarily only semi-quantitative because of the uncertainty about the most appropriate S-Rim end member. But the data support the concept that most or all S-Rim springs are sustained by North Rim water through South Rim infiltration and conveyance on South Rim fault systems. Additional spring monitoring and tracer studies (see below) can help to better quantify extent of mixing and the rates of transit to different locations.

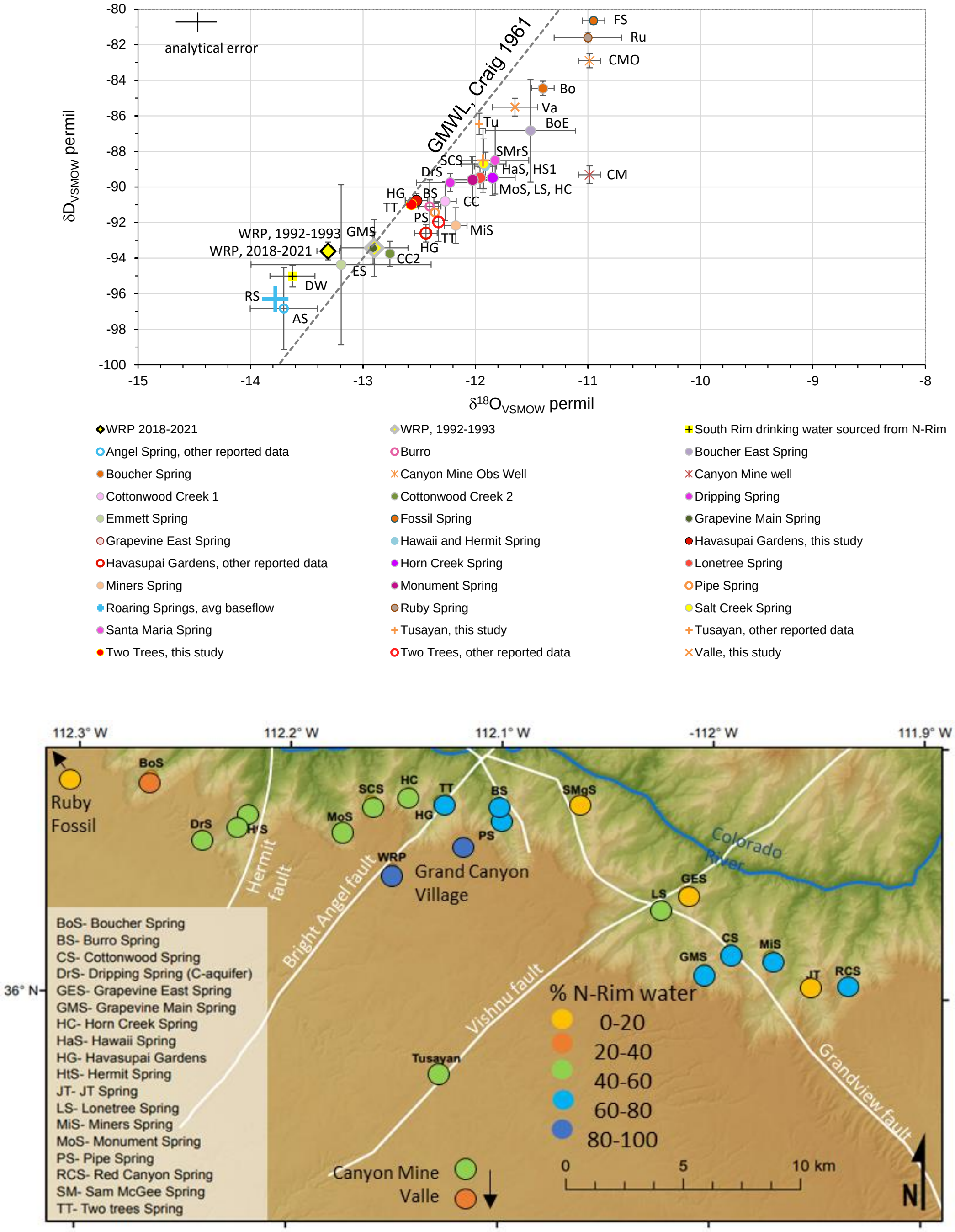

Figure 18. Stable isotope variation in South Rim springs and groundwaters. A) Mean stable isotope water values fall on a variation trend between a N-Rim end member (Roaring Springs base flow; blue plus) and Fossil Spring. B) Map shows spring locations and estimate of mixing proportion of N-Rim water in different springs from 18A due to infiltration of N-Rim water at Grand Canyon Village. This supports the hypothesis of significant groundwater connectivity between springs and Coconino Plateau groundwater wells, including the Canyon Uranium Mine.

An alternative hypothesis to explain the observed stable isotope groundwater variation was proposed by Solder and Beisner (2020). As shown in Figure 19, they compiled winter and summer precipitation data from the area and considered S-Rim groundwater variation (red oval) to reflect different mixtures of winter and summer recharge for different springs. Their meteoric mixing model explored different end members; their means of observed winter and summer precipitation do not encompass the groundwater data so they used a weighted model (mean modeled winter precipitation) mixing with mean summer surface runoff (green mixing line of Fig. 19).

In contrast, we explain the observed variation in stable isotope composition of springs and groundwater in terms of a groundwater mixing model (red mixing line) rather than different types of recharge. Our end member mixing line (red) more closely parallels the observed variation of S-Rim springs and groundwater. Their proposed model suggests that that there is a varying balance of winter and summer precipitation, and hence an important control that local recharge exerts on groundwater. We agree that this may be an important factor at subregional scales, but is likely a second order control relative to groundwater mixing for the relatively small region of the South Rim springs and groundwater of both studies.

A key but relatively poorly resolved aspect of our 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 Figure 5B. Scarcity of wells and poor public documentation of water level and historical data is such that additional data about geochemical variation of key wells at Tusayan 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, an early study done in 1999 showed that groundwater pumping had 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 to 65 l/s (Toll et al. 2020).

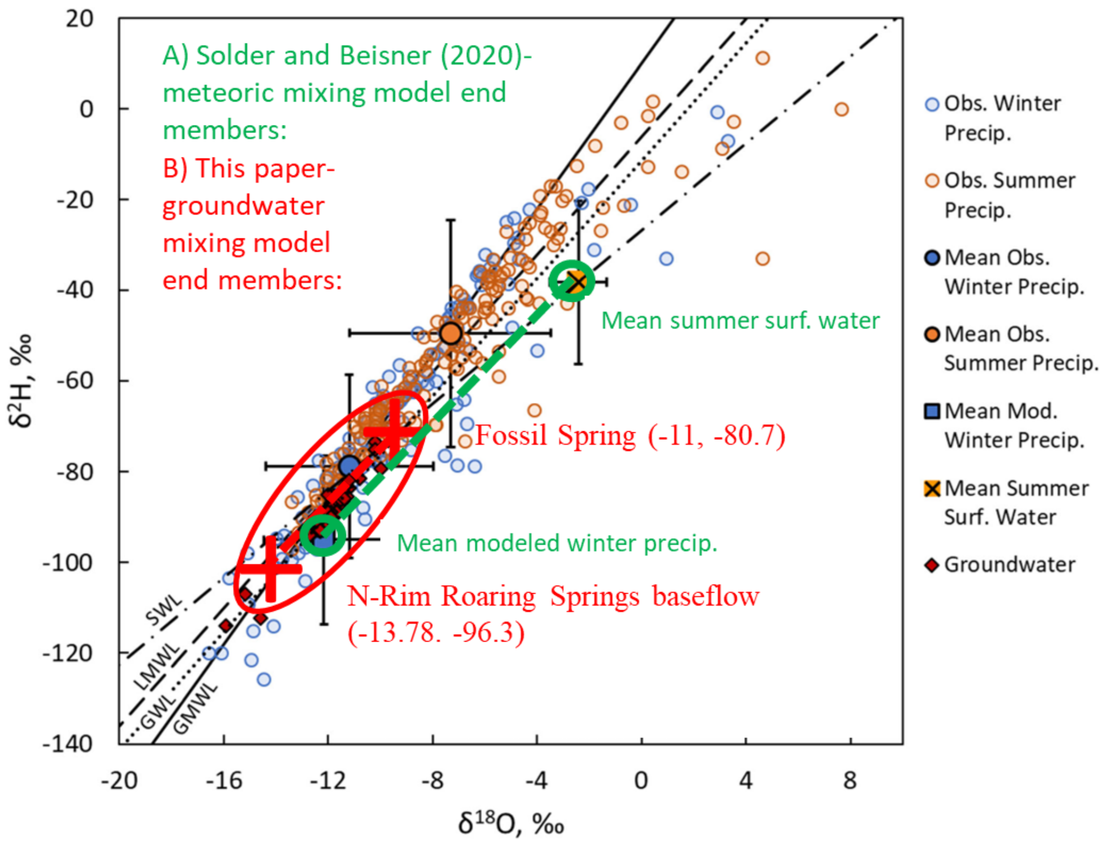

Figure 19. Alternate models (modified from Figure 3 of Solder and Beisner, 2020): A) meteoric mixing (green circles) proposes that variation in stable isotopes in groundwater (red diamonds) reflects mixing of modeled mean winter precipitation and mean summer runoff end members (Solder and Beisner, 2020). Note that the red oval of groundwater points excludes the most negative points from the San Francisco Peaks and the least negative points from Wupatki well that are outliers and distant from South Rim; versus B) groundwater mixing model (this paper, red pluses) proposes mixing of 80% N-Rim baseflow and a South Rim end member similar to Fossil Spring.

The recent evolution of the Tusayan divide has especially important implications for regional water use, drilling, and mining at Tusayan and Pinyon Plain Mine. Given the potential for fault-influenced flow combined with karst complexities, our hypothesis is that any change in head in the groundwater wells, especially near the divide, could affect South Rim springs.

Water quality as well as sustainability are concerns for South Rim springs considering local uranium mining. 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 an average of 0.67 L/s over the last 9 years from the shallow C-aquifer. Data suggest the shallow aquifer is connected to the RM aquifer and mining operations could have an impact on both. A USGS report published in 2021 presents uranium data for greater than 200 groundwater sites samples between 1981-2020. The study reports that 95% of the sites have uranium concentrations less than the USEPA MCL of 30 µg/L (Tilman 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 Monument, Horn Creek, and Salt Creek springs downslope from the Orphan Mine in waters that are about 50% N-Rim and S-Rim 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) but our hypothesis is that the uranium mine wells are well connected with Grand Canyon springs and R-M groundwater of the Coconino Plateau.

The Bright Angel fault as a fast pathway for recharge to Havasupai Garden Spring is provocative in terms of understanding the rate of water transit. Additional PPCPs work and other tracers should be used to test this fault connection. A dye tracer study using biodegradable anthropogenic tracers similar to Jones et al. (2018) would also test the fault network model for the South Rim and better quantify connectivity between springs and rates of fast-traveled water movement. Testing whether dyes injected at the WRP may potentially be detected in wells in Tusayan and Pinyon Plain Mine and in various springs could help better define the location of the groundwater water divide and detect a future or ongoing cone of depression from pumping. It is likely that the S-Rim fault network is like the North Rim network and will convey waters in days to weeks in many directions.

There are also implications of our 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 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 to 0.0036 DIC). However, a probable 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 U.S. have experienced an average decrease in snowpack of 19 percent 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).

7.0 Conclusions

The overall goal of this study is to evaluate an ongoing anthropogenic hydrologic "experiment" that the Park has been conducting over the past >50 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 Garden Spring is more depleted 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 especially in springs near Havasupai Garden Spring but also in many South Rim springs and groundwaters. Specific findings of this study are as follows.

1. North Rim water emerging from Roaring Springs varies in composition between a baseflow endmember and snowmelt or monsoonal faster-traveled inputs. This provides the variability in water composition of pipeline water reaching the South Rim (Brown 2011) and suggests an 80% base flow end member may be most appropriate for our mixing model.
2. South Rim spring and groundwater geochemistry is an extremely varied mix of North Rim and South Rim water as a result of both water flow pathways and the influence of infiltration of North Rim water from Grand Canyon Village, including reclaimed water, recharging the aquifer; the different fingerprints of different waters will be useful for future monitoring of changes in springs.
3. Groundwater recharge at Havasupai Garden Spring is ~50-70% each from North Rim and South Rim end members (depending on choice of mixing end members). We favor

the higher value using an end member near the extremes of our data, similar in composition to Fossil Spring.

