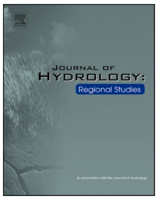
Journal of Hydrology: Regional Studies 48 (2023) 101461

Contents lists available at ScienceDirect

Journal of Hydrology: Regional Studies

journal homepage: www.elsevier.com/locate/ejrh



Utilizing anthropogenic compounds and geochemical tracers to identify preferential structurally controlled groundwater pathways influencing springs in Grand Canyon National Park, Arizona, USA

Kimberly R. Beisner [a,*], Nicholas V. Paretti [b], Jeramy R. Jasmann [c], Larry B. Barber [c]

[a] *U.S. Geological Survey, 6700 Edith Blvd NE, Albuquerque, NM 87113, USA*
[b] *U.S. Geological Survey, 520 N. Park Ave, Tucson, AZ 85719, USA*
[c] *U.S. Geological Survey, 3215 Marine St., Boulder, CO 80303, USA*

ARTICLE INFO

Key Words:
Anthropogenic
Grand Canyon
Fracture flow
Wastewater
Stable isotope
Per- and poly fluoroalkyl substances

ABSTRACT

Study region: This study focuses on the Colorado River watershed in the area along the South Rim of the Grand Canyon.
Study focus: This study utilizes anthropogenic chemical tracers to investigate the fate of treated wastewater effluent discharged within Grand Canyon National Park. Anthropogenic chemical tracers were used to discern preferential structurally controlled pathways in a complex regional network of faults and fractures in which some are conduits and others barriers to flow.
New hydrological insights for the region: Previous investigations on water resources of Grand Canyon have suggested two different discharge locations (Garden Springs versus Monument Spring) for the treated wastewater discharged on the South Rim of Grand Canyon yet the presence of wastewater at the springs remained unstudied for decades. The treated wastewater from Grand Canyon Village is released into Bright Angel Wash that flows along the surface expression of the Bright Angel Fault and past the inferred intersection with the perpendicular Monument Fault. Multiple anthropogenic compounds (pharmaceuticals, per- and polyfluoroalkyl substances (PFAS), and elevated nitrate) were found in Bright Angel Wash and Monument Spring. Stable isotopic measurements at Monument Spring show depletion over time also suggesting contribution from a depleted stable isotopic source found in the treated wastewater. The anthropogenic tracers utilized in this study provide good insight to which geologic structures are conduits versus barriers to flow and can be useful in other fracture flow and karst settings.

1. Introduction

On the dry-subhumid South Rim of the Grand Canyon water is a limited resource. Local populations and ecosystems are dependent on groundwater. Groundwater resources south of Grand Canyon are not sufficient to support the local water demand, and in 1970 a pipeline was completed to convey water from Roaring Spring north of Grand Canyon across the canyon and up to the South Rim to be used for around 6 million visitors a year (Ingraham et al., 2001). After water usage, the water is sent to a wastewater treatment plant

---

[*] Corresponding author.
E-mail address: kbeisner@usgs.gov (K.R. Beisner).

https://doi.org/10.1016/j.ejrh.2023.101461
Received 30 November 2022; Received in revised form 16 June 2023; Accepted 25 June 2023

located to the west of Grand Canyon Village (Fig. 1). The treated wastewater is discharged to Bright Angel Wash and flows south along the Bright Angel Fault then infiltrates into the subsurface. The fate of treated wastewater as it moves through the subsurface is not well understood.

Metzger (1961) assessed the potential water supply in Grand Canyon National Park and described two springs in Havasupai Gardens (one spring issuing from the slope east of Havasupai Gardens, which is referred to as Two Trees Spring or Pumphouse Spring in later publications, including this one, and a second spring issuing from the creek bed at the uppermost end of Havasupai Gardens, which we refer to as Garden Springs). Several early water chemistry studies list Horn, Salt, and Monument Springs as issuing from the Tapeats Sandstone (Goings, 1985; Zukosky, 1995; Fitzgerald, 1996; Ingraham et al., 2001), however the first issuance of water in these drainages is located at a higher elevation issuing from the Redwall-Muav aquifer then infiltrates into the alluvial material and re-emerges lower in the drainage. Metzger (1961) alluded to the water at Monument Spring as being supplied from higher in the Tonto Group (Frenchman Mountain Dolostone of Rowland et al., 2023 and Muav Limestone). Water chemistry from these earlier studies can be compared with water emerging lower in the drainage, but is not directly comparable to the water issuing from the Redwall-Muav aquifer higher up in the drainage. Ingraham et al. (2001) explored the possibility of using stable isotopes as a tracer for anthropogenic influence at Garden Springs suggesting that depleted isotopic values represented water from Roaring Springs piped across the Grand Canyon for water supply. Monroe et al. (2005) also explored the hydrogeochemistry of springs discharging along the South Rim of Grand Canyon using radiocarbon, strontium isotopes, and an extensive trace element suite and found elevated nitrate at Monument Spring and suggested treated wastewater may be contributing to the spring water.

Springer et al. (2017) analyzed stable isotopes of oxygen and hydrogen across western North America and in the Grand Canyon region found that stable isotope values can provide an indication of local versus regional sources of recharge. Tobin et al. (2017) provided a comprehensive review of the groundwater system of the Grand Canyon region and found that almost half of the springs

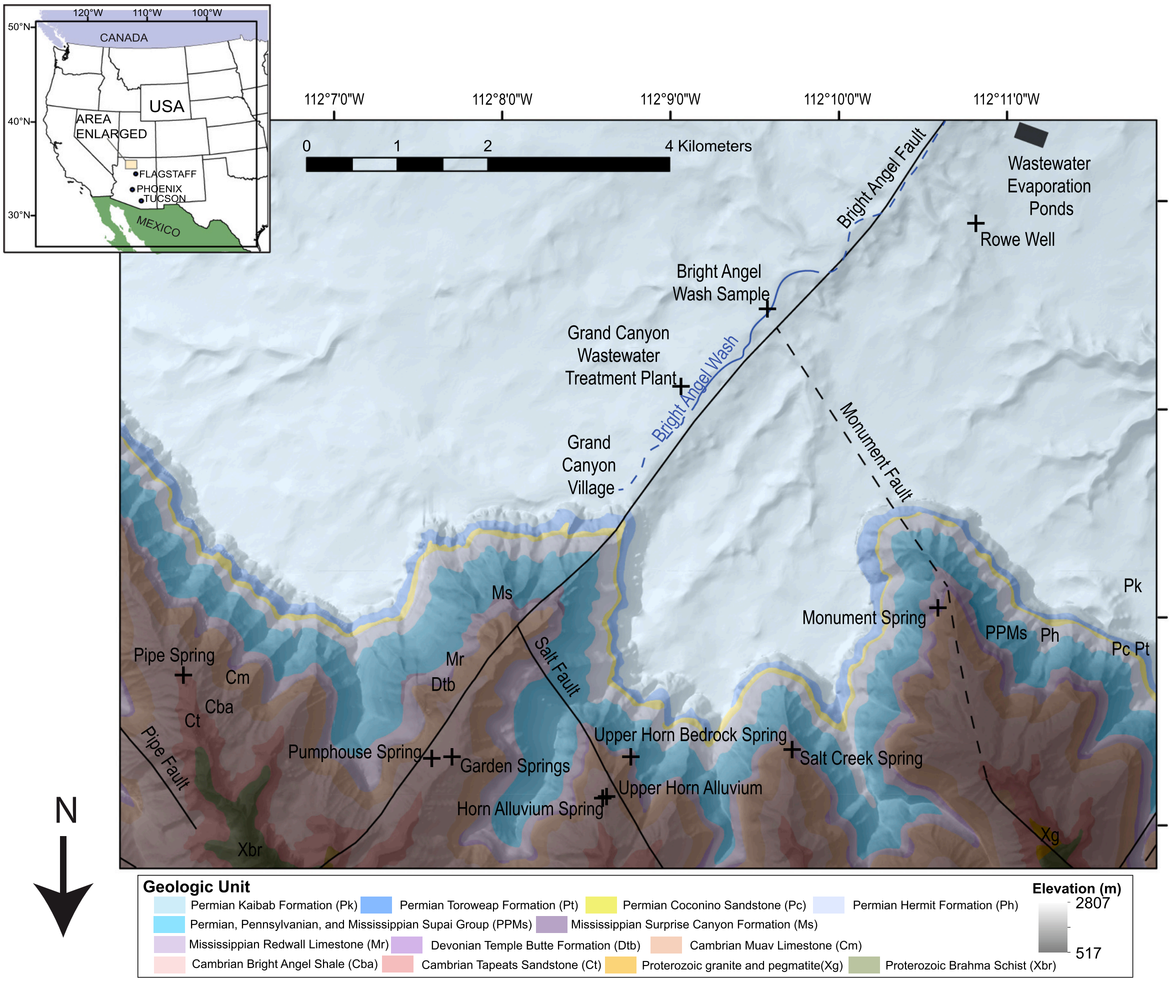


Fig. 1. Map showing the study area including sampling locations, Bright Angel Wash is a solid line for the reach perennially saturated by treated wastewater effluent. Geologic map layer from Billingsley (2000) with solid black lines representing faults (fault names from Maxson, 1961) and dashed Monument fault expression from Maxson (1961). Elevation data is from The National Map USGS Shaded Relief data from the National Elevation Dataset using North American Vertical Datum of 1988.

emerge from karst aquifers with high seasonal variability and evidence of fast flow pathways controlled by faults and fractures. A focused study at Cottonwood Creek (east of study area in this report) that utilized discharge and $\delta^{18}O$ indicates a 2–4 year delay between winter precipitation recharge and spring discharge in the Cottonwood drainage (Tobin et al., 2017). Burch (2021) analyzed water resources of Cottonwood Creek and found a decreasing discharge trend between 1994 and 2020, which may be related to climate factors or groundwater pumping in the region. Nuyttens (2022) also tested scenarios on an existing groundwater model to understand the potential influence of climate and groundwater pumping on spring discharge and found that climate change had a stronger influence on changing spring discharge compared with groundwater pumping. O'Connor (2022) conducted sampling at a limited number of springs along the South Rim including Garden, Pumphouse, and Pipe Springs for major ion, stable isotope, and personal care products and suggest that leaking pipeline infrastructure may be contributing to groundwater south of Grand Canyon, which is also published with some modifications in Curry et al. (2023).

