Arsenic in groundwater in the Grand Canyon region and an evaluation of potential pathways for arsenic contamination of groundwater from breccia pipe uranium mining

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Abstract

The Grand Canyon in northern Arizona is an international tourist destination, a home or sacred place to many Native Americans, and hosts some of the highest-grade uranium deposits in the United States. Although potential contamination of water resources by uranium from mining activities is a concern, other elements commonly associated with these uranium deposits may pose a greater risk to human populations in the area. This study presents an assessment of arsenic in groundwater in the Grand Canyon area. First, sampling results for arsenic are presented and areas with elevated arsenic concentrations are discussed. Potential pathways of groundwater contamination by arsenic from uranium mines are then discussed to elucidate situations and conditions under which elevated concentrations of arsenic might be expected to become mobilized from breccia-pipe uranium mining activities. Results for arsenic in groundwater in the study area were available for 652 samples collected from 230 sites. Arsenic concentrations in groundwater ranged from less than reporting limits in 60 samples to a maximum concentration of 875 μg/L at Pumpkin Spring. About 88% (202) of the sites sampled had a maximum arsenic concentration below the drinking water standard of 10 μg/L. Available data from near former or current breccia-pipe uranium mines in the area indicate limited evidence to-date of mining effects on elevated arsenic in groundwater, although slow groundwater flow paths in the region may result in extended times of decades or more for groundwater to reach discharge locations. Post-mining entry of groundwater into the shaft and underground mine workings, with subsequent transport of metal-enriched groundwater offsite, may be a potential pathway of groundwater arsenic contamination from mining, although concentrations would likely be attenuated by contact with sedimentary rock units and dilution with native groundwater along flow paths. Monitoring of perched groundwater at reclaimed mine sites post-reclamation could provide
Introduction

The Grand Canyon in northern Arizona is an international tourist destination and home or sacred place to many Native Americans (Fig 1). The Colorado River, which carved Grand Canyon over 3 million years ago, is an important water resource in the region, providing for the water needs of 40 million people in the United States (U.S.) and Mexico [1]. Groundwater, however, provides for almost all water needs of residents and visitors in the immediate Grand Canyon area, and may come under increased pressure with likely decreasing recharge in a warming climate [2]. The Grand Canyon area also hosts some of the highest-grade uranium deposits in the United States. In 2012, about 400,000 hectares of federal land near Grand Canyon was withdrawn from future uranium mining for 20 years, subject to valid existing rights, owing to, among other issues, uncertainties of mining effects on water resources in the region (Fig 1) [3]. Since that time, the U.S. Geological Survey (USGS) has collected environmental data (e.g., [4]) and published investigations (e.g., [5–8]) to address these uncertainties and to provide information to decision makers who will determine if the mining withdrawal should be eliminated, extended, or made permanent.

Although potential uranium contamination of water resources from mining activities is a concern, other elements commonly associated with these uranium deposits may pose a greater risk to human populations in the area. Arsenic is a commonly occurring element in soils and rocks throughout the United States and around the world [11] and water in contact with these geologic sources may contain naturally occurring arsenic [12–14]. Elevated concentrations of arsenic also are present in the mineralized breccia pipe deposits in the Grand Canyon region where uranium is mined [15–19]. There is substantial evidence that chronic exposure to drinking water with high (> 10 μg/L) arsenic concentrations is associated with negative effects on human health including skin lesions and cancer of the lung, bladder, kidney, and liver [20]. Arsenic has a U.S. Environmental Protection Agency (USEPA) and World Health Organization safe drinking water standard of 10 μg/L, which is one-third of the 30 μg/L standard for uranium [21, 22].

This study presents an assessment of arsenic in groundwater in the Grand Canyon area. First, sampling results for arsenic are presented and areas with elevated arsenic concentrations are discussed. Potential pathways of groundwater contamination from uranium mines are then discussed to elucidate conditions under which elevated concentrations of arsenic might be expected to become mobilized from breccia-pipe uranium mining activities. Science questions addressed in this study include 1) what are observed concentrations of arsenic in groundwater samples in the Grand Canyon region, 2) are there areas with elevated arsenic concentrations in groundwater and what are possible explanations for these elevated concentrations, and 3) how might breccia-pipe uranium mining activities contribute to arsenic mobilization and transport in groundwater in the region. Information and analyses of groundwater data from this study help establish baseline concentrations of arsenic in water resources in the area with which to compare future monitoring efforts to document change in water chemistry that may be caused by mining activities. Discussion of conditions of arsenic mobilization from mining activities to groundwater provides regulators and scientists a conceptual model of how
mining activities could negatively affect water resources in the region and insight into possible best practices for ensuring the health of groundwater systems in the area.