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. However, Havasupai Garden Spring does not see these high salts and its composition reflects 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 mixing of Roaring Springs (pipeline) water with groundwater across the South Rim part of the Coconino Plateau aquifer. Pumping at Tusayan and Valle and Pinyon Plain Mine may affect S-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. Conducting additional dye tracer study on the South Rim is needed to better quantify groundwater transit times and connectivity.
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, and worth it in terms of increased water supply. But this change has potential very adverse consequences in terms of increased downtime needed to settle turbidity after flashfloods and fire impacts.

Table 2. Sample Locations and Field Parameters (page 1/3)								
Sample ID	**Location**	**Sample Name**	**Date Sampled**	**Latitude**	**Longitude**	**Temp (°C)**	**pH**	**Conductivity (µS/cm)**
DW	N. Rim-drinking water	LC18 Paiute	1/3/2018	36.048208	-112.133917	14.1	7.57	314
DW2	N. Rim-drinking water	BO21-Market	2/28/2021	36.053125	-112.121025	36.9	7.1	296
Tu	Tusayan Best Western	LC18-TusBW	2018	35.969543	-112.129358	nr	nr	nr
Tu	Tusayan Best Western	BO21-Tusayan	2/27/2021	35.969543	-112.129358	22.4	7.01	700
Va	Valle Chevron Station	LC18- ValleChevron	2018	35.652782	-112.138673	nr	nr	nr
Va	Valle Chevron Station	BO21-Valle Chevron	2/27/2021	35.652782	-112.138673	13	7.07	767
WRP	Water Rec. Plant	LC18 REC1	1/3/2018	36.049689	-112.151311	13.69	6.46	952
WRP	Water Rec. Plant	BO21-WRP-1	2/27/2021	36.049657	-112.151633	8.1	6.17	877
WRP2	Water Rec. Plant	BO21-WRP-2	2/27/2021	36.049064	-112.151859	8.3	6.58	839
WRP	Water Rec. Plant	LC21 WRP	12/20/2021	36.049657	-112.151633	9.9	6.42	856
PC1	Pipe Creek	LC21 Pipe	12/18/2021	36.072810	-112.102830	4	6.2	635
PC2	Pipe Creek	LC18-Pipe Creek upper	1/1/2018	36.087452	-112.109862	7	7.87	1843
PC3	Pipe Creek	BO-21-Pipe Creek	2/28/2021	36.087986	-112.111506	18.3[f]	8.22[f]	1717[f]
PC3	Pipe Creek	BHO21-5-Pipe Creek	5/26/2021	36.087986	-112.111506	nr	nr	nr
PC4	Pipe Creek	BHO21-4-Pipe Creek abv Garden Ck Conf	5/26/2021	36.090845	-112.110639	nr	nr	nr
PC5	Pipe Creek	Pipe Creek A.C.	5/24/2017	36.093360	-112.111740	nr	7.89	1386
PC6	Pipe Creek	LC18-PipeCreek	1/1/2018	36.093396	-112.111694	10.7	7.64	376
PC7	Pipe Creek	Pipe Creek B.C.	5/24/2017	36.093560	-112.111820	nr	8.52	510
PC7	Pipe Creek	BHO21-2-Pipe Creek BC w Indian Gard	5/26/2021	36.093560	-112.111820	nr	nr	nr
PC8	Pipe Creek	BHO21-1-PC at CR	5/26/2021	36.098122	-112.111336	nr	nr	nr
PC8	Pipe Creek	LC18-PipeLower	1/1/2018	36.098122	-112.111336	10.2	7.15	429
PT1	Pipe Seep	LC17-PipeTrib1	12/31/2017	36.086919	-112.114976	12.1	7.21	3000
PT2	Pipe Seep at BA Fault	BHO21-6-Seep at BA Fault	5/26/2021	36.087227	-112.114681	nr	nr	nr
PT3	Trough Seep	LC18 Trough Seep	1/1/2018	36.087726	-112.114552	11.8	7.3	557
PT4	Fern Seep	LC18 Fern Seep	1/1/2018	36.088988	-112.114774	17.1	7.39	450
PT5	Pipe Cone Spring at BA Fault	BO-21-PC Cone	2/28/2021	36.088681	-112.112452	18.1[f]	8.21[f]	910[f]
PT5	Pipe Cone Spring at BA Fault	LC18- PipeCreek trav cone	1/1/2018	36.088681	-112.112452	11.1	7.72	813
PS	Pipe Creek[a]	Pipe Creek	5/22/2000	36.069308	-112.099906	22.1	7.77	614
PS	Pipe Creek[a]	Pipe Creek	12/7/2000	36.069308	-112.099906	13	7.38	588
PS	Pipe Creek[a]	Pipe Creek	4/8/2001	36.069308	-112.099906	13	7.28	554
HG2	Havasupai Gardens[b]	BHO21-HGU East	10/24/2021	36.077048	-112.128668	17.3	7.86	451
HG	Havasupai Gardens[b]	BHO21-HGU	10/24/2021	36.077174	-112.129002	19.6	7.07	430
HG	Havasupai Gardens[b]	LC21 Indian Garden Campground	12/19/2021	36.077174	-112.129002	18.5	7.06	434

Table 2. Sample Locations and Field Parameters (page 2/3)								
Sample ID	**Location**	**Sample Name**	**Date Sampled**	**Latitude**	**Longitude**	**Temp (°C)**	**pH**	**Conductivity (µS/cm)**
HG	Havasupai Gardens[b]	LC17-IGupper	12/31/2017	36.077174	-112.129002	21.3	6.72	449
HG	Havasupai Gardens[b]	BO21-HGU	2/28/2021	36.077174	-112.129002	18.2	6.99	450
GC1	Garden Creek	LC17-IG2	12/31/2017	36.077495	-112.128493	17.6	7.49	460
GC1	Garden Creek	BHO21-9-Garden Creek	5/26/2021	36.077495	-112.128493	nr	nr	nr
GC2	Garden Creek	Indian Garden Creek	5/24/2017	36.078610	-112.127550	nr	8.02	456
GC3	Garden Creek	LC17-IGlower	12/31/2017	36.086962	-112.118626	14.7	7.6	379
GC4	Garden Creek	BHO21-7-Garden Creek near unconformity	5/26/2021	36.088372	-112.115819	nr	nr	nr
GC5	Garden Creek	Lower IG	5/24/2017	36.093313	-112.111778	nr	8.51	431
GC5	Garden Creek	LC18-IGlowest	1/1/2018	36.093313	-112.111778	7.6	7.95	407
GC5	Garden Creek	BHO21-3-IG	5/26/2021	36.093313	-112.111778	nr	nr	nr
TT	Pumphouse Spring[a]	Pumphouse Spring	5/22/2000	36.077498	-112.126114	19.5	8.24	503
TT	Pumphouse Spring[a]	Pumphouse Spring	12/7/2000	36.077498	-112.126114	14.5	8.28	424
TT	Pumphouse Spring[a]	Pumphouse Spring	4/7/2001	36.077498	-112.126114	15.5	8.02	398
TT2	Two Trees Spring[c]	LC17-Two Trees	12/31/2017	36.077800	-112.125770	15.9	7.45	441
TT2	Two Trees Spring[c]	BO21-Two Trees	2/28/2021	36.077800	-112.125770	12.4	7.05	425
TT2	Two Trees Spring[c]	BHO21-Two Trees	10/24/2021	36.077800	-112.125770	18.3	7.1	423
TT2	Two Trees Spring[c]	LC21 Two Trees	12/19/2021	36.077800	-112.125770	9.9	7.87	430
TT3	Two Trees Spring[c]	LC21 Below Two Trees	12/19/2021	36.078360	-112.126340	18.7	7.45	415
PH	Pumphouse	Indian Garden below pumphouse	5/24/2017	36.078590	-112.126530	nr	8.19	424
PH	Pumphouse	LC17-IGeast	12/31/2017	36.078597	-112.126492	20.6	7.44	427
KS	Kolb Seep	BHO21- Kolb Seep	10/24/2021	36.059163	-112.142527	nr	nr	1265[f]
BS	Burro Spring	LC21 Burro	12/18/2021	36.076550	-112.101140	9	7.32	579
CC	Cottonwood Creek[a]	Cottonwood Creek No. 2	11/29/2000	36.018850	-111.991139	12	7.86	444
GMS	Grapevine Main Spring[a]	Grapevine Main Spring	4/30/2001	36.011058	-112.003277	12.5	8.1	370
HaS	Hawaii Spring[a]	Hawaii Spring	5/25/2000	36.070611	-112.219027	18	8.15	410
HtS	Hermit Spring[a]	Hermit Spring	4/11/2001	36.063156	-112.225626	10.6	8.16	417
HtS	Hermit Spring	LC 12 GC 95 HER-1	5/28/2012	36.065948	-112.223768	18.9	7.97	457
HC	Horn Creek[a]	Horn Creek	5/22/2000	36.08043176	-112.143673	17.9	8.17	668
LS	Lonetree Spring[a]	Lonetree Spring	5/1/2001	36.036000	-112.025000	11.7	7.7	660
MiS	Miners Spring[a]	Miners Spring	5/24/2000	36.016443	-111.972146	15.8	8.75	402

Table 2. Sample Locations and Field Parameters (page 3/3)								
Sample ID	**Location**	**Sample Name**	**Date Sampled**	**Latitude**	**Longitude**	**Temp (°C)**	**pH**	**Conductivity (µS/cm)**
MoS	Monument Spring[a]	Monument Spring	12/5/2000	36.065581	-112.176365	18	7.55	533
SCS	Salt Creek Spring[a]	Salt Creek Spring	5/23/2000	36.07683251(	-112.161741	18.7	8.46	706
BAC1	Bright Angel Creek	BO-BAC at Manzanita	9/11/2021	36.186030	-112.031722	15.3	8.73	308
BAC2	Bright Angel Creek	BO-BAC at Cottonwood	9/11/2021	36.169730	-112.041950	16.99	8.75	300
BAC3	Bright Angel Creek	BO-BAC above Ribbon	9/11/2021	36.159161	-112.052699	17.5	8.83	352
BAC4	Bright Angel Creek	BO-BAC-Below Ribbon	9/11/2021	36.156079	-112.054288	16.2	8.71	299
BAC5	Bright Angel Creek	LC17-BAUpper	5/24/2017	36.139408	-112.067038	nr	nr	nr
BAC6	Bright Angel Creek	BO-BAC at the box	9/11/2021	36.119337	-112.083813	17.64	8.6	442
BAC7	Bright Angel Creek	LC17-BA2AbovePhantom	5/24/2017	36.116274	-112.087326	20.4	8.7	284
BAC8	Bright Angel Creek	LC18-BA	1/1/2018	36.105830	-112.095432	11.2	7.3	347
BAC9	Bright Angel Creek	BO-BAC at bridge	9/10/2021	36.099658	-112.094210	23.36	8.67	308
BAC10	Bright Angel Creek	BO21-BA at CR	5/26/2021	36.099854	-112.093209	15.8	7.87	362
PhC	Phantom Creek	LC17-Phantom	5/24/2017	36.116304	-112.087438	24.5	8.78	371
PhC	Phantom Creek	BO-Phantom Creek	9/11/2021	36.116186	-112.087366	22.3	8.6	442
MS	Mint Spring	BO-Mint Spring	9/11/2021	36.140657	-112.066596	17.86	7.94	484
RF	Ribbon Falls	BO-Ribbon Falls	9/11/2021	36.158278	-112.055162	19.22	8.44	389
WC	Wall Creek	BO-Wall Creek	9/11/2021	36.163817	-112.046582	21.2	8.44	352
TC	Transept Creek	BO-Transept Creek	9/11/2021	36.171500	-112.040250	23.3	8.29	440
RC	Roaring Creek	BO-Roaring Creek	9/12/2021	36.193700	-112.033960	15.2	8.55	304
RS	Roaring Springs[d]	Roaring Springs	nr	36.19499[g]	-112.03574[g]	nr	nr	nr
RS	Roaring Springs[e]	Roaring Spring (North Rim)	4/1/1993	36.19499[g]	-112.03574[g]	nr	nr	nr
RS	Roaring Springs[e]	Roaring Spring (North Rim)	9/1/1993	36.19499[g]	-112.03574[g]	nr	nr	nr

nr = not recorded or not relevant

[a] Monroe et al. 2005

[b] Havasupai Gardens is the proposed new name for Indian Gardens. The name change is not formalized at this time.