Previous studies described above helped advance the hydrologic understanding of the system incrementally, however a comprehensive spatial investigation with multiple geochemical and anthropogenic tracers was needed to assess the contribution of human derived wastewater recharged on the rim of Grand Canyon. Whether there was evidence of non-natural human derived compounds at remote back country springs along the South Rim of Grand Canyon was unknown in addition to what other geochemical tracers were altered as a result of water moved across Grand Canyon by the transcanyon pipeline. Additionally, structural features in the region have a complicated history and little is known about their conductive properties. The objective of research presented in this paper is to provide novel understanding regarding these unresolved research questions to understand preferential pathways for water movement south of Grand Canyon using multiple geochemical and anthropogenic tracers.

1.1. Hydrogeologic setting

The study area is located in the Colorado Plateau physiographic province. The youngest rocks in the study area are Paleozoic sedimentary rocks underlain by Proterozoic igneous and metamorphic basement rocks (Billingsley, 2000). The majority of groundwater in this study was sampled from the Redwall-Muav aquifer, which occurs in older rock units of Mississippian to Cambrian age. Water is thought to recharge the system to the south of Grand Canyon near the high elevation peaks of the San Francisco volcanic field about 90 km away (Bills et al., 2007; Crossey et al., 2009; Solder et al., 2020) and some additional smaller areas of localized recharge closer to the South Rim have been proposed (Knight and Huntoon, 2022; Solder et al., 2020). For example, Rowe Well is a shallow well dug into the Kaibab Formation near the location of a seep (Metzger, 1961) that served as an early water source for Grand Canyon National Park. The water at the Rowe Well may represent localized recharge, since the area around the well at a higher elevation than the well for groundwater to infiltrate into the Kaibab Formation is only a few square kilometers, rather than the deeper flowpaths sourced from a large area to the south of Grand Canyon that feeds the Redwall-Muav springs along the South Rim of Grand Canyon.

Groundwater movement in the Grand Canyon region is dominated by fault and fracture controlled flowpaths where some geologic structures serve as barriers to flow and other structures have openings that provide pathways for rapid movement of water through the subsurface. Evidence of these different conductive properties is seen in recent dye traces along the Kaibab Plateau north of Grand Canyon (which may behave similarly to the Coconino Plateau south of the Grand Canyon) where dye placed in sinkholes moved through several hundred meters vertically and several kilometers horizontally to springs over a time period of less than a year (Jones et al., 2017). Master joints may also influence hydraulic conductivities of brittle rocks; they are commonly spaced around 100 ft to over a half mile from major structures and occur in lower carbonate rocks of the region (Huntoon, 1974). Northwest trending faults are present in Horn and Monument drainages and intersect the Bright Angel and Hermit Faults (Maxson, 1961) and may provide preferential pathways for groundwater movement. Springs are present in each of the major drainages that cut into the Grand Canyon South Rim and may also represent locations of preferential structurally controlled flowpaths as the springs occur at discrete locations rather than as saturated exposed cliff faces.

Development of water resources for visitors to Grand Canyon has been a limiting factor since the parks inception and the following information was presented in Metzger (1961). In 1928 a sewage disposal plant at Grand Canyon village was completed and allowed for the reuse of water at areas where potable water was not necessary. In 1932 a pipeline was completed to pump 731 liters per minute from Havasupai Gardens to Grand Canyon Village. Tourism increased following World War II and storage tanks were added such that 4 million gallons of water could be stored by 1958.

The water supply from Havasupai Gardens proved to be inadequate for the growing water demand and between 1965 and 1970 a pipeline was constructed to convey water from Roaring Spring (located near the Bright Angel Fault north of the Colorado River) 20 km to Grand Canyon Village and carries about 719 million liters of water per year (National Park Service, 2021). The wastewater treatment plant started releasing water at the Clearwell Overflow (located on the west side of the Grand Canyon Wastewater Treatment Plant in Bright Angel Wash) in 1987 according to Ingraham et al. (2001). Treated wastewater effluent is released into Bright Angel Wash which follows the surface expression of the Bright Angel Fault; surface flows in the wash move towards the south, then infiltrate into the subsurface within approximately 2 kilometers downstream. The Monument Fault intersects the Bright Angel Fault a few kilometers downstream of the Grand Canyon Wastewater Treatment Plant effluent release (Maxson, 1961) and may serve as a conduit for treated wastewater effluent to move towards Monument Spring (Fig. 1). Bright Angel Wash is ephemeral and only flows naturally following large scale precipitation events; the addition of treated wastewater effluent to the wash results in a short section of the wash having surface flow the majority of the year.

1.2. Purpose and scope

This study utilizes anthropogenic chemical tracers collected in April 2021 and 2022 to investigate the influence of anthropogenic activity within one of the most iconic outdoor destinations set aside for preservation and wilderness. Non-natural chemicals investigated in this study have human and environmental health implications, including the fate of treated wastewater effluent discharged within Grand Canyon National Park. The treated wastewater is discharged along the South Rim of Grand Canyon in an area of perpendicular faults (Bright Angel and Monument) where there are springs located near the fault expressions. A suite of multiple anthropogenic chemicals serve as tracers to discern which faults and fractures may be conduits and which may be barriers to flow, and the utilization of multiple anthropogenic tracers helps discern their persistence in the subsurface to assess usefulness for other studies. The anthropogenic tracers and stable isotopes of oxygen and hydrogen are used to test the decades old question of whether the treated wastewater in Grand Canyon contributes to Garden Springs or Monument Spring. Rapid fracture flow groundwater movement south of Grand Canyon has not been previously established and has implications for contaminant transport from breccia pipe uranium mines in the region as well as for artificial recharge including wastewater. Anthropogenic compounds associated with wastewater presented in this study show promise as tracers to discern preferential structurally controlled groundwater flowpaths.

2. Methods

2.1. Data collection

Water samples were collected for this study from 1 well, 7 spring sites, and 1 surface water site between April 27 and 30, 2021, and repeated at 5 springs and 1 surface water site between April 19 and 22, 2022 (Fig. 1). All samples were collected by the U.S. Geological Survey (USGS) using standard field methods (USGS, variously dated). Field parameters including pH, water temperature, specific conductance, dissolved oxygen, and barometric pressure were measured on site just before water samples were collected. Elbow length plastic gloves with nitrile gloves on top were worn with a clean pair used at each sampling site. Spring samples were collected as close to the point of issuance from the ground as possible using a peristaltic pump with a separate pre-cleaned flexible silicon tube used at each site for inorganic constituents, water was collected directly into sample bottles from the spring flow for organic constituents. The surface water sample from Bright Angel Wash was collected using a 1 L Teflon bottle dipped into the water and composited into a Teflon churn from which the raw samples were collected and the filtered samples were pumped out of. Samples for per- and polyfluoroalkyl substances (PFAS) were collected by dipping the sample bottles directly into the sampled water, and no sharpie marker or waterproof labels were used.

Samples for nutrients were filtered through 0.45 μm capsule filters and pharmaceutical samples were filtered though 0.70 μm syringe glass fiber filters using a pre-cleaned syringe and collected in 20 mL baked amber glass vials. Samples were collected unfiltered in 2 – 250 mL polycarbonate bottles for PFAS and in a 1 L baked amber glass bottle for wastewater tracer analysis at USGS Integrated Water Chemistry Analytical Lab (IWCAL) located in Boulder, Colorado. Samples were kept chilled immediately after sampling until analysis at the analytical laboratories.

Nitrate (NO_3) plus nitrite (NO_2) and nitrite were analyzed by colorimetry at the USGS National Water Quality Laboratory (NWQL) (Patton and Kryskalla, 2011) in Lakewood, Colorado. Stable isotopes of water ($\delta^{18}O$ and $\delta^{2}H$) were analyzed at the USGS Reston Stable Isotope Laboratory in Reston, Virginia using mass spectrometry following methods by Révész and Coplen (2008a,b), with precision of 0.9 per mil or better for $\delta^{2}H$ and 0.08 per mil or better for $\delta^{18}O$ on the basis of repeated internal standards.

Per- and polyfluoroalkyl substances (PFAS) were analyzed at SGS in Orlando, Florida by EPA modified 537.1 method (Shoemaker and Tettenhorst, 2018). Wastewater tracer compounds were analyzed at the IWCAL with continuous liquid-liquid extraction with methylene chloride followed by gas chromatography-tandem mass spectrometry (GC-MSMS) in multiple reaction monitoring mode following methods by Barber et al. (2000). Isotopically labeled surrogate standards were added prior to sample extraction and work-up procedures and non-labeled internal standards were added to the extracts prior to analysis. Pharmaceutical analysis was conducted by direct aqueous injection liquid chromatography-tandem mass spectrometry (LC-MSMS) using electrospray ionization, multiple monitoring mode, and isotopically labeled surrogate standards for quantitation at the NWQL (Furlong et al., 2014) for a subset of the sites.

2.2. Quality assurance

Three field blanks and two replicates were collected for the sample set. A field blank was collected with certified inorganic free blank water at Garden Springs for nutrients in 2021. An environmental replicate and a field blank were collected at Bright Angel Wash in 2021. A replicate and a source solution blank for PFAS were collected at Monument Spring in 2022. The blanks were collected with certified organic and PFAS free blank water.

No PFAS were detected in the field blanks from 2021 and 2022 and no pharmaceutical compounds were detected in the field blank analyzed by the NWQL in 2021. Cholesterol, 2,6-ditertbutyl 1–4 benzoquinone, and 4-tert-octylphenoltriethoxylate (4-t-OP3EO) analyzed at IWCAL in 2021 were present above the laboratory detection level in the field and lab blanks at similar concentrations to environmental samples and were not included in the discussion of anthropogenic compounds.