**Study area**

The Grand Canyon region is sparsely populated with few wells available with which to delineate groundwater basins and flow paths. For this investigation, topographic watershed boundaries are used as a proxy for groundwater basin boundaries. The study area for this
investigation is comprised of watershed boundaries that drain to the Colorado River between Lees Ferry in the east and the Grand Wash Cliffs (near the eastern edge of Lake Mead) in the west (Fig 1). Groundwater is present in two systems in the Grand Canyon area: a shallower perched system in the Permian-age Kaibab Formation, Toroweap Formation, and Coconino Sandstone, with most groundwater in the system about 300 m below plateau land surface; and a deeper regional system in the Mississippian-age Redwall Limestone, the Devonian-age Temple Butte Formation, and the underlying Cambrian-age Muav Limestone of the Tonto Group that is >1,000 m below the plateau surface. Perched groundwater is only locally present in the Grand Canyon region, but the Redwall–Muav aquifer is a groundwater system present throughout the region except where the aquifer units have been eroded away within canyons. Groundwater age varies widely across the region, with some springs sites along the Kaibab Plateau discharging water only days to months old [23, 24] and water at other well and spring sites in the region thousands of years old [25, 26].

Uranium ore in the Grand Canyon area is hosted in solution-collapse features known as breccia pipes. These uranium deposits are unique in the world and have a unique International Atomic Energy Agency uranium deposit classification category [27]. Ore zones in these breccia pipes are found mainly in Permian-age stratigraphic units (Fig 2), primarily at the Coconino Sandstone, Hermit Formation, and Esplanade Sandstone horizons. Large scale uranium mining began in the area in the 1950s within a breccia pipe on the South Rim of Grand Canyon at the Orphan copper mine [28]. There are presently 11 former and 2 current (both in standby status as of 2022) breccia pipe uranium mines in the Grand Canyon region (Fig 1). Mining shafts installed at breccia pipe uranium mines in the Grand Canyon region may encounter perched groundwater, but the bottom of mine shafts are often hundreds of meters above the regional Redwall–Muav aquifer (Fig 2). Trace elements other than uranium including antimony, arsenic, barium, cadmium, cobalt, copper, mercury, molybdenum, nickel, lead, silver, strontium, vanadium, and zinc also may be enriched in mineralized breccia pipes in the region [29]. Many of these trace elements also occur at substantially lower concentrations in rock units and surface soils in the area [30].

**Arsenic occurrence and geochemical controls**

Arsenic is a relatively minor, but widely present, naturally occurring element in the Earth’s crust [32] and is present in many common rock-forming minerals, although not as a major component [33]. Sedimentary rocks, which comprise both the perched and regional groundwater systems in the Grand Canyon area (Fig 2), typically have crustal average arsenic concentrations ~5–10 mg/kg [33]. Sandstones, composed mostly of quartz and feldspars, often have the lowest arsenic concentrations, with averages of ~4 mg/kg [33]. Argillaceous (e.g., claystone and shales) rocks have a broader range and higher average of arsenic concentrations than sandstones, with a typical average of ~13 mg/kg, reflecting a larger proportion of sulfide minerals, oxides, organic matter and clays [33]. Carbonate rocks typically have low arsenic concentrations of ~3 mg/kg [33]. In an analysis of over 700 surface soil samples on the Coconino Plateau in northern Arizona, background soils (i.e., not collected inside a collapse feature) had a median arsenic concentration of <10 mg/kg and a maximum of 70 mg/kg [30]. Geochemical analyses of aquifer-related, sedimentary rocks collected from surface exposures in Grand Canyon National Park [34] revealed arsenic concentrations >20 mg/kg in 2 of the 17 units sampled, with the highest concentration of 29.8 mg/kg found in the lower Muav Limestone. Arsenic concentrations in mineralized breccia-pipe deposits in the region, however, can be substantially higher than naturally occurring arsenic in surrounding country rock, and may become a source of elevated arsenic in groundwater under favorable conditions. Arsenic is
commonly present in greatest concentrations in sulfide minerals and the most abundant arsenic ore mineral is arsenopyrite (FeAsS) [33], with other phases of cobaltite (gersdorffite series, tennantite, and enarite) also found in breccia pipe ore [16–18]. Available geochemical data from waste rock and drill core material at breccia-pipe uranium mines in the region indicate enriched arsenic concentrations as high as 5,060 mg/kg in Pigeon Mine waste rock [15]; 1,980
mg/kg in Kanab North Mine waste rock [15]; 15,300 mg/kg in Hack II Mine drill core [16]; and 105,000 mg/kg in the Pinyon Plain Mine deposit [17].