[c] Two Trees Spring and Pumphouse Spring are synonymous

[d] data from Tobin et al. 2018

[e] data from Ingraham et al. 2001

[f] Measured in lab rather than in the field

[g] Roaring Springs location approximate for protection of caves

Table 3. Major Ion Chemistry (page 1/3)												
Sample ID	**Location**	**Date Sampled**	**Ca (mg/L)**	**Mg (mg/L)**	**Na (mg/L)**	**K (mg/L)**	**Alkalinity (mg/L HCO_3)**	**Cl (mg/L)**	**SO4 (mg/L)**	**NO3 (mg/L)**	**TDS[e] (mg/L)**	**Percent Error[f]**
DW	N. Rim-drinking water	1/3/2018	37.91	16.43	1.13	0.92	191	4.32	2.68	1.54	254	0.12
DW2	N. Rim-drinking water	2/28/2021	31.19	16.26	1.03	0.78	176	3.16	2.19	1.19	230	-0.95
Tu	Tusayan Best Western	2018	nr	nr	nr	nr	287	24.10	13.66	8.71	324	0.00
Tu	Tusayan Best Western	2/27/2021	17.52	22.08	87.17	1.78	301	49.94	14.68	14.03	495	-0.97
Va	Valle Chevron Station	2018	nr	nr	nr	nr	233	38.68	191.87	2.61	463	0.00
Va	Valle Chevron Station	2/27/2021	71.54	38.34	18.87	2.52	232	37.69	141.00	2.64	542	-1.23
WRP	Water Rec. Plant	1/3/2018	45.95	28.41	75.24	21.77	140	92.15	57.46	178.20	461	-2.87
WRP	Water Rec. Plant	2/27/2021	37.18	19.16	79.15	14.07	44	100.11	88.92	128.58	383	-2.02
WRP2	Water Rec. Plant	2/27/2021	38.82	20.51	80.21	14.19	45	98.47	85.86	127.90	383	0.31
WRP	Water Rec. Plant	12/20/2021	43.62	25.75	76.20	18.45	45	95.06	35.05	227.90	339	1.60
PC1	Pipe Creek	12/18/2021	65.57	41.42	10.80	3.84	311	17.39	55.41	0.70	506	3.59
PC2	Pipe Creek	1/1/2018	77.66	81.27	174.60	16.14	286	211.52	359.23	1.34	1206	1.21
PC3	Pipe Creek	2/28/2021	73.41	75.53	192.10	17.87	249	252.99	372.13	0.79	1233	-0.73
PC3	Pipe Creek	5/26/2021	83.66	62.78	196.60	21.51	270	240.24	354.30	0.64	1229	-0.36
PC4	Pipe Creek	5/26/2021	53.12	48.68	102.70	11.27	286	122.31	142.83	0.60	766	1.36
PC7	Pipe Creek	5/24/2017	48.13	31.00	16.41	2.09	250	25.50	29.72	3.68	403	2.48
PC7	Pipe Creek	5/26/2021	48.54	31.12	8.21	1.24	259	12.87	14.50	nd	375	4.53
PC8	Pipe Creek	5/26/2021	48.20	31.26	10.58	1.42	259	16.14	18.38	nd	385	3.74
PC8	Pipe Creek	1/1/2018	45.18	24.26	9.40	1.72	245	17.27	19.86	0.95	363	-2.29
PT2	Pipe Seep at BA Fault	5/26/2021	446.80	207.40	2109.00	127.90	353	nr	nr	nr	3244	nr
PT3	Trough Seep	1/1/2018	57.28	31.14	7.71	2.11	321	13.34	12.14	1.54	445	-0.71
PT4	Fern Seep	1/1/2018	nr	nr	nr	nr	261	4.40	4.46	nd	270	0.00
PT5	Pipe Cone Spring at BA Fault	2/28/2021	46.92	37.27	81.73	5.31	248	123.16	70.50	0.56	613	0.53
PT5	Pipe Cone Spring at BA Fault	1/1/2018	44.71	41.57	58.93	4.32	262	119.88	74.03	1.21	606	-5.12
PS	Pipe Creek[a]	5/22/2000	54.18	37.56	12.16	3.75	305	19.04	63.12	nr	495	-3.31
PS	Pipe Creek[a]	12/7/2000	55.49	36.36	9.96	3.62	293	17.13	55.17	nr	471	-1.14
PS	Pipe Creek[a]	4/8/2001	51.37	35.11	9.51	3.50	265	14.29	58.49	nr	437	-0.15
HG2	Havasupai Gardens[b]	10/24/2021	49.27	31.79	5.57	1.43	279	10.70	13.25	1.31	391	1.64
HG	Havasupai Gardens[b]	10/24/2021	43.41	30.73	5.38	1.42	255	10.19	13.20	2.11	359	1.93
HG	Havasupai Gardens[b]	12/19/2021	43.89	30.52	5.63	1.53	248	10.06	12.82	2.05	352	3.53
HG	Havasupai Gardens[b]	12/31/2017	43.19	27.48	5.35	1.63	259	12.44	15.87	2.50	365	-2.51
HG	Havasupai Gardens[b]	2/28/2021	40.76	28.65	5.17	1.43	247	10.50	13.73	2.11	347	0.32
GC1	Garden Creek	12/31/2017	44.12	27.70	5.42	1.70	260	12.34	16.12	2.24	367	-1.91

Table 3. Major Ion Chemistry (page 2/3)												
Sample ID	Location	Date Sampled	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Alkalinity (mg/L HCO_3)	Cl (mg/L)	SO4 (mg/L)	NO3 (mg/L)	TDS[e] (mg/L)	Percent Error[f]
GC1	Garden Creek	5/26/2021	43.94	31.82	5.49	1.48	249	9.93	15.29	2.08	357	3.82
GC2	Garden Creek	5/24/2017	49.06	31.13	5.84	1.39	262	10.35	13.45	3.66	373	4.29
GC3	Garden Creek	12/31/2017	44.98	22.39	3.12	1.25	237	8.30	8.63	1.41	326	-0.52
GC4	Garden Creek	5/26/2021	49.70	30.24	5.04	1.13	270	8.63	9.60	0.65	374	3.38
GC5	Garden Creek	5/24/2017	45.82	29.00	5.45	1.21	249	10.01	11.42	3.40	352	3.56
GC5	Garden Creek	1/1/2018	43.79	22.98	3.22	1.20	238	8.12	8.55	1.04	326	-0.71
GC5	Garden Creek	5/26/2021	43.44	30.18	4.80	1.00	236	15.41	11.74	nd	342	3.66
TT	Pumphouse Spring[a]	5/22/2000	41.40	29.48	6.76	1.76	261	11.02	14.05	nr	365	-0.57
TT	Pumphouse Spring[a]	12/7/2000	39.20	28.62	6.09	1.48	244	11.60	13.81	nr	345	-0.05
TT	Pumphouse Spring[a]	4/7/2001	39.81	27.96	5.84	1.56	251	10.32	15.14	nr	351	-1.66
TT2	Two Trees Spring[c]	12/31/2017	40.48	26.99	5.74	1.88	240	14.25	17.98	4.14	348	-1.93
TT2	Two Trees Spring[c]	2/28/2021	37.99	28.15	5.47	1.66	237	11.91	15.04	2.60	337	-0.42
TT2	Two Trees Spring[c]	10/24/2021	40.29	30.49	5.62	1.55	240	11.66	14.42	2.97	344	1.97
TT2	Two Trees Spring[c]	12/19/2021	41.02	29.87	5.98	1.70	233	11.31	14.39	2.57	337	3.52
TT3	Two Trees Spring[c]	12/19/2021	37.65	28.44	5.47	1.59	231	11.25	14.03	2.14	329	0.81
PH	Pumphouse	5/24/2017	42.03	29.61	5.82	1.50	228	11.57	16.29	7.25	334	4.65
PH	Pumphouse	12/31/2017	38.55	26.37	5.49	1.84	242	13.92	17.77	3.49	346	-3.89
BS	Burro Spring	12/18/2021	55.06	39.69	13.69	4.47	282	19.70	48.27	1.82	463	3.96
CC	Cottonwood Creek[a]	11/29/2000	41.96	28.30	5.35	2.19	256	9.54	18.43	nr	362	-1.48
GMS	Grapevine Main Spring[a]	4/30/2001	35.48	22.67	3.85	1.38	225	5.70	6.03	nr	300	-1.84
HaS	Hawaii Spring[a]	5/25/2000	45.36	31.33	12.50	2.71	266	13.03	33.40	nr	404	0.16
HtS	Hermit Spring[a]	4/11/2001	42.76	26.86	5.47	1.49	235	9.41	13.27	nr	334	2.30
HtS	Hermit Spring	5/28/2012	40.68	24.92	6.63	1.71	258	12.07	15.80	2.93	360	-5.22
HC	Horn Creek[a]	5/22/2000	51.00	40.06	22.47	5.98	259	34.66	99.27	nr	512	-2.42
LS	Lonetree Spring[a]	5/1/2001	59.64	42.01	26.53	10.73	198	19.70	190.00	nr	547	0.59
MiS	Miners Spring[a]	5/24/2000	22.02	27.46	11.87	3.60	142	19.09	35.24	nr	261	4.47
MoS	Monument Spring[a]	12/5/2000	43.11	30.43	18.35	1.65	246	43.38	20.36	nr	403	-2.41
SCS	Salt Creek Spring[a]	5/23/2000	55.54	43.08	17.08	4.38	176	17.66	168.81	nr	483	1.83
BAC1	Bright Angel Creek	9/11/2021	39.50	18.71	1.11	0.79	199	1.96	2.27	0.87	263	3.10
BAC2	Bright Angel Creek	9/11/2021	40.43	19.42	1.26	0.83	213	2.03	2.89	0.78	280	1.14
BAC3	Bright Angel Creek	9/11/2021	40.80	20.40	1.38	0.84	215	2.10	3.30	0.76	284	1.98
BAC4	Bright Angel Creek	9/11/2021	41.66	20.80	1.47	0.87	220	2.20	3.46	0.73	290	1.86
BAC5	Bright Angel Creek	5/24/2017	nr	nr	nr	nr	171	0.34	0.32	n.a.	172	nr

Table 3. Major Ion Chemistry (page 3/3)												
Sample ID	Location	Date Sampled	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Alkalinity (mg/L HCO_3)	Cl (mg/L)	SO4 (mg/L)	NO3 (mg/L)	TDS[e] (mg/L)	Percent Error[f]
BAC6	Bright Angel Creek	9/11/2021	42.05	21.61	2.73	1.06	226	3.12	4.66	0.74	301	1.73
BAC7	Bright Angel Creek	5/24/2017	36.13	17.56	1.99	0.82	173	2.64	4.43	0.03	237	5.54
BAC8	Bright Angel Creek	1/1/2018	42.63	20.81	12.51	1.26	231	5.65	7.58	0.94	321	3.73
BAC9	Bright Angel Creek	9/10/2021	35.22	21.56	3.89	1.21	198	4.60	5.17	0.75	269	3.51
BAC10	Bright Angel Creek	5/26/2021	42.07	20.85	3.50	0.95	221	4.17	5.66	0.61	298	1.72
PhC	Phantom Creek	9/11/2021	38.41	28.92	16.22	3.02	249	22.11	9.23	0.74	367	1.83
MS	Mint Spring	9/11/2021	54.75	28.09	11.47	2.39	282	6.25	34.37	0.73	419	0.81
RF	Ribbon Falls	9/11/2021	46.59	28.66	2.77	1.49	278	3.00	2.07	0.75	363	1.60
WC	Wall Creek	9/11/2021	39.89	23.66	2.44	1.33	237	2.94	3.82	0.74	311	0.42
TC	Transept Creek	9/11/2021	42.63	28.70	6.32	3.03	267	4.26	16.52	0.74	369	-0.04
RC	Roaring Creek	9/12/2021	38.97	17.69	1.16	0.87	201	1.98	2.49	1.11	265	0.67
RS	Roaring Springs[d]	nr	34.00	17.00	1.70	0.60	170	5.60	3.90	nr	233	2.56

Method detection limit (mg/L): 0.02

nd = not detected

nr = not recorded

[a] Monroe et al. 2005

[b] Havasupai Gardens is the proposed new name for Indian Gardens. The name change is not formalized at this time.