The replicate sample collected at Bright Angel Wash in 2021 showed good agreement with the environmental sample for most PFAS: the relative percent differences for compounds detected in the samples were PFPeA (2 %), PFHxA (4 %), PFHpA (5 %), PFOA (4 %), PFNA (7 %), PFDA (0 %), PFBA (58 %), and PFOS (40 %). In 2022, the replicate sample from Monument Spring had similar recoveries for detected compounds PFPeA (0 %), PFHxA (0 %), PFOA (13 %), and PFOS (42 %). The higher variability for PFOS results from low estimated concentrations (1.8 and 1.2 ng/L) above the laboratory detection level but below the laboratory reporting level. Pharmaceutical replicate samples from NWQL in 2021 showed good agreement with environmental samples, with the majority of compounds less than 10 % difference and the following compounds had higher variability: caffeine (16 %), sulfamethoxazole (30 %), pseudoephederine +ephedrine (11 %), meprobamate (14 %), fexofenadine (12 %), and nordiazepam (31 %). Of these, caffeine, sulfamethoxazole, and nordiazepam had values below the laboratory reporting level but above the laboratory detection level and may represent values with greater quantitative uncertainty. Wastewater tracer replicate samples from IWCAL in 2021 also showed good agreement with environmental samples, with the majority of compounds less than 10 % difference and the following compounds had higher variability DEET (38 %), diphenhydramine (20 %), galaxolide (17 %), 4-NP2EO (14 %), and 4-t-OP1EO (11 %). 4-t-OP2EO and 5-methyl-1-H-benzotriazole had a value detected in the environmental sample but not in the replicate sample.

3. Results

3.1. Water chemistry

Field parameters of samples collected in the study indicate oxic, near neutral to slightly alkaline fresh-water conditions. Groundwater temperature ranged from 10.7 to 18.6 °C, pH ranged from 7.2 to 8.5, specific conductance ranged from 392 to 1080 μS/cm, and dissolved oxygen ranged from 6.2 to 9.2 mg/L (U.S. Geological Survey, 2022). Surface water at Bright Angel Wash, comprised primarily of treated wastewater, had some parameters similar to the groundwater with dissolved oxygen of 7.9 and 11.5 mg/L, pH (8.2 and 8.7), higher specific conductance (1170 and 1270 μS/cm), and variable temperature (7.3 and 22.8 °C) (U.S. Geological Survey, 2022).

Groundwater temperature was lowest (10.7 °C) at the Rowe Well, which is a shallow seep in the upper stratigraphic unit (Kaibab Formation) located on the South Rim about a thousand meters above where the Redwall-Muav aquifer springs discharge below the rim. Pipe, Pumphouse, and Garden Springs had the warmest temperatures (17.7–18.6 °C) and springs to the west of the Bright Angel Fault (Horn, Salt, and Monument) had lower temperatures (12–14.8 °C). The decrease in temperature across the fault may suggest different flowpaths supply water to springs on each side of the fault, and continuous temperature measurements at the springs could provide insight into temperature fluctuation throughout the year to help discern more integrated regional sources of water compared with variable locally derived sources of water.

Specific conductance indicates the amount of dissolved charged ions in solution as a result of dissolution of minerals along a flowpath, or addition of salts as the water passes through human digestive systems and hygienic activities in addition to chemicals added during the treatment of the water before and after human use. Specific conductance was highest in Bright Angel Wash (1270 μS/cm) and lowest at Pumphouse and Garden Springs (417 and 437 μS/cm) for samples from 2021 (Fig. 2), with similar values in 2022. Of the other springs, Upper Horn Bedrock Spring had the highest specific conductance (1080 μS/cm) (Fig. 2), which may be related to water moving through the nearby mineralized deposit at the Orphan Mine (Beisner and Tillman, 2019).

Nitrate ranged from 0.355 to 68.3 mg/L as N for samples collected in this study, with the highest value from Bright Angel Wash (Fig. 2). All spring sample concentrations of nitrate were below the USEPA drinking water MCL of 10 mg/L (U.S. Environmental Protection Agency, 2022), and Monument Spring had the highest concentration of 6.1 in 2021 and 6.49 in 2022 as mg/L as N. Nitrate has been elevated at Monument Spring in every sample collected by USGS since 2000 and ranged from 5.1 to 7.02 mg/L as N (Monroe et al., 2005; U.S. Geological Survey, 2022). Additionally, there is a warning given by Grand Canyon National Park for back country hikers camping at Monument Campsite regarding elevated nitrate in Monument Creek.

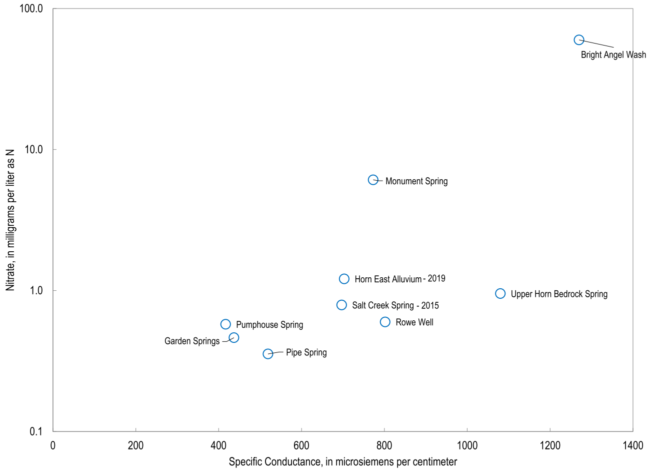


Fig. 2. Specific conductance versus nitrate for water samples along South Rim of Grand Canyon, where values are from samples collected in 2021 unless otherwise noted.

3.2. Anthropogenic organic compounds

The anthropogenic PFAS do not occur naturally and are persistent in the environment suggesting that the presence of PFAS in water samples is related to water in contact with human influenced sources such as cookware, adhesives, paper, and packaging that often end up at wastewater treatment plants (Ahrens et al., 2009). Of the 28 PFAS analyzed in water samples, 9 were detected in environmental samples in 2021 (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, and PFOS; Table 1). The majority of PFAS were detected in Bright Angel Wash (all but PFBS). Monument Spring had several detections of PFAS (PFPeA, PFHxA, PFOA, PFBS, and PFOS). Upper Horn Bedrock Spring had detections of PFBA and PFBS (Fig. 3) and no other sampling sites had any detections of PFAS. Repeat sampling in 2022 showed similar PFAS compounds at Bright Angel Wash although the concentration was lower for PFOA, and the following compounds were not detected PFBA, PFHpA, PFNA, and PFDA (Table 1). PFAS compounds and concentrations at Monument Spring in 2022 were very similar to 2022. Upper Horn Bedrock Spring did not have any PFAS compounds above the laboratory detection level in the 2022 sample.

Wastewater compounds were analyzed at IWCAL and at a subset of the sites (Bright Angel Wash, Monument, Gardens, and Upper Horn Bedrock Springs) at the NWQL. 37 compounds were analyzed at IWCAL, and of those, 13 were detected in Bright Angel Wash and 2 of those were also detected at Monument Spring. 154 human-use pharmaceuticals were analyzed at the NWQL of which 28 compounds were detected in Bright Angel Wash and 6 of those were also detected at Monument Spring (Table 2). Carbamazepine and diphenhydramine were analyzed at both IWCAL and NWQL. Both labs detected these compounds at Bright Angel Wash and carbamazepine at Monument Spring but only IWCAL detected estimated concentrations of diphenhydramine at Monument Spring. IWCAL samples were collected unfiltered and concentrations for carbamazepine and diphenhydramine were higher than filtered samples analyzed at NWQL and may suggest either variability between colloidal and dissolved partitions, separate bottles used for sample analysis, or variability between the analytical methods.

4. Discussion

4.1. Anthropogenic influence on Grand Canyon springs

The intersection of human influence on a landscape set aside for preservation and wilderness in Grand Canyon, one of the most iconic outdoor destinations, has human and environmental health implications. The majority of Grand Canyon National Park is managed as wilderness, but there are areas of intense visitor use (primarily along the Bright Angel Trail corridor) within the park that are utilized heavily and have a developed an anthropogenic footprint. At the time of this publication, more than 6 million people visit Grand Canyon National Park per year and the infrastructure to accommodate the majority of visitors and park staff is concentrated in a small spatial area near Grand Canyon Village (Ingraham et al., 2001). The treated wastewater from Grand Canyon Village is reused for graywater, firefighting, and discharged to Bright Angel Wash which infiltrates into the subsurface (Metzger, 1961), but the fate of the treated wastewater after discharge has been generally unknown.

The springs sampled in this study are located below the rim of Grand Canyon and at Monument, Salt, Upper Horn Bedrock Springs the groundwater emerges from bedrock outcrops, which are accessed by hiking up the alluvial drainages away from the established trails to remote areas which are not or rarely accessed by visitors. No trash or other anthropogenic materials have been found at the aforementioned springs. Monument and Upper Horn Bedrock Springs are the only two springs in this study that had detectable PFAS and were sampled right as the water emerges from the bedrock suggesting the possibility of local contamination is minimal. Other springs in the study, Garden, Pumphouse, and Pipe Springs are located in closer proximity to trails frequented by visitors and Garden Springs in particular is located directly adjacent to a campsite in Havasupai Gardens. Pumphouse Spring is located up a hill from a pumphouse that pushes water in a pipeline originating at Roaring Spring up to the South Rim of Grand Canyon and there are periodically leaks in the pipeline that influence the chemistry of the water in Garden Creek located below the spring discharge location (Curry et al., 2023). Garden and Pumphouse Springs in closer proximity to visitor traffic did not have any anthropogenic compounds

Table 1

Concentrations of per- and polyfluoroalkyl substances for sites with at least one sample above the laboratory detection level in surface and groundwater samples collected in April 2021 and 2022 (U.S. Geological Survey, 2022).