Arsenic may easily be released into waters under certain geochemical conditions. The transport and fate of arsenic in groundwater, however, may be difficult to predict because of the complex interplay of multiple controlling factors [35]. Indeed, a common characteristic of areas with elevated arsenic in groundwater is the large spatial variability in concentrations, leading to great difficulty in reliably predicting arsenic concentrations in a particular well even when results from nearby wells are available [33]. Geochemical controls on arsenic in groundwater include pH and oxidation-reduction potential, as well as the presence of iron oxides. Smedley and Kinniburgh [33] describe arsenic as possibly unique among the heavy metalloids and oxyanion-forming elements such as uranium, selenium, vanadium, and others, in that it is sensitive to mobilization at typical groundwater pH values (pH 6.5–8.5) and under both oxidizing and reducing conditions. In solution in water, the stable forms of arsenic are arsenate (As$^{5+}$) or arsenite (As$^{3+}$) oxyanions [36]. The aqueous monovalent arsenate anion H$_2$AsO$_4^-$ is expected to predominate in waters with pH between 3 and 7 and the divalent arsenic species HAsO$_4^{2-}$ would predominate in pH 7–11 (Fig 3) [37]. In mildly reducing groundwater, the uncharged arsenite ion HAsO$_2^{(aq)}$ would be favored [36]. The uncharged arsenite ion is less likely to be adsorbed on most mineral surfaces and is therefore more mobile than the more negatively charged arsenate oxyanion [38]. The sorption and desorption of arsenic onto aquifer materials also has been shown to be pH-dependent, with greater sorption of arsenate onto iron oxides found at pH values less than about 8.0 [13, 39] and elevated arsenic concentrations in groundwater through desorption of arsenic from metal oxides observed at values of pH exceeding about 8.5 [40]. In California’s Central Valley and in the Middle Rio Grande Basin of New Mexico, high pH values were cited as being conducive to desorption of arsenic from metal oxides in aquifer sediments [13]. In a water-quality investigation of principal aquifers of the western United States, Rosecrans and Musgrove [41] found that elevated arsenic concentrations in groundwater occurred more often under oxic groundwater conditions at pH values greater than 7 compared to arsenic concentrations in anoxic groundwater.

High arsenic concentrations in groundwater may be found in several environments [33]. Three that are relevant to this study are geothermal waters, aquifers with specific geochemical and hydrologic conditions, and areas with mining activity. Hydrothermal sources of arsenic are related to magmatic activity, including volcanic ash, and high concentrations of arsenic in hydrothermal waters result from arsenic being a volatile component of magma and highly water-soluble [32]. Hot springs may contain very high arsenic concentrations—for example, hot springs in Yellowstone National Park have arsenic concentrations as high as 10 mg/L [32]. Although the presence of high arsenic rocks or sediments along a groundwater flow path may be an important factor affecting arsenic concentrations in groundwater [13], aquifers may contain elevated concentrations of arsenic even when the sediments themselves are not particularly enriched. For example, high arsenic concentrations observed in groundwater (as high as 3.2 mg/L) in the Bengal Basin of Bangladesh are associated with sediment arsenic concentrations of <2–20 mg/kg [33]. What appears to be important in high arsenic groundwater sourced from sediments is long residence times that allow for extended groundwater-sediment contact without flushing arsenic out of the source material [33]. In a study of aquifers in the western United States, elevated arsenic in groundwater was mostly associated with premodern or mixed age groundwater [41] and the presence of groundwater with long travel times was cited as an important control on arsenic concentrations in the Central Valley in California, the Middle Rio Grande in New Mexico, and the Salt Lake Valley in Utah [13]. Additionally, geochemical conditions favorable for the accumulation of arsenic in groundwater include oxidizing conditions under high pH (>8.5) or strongly reducing conditions at circumneutral pH.
values \cite{33}. Finally, concentrations of arsenic in aquifers have the potential to become elevated when groundwater is exposed to mining ore or waste rock \cite{15, 42}. Processes for elevated arsenic concentrations in water often involve the release of arsenic from sulfide minerals as they are oxidized during mining operations \cite{33}.