[c] Two Trees Spring and Pumphouse Spring are synonymous

[d] data from Tobin et al. 2018

[e] total dissolved solids calculated as sum of major cations and anions in mg/L

[f] charge balance error calculated as (Σcations-Σanions)/(Σcations+Σanions) in meq/L

Table 4. Trace Elements, $^{87}Sr/^{86}Sr$ Ratios, and Stable Isotopes (page 1/3)											
Sample ID	Location	Date Sampled	F (mg/L)	Br (mg/L)	Ba (mg/L)	Li (mg/L)	Si (mg/L)	Sr (mg/L)	$^{87}Sr/^{86}Sr$	δD (‰)	$\delta^{18}O$ (‰)
DW	N. Rim-drinking water	1/3/2018	1.38	nd	0.07	nd	1.39	0.02	0.71106	-94.6	-13.5
DW2	N. Rim-drinking water	2/28/2021	0.27	nd	0.06	nd	2.67	nd	nr	-95.4	-13.7
Tu	Tusayan Best Western	2018	1.49	nd	0.00	0.00	0.00	0.00	nr	-86.9	-12.0
Tu	Tusayan Best Western	2/27/2021	0.33	0.56	0.04	nd	4.40	nd	0.70985	-86.0	-11.9
Va	Valle Chevron Station	2018	1.86	0.97	nr	nr	nr	nr	nr	-85.1	-11.5
Va	Valle Chevron Station	2/27/2021	0.78	nd	nd	nd	4.86	0.74	0.70990	-85.9	-11.8
WRP	Water Rec. Plant	1/3/2018	1.41	nd	0.02	nd	1.46	0.04	nr	-92.8	-13.2
WRP	Water Rec. Plant	2/27/2021	n.a.	n.a.	<0.02	nd	2.87	nd	0.71055	-93.9	-13.4
WRP2	Water Rec. Plant	2/27/2021	0.25	n.a.	<0.02	nd	2.74	nd	nr	-93.7	-13.3
WRP	Water Rec. Plant	12/20/2021	nd	nd	0.02	nd	2.44	0.02	nr	-94.0	-13.3
PC1	Pipe Creek	12/18/2021	1.02	0.78	0.06	nd	5.17	0.15	nr	-88.6	-12.1
PC2	Pipe Creek	1/1/2018	1.60	2.92	0.02	0.04	3.91	0.96	0.72816	-82.6	-10.8
PC3	Pipe Creek	2/28/2021	0.51	1.16	nd	nd	4.86	0.85	nr	-84.0	-11.1
PC3	Pipe Creek	5/26/2021	0.50	1.55	0.04	0.37	6.94	1.01	nr	-84.9	-11.0
PC4	Pipe Creek	5/26/2021	0.42	0.86	0.11	0.25	6.36	0.56	nr	-88.6	-12.0
PC5	Pipe Creek	5/24/2017	n.a.	n.a.	nr	nr	nr	nr	nr	-83.6	-11.2
PC6	Pipe Creek	1/1/2018	1.54	2.05	0.20	nd	2.04	0.06	nr	-89.9	-12.5
PC7	Pipe Creek	5/24/2017	n.a.	n.a.	nr	nr	nr	nr	nr	-89.7	-12.4
PC7	Pipe Creek	5/26/2021	0.40	0.55	0.24	0.08	3.91	0.11	nr	-91.8	-12.6
PC8	Pipe Creek	5/26/2021	0.35	0.57	0.23	0.08	3.67	0.12	nr	-91.9	-12.7
PC8	Pipe Creek	1/1/2018	1.49	1.17	0.17	nd	1.93	0.09	0.71714	-92.1	-12.9
PT1	Pipe Seep	12/31/2017	1.38	13.93	0.00	1.03	5.28	4.10	0.73362	-84.3	-10.7
PT2	Pipe Seep at BA Fault	5/26/2021	nd	nd	0.26	0.07	4.05	0.10	nr	-78.2	-8.4
PT3	Fern Seep	1/1/2018	1.51	0.96	0.31	nd	4.11	0.11	nr	-91.3	-12.8
PT4	Pipe Creek Cone	1/1/2018	1.40	nd	nr	nr	nr	nr	nr	-91.4	-12.8
PT5	Pipe Cone Spring at BA Fault	2/28/2021	0.37	0.86	0.23	nd	5.16	0.27	nr	-90.3	-12.6
PT5	Pipe Cone Spring at BA Fault	1/1/2018	1.55	2.13	0.28	nd	4.17	0.25	nr	-90.1	-12.5
PS	Pipe Creek[a]	5/22/2000	0.22	0.00	0.07	0.01	0.00	0.18	nr	-91.9	-12.3
PS	Pipe Creek[a]	12/7/2000	0.00	0.04	0.07	0.01	0.00	0.17	nr	-91.5	-12.4
PS	Pipe Creek[a]	4/8/2001	0.26	0.04	0.06	0.01	0.00	0.16	nr	-90.9	-12.4
HG2	Havasupai Gardens[b]	10/24/2021	0.26	1.04	0.28	0.06	4.60	0.07	nr	-90.5	-12.4
HG	Havasupai Gardens[b]	10/24/2021	0.25	1.07	0.27	0.06	4.60	0.06	nr	-91.2	-12.6
HG	Havasupai Gardens[b]	12/19/2021	0.98	0.63	0.30	nd	4.78	0.08	nr	-90.3	-12.5

Table 4. Trace Elements, $^{87}Sr/^{86}Sr$ Ratios, and Stable Isotopes (page 2/3)											
Sample ID	Location	Date Sampled	F (mg/L)	Br (mg/L)	Ba (mg/L)	Li (mg/L)	Si (mg/L)	Sr (mg/L)	$^{87}Sr/^{86}Sr$	δD (‰)	$\delta^{18}O$ (‰)
HG	Havasupai Gardens[b]	12/31/2017	1.42	1.02	0.29	nd	3.10	0.09	nr	-90.8	-12.5
HG	Havasupai Gardens[b]	2/28/2021	0.31	0.60	0.27	nd	4.37	0.04	0.71122	-91.0	-12.6
GC1	Garden Creek	12/31/2017	1.43	0.98	0.30	nd	3.23	0.09	nr	-90.8	-12.5
GC1	Garden Creek	5/26/2021	0.39	0.62	0.00	0.00	0.00	0.00	nr	-91.8	-12.6
GC2	Garden Creek	5/24/2017	n.a.	n.a.	nr	nr	nr	nr	nr	-90.7	-12.6
GC3	Garden Creek	12/31/2017	1.49	0.98	0.18	nd	2.32	0.05	0.71160	-93.0	-13.1
GC4	Garden Creek	5/26/2021	0.34	0.55	0.31	0.08	4.81	0.11	nr	-92.3	-12.8
GC5	Garden Creek	5/24/2017	nr	nr	nr	nr	nr	nr	nr	-89.8	-12.6
GC5	Garden Creek	1/1/2018	1.41	nd	0.17	nd	2.07	0.05	nr	-92.3	-13.0
GC5	Garden Creek	5/26/2021	0.34	0.55	0.23	0.07	3.84	0.09	nr	-91.6	-12.7
TT	Pumphouse Spring[a]	5/22/2000	0.06	0.00	0.28	0.01	0.00	0.11	nr	-92.6	-12.3
TT	Pumphouse Spring[a]	12/7/2000	0.00	0.03	0.27	0.01	0.00	0.11	nr	-93.1	-12.3
TT	Pumphouse Spring[a]	4/7/2001	0.25	0.03	0.28	0.01	0.00	0.11	nr	-92.8	-12.3
TT2	Two Trees Spring[c]	12/31/2017	1.46	1.08	0.27	nd	3.05	0.09	nr	-90.9	-12.5
TT2	Two Trees Spring[c]	2/28/2021	0.32	0.61	0.24	nd	4.37	0.04	0.71183	-91.0	-12.5
TT2	Two Trees Spring[c]	10/24/2021	0.28	1.14	0.24	0.06	4.56	0.06	nr	-91.2	-12.6
TT2	Two Trees Spring[c]	12/19/2021	0.95	0.64	0.26	nd	4.69	0.08	nr	-90.8	-12.6
TT3	Two Trees Spring[c]	12/19/2021	0.96	0.60	0.27	0.11	4.34	0.09	nr	-91.1	-12.6
PH	Pumphouse	5/24/2017	n.a.	n.a.	nr	nr	nr	nr	nr	-90.9	-12.6
PH	Pumphouse	12/31/2017	1.52	1.14	0.25	nd	3.12	0.08	nr	-90.8	-12.5
KS	Kolb Seep	10/24/2021	0.68	0.84	0.10	0.08	7.43	0.10	nr	-84.3	-11.7
BS	Burro Spring	12/18/2021	1.04	0.70	0.08	nd	5.68	0.17	nr	-89.4	-12.5
CC	Cottonwood Creek[a]	11/29/2000	0.00	0.02	0.24	0.01	0.00	0.12	0.71264	-93.9	-12.7
GMS	Grapevine Main Spring[a]	4/30/2001	0.15	0.02	0.36	0.00	0.00	0.08	0.71140	-92.7	-12.9
HaS	Hawaii Spring[a]	5/25/2000	0.00	0.03	0.11	0.01	0.00	0.23	0.71152	-89.1	-11.9
HtS	Hermit Spring[a]	4/11/2001	0.27	0.03	0.21	0.01	0.00	0.15	0.71009	-88.2	-11.8
HtS	Hermit Spring	5/28/2012	0.53	0.13	0.19	0.00	4.00	0.12	nr	-88.8	-11.9
HC	Horn Creek[a]	5/22/2000	0.26	0.00	0.05	0.02	0.00	0.24	0.70363	-88.8	-11.9
LS	Lonetree Spring[a]	5/1/2001	0.27	0.05	0.04	0.04	0.00	0.33	0.71327	-89.9	-12.0
MiS	Miners Spring[a]	5/24/2000	0.19	0.00	0.13	0.01	0.00	0.17	0.71196	-93.1	-12.3
MoS	Monument Spring[a]	12/5/2000	0.00	0.04	0.28	0.01	0.00	0.13	0.71070	-91.1	-12.2

Table 4. Trace Elements, $^{87}Sr/^{86}Sr$ Ratios, and Stable Isotopes (page 3/3)

Sample ID	Location	Date Sampled	F (mg/L)	Br (mg/L)	Ba (mg/L)	Li (mg/L)	Si (mg/L)	Sr (mg/L)	$^{87}Sr/^{86}Sr$	δD (‰)	$\delta^{18}O$ (‰)
SCS	Salt Creek Spring[a]	5/23/2000	0.22	0.00	0.03	0.02	0.00	0.25	0.71248	-87.3	-11.8
BAC1	Bright Angel Creek	9/11/2021	0.78	0.64	0.12	nd	2.77	nd	nr	-96.2	-13.9
BAC2	Bright Angel Creek	9/11/2021	0.79	nd	0.12	nd	2.37	0.00	nr	-95.8	-13.7
BAC3	Bright Angel Creek	9/11/2021	0.81	0.66	0.13	nd	2.19	nd	nr	-95.7	-13.7
BAC4	Bright Angel Creek	9/11/2021	0.78	0.64	0.13	nd	2.25	nd	nr	-95.2	-13.5
BAC5	Bright Angel Creek	5/24/2017	n.a.	n.a.	0.00	0.00	0.00	0.00	nr	-92.2	-13.1
BAC6	Bright Angel Creek	9/11/2021	0.79	0.64	0.13	nd	2.08	nd	nr	-95.5	-13.7
BAC7	Bright Angel Creek	5/24/2017	0.03	n.a.	0.00	0.00	0.00	0.00	nr	-92.8	-13.2
BAC8	Bright Angel Creek	1/1/2018	1.38	nd	0.11	nd	1.35	0.06	nr	-94.4	-13.4
BAC9	Bright Angel Creek	9/10/2021	0.79	0.66	0.12	nd	2.18	0.02	nr	-93.6	-13.2
BAC10	Bright Angel Creek	5/26/2021	0.31	0.50	0.14	0.08	2.09	0.06	0.71387	-95.5	-13.5
PhC	Phantom Creek	5/24/2017	nr	nr	nr	nr	nr	nr	nr	-91.6	-12.8
PhC	Phantom Creek	9/11/2021	0.79	0.70	0.12	nd	3.84	0.08	nr	-89.6	-12.6
MS	Mint Spring	9/11/2021	0.79	0.65	0.14	nd	5.07	0.13	nr	-94.7	-13.5
RF	Ribbon Falls	9/11/2021	0.79	0.65	0.14	nd	4.63	0.04	nr	-93.0	-13.2
WC	Wall Creek	9/11/2021	0.79	0.65	0.23	nd	4.27	0.03	nr	-94.6	-13.4
TC	Transept Creek	9/11/2021	0.80	0.64	0.13	nd	4.47	0.07	nr	-91.9	-13.0
RC	Roaring Creek	9/12/2021	0.79	0.65	0.10	nd	2.93	nd	nr	-95.3	-13.6
RS	Roaring Springs[d]	nr	nr	nr	nr	nr	nr	nr	nr	-95.0	-13.5
RS	Roaring Springs[d]	9/1/1993	nr	nr	nr	nr	nr	nr	nr	-97.0	-13.5

[a] Monroe et al. 2005

[b] Havasupai Gardens is the proposed new name for Indian Gardens. The name change is not formalized at this time.