Site Name ->	Bright Angel Wash		Monument Spring		Upper Horn Bedrock Spring	
Sample Date ->	4–30–21	4–22–22	4–28–21	4–19–22	4–27–21	4–20–22
Perfluorobutanoic acid (PFBA)	5.6	< 3.6	< 3.6	< 3.6	6	< 5.6
Perfluoropentanoic acid (PFPeA)	25.9	17.1	3.2	4.9	< 2.0	< 2.8
Perfluorohexanoic acid (PFHxA)	18.4	12.0	1.8	2.6	< 2.0	< 2.8
Perfluoroheptanoic acid (PFHpA)	5.7	< 1.8	< 1.8	< 1.8	< 2.0	< 2.8
Perfluorooctanoic acid (PFOA)	84.6	9.0	2.7	2.9	< 2.0	< 2.8
Perfluorononanoic acid (PFNA)	E 1.4	< 1.8	< 1.8	< 1.8	< 2.0	< 2.8
Perfluorodecanoic acid (PFDA)	2.7	< 1.8	< 1.8	< 1.8	< 2.0	< 2.8
Perfluorobutanesulfonic acid (PFBS)	< 1.9	< 1.8	3.8	3.0	E 1.5	< 2.8
Perfluorooctanesulfonic acid (PFOS)	E 1.8	E 1.3	E 1.5	E 1.5	< 2.0	< 2.8

[Compound abbreviations used in text shown in parentheses; values are in ng/L, nanograms per liter; < , value is less than the laboratory reporting and detection level; E, value is above laboratory detection level but below laboratory reporting level]

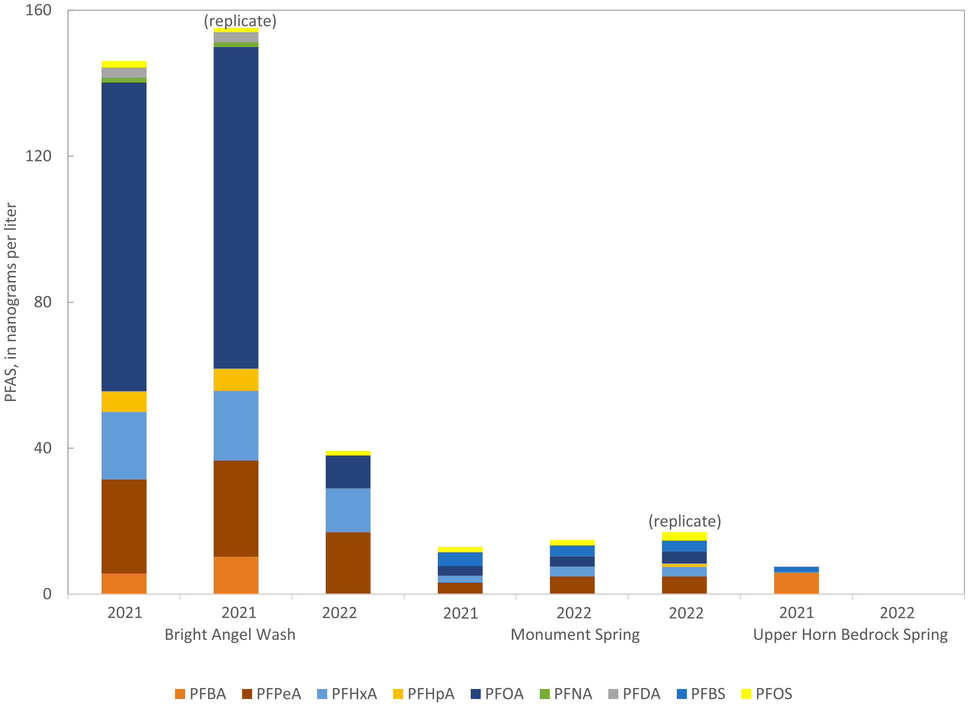


Fig. 3. Proportions of individual per- and polyfluoroalkyl substance detected in surface and groundwater samples along South Rim of Grand Canyon.

detected, and tritium is below the laboratory reporting level (Solder et al., 2020), suggesting that the leaking pipeline infrastructure (leaks from which are composed of young tritiated water) did not contribute substantially to the water at the springs. Additionally, Garden and Pumphouse Springs were present prior to the pipeline infrastructure and were known to be perennial sources of groundwater.

Monument Spring had the highest nitrate concentration (6.1 in 2021 and 6.49 in 2022 mg/L as N) of any Redwall-Muav groundwater in the Grand Canyon region. There are some earlier samples that provide context for baseline conditions (before treated wastewater effluent contribution) such as Metzger (1961) which gives a value of 1.0 mg/L for nitrate from a sample collected in October of 1957. Zukosky (1995) presented values of nitrate from the Clearwell Overflow and springs along the South Rim of Grand Canyon including Monument Spring. Nitrate presented in Zukosky (1995) appears to be reported as nitrate and when converted to nitrate as N range from 1.33 to 1.92 mg/L as N. Fitzgerald (1996) reports a nitrate concentration from July, 1995 from Monument Spring as 2.18 mg/L as N. The samples from Metzger (1961), Zukosky (1995), and Fitzgerald (1996) were collected lower in the Monument Creek drainage where water re-emerges after infiltrating into the alluvial material and resurfacing due to thinning of the alluvial material downgradient. Monroe et al. (2005) also sampled Monument Spring at first issuance from the bedrock as in our study and had nitrate concentrations of 5.7 and 6.8 mg/L of N in December, 2000 and April, 2001 and then lower in Monument Creek with 4.5 mg/L of N at a different date (May, 2000). The concentration of nitrate collected from Monument Creek about 2 kilometers below the spring emergence from Monroe et al. (2005) is higher than any other spring along the South Rim of Grand Canyon (1.4 mg/L as N (Beisner et al., 2020)) and higher compared with previous studies (Ingraham et al., 2001; Monroe et al., 2005) suggesting water emerging from the alluvium lower in Monument Creek may show elevated nitrate concentrations related to the upper spring source.

Natural processes from nitrogen fixing plants in the Semidesert Grassland, Mojave Desertscrub, Sonoran Desertscrub-Arizona Uplands, and Sonoran Desertscrub-Lower Colorado River Valley biotic communities of the southwest have only been shown to produce groundwater nitrate concentrations of 2 – 4.9 mg/L (Anning et al., 2012). Some of these and similar biotic communities are present in the study area; the Mojave Desertscrub occurs along the Colorado River through Grand Canyon, Great Basin Desertscrub in the inner corridor of the canyon, and Plains and Great Basin Grassland occur along the uplands draining to Cataract Creek to the west of our study area. Bexfield et al. (2011) suggest occurrence of nitrate concentrations greater than 5.0 mg/L is generally controlled by the presence of human-related sources of nitrogen on the land surface, transport to the aquifer by natural and human-related recharge mechanisms, and/or persistence in the aquifer as a result of favorable geochemical conditions.

The concentration of nitrate in Bright Angel Wash, which was composed entirely of treated wastewater, was very high at 59.9 in 2021 and 68.3 in 2022 mg/L as N. Assuming that nitrogen does not degrade as it moves through the subsurface and the baseline value of nitrate at Monument Spring would be 1 mg/L or less (sample from Monument Spring in 1957 was 1 mg/L; Metzger, 1961), then the proportion of treated wastewater present at Monument Spring in 2021 would be around 8 % (dividing the Monument Spring nitrate concentration minus 1 by the value from Bright Angel Wash). Proportion of treated wastewater present at Monument Spring using total

Table 2
Concentrations of wastewater compounds for samples with at least one value above the laboratory detection level collected from April 27–30, 2021 (U.S. Geological Survey, 2022). [values are in ng/L, nanograms per liter; < , value is less than the laboratory reporting and detection level; E, value is an estimated concentration above laboratory detection level but below laboratory reporting level or associated with additional quantitative uncertainty].

Compound (ng/L)	Analytical Laboratory	Bright Angel Wash	Monument Spring
Guanylurea	NWQL	702	< 140
Bupropion	NWQL	131	< 18
Caffeine	NWQL	E 50.6	< 91
Cotinine	NWQL	32	< 6.4
Sulfamethoxazole	NWQL	16.8	12.4
Thiabendazole	NWQL	E 12.3	< 4
Trimethoprim	NWQL	6.98	< 20
Pseudoephedrine + Ephedrine	NWQL	25.7	< 6
Lidocaine	NWQL	12	< 4
Meprobamate	NWQL	70.9	< 12
Desvenlafaxine	NWQL	E 21.3	< 84
Dextromethorphan	NWQL	2.34	< 8.2
Temazepam	NWQL	60.1	< 18
Triamterene	NWQL	8.42	< 5.2
Fluconazole	NWQL	570	32.6
Loratadine	NWQL	E 9.29	< 7
Metformin	NWQL	992	7.58
Methocarbamol	NWQL	725	< 11
Atenolol	NWQL	85.6	< 20
Citalopram	NWQL	E 16.6	< 6.6
Fexofenadine	NWQL	E 256	< 44
Methyl-1H-benzotriazole	NWQL	E 236	< 80
Tramadol	NWQL	13.2	4.3
Metoprolol	NWQL	27	< 10
Sitagliptin	NWQL	720	< 97
Venlafaxine	NWQL	23	2.11
Nordiazepam	NWQL	4.18	< 20
Carbamazepine	NWQL	399	49.5
Carbamazepine	IWCAL	529	133
Diphenhydramine	NWQL	15.8	< 48
Diphenhydramine	IWCAL	E 2349	E 106
Bisphenol A	IWCAL	E 135	< 50
Coprostanol	IWCAL	220	< 125
DEET	IWCAL	E 51.9	< 28.4
Galaxolide	IWCAL	184	< 27
5-methyl-1H-Benzotriazole	IWCAL	E 323	< 102.2
4-Methylphenol	IWCAL	91.3	< 28.3
4-NP1EO	IWCAL	328	< 258.7
4-NP2EO	IWCAL	416	< 270.2
4-t-OP1EO	IWCAL	E 11.5	< 10.2
4-t-OP2EO	IWCAL	91.7	< 86
Triclosan	IWCAL	78.5	< 27.4

PFAS (dividing total PFAS from Monument Spring by the total PFAS from Bright Angel Wash sample) gives a similar value of 9 %. Previous sampling of treated wastewater flowing into Bright Angel Wash in 2002 by USGS had nitrate of 37 mg/L as N, with a corresponding concentration in Monument Spring of 5.7 mg/L as N, with a proportion of treated wastewater of approximately 13 %. Since the lag time of water from Bright Angel Wash through the subsurface to Monument Spring is unknown, the proportion values serve as estimates of wastewater contribution.

Several PFAS compounds (PFBS, PFHxA, PFOA, PFOS, and PFPeA) were detected at Monument Spring in both 2021 and 2022. These compounds were also present in the Bright Angel Wash treated wastewater effluent samples with the exception of PFBS. Longer chain PFAS compounds tend to sorb to the solid phase, while shorter chain PFAS partition to the aqueous phase (Coggan et al., 2019), which may explain why long chain PFNA and PFDA are only present in the Bright Angel Wash samples and not at Monument Spring. PFBS has been found to be a breakdown product of other PFAS compounds (Singh et al., 2019; Lenka et al., 2021) and may represent changes occurring as the treated wastewater effluent moves through the subsurface. Another explanation could be temporal variability in the Bright Angel Wash PFAS compounds, which we see between the 2021 and 2022 samples (Table 1) and analytical variability as seen with the replicate samples (Fig. 3). Additionally, Bright Angel Wash treated wastewater effluent was sampled during the same week as the spring samples, and there is a lag time for the water to move through the subsurface to the springs. More frequent sampling of the Bright Angel Wash site could help identify PFAS changes over time and studies on the lag time for treated wastewater moving through the subsurface to the spring discharge locations could help identify if PFBS is a transformation byproduct of other PFAS compounds or is highly variable in the wastewater treatment plant effluent.