**Data and methods**

Arsenic concentrations in groundwater samples from springs and wells in the Grand Canyon region were obtained from the USGS National Water Information System (NWIS) database \cite{43}. Analytical results from many of these sites have been broadly discussed in other studies of groundwater geochemistry in the region \cite{5, 25, 44–46}. Groundwater arsenic concentration data also were available from a USGS–National Park Service (NPS) sampling partnership from 2016 through 2017, during which time Grand Canyon National Park staff collected additional water samples for analyses by USGS laboratories while visiting spring locations in the park. These analytical results are publicly available from Unema et al. \cite{4}. Groundwater samples were collected with permission from the U.S. National Park Service (Research Permit GRCA-2019-SCI-0007) and the U.S. Forest Service (Authorization ID KAI93).
Samples from spring and well sites were collected in acid-rinsed sample containers, filtered through 0.45 μm capsule (Versapor® acrylic copolymer membrane) or Luer-Lok syringe (polymethersulfone) filters, and preserved to pH < 2 with Ultrax® grade nitric acid. For sample collection at well sites, first the wells were purged a minimum of three casing volumes and until stable parameters were reached (i.e., pH, water temperature, specific conductance, dissolved oxygen, and barometric pressure) [47]. Results from the collection, processing, and analysis of blanks and replicate samples were used to quality assure groundwater sample results. Inductively coupled plasma–mass spectrometry (ICP–MS) methods were used by USGS laboratories for quantifying arsenic concentrations in the filtered and preserved groundwater samples. Because groundwater samples were collected from sites near Grand Canyon over a period of decades, detection and reporting limits for arsenic results varied over time. For samples collected since 2009, the USGS Analytical Trace Element Chemistry Laboratory in Boulder, Colorado was used for laboratory analyses, and arsenic reporting limit and laboratory quality control results for the Boulder lab are discussed here. Mean and median detection limits for arsenic reported by the Boulder lab’s method are 0.04 and 0.01 μg/L respectively, based on 20 separate analysis runs of 18 blanks each [48]. This method calculates detection limits as the standard deviation of n blanks multiplied by the Student’s t-statistic at the 98.5% confidence level for (n-1) degrees of freedom. Quality control standard reference material (SRM) samples are analyzed by the Boulder lab in each analysis run at a frequency which exceeds 30% of all analyses, and the SRM standards are interspersed throughout the run to determine precision, accuracy, and instrument stability. Method accuracy and precision for arsenic results from National Institute of Standards and Technology (NIST) standard reference material SRM 1643d are 99% (based on percent recovery) and 0.8% (percent relative median absolute deviation), respectively [48]. Results presented with “<” in this manuscript are less than the reporting limit for samples analyzed during the sample-collection time period. Additional data on arsenic concentrations in water at breccia-pipe uranium mining sites near Grand Canyon from mining company reports were obtained from the Arizona Department of Environmental Quality (https://azdeq.gov/request-record). Geochemist’s Workbench software [49] was used to generate arsenic stability diagrams discussed in this manuscript. Descriptive and statistical analyses were performed using the R statistical platform and the NADA package for data analysis of censored environmental data [50, 51].