[c] Two Trees Spring and Pumphouse Spring are synonymous

[d] data from Ingraham et al. 2001

Table 5. PHREEQC-Calculated Saturation Indices and Dissolved Inorganic Carbon (page 1/2)								
Sample ID	**Location**	**Date Sampled**	**Calcite**	**CO_2**	**Dolomite**	**Gypsum**	**Halite**	**DIC[d]**
DW	N. Rim-drinking water	1/3/2018	-0.1	-2.36	-0.5	-3.3	-9.8	3.33E-03
DW2	N. Rim-drinking water	2/28/2021	-0.4	-1.78	-0.6	-3.5	-10.0	3.30E-03
Tu	Tusayan Best Western	2/27/2021	-0.8	-1.56	-1.1	-3.0	-6.9	5.95E-03
Va	Valle Chevron Station	2/27/2021	-0.4	-1.80	-0.9	-1.5	-7.7	4.57E-03
WRP	Water Rec. Plant	1/3/2018	-1.4	-1.40	-2.8	-2.0	-6.7	4.19E-03
WRP	Water Rec. Plant	2/27/2021	-2.3	-1.63	-4.9	-1.9	-6.7	2.05E-03
WRP2	Water Rec. Plant	2/27/2021	-1.9	-2.03	-4.0	-1.9	-6.7	1.27E-03
WRP	Water Rec. Plant	12/20/2021	-2.0	-1.86	-4.0	-2.2	-6.7	1.48E-03
PC1	Pipe Creek	12/18/2021	-1.3	-0.84	-2.8	-1.9	-8.3	1.47E-02
PC2	Pipe Creek	1/1/2018	0.3	-2.56	0.7	-1.2	-6.0	4.81E-03
PC6	Pipe Creek	1/1/2018	0.0	-2.34	-0.1	-1.7	-8.0	4.36E-03
PC8	Pipe Creek	1/1/2018	-0.5	-1.86	-1.1	-2.4	-8.3	4.76E-03
PT1	Pipe Seep	12/31/2017	0.0	-1.92	-0.2	-0.6	-4.3	5.27E-03
PT3	Fern Seep	1/1/2018	-0.1	-1.89	-0.3	-2.6	-8.5	5.91E-03
PT5	Pipe Cone Spring at BA Fault	1/1/2018	0.1	-2.41	0.2	-1.9	-6.7	4.48E-03
PS	Pipe Creek[a]	5/22/2000	0.4	-2.33	1.0	-1.9	-8.2	5.13E-03
PS	Pipe Creek[a]	12/7/2000	-0.1	-2.00	-0.2	-2.0	-8.3	5.28E-03
PS	Pipe Creek[a]	4/8/2001	-0.2	-1.94	-0.5	-1.9	-8.4	4.89E-03
HG2	Havasupai Gardens[b]	10/24/2021	0.4	-2.48	0.9	-2.6	-8.8	4.68E-03
HG	Havasupai Gardens[b]	10/24/2021	-0.4	-1.71	-0.7	-2.6	-8.8	4.95E-03
HG	Havasupai Gardens[b]	12/19/2021	-0.4	-1.72	-0.8	-2.6	-8.8	4.84E-03
HG	Havasupai Gardens[b]	12/31/2017	-0.7	-1.34	-1.4	-2.6	-8.7	5.97E-03
HG	Havasupai Gardens[b]	2/28/2021	-0.6	-1.65	-1.0	-2.6	-8.8	4.96E-03
GC1	Garden Creek	12/31/2017	0.0	-2.13	0.0	-2.5	-8.7	4.56E-03
GC3	Garden Creek	12/31/2017	0.0	-2.30	0.0	-2.8	-9.1	4.10E-03
GC5	Garden Creek	1/1/2018	0.3	-2.68	0.3	-2.8	-9.1	3.99E-03
TT	Pumphouse Spring[a]	5/22/2000	0.7	-2.88	1.6	-2.6	-8.7	4.24E-03
TT	Pumphouse Spring[a]	12/7/2000	0.6	-2.98	1.3	-2.6	-8.7	3.97E-03
TT	Pumphouse Spring[a]	4/7/2001	0.4	-2.70	0.9	-2.6	-8.8	4.16E-03
TT2	Two Trees Spring[c]	12/31/2017	-0.1	-2.13	-0.2	-2.5	-8.6	4.25E-03
TT2	Two Trees Spring[c]	2/28/2021	-0.6	-1.76	-1.2	-2.6	-8.7	4.74E-03
TT2	Two Trees Spring[c]	10/24/2021	-0.5	-1.77	-0.8	-2.6	-8.7	4.63E-03

Sample ID	Location	Date Sampled	Calcite	CO_2	Dolomite	Gypsum	Halite	DIC[d]
TT2	Two Trees Spring[c]	12/19/2021	0.2	-2.60	0.3	-2.6	-8.7	3.93E-03
TT3	Two Trees Spring[c]	12/19/2021	-0.1	-2.14	-0.2	-2.7	-8.8	4.07E-03
PH	Pumphouse	12/31/2017	-0.1	-2.09	-0.1	-2.6	-8.7	4.27E-03
BS	Burro Spring	12/18/2021	-0.2	-1.98	-0.5	-2.0	-8.1	5.20E-03
CC	Cottonwood Creek[a]	11/29/2000	0.2	-2.54	0.5	-2.5	-8.8	4.31E-03
HaS	Hawaii Spring[a]	5/25/2000	0.6	-2.79	1.4	-2.2	-8.3	4.36E-03
HtS	Hermit Spring[a]	4/11/2001	0.4	-2.61	0.9	-2.6	-8.6	4.28E-03
MiS	Miners Spring[a]	5/24/2000	0.6	-3.70	1.6	-2.5	-8.2	2.23E-03
MoS	Monument Spring[a]	12/5/2000	0.0	-2.22	0.1	-2.5	-7.7	4.27E-03
BAC2	Bright Angel Creek	9/11/2021	1.0	-3.54	1.9	-3.1	-9.8	2.71E-03
BAC3	Bright Angel Creek	9/11/2021	-0.3	-2.03	-0.9	-2.8	-8.7	4.26E-03
BAC4	Bright Angel Creek	9/11/2021	0.3	-2.59	0.4	-3.0	-9.4	3.71E-03
BAC5	Bright Angel Creek	5/24/2017	1.0	-3.44	2.1	-3.1	-9.3	3.08E-03
BAC6	Bright Angel Creek	9/11/2021	1.0	-3.33	1.9	-3.1	-9.6	3.57E-03
BAC7	Bright Angel Creek	5/24/2017	1.1	-3.47	2.0	-3.2	-10.0	3.44E-03
BAC8	Bright Angel Creek	1/1/2018	1.2	-3.61	2.3	-3.2	-10.1	3.31E-03
BAC9	Bright Angel Creek	9/10/2021	1.1	-3.52	2.1	-3.3	-10.1	3.32E-03
BAC10	Bright Angel Creek	5/26/2021	1.0	-3.54	1.9	-3.4	-10.2	3.12E-03
PhC	Phantom Creek	9/11/2021	1.0	-3.27	2.3	-2.9	-8.0	3.91E-03
MS	Mint Spring	9/11/2021	0.5	-2.56	1.1	-2.2	-8.7	4.69E-03
RF	Ribbon Falls	9/11/2021	1.0	-3.07	2.0	-3.4	-9.6	4.45E-03
WC	Wall Creek	9/11/2021	0.9	-3.12	1.8	-3.2	-9.7	3.78E-03
TC	Transept Creek	9/11/2021	0.8	-2.91	1.8	-2.6	-9.1	4.31E-03
RC	Roaring Creek	9/12/2021	0.8	-3.34	1.6	-3.4	-10.2	3.21E-03

Table 5. PHREEQC-Calculated Saturation Indices and Dissolved Inorganic Carbon (page 2/2)

[a] Monroe et al. 2005

[b] Havasupai Gardens is the proposed new name for Indian Gardens. The name change is not formalized at this time.

[c] Two Trees Spring and Pumphouse Spring are synonymous

[d] dissolved inorganic carbon computed in PHREEQ-C as the sum of all inorganic carbon species

Table 6. Oxygen and Hydrogen Stable Isotopes and Chloride (page 1/11)						
Sample ID	**Location**	**Data Source**	**Date Sampled**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Cl (mg/L)**
DW	N. Rim-drinking water	this study	1/3/2018	-13.5	-94.6	4.3
DW2	N. Rim-drinking water	this study	2/28/2021	-13.7	-95.4	3.2
Tu	Tusayan Best Western	this study	7/10/1905	-12.0	-86.9	24.1
Tu	Tusayan Best Western	this study	2/27/2021	-11.9	-86.0	49.9
Tu	Tusayan Well	Zukosky 1995	12/1/1992	-11.7	-89.0	nr
Tu	Tusayan Well	Zukosky 1995	1/1/1993	-11.9	-89.0	nr
Tu	Tusayan Well	Zukosky 1995	3/1/1993	-12.1	-89.0	nr
Tu	Tusayan Well	Zukosky 1995	4/1/1993	-12.0	-89.0	nr
Tu	Tusayan Well	Zukosky 1995	5/1/1993	-11.9	-90.0	nr
Tu	Tusayan Well	Zukosky 1995	9/1/1993	-12.0	-85.0	nr
Va	Valle, average value	calculated	nr	-11.6	-85.5	nr
Va	Valle Chevron Station	this study	2018	-11.5	-85.1	38.7
Va	Valle Chevron Station	this study	2/27/2021	-11.8	-85.9	37.7
WRP	Water Rec. Plant	this study	1/3/2018	-13.2	-92.8	92.1
WRP	Water Rec. Plant	this study	2/27/2021	-13.4	-93.9	100.1
WRP2	Water Rec. Plant	this study	2/27/2021	-13.3	-93.7	98.5
WRP	Water Rec. Plant	this study	12/20/2021	-13.3	-94.0	95.1
PC1	Pipe Creek	this study	12/18/2021	-12.1	-88.6	17.4
PC2	Pipe Creek	this study	1/1/2018	-10.8	-82.6	211.5
PC3	Pipe Creek	this study	2/28/2021	-11.1	-84.0	253.0
PC3	Pipe Creek	this study	5/26/2021	-11.0	-84.9	240.2
PC4	Pipe Creek	this study	5/26/2021	-12.0	-88.6	122.3
PC5	Pipe Creek	this study	5/24/2017	-11.2	-83.6	233.4
PC6	Pipe Creek	this study	1/1/2018	-12.5	-89.9	87.6
PC7	Pipe Creek	this study	5/24/2017	-12.4	-89.7	25.5
PC7	Pipe Creek	this study	5/26/2021	-12.6	-91.8	12.9
PC8	Pipe Creek	this study	5/26/2021	-12.7	-91.9	16.1
PC8	Pipe Creek	this study	1/1/2018	-12.9	-92.1	17.3
PT1	Pipe Seep	this study	12/31/2017	-10.7	-84.3	2263.6
PT2	Pipe Seep at BA Fault	this study	5/26/2021	-8.4	-78.2	nr