Upper Horn Bedrock Spring was the only other spring in this study to have PFAS compounds (PFBA and PFBS) present although fewer compounds were present, at lower concentrations, and were only detected in 2021 not in 2022 (Fig. 3) in comparison with Monument Spring PFAS results. The spring had the second highest nitrate concentration (0.95 mg/L as N) from the samples collected in April 2021, but was similar to nitrate concentrations from previous samples in Horn and Salt Creek Springs that are slightly elevated compared with Garden, Pumphouse, and Pipe Creek Springs (0.4–0.6 mg/L as N). PFAS was not detected in groundwater emerging from the alluvium lower in the Horn Creek drainage. April 2021 had low flow conditions at Horn Creek Springs compared to previous years and there are other studies suggesting there are chemical changes (including decrease in uranium and sulfate) and contribution of younger water between the Upper Horn Bedrock Spring and the Horn Alluvium Spring (Liebe, 2003; Beisner and Tillman, 2019). The PFAS compounds detected at Upper Horn Bedrock may also be related to past mining activities at the nearby Orphan Mine and additional investigation could provide insight into the variability and repeatability of the PFAS detections.

Pharmaceutical compounds were detected only in water samples from Bright Angel Wash and Monument Spring. Carbamazepine, sulfamethoxazole, and other select pharmaceuticals have been found in other studies of wastewater effluent and are persistent in environmental water samples, while other pharmaceutical compounds present at Bright Angel Wash may degrade as they move through the subsurface environment (Andreozzi et al., 2002; Bexfield et al., 2019; Zainab et al., 2020; Bavumiragira et al., 2022).

O'Connor (2022) also sampled for personal care products at the Grand Canyon Wastewater Treatment Plant Outfall and at Garden, Pumphouse, and Pipe Springs in 2021, which was subsequently published as Curry et al. (2023). Fourteen compounds were detected in the wastewater treatment effluent from samples in February and December 2021 and ten other compounds were detected in at least one of the wastewater treatment effluent samples, but there were no detections from their first round of sampling of the springs in February 2021. Subsequent sampling events in October and December 2021 showed low level detections of several compounds including 1,7-dimethylxanthine, albuterol, caffeine, DEA, phenazone, salicylic acid, sulfadiazine, theobromine, and theophylline detected at the springs, of which only albuterol and caffeine were detected from the wastewater treatment effluent samples in the December 2021 sample. Our study also analyzed for 1,7-dimethylxanthine, albuterol, caffeine, and theophylline, and only caffeine had estimated concentrations (below the laboratory reporting level) from the Bright Angel Wash (treated wastewater effluent) site. Compounds detected by O'Connor (2022) in the latter two sampling events are not persistent compounds in the subsurface environment and may represent local contamination or as a result of laboratory positive bias. Monument Spring was not sampled by O'Connor (2022), so direct comparison with the only spring from our study to have pharmaceutical compound detections was not possible.

Discharge measurements from springs along the South Rim of the Grand Canyon were reported by Monroe et al. (2005) and are presented in Table 3. More discharge measurements were made between 2001 and 2003 in Pumphouse Wash, Monument Creek, and Pipe Creek below the spring discharge locations (U.S. Geological Survey, 2022). Monument Creek stream flow was variable over a period of three years while Pumphouse Wash and Pipe Spring flow was more consistent (Fig. 4). Nuyttens (2022) assessed discharge values from several south-rim springs and found Pumphouse Wash to be a heavily base-flow dependent system (with a mean base-flow index of 95 %). Variable flow at Monument Creek suggests the influence from changes in treated wastewater effluent contributions. Further study could enhance the understanding of the variability in discharge at Monument Spring and the transport time of treated wastewater through the subsurface.

4.2. Stable isotopic indication of water source

Ratios of the stable isotopes of oxygen and hydrogen of the water molecule provide evidence of the groundwater recharge elevation, seasonality, and evaporation. High elevation winter precipitation in the region has the most depleted stable isotopic ratio and low elevation summer precipitation has the most enriched stable isotopic ratio (Beisner et al., 2016). Stable isotope groundwater

Table 3
Discharge measurements for springs and streams along the South Rim of Grand Canyon from Monroe et al. (2005) and Nuyttens (2022)* .

USGS site name	Date	Discharge (L/min)
Pipe Creek	5–22–00	15
	12–7–00	44
	04–08–01	37
	5–6–21	16.8*
	10–22–21	17.4*
Pumphouse Wash Gage	12–7–00	170
	12–9–00	170
Horn Creek	5–22–00	3.4
	12–6–00	5.1
	4–7–01	9.5
Salt Creek Spring	5–23–00	1.7
	12–6–00	3.4
	4–10–01	4.9
Monument Spring	12–5–00	221
	4–9–01	337
Monument Creek	5–24–00	204
	11–6–21	73.2*

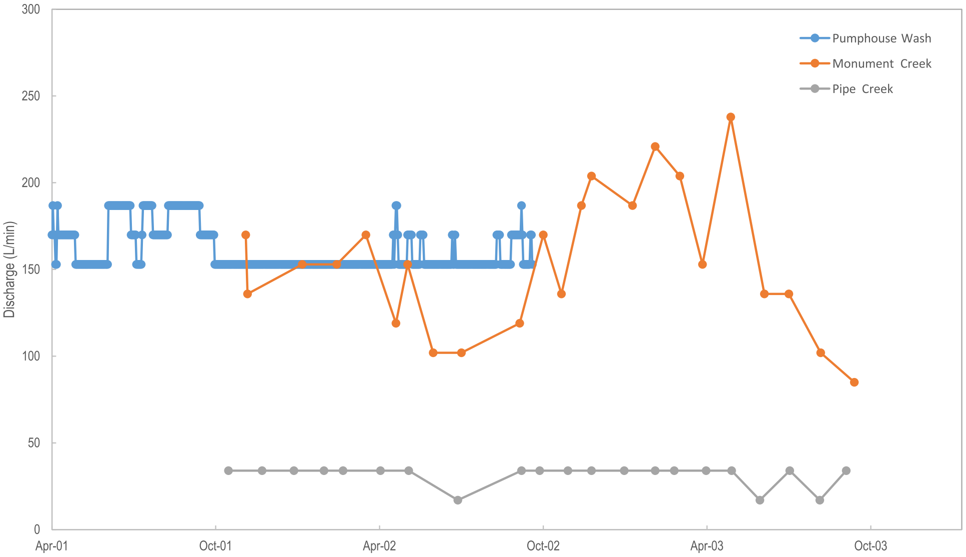


Fig. 4. Discharge measurements from USGS gages (Pumphouse Wash- 09403013; Monument Creek- 09403033; and Pipe Creek- 09403010) below the South Rim of Grand Canyon (USGS, 2022).

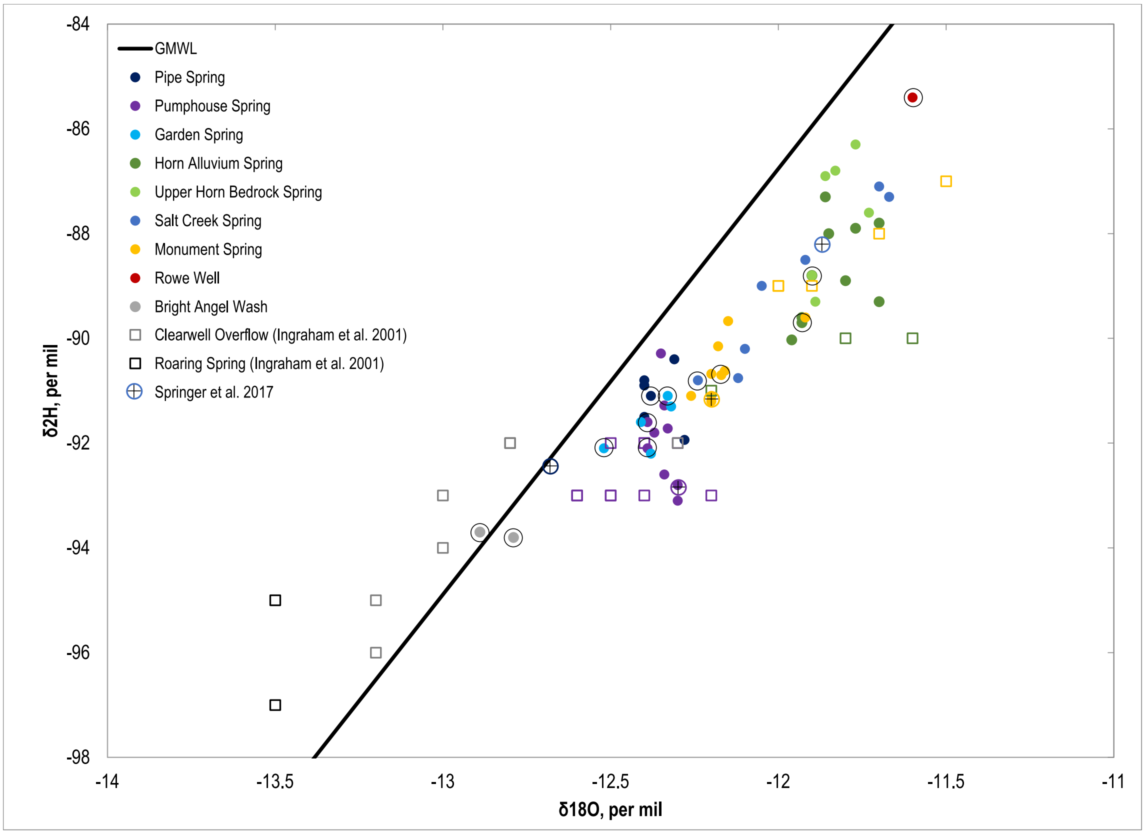


Fig. 5. Stable isotopic ratios of oxygen and hydrogen from select water samples collected from the Grand Canyon. Colored circle symbols represent samples collected by USGS (including samples from Monroe et al., 2005), with an outlining circle around samples collected in April 2021 and 2022, and open square symbols represent samples collected by Ingraham et al. (2001) and plus symbols with surrounding circle from samples in Springer et al. (2017). Global meteoric water line (GMWL) from Craig (1961).

sample ratios near the South Rim of Grand Canyon fall within the range of winter precipitation values (Solder and Beisner, 2020).