Results and discussion

Assessment of arsenic in groundwater in the Grand Canyon region

Quality control results. Eighty-seven pairs of environmental and replicate sample results for arsenic were available for the study area. Seven of these replicate pairs had arsenic values that exceeded the USEPA Maximum Contaminant Level (MCL) of 10 μg/L; these pairs had less than 2% difference between the environmental and replicate samples. The difference between all environmental and replicate samples ranged from 0 μg/L to a maximum difference of 1.2 μg/L (Fig A in S1 Fig, Table A in S1 Table). Dissolved arsenic results were available for 42 blank analyses. All but two were below the reporting limits; the two blank samples with recorded arsenic were both 0.02 μg/L. Based on this evaluation of replicate and blank quality assurance results, there is high confidence in environmental sample results > 1 μg/L and expected sampling and laboratory variability is ≤ 1.2 μg/L. Available replicate and blank results for other parameters and elements discussed in this manuscript are provided in Table A in S1 Table. To summarize these quality-control data, there is high confidence in sulfate and uranium results at similar levels as arsenic (i.e., > 1 μg/L), total dissolved solids at > 1 mg/L, tritium at > 0.5 pCi/L (based on 2 replicates), pH at 0.1 standard units (based on 2 replicates),
and dissolved oxygen at 0.1 mg/L (based on 2 replicates). Iron quality-assurance results periodically indicate the presence of sample contamination, with iron detections in blank samples as high as 5.7 µg/L and substantial discrepancies between replicates at <100 µg/L iron concentrations (e.g., replicates of 32 and 17 µg/L, 4 and 10 µg/L, 7.8 and 0.9 µg/L, 7 and 40 µg/L). Therefore, there is low confidence in accuracy or precision of iron concentrations below about 100 µg/L.

**Site-wide observations on arsenic concentrations.** Analytical results for arsenic in groundwater in the Grand Canyon region were available for 652 samples collected from 230 sites between June 1, 1977, and September 30, 2022. Site information and analytical results for all samples are available in Tables B and C in S1 Table, and mapped results are presented in Fig 4 [43]. Additionally, arsenic concentration results in this study may be further explored in the USGS online interactive map “Uranium and Arsenic in Groundwater in the Grand Canyon Region” (https://webapps.usgs.gov/uraniummap/). Of the 230 groundwater sites sampled, 48 are wells and 182 are springs. Springs primarily discharge along canyon walls and floors, located above, within, and below the Permian strata that host uranium ore in breccia pipes in the area. Wells are located on the plateaus above the Grand Canyon and have depths ranging from 24 m to more than 1,100 m (Table B in S1 Table).

Maximum observed arsenic concentrations at groundwater sites in the Grand Canyon region ranged from <1 µg/L at 52 sites to 875 µg/L at Pumpkin Spring (USGS Site ID 355459113195900, S1 in Fig 4). About 88% (202) of the 230 groundwater sites had a maximum arsenic concentration at or below the USEPA MCL of 10 µg/L (Figs 4 and 5), substantially less than the 95% of groundwater sites with uranium concentrations below the uranium MCL reported by Tillman et al. [8]. Of the remaining 12% of sites, all but three had maximum concentrations <40 µg/L. The sites with a maximum arsenic concentration above the MCL are scattered throughout the study area, but some general observations can be made. Of the 22 spring sites with a maximum arsenic concentration above the MCL that discharge along the Colorado River or its tributaries, all but Saddle Canyon spring (USGS Site ID 362135111541801, S2 in Fig 4) and Fence Fault Left spring (USGS Site ID 363100111504701, S3 in Fig 4) are located on the South Rim of the Grand Canyon. The springs with the highest maximum arsenic concentration are in the southwestern region of the study area on or near the Hualapai Indian Reservation.