Table 6. Oxygen and Hydrogen Stable Isotopes and Chloride (page 2/11)						
Sample ID	**Location**	**Data Source**	**Date Sampled**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Cl (mg/L)**
PT3	Trough Seep	this study	1/1/2018	-12.8	-91.3	13.3
PT4	Fern Seep	this study	1/1/2018	-12.8	-91.4	4.4
PT5	Pipe Cone Spring at BA Fault	this study	2/28/2021	-12.6	-90.3	123.2
PT5	Pipe Cone Spring at BA Fault	this study	1/1/2018	-12.5	-90.1	119.9
PS	Pipe Creek	Monroe et al. 2005	5/22/2000	-12.3	-91.9	19.0
PS	Pipe Creek	Monroe et al. 2005	12/7/2000	-12.4	-91.5	17.1
PS	Pipe Creek	Monroe et al. 2005	4/8/2001	-12.4	-90.9	14.3
PS	Pipe Creek Spring	USGS 2019	nr	-12.4	-90.8	nr
HG2	Havasupai Gardens[b]	this study	10/24/2021	-12.4	-90.5	10.7
HG	Havasupai Gardens[b]	this study	10/24/2021	-12.6	-91.2	10.2
HG	Havasupai Gardens[b]	this study	12/19/2021	-12.5	-90.3	10.1
HG	Havasupai Gardens[b]	this study	12/31/2017	-12.5	-90.8	12.4
HG	Havasupai Gardens[b]	this study	2/28/2021	-12.6	-91.0	10.5
HGU	Indian Garden Spring	Ingraham et al. 2001	9/1/1992	-12.5	-93.0	nr
HGU	Indian Garden Spring	Ingraham et al. 2001	12/1/1992	-12.2	-93.0	nr
HGU	Indian Garden Spring	Ingraham et al. 2001	1/1/1993	-12.4	-92.0	nr
HGU	Indian Garden Spring	Ingraham et al. 2001	3/1/1993	-12.4	-92.0	nr
HGU	Indian Garden Spring	Ingraham et al. 2001	4/1/1993	-12.3	-92.0	nr
HGU	Indian Garden Spring	Ingraham et al. 2001	5/1/1993	-12.5	-93.0	nr
HGU	Indian Garden Spring	Ingraham et al. 2001	6/1/1993	-12.6	-93.0	nr
HGU	Indian Garden Spring	Ingraham et al. 2001	7/1/1993	-12.6	-93.0	nr
HGU	Indian Garden Spring	Ingraham et al. 2001	8/1/1993	-12.4	-93.0	nr
HGU	Indian Garden Spring	Ingraham et al. 2001	10/1/1993	-12.5	-92.0	nr
HGU	Indian Garden Spring Avg, 1993	Ingraham et al 2001	1993	-12.4	-92.6	12.8
HGU	Indian Garden Spring Max, 1993	Ingraham et al 2001	1993	-12.2	-92.0	15.0
HGU	Indian Garden Spring Min, 1993	Ingraham et al 2001	1993	-12.6	-93.0	11.0
HGU	Indian Garden Spring	USGS 2019	9/27/2016	-12.4	-92.2	nr
GC1	Garden Creek	this study	12/31/2017	-12.5	-90.8	12.3
GC1	Garden Creek	this study	5/26/2021	-12.6	-91.8	9.9

Table 6. Oxygen and Hydrogen Stable Isotopes and Chloride (page 3/11)						
Sample ID	**Location**	**Data Source**	**Date Sampled**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Cl (mg/L)**
GC2	Garden Creek	this study	5/24/2017	-12.6	-90.7	10.3
GC3	Garden Creek	this study	12/31/2017	-13.1	-93.0	8.3
GC4	Garden Creek	this study	5/26/2021	-12.8	-92.3	8.6
GC5	Garden Creek	this study	5/24/2017	-12.6	-89.8	10.0
GC5	Garden Creek	this study	1/1/2018	-13.0	-92.3	8.1
GC5	Garden Creek	this study	5/26/2021	-12.7	-91.6	15.4
TT	Pumphouse Spring	Monroe et al. 2005	5/22/2000	-12.3	-92.6	11.0
TT	Pumphouse Spring	Monroe et al. 2005	12/7/2000	-12.3	-93.1	11.6
TT	Pumphouse Spring	Monroe et al. 2005	4/7/2001	-12.3	-92.8	10.3
TT	Pumphouse Spring	Bills et al. 2007	11/19/2001	-12.4	-90.3	nr
TT	Pumphouse Spring	Bills et al. 2007	6/12/2002	-12.3	-91.3	nr
TT	Pumphouse Spring	Bills et al. 2007	11/23/2002	-12.3	-91.7	nr
TT2	Two Trees Spring[c]	this study	2/28/2021	-12.5	-91.0	11.9
TT2	Two Trees Spring[c]	this study	10/24/2021	-12.6	-91.2	11.7
TT2	Two Trees Spring[c]	this study	12/19/2021	-12.6	-90.8	11.3
TT3	Two Trees Spring[c]	Monroe et al. 2005	12/19/2021	-12.6	-91.1	11.3
PH	Pumphouse Gage	Monroe et al. 2005	12/7/2000	-12.3	-93.1	11.8
PH	Pumphouse	this study	5/24/2017	-12.6	-90.9	11.6
PH	Pumphouse	this study	12/31/2017	-12.5	-90.8	13.9
KS	Kolb Seep	this study	10/24/2021	-11.7	-84.3	90.9
BAC1	Bright Angel Creek	this study	9/11/2021	-13.9	-96.2	2.0
BAC2	Bright Angel Creek	this study	9/11/2021	-13.7	-95.8	2.0
BAC3	Bright Angel Creek	this study	9/11/2021	-13.7	-95.7	2.1
BAC4	Bright Angel Creek	this study	9/11/2021	-13.5	-95.2	2.2
BAC5	Bright Angel Creek	this study	5/24/2017	-13.1	-92.2	0.3
BAC6	Bright Angel Creek	this study	9/11/2021	-13.7	-95.5	3.1
BAC7	Bright Angel Creek	this study	5/24/2017	-13.2	-92.8	2.6
BAC8	Bright Angel Creek	this study	1/1/2018	-13.4	-94.4	5.7
BAC9	Bright Angel Creek	this study	9/10/2021	-13.2	-93.6	4.6

Table 6. Oxygen and Hydrogen Stable Isotopes and Chloride (page 4/11)						
Sample ID	**Location**	**Data Source**	**Date Sampled**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Cl (mg/L)**
BAC10	Bright Angel Creek	this study	5/26/2021	-13.5	-95.5	4.2
PhC	Phantom Creek	this study	5/24/2017	-12.8	-91.6	10.5
PhC	Phantom Creek	this study	9/11/2021	-12.6	-89.6	22.1
MS	Mint Spring	this study	9/11/2021	-13.5	-94.7	6.2
RF	Ribbon Falls	this study	9/11/2021	-13.2	-93.0	3.0
WC	Wall Creek	this study	9/11/2021	-13.4	-94.6	2.9
TC	Transept Creek	this study	9/11/2021	-13.0	-91.9	4.3
RC	Roaring Creek	this study	9/12/2021	-13.6	-95.3	2.0
RS	Roaring Springs, avg baseflow	Brown 2011	2003-2008	-13.8	-96.3	nr
RS	Roaring Spring (North Rim)	Ingraham et al. 2001	4/1/1993	-13.5	-95.0	nr
RS	Roaring Spring (North Rim)	Ingraham et al. 2001	9/1/1993	-13.5	-97.0	nr
RS	Roaring Springs	Tobin et al. 2018	9/14/1993	-13.4	-99.0	nr
RS	Roaring Springs	Tobin et al. 2018	10/4/2007	-13.8	-95.9	nr
RS	Roaring Springs	Tobin et al. 2018	11/15/2007	-13.8	-95.8	nr
RS	Roaring Springs Source1	Brown 2011	3/7/2003	-13.50	-90.18	nr
RS	Roaring Springs Source1	Brown 2011	4/11/2003	-12.77	-84.83	nr
RS	Roaring Springs Source1	Brown 2011	5/17/2003	-12.76	-88.43	nr
RS	Roaring Springs Source1	Brown 2011	6/14/2003	-13.18	-88.82	nr
RS	Roaring Springs Source1	Brown 2011	7/13/2003	-13.40	-93.28	nr
RS	Roaring Springs Source1	Brown 2011	9/3/2003	-13.65	-91.84	nr
RS	Roaring Springs Source1	Brown 2011	10/10/2003	-13.54	-94.66	nr
RS	Roaring Springs Source1	Brown 2011	4/?/2005	-13.25	-91.75	nr
RS	Roaring Springs Cave Pipe	Brown 2011	8/7/2007	-13.39	-98.60	nr
RS	Roaring Springs Cave Pipe	Brown 2011	8/8/2007	-13.41	-97.02	nr
RS	Roaring Springs Cave Pipe	Brown 2011	8/24/2007	-13.25	-99.49	nr
RS	Roaring Springs Cave Pipe	Brown 2011	9/14/2007	-13.35	-99.00	0.9
RS	Roaring Springs Cave Pipe	Brown 2011	10/4/2007	-13.80	-95.87	0.9
RS	Roaring Springs Cave Pipe	Brown 2011	11/15/2007	-13.77	-95.77	0.9
RS	Roaring Springs Cave Pipe	Brown 2011	12/17/2007	-13.82	-95.84	1.0
RS	Roaring Springs Cave Pipe	Brown 2011	1/24/2008	-13.88	-95.91	nr

Table 6. Oxygen and Hydrogen Stable Isotopes and Chloride (page 5/11)						
Sample ID	**Location**	**Data Source**	**Date Sampled**	**δ^{18}O (‰)**	**δD (‰)**	**Cl (mg/L)**
RS	Roaring Springs Cave Pipe	Brown 2011	1/24/2008	-13.69	-95.82	nr
RS	Roaring Springs Cave Pipe	Brown 2011	3/17/2008	-13.68	-97.42	nr
RS	Roaring Springs Cave Pipe	Brown 2011	3/17/2008	-13.80	-97.42	nr
RS	Roaring Springs Cave Pipe (20:00)	Brown 2011	4/26/2008	-13.11	-91.70	1.0
RS	Roaring Springs Cave Pipe (0:00)	Brown 2011	4/27/2008	-12.66	-91.01	1.0
RS	Roaring Springs Cave Pipe (4:00)	Brown 2011	4/27/2008	-12.82	-91.62	1.0
RS	Roaring Springs Cave Pipe (8:00)	Brown 2011	4/27/2008	-12.87	-91.45	nr
RS	Roaring Springs Cave Pipe (12:00)	Brown 2011	4/27/2008	-12.98	-92.58	nr
RS	Roaring Springs Cave Pipe (16:00)	Brown 2011	4/27/2008	-13.41	-94.13	1.4
RS	Roaring Springs Cave Pipe (20:00)	Brown 2011	4/27/2008	-13.30	-93.76	1.0
RS	Roaring Springs Cave Pipe (0:00)	Brown 2011	4/28/2008	-13.41	-93.99	1.0
RS	Roaring Springs Cave Pipe (4:00)	Brown 2011	4/28/2008	-13.48	-94.77	0.9
RS	Roaring Springs Cave Pipe	Brown 2011	7/10/2008	-13.2	-95.3	3.2
RS	Roaring Springs Cave Pipe	Brown 2011	8/14/2008	-12.9	-91.5	3.2
RS	Roaring Springs Cave Pipe - NPS	Schindel 2015	10/15/2008	-13.6	-97.3	nr
RS	Roaring Springs Cave Pipe - NPS	Schindel 2015	6/5/2009	-14.3	-97.2	nr
RS	Roaring Springs Cave Pipe - NPS	Schindel 2015	7/16/2009	-14.3	-98.1	nr
RS	Roaring Springs Cave Pipe - NPS	Schindel 2015	11/9/2009	-13.6	-95.4	nr
RS	Roaring Springs Cave - NPS	Schindel 2015	4/6/2013	-13.6	-95.4	nr
RS	Roaring Springs Cave	Schindel 2015	5/12/2014	-13.5	-96.5	nr
RS	Roaring Springs Cave	Schindel 2015	7/16/2014	-13.5	-96.8	nr
RS	Roaring Spring Cave - Deep	NPS, unpublished	2/10/2019	-13.6	-94.0	nr
RS	Roaring Deep	NPS, unpublished	7/16/2019	-13.3	-95.3	nr
RS	Roaring Deep	NPS, unpublished	9/14/2019	-13.9	-94.5	nr
RS	Roaring Spring Cave - Deep	NPS, unpublished	1/15/2020	-12.8	-95.5	nr
RS	Roaring Spring Cave - Deep	NPS, unpublished	3/14/2020	-12.5	-92.3	nr
RS	Roaring Springs Cave Shallow	NPS, unpublished	9/13/2020	-13.3	-94.8	nr
RS	Roaring Springs Cave Deep	NPS, unpublished	12/4/2020	-13.5	-96.4	nr
RS	Roaring Springs Cave Deep	NPS, unpublished	4/5/2021	-13.7	-95.6	nr
AS	Angel Springs	Brown 2011	9/13/2007	-13.6	-100.5	nr