Ingraham et al. (2001) suggested that groundwater discharging at Havasupai Gardens was derived from treated wastewater discharged on the South Rim along the Bright Angel Fault based on the depleted stable isotopic signature of the water used at Grand Canyon Village, which is derived from Roaring Spring (located north of the Colorado River and piped to the South Rim). Roaring Spring has a more depleted stable isotopic signature than most springs on the South Rim of the Grand Canyon as does water discharging from the Grand Canyon Wastewater Treatment Plant at Bright Angel Wash (Fig. 5).

O'Connor (2022) also suggests that groundwater south of Grand Canyon is derived from water originating from Roaring Spring though pipeline leakage using stable isotopic evidence, however the quantification of the fraction of leaking pipeline water is driven by utilizing either Fossil Spring or Valle groundwater as an endmember. O'Connor (2022) then uses stable isotopic data to quantify the percentage of north rim water (derived from Roaring Spring) that is present at all groundwater sites south of Grand Canyon utilizing Fossil Spring or Valle groundwater as a representative end member (Curry et al., 2023 only used Valle groundwater as an endmember). The use of a single endmember to represent all groundwaters along the South Rim of Grand Canyon could oversimplify the complex groundwater system and likely does not account for spatial variability described by Monroe et al. (2005), and Solder and Beisner (2020).

Stable isotopic values for waters from this study plot below the global meteoric water line suggesting the water may have undergone evaporation either during precipitation or as it moved through the unsaturated zone towards the water table. The Rowe Well had the most enriched stable isotopic ratios (Fig. 5) and may represent an endmember of water recharged locally along the South Rim rather than originating to the south of Grand Canyon near the San Francisco Peaks (Crossey et al., 2009; Solder et al., 2020). Water in Bright Angel Wash had the most depleted stable isotopic ratios from this study and likely represents an artificial end member as it is treated wastewater effluent primarily derived from Roaring Spring water which has a depleted stable isotopic signature. Monroe et al. (2005) identified a trend of decreasing stable isotopic values towards the east for springs along the South Rim of the Grand Canyon. The

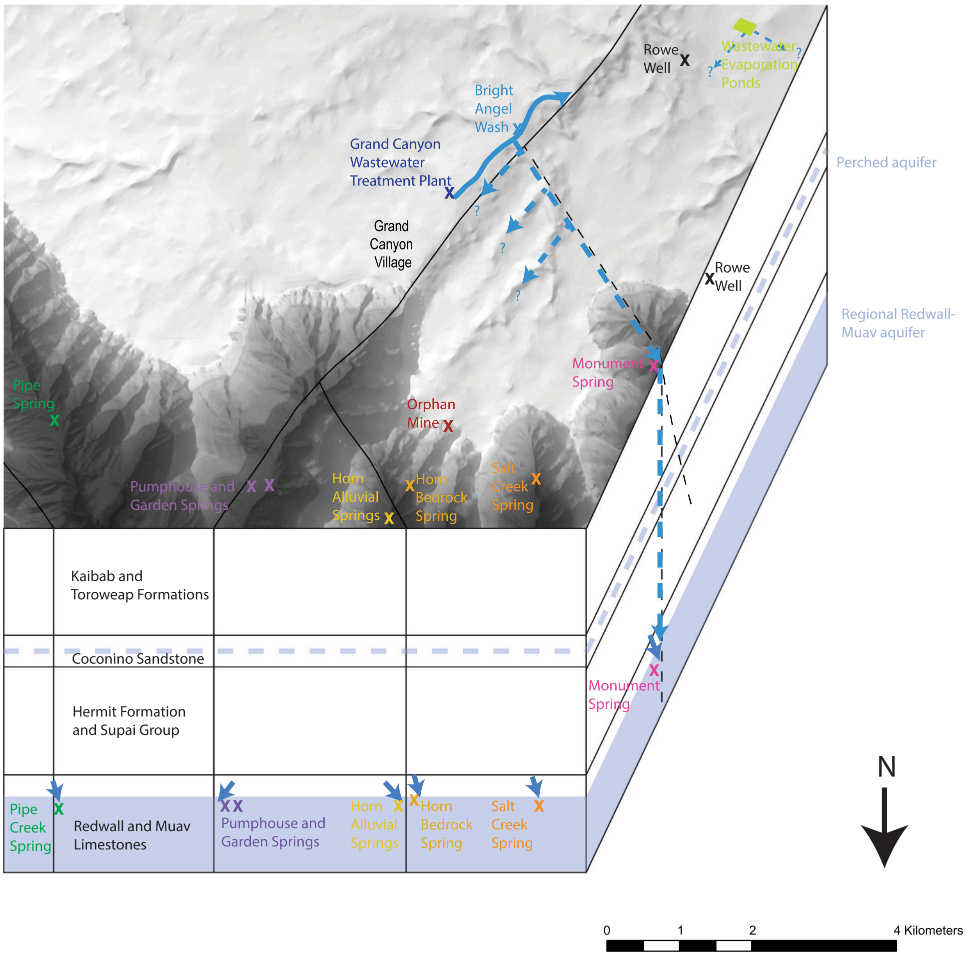


Fig. 6. Conceptual depiction of movement of treated wastewater effluent discharged into Bright Angel Wash (solid blue line) demonstrating preferential groundwater flow pathways (dashed blue lines) facilitated by structural features with solid black lines representing faults and dashed black line representing Monument fault expression from Maxson (1961). Elevation data is from The National Map USGS Shaded Relief data from the National Elevation Dataset using North American Vertical Datum of 1988.

subset of springs included in this study show a similar trend with Pipe, Pumphouse, and Gardens Springs having the most depleted stable isotopic values (Fig. 5).

Several springs included in this study were sampled by Ingraham et al. (2001) and Monroe et al. (2005) and are presented in Fig. 5 together with the values collected by USGS between October, 2012 and April, 2022 (U.S. Geological Survey, 2022). Pumphouse Spring showed similar isotopic values from all studies while Horn and Salt Creek Springs show large variability over time. Pumphouse and Garden Springs have tritium values below the laboratory reporting level and radiocarbon age of around 2000 years old and may represent older water with a long deep flowpath compared with Horn Creek Springs which contain elevated values of tritium and radiocarbon data suggesting young water (Monroe et al., 2005; Solder et al., 2020). Monument Spring shows a distinct shift from the more enriched samples collected by Ingraham et al. (2001) with the more depleted samples collected by USGS at later dates. The Ingraham et al. (2001) samples were collected in 1992 and 1993 a few years after the wastewater treatment plant effluent began releasing water to Bright Angel Wash and may represent values prior to the contribution of the more depleted wastewater source from Roaring Spring (located north of the Colorado River and piped over to the South Rim) due to travel time of the effluent. Zukosky (1995) reported low nitrate values for the same samples presented in Ingraham et al. (2001) from 1992 and 1993, which supports the concept that these samples represent baseline conditions prior to treated wastewater contribution. The samples from Clearwell Overflow collected by Ingraham et al. (2001) were also highly variable and the lag time from infiltration into Bright Angel Wash and movement through the subsurface to Monument Spring is not well characterized.

The Ingraham et al. (2001) study states that after their sampling a leak was detected in the buried transcanyon pipeline above where their samples for Gardens Spring were collected (below the Tonto Trail from emergence of groundwater from spring referred to as Pumphouse Spring in Monroe et al., 2005 and this study) and may have contributed to the depleted stable isotopic values. Some of the samples from Pumphouse Spring from Ingraham et al. (2001) do plot to the left of the samples collected by USGS at Pumphouse Spring and may represent a contribution from transcanyon pipeline water (Fig. 5). Fitzgerald (1996) presents data from Pumphouse Spring collected on the hillslope upgradient of the transcanyon pipeline in 1994 with values of −12.2 and −93 ‰ and −12.3 ‰ and 91 for δ^{18}O and δ^{2}H respectively that are within the range of USGS and the farthest right Ingraham et al. (2001) point. Monroe et al. (2005) and our study sampled Pumphouse Spring above the pipeline infrastructure and the similarity of the stable isotopes at Pumphouse, Gardens, and Pipe Springs suggest the depleted stable isotopic signatures at those sites are representative of older deeply sourced groundwater flowpaths that may originate to the south near the San Francisco Peaks (Crossey et al., 2009; Solder et al., 2020).

The spatial and temporal variability and context derived from baseline conditions suggest that stable isotopic values are best used as supporting evidence, rather than as the primary line of evidence, for treated wastewater contribution in the system when a full range of variability of stable isotopic ratios is understood. The contribution of treated wastewater to Monument Spring based on available stable isotope and nitrate data can be constrained to the time window between 1994 and 2000, which suggests the movement of treated wastewater from the rim down a vertical distance of about 720 m and a horizontal distance of 3 km to Monument Spring (Fig. 6) may occur in less than a decade. Elevated nitrate, PFAS, persistent pharmaceuticals, and a shift towards a depleted stable isotopic endmember at Monument Spring suggest anthropogenic influence on the spring that is likely related to treated wastewater infiltration along Bright Angel Wash.

4.3. Wastewater as a tracer of structural controls on groundwater flow

Spring locations along the South Rim of Grand Canyon are controlled by structural features where water flows along more preferable permeable pathways. Historical evidence suggests all of the springs in this study were present in the canyon prior to the additional recharge from the wastewater up on the rim. Current understanding of areas that have a positive soil water balance which recharges the groundwater system indicate that recharge areas are located to the southeast near the San Francisco Volcanic Field and a smaller area to the east of the Bright Angel Fault south of the rim of the canyon (Knight and Huntoon, 2022). The naturally recharged water flows along preferential structurally controlled pathways and may move quickly from the upper stratigraphic units to the lower Redwall-Muav aquifer along deep penetrating fractures (Gettings and Bultman, 2005). A groundwater divide near the South Rim of Grand Canyon is referenced in Crossey et al. (2009) and Knight and Huntoon (2022), but the location of the divide is based on several decades old groundwater elevation data and could be reassessed with more recent data to understand current groundwater flow directions. Additionally, more information is needed to understand the influence of the Bright Angel Fault on the groundwater potentiometric surface.