Table 6. Oxygen and Hydrogen Stable Isotopes and Chloride (page 6/11)						
Sample ID	**Location**	**Data Source**	**Date Sampled**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Cl (mg/L)**
AS	Angel Springs	Brown 2011	6/2/2008	-13.3	-94.8	nr
AS	Angel Springs	Brown 2011	6/2/2008	-13.5	-94.3	nr
AS	Angel Spring - NPS	Schindel 2015	7/10/2008	-13.9	-96.4	nr
AS	Angel Spring - NPS	Schindel 2015	6/3/2009	-14.1	-97.8	nr
AS	Angel Spring - NPS	Schindel 2015	4/6/2013	-13.9	-97.3	nr
BoE	Boucher East Spring	Monroe et al. 2005	5/26/2000	-11.4	-84.1	nr
BoE	Boucher East Spring	Monroe et al. 2005	4/12/2001	-11.2	-86.6	nr
BoE	Boucher East Spring	USGS 2019	4/8/2017	-11.9	-89.8	nr
Bo	Boucher Spring	Bills et al. 2007	4/25/2002	-11.5	-84.2	nr
Bo	Boucher Spring	Bills et al. 2007	10/21/2002	-11.3	-84.7	nr
BS	LC21 Burro	this study	12/18/2021	-12.5	-89.4	19.7
BS	Burro Spring	Monroe et al. 2005	5/22/2000	-12.4	-91.0	18.6
BS	Burro Spring	Monroe et al. 2005	12/7/2000	-12.3	-92.9	19.9
BS	Burro Spring	Monroe et al. 2005	4/8/2001	-12.5	-91.1	18.4
WRP	Clearwell Overflow	Ingraham et al. 2001	9/1/1992	-12.3	-92.0	nr
WRP	Clearwell Overflow	Ingraham et al. 2001	1/1/1993	-13.2	-96.0	nr
WRP	Clearwell Overflow	Ingraham et al. 2001	2/1/1993	-13.2	-95.0	nr
WRP	Clearwell Overflow	Ingraham et al. 2001	3/1/1993	-13.0	-94.0	nr
WRP	Clearwell Overflow	Ingraham et al. 2001	4/1/1993	-13.0	-93.0	nr
WRP	Clearwell Overflow	Ingraham et al. 2001	8/1/1993	-12.8	-92.0	nr
WRP	Clearwell Overflow	Ingraham et al. 2001	9/1/1993	-12.8	-92.0	nr
WRP	Clearwell Overflow Avg, 1993	Ingraham et al 2001	1993	-12.9	-93.4	125.6
WRP	Clearwell Overflow Max, 1993	Ingraham et al 2001	1993	-12.3	-92.0	180.3
WRP	Clearwell Overflow Min, 1993	Ingraham et al 2001	1993	-13.2	-96.0	77.9
CMO	Canyon Mine Observation Well	USGS 2019	7/20/2017	-10.9	-83.0	nr
CMO	Canyon Mine Observation Well	USGS 2019	11/21/2017	-11.1	-83.2	nr
CMO	Canyon Mine Observation Well	USGS 2019	1/31/2018	-10.9	-82.3	nr
CMO	Canyon Mine Observation Well	USGS 2019	5/9/2019	-11.1	-83.1	nr
CM	Canyon Mine Well	Zukosky 1995	5/1/1993	-12.3	-90.0	nr
CM	Canyon Mine Well	Bills et al. 2007	5/20/2003	-12.2	-89.5	nr

Table 6. Oxygen and Hydrogen Stable Isotopes and Chloride (page 7/11)						
Sample ID	**Location**	**Data Source**	**Date Sampled**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Cl (mg/L)**
CM	Canyon Mine Well	USGS 2019	9/18/2009	-12.1	-89.2	nr
CM	Canyon Mine Well	USGS 2019	6/26/2013	-12.1	-89.7	nr
CM	Canyon Mine Well	USGS 2019	6/28/2016	-12.2	-89.0	nr
CM	Canyon Mine Well	USGS 2019	9/14/2017	-12.1	-88.5	nr
CC	Cottonwood Creek No. 1	Monroe et al. 2005	5/25/2000	-12.3	-91.6	15.6
CC	Cottonwood Creek No. 1	Bills et al. 2007	10/7/2002	-12.2	-90.0	nr
CC	Cottonwood Creek No. 2	Monroe et al. 2005	11/29/2000	-12.7	-93.9	9.5
CC	Cottonwood Creek No. 2	Monroe et al. 2005	4/9/2001	-12.8	-93.8	9.4
CC	Cottonwood Creek No. 2	Bills et al. 2007	3/7/2002	-12.8	-93.8	nr
CC	Cottonwood Creek No. 2	Bills et al. 2007	6/5/2002	-12.7	-92.7	nr
CC	Cottonwood Creek No. 2	Bills et al. 2007	10/8/2002	-12.8	-94.6	nr
CC	Cottonwood Creek No. 3	Monroe et al. 2005	4/9/2001	-12.8	-93.8	nr
DrS	Dripping Spring	Ingraham et al. 2001	10/1/1992	-12.4	-90.0	nr
DrS	Dripping Spring	Ingraham et al. 2001	2/1/1993	-12.5	-90.0	nr
DrS	Dripping Spring	Ingraham et al. 2001	4/1/1993	-12.0	-89.0	nr
DrS	Dripping Spring	Ingraham et al. 2001	9/1/1993	-12.0	-90.0	nr
ES	Emmett Spring	Brown, 2011	9/13/2007	-13.3	-99.5	nr
ES	Emmett Spring	Brown, 2011	11/15/2007	-14.0	-97.5	nr
ES	Emmett Spring	Brown, 2011	6/1/2008	-13.0	-93.8	nr
ES	Emmett Spring	Brown, 2011	6/1/2008	-13.4	-94.0	nr
ES	Emmett Spr. Pool below falls	NPS, unpublished	9/15/2019	-13.4	-94.40	nr
ES	Emmett Spring	NPS, unpublished	7/16/2019	-13.0	-94.51	nr
ES	Emmett Spring	NPS, unpublished	9/12/2020	-13.2	-94.65	nr
ES	Emmett Spring	NPS, unpublished	12/3/2020	-13.6	-96.01	nr
ES	Emmett Spring	NPS, unpublished	4/4/2021	-13.9	-96.56	nr
Fe	Fern Spring	Bills et al. 2007	8/24/1994	-11.7	-85.4	nr
Fe	Fern Spring	USGS, 2019	10/12/2016	-11.7	-85.2	nr
FC	Forster Canyon Spring	Bills et al. 2007	1/20/2002	-12.3	-93.0	nr
FC	Forster Canyon Spring	Bills et al. 2007	5/3/2002	-12.4	-92.7	nr
FC	Forster Canyon Spring	Bills et al. 2007	11/2/2002	-12.3	-92.8	nr

Table 6. Oxygen and Hydrogen Stable Isotopes and Chloride (page 8/11)						
Sample ID	**Location**	**Data Source**	**Date Sampled**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Cl (mg/L)**
Fo	Fossil Spring	Bills et al. 2007	5/18/2002	-11.0	-80.8	40.0
Fo	Fossil Spring	Bills et al. 2007	11/2/2002	-10.9	-80.5	35.0
GC1	GC-1 Well	Bills et al. 2007	2/16/2002	-11.3	-81.3	nr
GES	Grapevine East Spring	Monroe et al. 2005	5/25/2000	-9.1	-73.6	25.5
GES	Grapevine East Spring	Monroe et al. 2005	12/12/2000	-8.9	-74.8	nr
GES	Grapevine East Spring	Monroe et al. 2005	4/9/2001	-8.5	-71.0	34.7
GES	Grapevine East Spring	Bills et al. 2007	11/14/2001	-9.6	-74.9	nr
GMS	Grapevine Main Spring	Monroe et al. 2005	4/10/2001	-12.9	-94.6	5.6
GMS	Grapevine Main Spring	Monroe et al. 2005	4/30/2001	-12.9	-92.7	5.7
GMS	Grapevine Main Spring	Bills et al. 2007	11/15/2001	-12.9	-92.7	nr
GMS	Grapevine Main Spring	USGS, 2019	5/19/2018	-12.9	-93.7	nr
HavS	Havasu Spring	Bills et al. 2007	8/24/1994	-11.8	-86.3	nr
HavS	Havasu Spring	USGS, 2019	10/11/2016	-11.8	-86.2	nr
HavW	Havasupai Well	Bills et al. 2007	8/23/1994	-11.6	-85.0	nr
HavW	Havasupai Well	USGS, 2019	10/12/2016	-11.8	-85.9	nr
HaS	Hawaii Spring	Ingraham et al. 2001	9/1/1992	-12.0	-88.0	nr
HaS	Hawaii Spring	Ingraham et al. 2001	4/1/1993	-11.8	-88.0	nr
HaS	Hawaii Spring	Ingraham et al. 2001	9/1/1993	-12.1	-90.0	nr
HaS	Hawaii Spring	Monroe et al. 2005	5/25/2000	-11.9	-89.1	13.0
HaS	Hawaii Spring	Monroe et al. 2005	12/4/2000	-11.9	-88.3	13.8
HaS	Hawaii Spring	Monroe et al. 2005	4/11/2001	-11.9	-88.9	12.8
HS1	Hermit Spring	Ingraham et al. 2001	2/1/1993	-11.9	-87.0	nr
HS1	Hermit Spring	Ingraham et al. 2001	4/1/1993	-12.0	-89.0	nr
HS1	Hermit Spring	Ingraham et al. 2001	7/1/1993	-11.8	-90.0	nr
HS1	Hermit Spring	Ingraham et al. 2001	9/1/1993	-11.7	-89.0	nr
HS1	Hermit Spring	Monroe et al. 2005	12/4/2000	-12.0	-89.7	10.6
HS1	Hermit Spring	Monroe et al. 2005	4/11/2001	-11.8	-88.2	9.4
HS1	Hermit Spring	Bills et al. 2007	11/19/2001	-12.0	-88.8	nr
HS1	Hermit Spring	Bills et al. 2007	11/21/2002	-12.0	-89.1	nr
HtS	LC 12 GC 95 HER-1	this study	5/28/2012	-11.9	-88.8	12.1

Table 6. Oxygen and Hydrogen Stable Isotopes and Chloride (page 9/11)						
Sample ID	**Location**	**Data Source**	**Date Sampled**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Cl (mg/L)**
HS1	Hermit Spring	USGS 2019	4/9/2017	-11.9	-89.5	nr
HC	Horn Spring	Ingraham et al. 2001	4/1/1993	-11.6	-90.0	nr
HC	Horn Spring	Ingraham et al. 2001	6/1/1993	-12.2	-91.0	nr
HC	Horn Spring	Ingraham et al. 2001	9/1/1993	-11.8	-90.0	nr
HC	Horn Creek	Monroe et al. 2005	5/22/2000	-11.9	-88.8	34.7
HC	Horn Creek	Monroe et al. 2005	12/6/2000	-11.7	-89.3	30.8
HC	Horn Creek	Monroe et al. 2005	4/7/2001	-11.8	-88.9	27.5
HC	Horn Creek Spring	Bills et al. 2007	11/22/2002	-12.0	-90.0	nr
HC	Horn Creek Spring	USGS 2019	9/27/2016	-11.7	-87.8	nr
JT	JT Spring	Monroe et al. 2005	4/8/2001	-9.4	-73.1	nr
JT	JT Spring	Monroe et al. 2005	5/11/2001	-12.2	-91.4	nr
LS	Lonetree Spring	Monroe et al. 2005	4/11/2001	-11.9	-89.1	19.5
LS	Lonetree Spring	Monroe et al. 2005	5/1/2001	-12.0	-89.9	19.7
MaS	Matkatamiba Spring	Bills et al. 2007	1/21/2002	-11.7	-87.8	nr
MaS	Matkatamiba Spring	Bills et al. 2007	4/29/2002	-11.7	-87.5	nr
MaS	Matkatamiba Spring	Bills et al. 2007	5/5/2002	-11.7	-87.8	nr
MaS	Matkatamiba Spring	Bills et al. 2007	11/4/2002	-11.7	-89.0	nr
MiS	Miners Spring	Monroe et al. 2005	5/24/2000	-12.3	-93.1	19.1
MiS	Miners Spring	Monroe et al. 2005	11/28/2000	-12.2	-90.7	19.3
MiS	Miners Spring	Monroe et al. 2005	4/7/2001	-12.1	-92.3	17.2
MiS	Miners Spring	Bills et al. 2007	6/6/2002	-12.1	-92.5	nr
MCS	Mohawk Canyon Spring	Bills et al. 2007	9/18/2001	-11.2	-83.7	nr
MCS	Mohawk Canyon Spring	Bills et al. 2007	5/19/2002	-11.2	-83.7	nr
MoS	Monument Spring	Ingraham et al. 2001	9/1/1992	-12.0	-89.0	nr
MoS	Monument Spring	Ingraham et al. 2001	12/1/1992	-11.7	-88.0	nr
MoS	Monument Spring	Ingraham et al. 2001	4/1/1993	-11.5	-87.0	nr
MoS	Monument Spring	Ingraham et al. 2001	7/1/1993	-12.0	-89.0	nr
MoS	Monument Spring	Ingraham et al. 2001	9/1/1993	-11.9	-89.0	nr
MoS	Monument Spring	Monroe et al. 2005	12/5/2000	-12.2	-91.1	43.4
MoS	Monument Spring	Monroe et al. 2005	4/9/2001	-12.2	-91.2	39.6

Table 6. Oxygen and Hydrogen Stable Isotopes and Chloride (page 10/11)						
Sample ID	**Location**	**Data Source**	**Date Sampled**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Cl (mg/L)**
MoS	Monument Spring	Bills et al. 2007	11/19/2001	-12.2	-90.2	nr
MoS	Monument Spring	Bills et al. 2007	5/2/2002	-12.2	-90.7	nr
MoS	Monument Spring	Bills et al. 2007	5/16/2002	-12.2	-89.7	nr
MoS	Monument Spring	Bills et al. 2007	11/21/2002	-12.2	-90.6	nr
NC	National Canyon Spring	Bills et al. 2007	5/6/2002	-11.8	-89.5	nr
NC	National Canyon Spring	Bills et al. 2007	11/6/2002	-11.9	-90.4	nr
NC	National Canyon Spring	USGS 2019	2/27/2018	-11.3	-85.5	nr
WuHQ	NPS Wupatki HQ Well	Bills et al. 2007	6/26/1996	-10.2	-73.5	nr
WuHQ	NPS Wupatki HQ Well	Bills et al. 2007	7/9/1996	-10.2	-75.2	nr
PKW	Patch Karr Well	Bills et al. 2007	4/13/2004	-11.6	-86.7	nr
RCS	Red Canyon Spring	Monroe et al. 2005	9/26/2001	-12.7	-94.2	nr
RCS	Red Canyon Spring	Bills et al. 2007	6/3/2002	-12.7	-93.9	nr
RAS	Royal Arch Spring	Bills et al. 2007	3/23/2002	-11.3	-83.0	nr
RAS	Royal Arch Spring	USGS 2019	5/24/2018	-11.4	-84.5	nr
Ru	Ruby Spring	Bills et al. 2007	4/21/2002	-10.8	-81.4	nr
Ru	Ruby Spring	Bills et al. 2007	10/24/2002	-11.2	-81.8	nr
SCS	Salt Creek Spring	Zukosky 1995	9/1/1993	-11.9	-88.0	nr
SCS	Salt Creek Spring	Monroe et al. 2005	5/23/2000	-11.8	-87.3	17.7
SCS	Salt Creek Spring	Monroe et al. 2005	12/6/2000	-12.1	-90.2	18.1
SCS	Salt Creek Spring	Monroe et al. 2005	4/10/2001	-11.7	-87.1	16.1
SCS	Salt Creek Spring	Bills et al. 2007	11/22/2002	-12.1	-90.8	nr
SCS	Salt Creek Spring	USGS 2019	10/24/2012	-12.1	-89.0	nr
SCS	Salt Creek Spring	USGS 2019	9/5/2015	-11.9	-88.5	nr
SMgS	Sam Magee Spring	Monroe et al. 2005	4/20/2001	-10.0	-79.4	nr
SaS	Sapphire Spring	Bills et al. 2007	4/23/2002	-11.9	-89.0	nr
SaS	Sapphire Spring	Bills et al. 2007	10/23/2002	-11.8	-87.7	nr
SeS	Serpentine Spring	Bills et al. 2007	4/21/2002	-12.1	-91.1	nr
SeS	Serpentine Spring	Bills et al. 2007	10/24/2002	-11.9	-89.1	nr
SFPW	SF Peaks Well	USGS 2019	7/2/1996	-13.1	-93.8	nr
SFPW	SF Peaks Well	USGS 2019	1/15/1997	-15.2	-107.0	nr

Table 6. Oxygen and Hydrogen Stable Isotopes and Chloride (page 11/11)						
Sample ID	**Location**	**Data Source**	**Date Sampled**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Cl (mg/L)**
SFPW	SF Peaks Well	USGS 2019	1/29/1997	-15.9	-114.0	nr
SMrS	Santa Maria Spring	Ingraham et al. 2001	12/1/1992	-11.8	-90.0	nr
SMrS	Santa Maria Spring	Ingraham et al. 2001	2/1/1993	-11.9	-88.0	nr
SMrS	Santa Maria Spring	Ingraham et al. 2001	4/1/1993	-11.4	-86.0	nr
SMrS	Santa Maria Spring	Ingraham et al. 2001	9/1/1993	-12.2	-90.0	nr
SCW	Sunset Crater Well	USGS 2019	8/17/2017	-11.8	-85.3	nr
TS	Turquoise Spring	Bills et al. 2007	10/23/2002	-12.0	-90.0	nr

nr = not reported

Table 7. PPCPs detections in all samples (ng/L)								
Analyte	**WRP**	**WRP**	**Havasupai Garden Spring**	**Two Trees Spring**	**Two Trees Spring, below (TT3)**	**Pipe Spring**	**Field Blank**	**Field Blank**
	2/27/2021	12/21/2021	10/24/2021	10/24/2021	12/19/2021	12/18/2021	2/27/2021	12/21/2021
1,7-Dimethylxannthine	---	---	---	---	---	21	---	---
Acesulfame-K	16000	160	---	---	---	---	---	---
Albuterol	---	6.4	8.4	12	---	---	---	---
Atenolol	160	42	---	---	---	---	---	---
Bezafibrate	13	---	---	---	---	---	---	---
Butalbital	18	19	---	---	---	---	---	---
Caffeine	38	15	66	---	---	48	---	---
Carbamazepine	240	66	---	---	---	---	---	---
Carisoprodol	---	26	---	---	---	---	---	---
Cotinine	51	38	---	---	---	---	---	---
DEA	---	---	100	84	---	---	---	---
DEET	120	22	---	---	---	---	35	120
Dilantin	25	55	---	---	---	---	---	---
Diuron	22	---	---	---	---	---	---	---
Fluoxetine	44	110	---	---	---	---	---	---
Gemfibrozil	5.8	---	---	---	---	---	---	---
Ibuprofen	120	---	---	---	---	---	---	---
Ketoprofen	8	---	---	---	---	---	---	---
Lidocaine	6.7	---	---	---	---	---	---	---
Lopressor	---	49	---	---	---	---	---	---
Meprobamate	33	81	---	---	---	---	---	---
Phenazone	---	---	38	---	---	---	---	---
Primidone	190	58	---	---	---	---	---	---
Propylparaben	---	---	6.1	---	---	---	---	---
Salicylic Acid	---	---	---	---	---	300	230	---
Sucralose	66000	92000	---	---	---	---	---	---
Sulfadiazine	---	---	8.1	10	---	---	---	---
TCEP	94	68	---	---	---	---	26	---
TCPP	730	280	---	---	---	---	230	---
TDCPP	350	140	---	---	---	---	---	---
Thiabendazole	---	20	---	---	---	---	---	---
Theobromine	---	---	78	56	65	180	---	---
Theophylline	---	---	---	---	---	37	---	---

2/28/21 Havasupai Garden Spring had no detections

2/28/21 Two Trees Spring had no detections

--- = non-detect

Table 8. PPCPs detections in springs sampled in October and December 2021 (ng/L)					
Analyte	**Water Reclamation Plant**	**Havasupai Garden Spring**	**Two Trees Spring**	**Two Trees Spring, below (TT3)**	**Pipe Spring**
	12/21/2021	10/24/2021	10/24/2021	12/19/2021	12/18/2021
1,7-Dimethylxannthine					21
Albuterol	6.4	8.4	12		
Caffeine	15	66			48
DEA		100	84		
Phenazone		38			
Propylparaben		6.1			
Salicylic Acid					300*
Sulfadiazine		8.1	10		
Theobromine		78	56	65	180
Theophylline					37

*Detection also in field blank sample

Table 9. Averages for Oxygen and Hydrogen Stable Isotopes and Chloride Concentration							
Sample ID	**Abreviation**	**Dates Sampled**	**Avg $\delta^{18}O$ (‰)**	**Std $\delta^{18}O$ (‰)**	**Avg δD (‰)**	**Std δD (‰)**	**Avg Cl (mg/L)**
Grand Canyon Village Drinking Water, this study	DW	2018-2021	-13.6	0.2	-95.0	0.6	3.7
Tusayan, this study	Tu	2018-2021	-12.0	0.0	-86.4	0.6	37.0
Tusayan, other reported data	Tu	1992-1993	-11.9	0.1	-88.5	1.8	nr
Valle, this study	Va	2018-2021	-11.6	0.2	-85.5	0.5	38.2
WRP, this study	WRP	2018-2021	-13.3	0.1	-93.6	0.5	96.4
Clearwell Overflow Avg, 1993	WRP	1993	-12.9	0.3	-93.4	1.6	125.6
Pipe Creek	PS	2000-2001	-12.4	0.0	-91.4	0.5	16.8
Havasupai Garden Spring, this study	HG	2017-2021	-12.5	0.1	-90.8	0.4	10.8
Indian Garden Spring Avg, 1993	HGU	1993	-12.4	0.1	-92.6	0.5	12.8
Two Trees Spring, other reported data	TT	2000-2002	-12.3	0.0	-92.0	1.1	11.0
Two Trees Spring, this study	TT	2021	-12.6	0.0	-91.0	0.2	11.6
Roaring Springs, avg baseflow	RS	2003 - 2008	-13.8	na	-96.3	nr	1.3
Angel Spring, other reported data	AS	2011-2015	-13.7	0.3	-96.8	2.3	nr
Boucher East Spring, other reported data	BoE	2000-2017	-11.5	0.4	-86.8	2.9	nr
Boucher Spring, other reported data	Bo	2002	-11.4	0.1	-84.5	0.4	nr
Burro Spring, this study and other reported data	BS	2000-2021	-12.4	0.1	-91.1	1.5	19.2
Canyon Mine Observation Well, other reported data	CMO	2017-2019	-11.0	0.1	-82.9	0.4	nr
Canyon Mine Well, other reported data	CM	1993-2017	-12.2	0.1	-89.3	0.5	nr
Cottonwood Creek No. 1, other reported data	CC	2000-2002	-12.3	0.1	-90.8	1.1	nr
Cottonwood Creek No. 2, other reported data	CC	2000-2002	-12.8	0.0	-93.8	0.7	nr
Dripping Spring, other reported data	DrS	1992-1993	-12.2	0.3	-89.8	0.5	nr
Emmett Spring, other reported data	ES	2007-2021	-13.2	0.8	-94.4	4.5	nr
Fossil Spring, other reported data	Fo	2002	-10.95	0.1	-80.65	0.2	37.5
Grapevine East Spring, other reported data	GES	2000-2001	-9.0	0.4	-73.6	1.8	nr
Grapevine Main Spring, other reported data	GMS	2001-2018	-12.9	0.0	-93.4	0.9	nr
Hawaii Spring, other reported data	HaS	1992-2001	-11.9	0.1	-88.7	0.8	13.2
Hermit Spring, this study and other reported data	HS	1993-2017	-11.9	0.1	-88.9	0.8	10.7
Hawaii and Hermit Spring	HaS and HS	1992-2017	-11.9	0.1	-88.8	0.8	12.0
Horn Creek Spring, other reported data	HC	1993-2016	-11.8	0.2	-89.5	1.0	31.0
Lonetree Spring, other reported data	LS	6/23/1905	-12.0	0.0	-89.5	0.6	19.6
Miners Spring, other reported data	MiS	2000-2002	-12.2	0.1	-92.2	1.0	18.5
Monument Spring, other reported data	MoS	2000-2002	-12.0	0.2	-89.6	1.3	41.5
Ruby Spring	Ru	2002.00	-11.00	0.3	-81.60	0.3	nr
Salt Creek Spring, other reported data	SCS	1993-2015	-11.9	0.2	-88.7	1.4	17.3
Santa Maria Spring, other reported data	SMrS	1992-1993	-11.8	0.3	-88.5	1.9	nr

nr = not reported

8.0 References

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