The wastewater is recharged along a large structural feature, the Bright Angel Fault, which has had a complex history of deformation. Huntoon and Sears (1975) provide a detailed history of the Bright Angel Fault as a northeast trending fault that parallels basement foliation and activity on the fault dates to the Precambrian, where evidence suggests it began as a reverse fault with the east side up. Later evidence suggests a series of northwest trending normal faults broke up the Precambrian Chuar Group and caused minor adjustments along the Bright Angel Fault. Reverse movement occurred along pre-existing northwest-trending Precambrian faults then tensional faulting in Miocene or Pliocene caused downfaulting along the Bright Angel Fault with a dip of about 85 degrees with east side down. Beds on the east side of the fault dip toward the fault plane at a slight angle representing reverse drag. The Monument, Salt, and Pipe Faults were identified by Maxson (1961) and may represent perpendicular to Bright Angel Fault northwest trending structures that originated in the Precambrian and have been offset by subsequent tectonic stresses, which may have opened up preferential subsurface pathways.

Dutson (2005) investigated groundwater discharge along the Virgin River, Utah near the Hurricane Fault and found that groundwater discharge occurred discontinuously to the east of the fault presumably in the damage zone around the main fault plane (core zone which is considered to have low permeability). Additionally, the pattern of groundwater discharge may also be controlled by a secondary structural fabric intersecting with the damage zone to produce areas of higher permeability (Dutson, 2005). The findings of Dutson (2005) provide a similar example in the region and suggest that groundwater movement within major fault zones is complex and dependent on intersecting structural fabrics that provide preferential pathways for groundwater flow.

The anthropogenic compounds associated with the wastewater in this study provide a tracer to test the direction of water flow through the subsurface within the damage zone of the Bright Angel Fault and suggest that the water is following a preferential pathway from a different structural fabric around the Bright Angel Fault as it moves through the subsurface. Similar behavior was observed in a dye tracer study north of Grand Canyon where the dye moved quickly in perpendicular directions to the known large surface fault network (Jones et al., 2017). The Jones et al. (2017) study also discussed the karst characteristics of the Redwall-Muav aquifer system north of Grand Canyon and assessed the dense sinkhole network present on the surface. The wastewater recharged along Bright Angel Wash terminates at a sinkhole and there are likely karst characteristics present in the groundwater system south of the Colorado River as well, although this is not as well characterized and receives less surface moisture compared to the north side.

The presence of anthropogenic tracers in a remote backcountry spring (Monument Spring) suggest fracture and karst flow is an important component of groundwater flow in the region and has implications for the region where water is artificially recharged. Breccia pipe uranium mines open up artificial pathways in the subsurface and allow water to move down into new subsurface environments where accumulated water may move along structurally controlled preferential pathways not previously utilized by the natural groundwater system. Additional research into the fate of the treated wastewater in Bright Angel Wash, the wastewater evaporation ponds, and leaky wastewater pipeline infrastructure in Grand Canyon Village could provide a comprehensive understanding of the anthropogenic influence on water resources near Grand Canyon Village.

5. Conclusions

This study utilizes anthropogenic compounds to elucidate the influence of the Grand Canyon Wastewater Treatment Plant effluent on water resources of Grand Canyon. Previously there were two investigations (Ingraham et al., 2001; Monroe et al., 2005) on water resources in Grand Canyon that suggested different discharge locations (Garden Springs versus Monument Spring) for the treated wastewater discharged on the South Rim of Grand Canyon. The two theories remained for more than a decade without follow up sampling leaving uncertainty about the fate of the treated effluent. This study found elevated nitrate, PFAS, and pharmaceutical compounds (carbamazepine, diphenhydramine, fluconazole, metformin, sulfamethazole, tramadol, and venlaflaxine) at Monument Spring and low level PFAS compounds at Upper Horn Bedrock Spring but not at any other spring including Garden Springs. The compounds found at Monument Spring suggest the movement of treated wastewater discharged on the rim along Bright Angel Wash down a vertical distance of about 720 m and a horizontal distance of 3 km to Monument Spring. Stable isotopic data from Monument Spring also suggest a shift towards a more depleted endmember similar to the treated wastewater effluent that occurred in less than a decade.

Lag time from infiltration of treated wastewater in Bright Angel Wash to Monument Spring is unknown and may vary depending on the volume of water being released which increases or slows the speed of the water moving through the fractured groundwater system. Volumetric discharge measurements on the spring sites below the South Rim of Grand Canyon and of treated wastewater discharge over time could help better characterize natural fluctuations versus influence from treated wastewater effluent influence. A dye trace study on the treated wastewater effluent would help quantify the transit time through the system as well as the magnitude of effluent contributing to Monument Spring. Repeat sampling of anthropogenic compounds at shorter timescales could provide understanding of the variability of treated wastewater effluent moving through the subsurface especially at Monument and Upper Horn Bedrock Springs. Current understanding of groundwater flow direction between Flagstaff, Ariz. and Grand Canyon Village is limited due to a lack of groundwater wells and water level measurements at existing wells over time. There are other possible groundwater flowpaths that the infiltrated treated wastewater in Bright Angel Wash may follow as well as other areas where treated wastewater may move into the subsurface including the wastewater evaporation ponds and leaky wastewater pipeline infrastructure in Grand Canyon Village. Additional sampling of anthropogenic compounds at other groundwater sites in the area could provide valuable information and lead to further understanding of the complex structurally altered stratigraphic subsurface of the region.

The anthropogenic compounds used in this study (namely PFAS, nitrate, and persistent pharmaceuticals) serve as indicators of wastewater. They also serve as tracers for preferential fracture-controlled groundwater flowpaths, which in this case helped differentiate flowpaths in an area with a perpendicular fault network where some structures are conductive, and some are barriers to flow. Treated wastewater, which contains anthropogenic compounds (PFAS, pharmaceuticals, personal care products) that are not removed during the wastewater treatment process, is increasingly being reused for irrigation, snowmaking, and recharged to augment water supply resources. These tracers may be utilized in other areas in the arid southwest and around the world where treated wastewater effluent is recharged to groundwater resources.

CRediT authorship contribution statement

Kimberly R. Beisner: Project conceptualization, methodology, formal analysis, investigation, resources, writing original draft, writing review and editing, visualization of figures, supervision of project staff, project administration, and funding acquisition, **Nicholas V. Paretti:** Project conceptualization, project methodology, writing review and editing, validation of data, supervision of project staff, project administration, and funding acquisition, **Jeramy R. Jasmann:** Project conceptualization, formal analysis, writing review and editing, **Larry B. Barber:** Project conceptualization, writing review and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data presented in this paper are publicly available at the USGS NWIS database which can be accessed at https://doi.org/10.5066/F7P55KJN and at USGS Water Quality Samples for USA: Sample Data for specific sites used in this paper.

Acknowledgments

The authors would like to thank Jay Cederberg, Sarah Shepherd, Kat Cooney, and Jessica Anderson from the USGS in Arizona for their help collecting the water samples from remote physically challenging locations. We would like to acknowledge support from Grand Canyon National Park that was critical to the logistical challenges of collecting the samples. We thank Kenneth Skinner and three anonymous journal reviewers that helped improve the paper. The funding for this research was provided by the USGS-NPS Water Quality Partnership Program and the USGS Environmental Health Program (Toxic Substances Hydrology). The research was conducted under National Park Service research permits GRCA-2021-SCI-0038 and GRCA-2022-SCI-0041.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ejrh.2023.101461.

References

Ahrens, L., Felizeter, S., Sturm, R., Xie, Z., Ebinghaus, R., 2009. Polyfluorinated compounds in wastewater treatment plant effluents and surface waters along the River Elbe. Ger. Mar. Poll. Bull. 58 (9), 1326–1333. https://doi.org/10.1016/j.marpolbul.2009.04.028.

Andreozzi, R., Marotta, R., Pinto, G., Pollio, A., 2002. Carbamazepine in water: persistence in the environment, ozonation treatment and preliminary assessment on algal toxicity. Water Res 36 (11), 2869–2877.

Anning, D.W., Paul, A.P., McKinney, T.S., Huntington, J.M., Bexfield, L.M., Thiros, S.A., 2012. Predicted nitrate and arsenic concentrations in basin-fill aquifers of the Southwestern United States. U. S. Geol. Surv. Sci. Investig. Rep. 78, 2012–5065.

Barber, L.B., Brown, G.K., Zaugg, S.D., 2000. Potential endocrine disrupting organic chemicals in treated municipal wastewater and river water. In: Keith, L.H., Jones-Lepp, T.L., Needham, L.L. (Eds.), in Analysis of Environmental Endocrine Disruptors, 747. American Chemical Society Symposium Series, Washington, DC, pp. 97–123.

Bavumiragira, J.P., Ge, J., Yin, H., 2022. Fate and transport of pharmaceuticals in water systems: A process review. Sci. Tot. Environ. 823, 153635.

Beisner, K.R., Tillman, F.D., 2019. Assessing spatial differences in uranium concentrations in groundwater along the Horn Creek Drainage in Grand Canyon National Park, Arizona. 11th National Monitoring Conference abstract with program, March 25–29, 2019 Denver, CO.

Beisner, K.R., Paretti, N.V., Tucci, R.S., 2016. Analysis of stable isotope ratios ($\delta^{18}O$ and $\delta^{2}H$) in precipitation of the Verde River watershed, Arizona, 2003 through 2014. U. S. Geol. Surv. Open-File Rep. 2016–1053, 11.

Beisner, K.R., Solder, J.E., Tillman, F.D., Anderson, J.R., Antweiler, R.C., 2020. Geochemical characterization of groundwater evolution south of Grand Canyon, Arizona (USA). Hydrogeol. J. 28 (5), 1615–1633.

Bexfield, L.M., Thiros, S.A., Anning, D.W., Huntington, J.M., McKinney, T.S., 2011. Effects of natural and human factors on groundwater quality of basin-fill aquifers in the southwestern United States—conceptual models for selected contaminants. U. S. Geol. Surv. Sci. Investig. Rep. 90, 2011–5020.

Bexfield, L.M., Toccalino, P.L., Belitz, K., Foreman, W.T., Furlong, E.T., 2019. Hormones and pharmaceuticals in groundwater used as a source of drinking water across the United States. Environ. Sci. Technol. 53, 2950–2960.

Billingsley, G.H., 2000. Geologic map of the Grand Canyon 30' x 60' quadrangle, Coconino and Mohave Counties, Northwestern Arizona. U. S. Geol. Surv. Geol. Invest. Series I-2688.

Bills, D.J., Flynn, M.E., Monroe, S.A., 2007. Hydrogeology of the Coconino Plateau and adjacent areas, Coconino and Yavapai Counties, 4 plates Ariz. U. S. Geol. Surv. Sci. Investig. Rep. 2005–5222, Version 1 (1), 101. https://doi.org/10.3133/sir20055222v1.1.

Burch, S.J., 2021. Assessing fire impacts to a spring-fed riparian ecosystem during a dry climate cycle in Grand Canyon National Park, USA, M.S. Thesis, Northern Arizona University.

Coggan, T.L., Moodie, D., Kolobaric, A., Szabo, D., Shimeta, J., Crosbie, N.D., Lee, E., Fernandes, M., Clarke, B.O., 2019. An investigation into per- and polyfluoroalkyl substances (PFAS) in nineteen Australian wastewater treatment plants (WWTPs). Heliyon 5, e02316. https://doi.org/10.1016/j.heliyon.2019.e02316.

Craig, H., 1961. Isotopic variations in meteoric waters. Science 133, 1702–1703.

Crossey, L.J., Karlstrom, K.E., Springer, A.E., Newell, D., Hilton, D.R., Fischer, T., 2009. Degassing of mantle derived CO_2 and He from springs in the southern Colorado Plateau region- Neotectonic connections and implications for groundwater systems: Geol. Soc. Am. Bull. 121 (7–8), 1034–1053.

Curry, B.H., Crossey, L.J., Karlstrom, K.E., 2023. The Grand Canyon National Park (USA) water corridor: water supply, water quality, and recharge along the Bright Angel Fault. Hydrogeol. J. https://doi.org/10.1007/s10040-023-02633-6.

Dutson, S.J., 2005. Effects of Hurricane Fault Architecture on Groundwater Flow in the Timpoweap Canyon of Southwestern, Utah, Bringham Young University- Provo masters thesis.

Fitzgerald, J., 1996. Residence time of groundwater issuing from the south rim aquifer in the eastern Grand Canyon, Arizona. Las Vegas, University of Nevada, unpublished master's thesis, 103 p.

Furlong, E.T., Noriega, M.C., Kanagy, C.J., Kanagy, L.K., Coffey, L.J., Burkhardt, M.R., 2014. Determination of human-use pharmaceuticals in filtered water by direct aqueous injection-high-performance liquid chromatography/tandem mass spectrometry. U. S. Geol. Surv. Tech. Meth., Book 5, chap. B10 49.

Gettings, M.E., Bultman, M.W., 2005. Candidate-penetrative-fracture mapping of the Grand Canyon area, Arizona, from spatial correlation of deep geophysical features and surficial lineaments. U. S. Geol. Surv. Data Ser. 121.

Goings, D.B., 1985. Spring flow in a portion of Grand Canyon National Park, Arizona. Las Vegas, University of Nevada, unpublished master's thesis.

Huntoon, P.W., 1974. The karstic groundwater basins of the Kaibab Plateau. Ariz. Wat. Res. Res. 10 (3), 579–590.

Huntoon, P.W., Sears, J.W., 1975. Bright Angel and Eminence Faults, Eastern Grand Canyon, Arizona, Geol. Soc. Am. Bull. v. 86, 465–472.

Ingraham, N.L., Zukosky, K., Kreamer, D.K., 2001. Application of stable isotopes to identify problems in large-scale water transfer in Grand Canyon National Park. Environ. Sci. Technol. 35, 1299–1302.

Jones, C.J.R., Springer, A.E., Tobin, B.W., Zappitello, S.J., Jones, N.A., 2017. Characterization and hydraulic behavior of the complex karst of the Kaibab Plateau and Grand Canyon National Park, USA. Geol. Soc. Lond., Spec. Publ. 466, 237–260. https://doi.org/10.1144/SP466.5.

Knight, J., Huntoon, P.W., 2022. Conceptual models of groundwater flow in the Grand Canyon Region. Ariz. U. S. Geol. Surv. Sci. Investig. Rep. 2022–5037, 51. https://doi.org/10.3133/sir20225037.

Lenka, S.P., Kah, M., Padhye, L.P., 2021. A review of the occurrence, transformation, and removal of poly- and perfluoroalkyl substances (PFAS) in wastewater treatment plants. Water Res. 199, 117187 https://doi.org/10.1016/j.watres.2021.117187.

Liebe, D., 2003. The use of the ^{234}U/^{238}U activity ratio at the characterization of springs and surface streams in Grand Canyon National Park, Arizona. Hochschule fur Technik und Wirtschaft Dresden, Germany, M.S. Thesis 105.

Maxson, J.H., 1961. Geologic map of the Bright Angel quadrangle, Grand Canyon National Park, Arizona. Grand Canyon National Park, Arizona. Grand Canyon Nat. Hist. Assoc., 2 plates.

Metzger, D., 1961. Geology in relation to availability of water along the south-rim, Grand Canyon National Park, Arizona. U. S. Geol. Surv. Water-Supply Pap. 1475-C. 100–130.

Monroe, S.A., Antweiler, R.C., Hart, R.J., Taylor, H.E., Truini, M., Rihs, J.R., Felger, T.J., 2005. Chemical characteristics of ground-water discharge along the south rim of Grand Canyon in Grand Canyon National Park, Arizona, 2000–2001. U. S. Geol. Surv. Sci. Investig. Rep. 2004–5146 59.

National Park Service. 2021. Grand Canyon National Park Features Trans-Canyon Waterline to Celebrate Engineers Week 2021 Grand Canyon National Park Features Trans-Canyon Waterline to Celebrate Engineers Week 2021 (U.S. National Park Service) (nps.gov) accessed May 18, 2022.

Nuyttens, K. 2022. Ecohydrogeology of springs below the Grand Canyon's South Rim, Grand Canyon National Park, Arizona. M.S. Thesis, Northern Arizona University.

O'Connor, B. 2022. Grand Canyon National Park's Water Corridor: Water Supply, Water Quality, and Recharge Along the Bright Angel Fault, M.S. Thesis, University of New Mexico, ⟨https://digitalrepository.unm.edu/eps_etds/300⟩.

Patton, C.J., Kryskalla, J.R., 2011. Colorimetric determination of nitrate plus nitrite in water by enzymatic reduction, automated discrete analyzer methods. U. S. Geol. Surv. Tech. Meth., Book 5, chap 34, B8.

Révész, K., Coplen, T.B., 2008a. Determination of the δ2H/1H, of water—RSIL lab code 1574: U.S. Geol. Surv. Tech. Meth., Book 10, chap 27, C1.

Révész, K., Coplen, T.B., 2008b. Determination of the δ18O/16O of water—RSIL lab code 489: U.S. Geol. Surv. Tech. Meth., Book 10, chap 28, C2.

Rowland, S.M., Korolev, S., Hagadorn, J.W., Ghosh, K., 2023. Frenchman Mountain Dolostone: A new formation of the Cambrian Tonto Group, Grand Canyon and Basin and Range. USA: Geosph. v. 19 https://doi.org/10.1130/GES02514.1.

Shoemaker, J., Tettenhorst, D., 2018. Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington, DC.

Singh, R.K., Fernando, S., Baygi, S.F., Multari, N., Thagard, S.M., Holsen, T.M., 2019. Breakdown products from perfluorinated alkyl substances (PFAS) degradation in a plasma-based water treatment process. Environ. Sci. Technol. 2019 53 (5), 2731–2738. https://doi.org/10.1021/acs.est.8b07031.

Solder, J.E., Beisner, K.R., 2020. Critical evaluation of stable isotope mixing end-members for estimating groundwater recharge sources: case study from the South Rim of the Grand Canyon, Arizona, USA. Hydrogeol. J. 28 (5), 1575–1591. https://doi.org/10.1007/s10040-020-02194-y.

Solder, J.E., Beisner, K.R., Anderson, J.R., Bills, D., 2020. Rethinking groundwater flow on the South Rim of the Grand Canyon, USA: characterizing recharge sources to South Rim springs with noble gas data and groundwater age estimates. Hydrogeol. J. 28 (5), 1593–1613. https://doi.org/10.1007/s10040-020-02193-z.

Springer, A.E., Boldt, E.M., Junghans, K.M., 2017. Local vs. regional groundwater flow delineation from stable isotopes at western North America springs. Groundwater 55 (1), 100–109. https://doi.org/10.1111/gwat.12442.

Tobin, B.W., Springer, A.E., Kreamer, D.K., Schenk, E., 2017. Review: The distribution, flow, and quality of Grand Canyon Springs, Arizona (USA). Hydrogeol. J. 26, 721–732. https://doi.org/10.1007/s10040-017-1688-8.

U.S. Geological Surveyvariously dated, National field manual for the collection of water-quality data U. S. Geol. Surv. Tech. Meth. Water-Resour. Invest., Book 9, chapt 2022 A1 A10. http://pubs.water.usgs.gov/twri9A.

U.S. Environmental Protection Agency, 2022. Drinking water contaminants. U.S. Environmental Protection Agency database. [Accessed May 19, 2022, at https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations].

U.S. Geological Survey, 2022. USGS water data for the Nation: U.S. Geological Survey National Water Information System database. [Accessed May 19, 2022, at https://doi.org/10.5066/F7P55KJN].

Zainab, S.M., Junaid, M., Xu, N., Malik, R.N., 2020. Antibiotics and antibiotic resistant genes (ARGs) in groundwater: A global review on dissemination, sources, interactions, environmental and human health risks. Water Res 187, 116455.

Zukosky, K., 1995. An assessment of the potential to use water chemistry parameters to define ground water flow pathways at Grand Canyon National Park, Arizona. Las Vegas, University of Nevada, Retrospective Theses Dissertations 493.