Previous studies have indicated likely pH and redox controls on arsenic mobilization and transport in groundwater, and possible relations between arsenic and other water-chemistry constituents and properties including concentrations of sulfate, iron, total dissolved solids (TDS), and groundwater age, among others. Paired results for pH and maximum arsenic concentration at a groundwater site were available for 173 sites in the study area. For these samples, pH values ranged from 3.8 to 8.8, with a median of 7.7 (Fig B in S1 Fig), and arsenic was significantly (p-value = 0.003) but weakly (0.15) correlated with pH (Kendall’s tau; Fig B in S1 Fig). Paired dissolved oxygen (DO) and maximum arsenic concentrations were available for 152 groundwater sites. DO at these sites ranged from <1 mg/L to 11.5 mg/L, with a median of 7.2 mg/L. Based on the definition by Thiros et al. [52] of oxic waters having DO concentrations ≥ 0.5 mg/L, 10 sites (2.3%) in the study area are considered anoxic. DO was not correlated with arsenic concentrations at study area sites (Kendall’s tau; p-value > 0.05; Fig B in S1 Fig). Oxidation of sulfide minerals, especially in mining or mineralized areas, may influence arsenic levels in groundwater [33]. Maximum arsenic concentrations and available paired sulfate concentrations were evaluated for 185 sites in the study area, with sulfate ranging from 1.5 mg/L to 3,450 mg/L with a median of 73.0 mg/L (Fig B in S1 Fig). Sulfate was not correlated with arsenic concentrations at study area groundwater sites (Kendall’s tau; p-value > 0.05). Iron and arsenic concentrations may be correlated in sediments and reductive
dissolution of iron oxides may be important for mobilizing arsenic in groundwater [33]. Maximum arsenic concentrations and available paired iron concentrations were evaluated for 187 sites in the study area, with iron ranging from < 0.2 μg/L to 10,300 μg/L with a median of 4 μg/L (Fig B in S1 Fig). Iron was not correlated with arsenic concentrations at study area groundwater sites (Kendall’s tau; p-value > 0.05), although further investigation of iron in different oxidation states in water may provide more insight about the relationship. In an investigation of principal aquifers in the western United States, Rosecrans and Musgrove [41] found high arsenic concentrations to be associated with TDS concentrations greater than 500 mg/L. Paired arsenic and TDS sample results were available for 183 groundwater sites, with TDS concentrations ranging from 69 mg/L to 9,630 mg/L, with a median of 459 mg/L (Fig B in S1 Fig). TDS was not correlated with arsenic concentrations at study area groundwater sites (Kendall’s
Elevated arsenic has commonly been found in premodern or mixed-age groundwater in the western United States [41]. As a broad estimation of groundwater age in the study area, paired tritium and maximum arsenic concentrations were compared for 138 sites (Fig B in S1 Fig). Tritium samples at these sites ranged from -1 pCi/L to 33 pCi/L, with a median of 2.2 pCi/L. Elevated arsenic concentrations were not associated with either premodern (\(< 1.3 \text{ pCi/L} \) [25]) or modern groundwater in the study area. Although not known to be a control on, or commonly related to, arsenic in groundwater, uranium concentrations also were evaluated with arsenic at groundwater sites, owing to concern about uranium mining effects on groundwater-quality in the region (Fig C in S1 Fig). Paired results for uranium and maximum arsenic concentration at groundwater sites were available for 205 sites in the study area. For these samples, uranium values ranged from 0.114 μg/L to 231 μg/L, with a median of 3.7 μg/L. Uranium was not correlated with arsenic concentrations at study-area sites (Kendall’s \( \tau \); p-value > 0.05).

The specific geology and stratigraphic unit that spring sites discharge from is not always known for samples in this study, but some of the high arsenic values were found in travertine springs. Modern travertine-depositing springs and inactive travertine deposits are often located along faults in the Grand Canyon [26]. Pumpkin Spring (S1 in Fig 4), Travertine Falls Spring (maximum arsenic concentration = 243 μg/L, USGS Site ID 354522113264800, S4 in...
Fig 4) and Travertine Canyon above the mouth at River Mile 229 (maximum arsenic concentration = 100 μg/L, USGS Site ID 354503113252600, S5 in Fig 4) are active travertine-depositing springs on the Hualapai Indian Reservation in the western part of the Grand Canyon region. Pumpkin Spring is fault-controlled, and although it discharges from the saline Tapeats Sandstone, its warm temperature may indicate a deeper, geothermal source [26, 53]. Fence Spring (maximum arsenic concentration = 16.4 μg/L, USGS Site ID 363123111503101, S6 in Fig 4), located in the eastern portion of the Grand Canyon region and along the Fence fault zone, also is a travertine-depositing spring. High arsenic concentrations at these sites may be influenced by deep mantle mixing [26] and carbonate concentrations in groundwater [54]. Relationships between high arsenic and travertine have been found throughout the western United States, including Mammoth Hot Springs in Yellowstone National Park of Wyoming [55] and Montezuma Well located in the Verde Valley of Arizona [56, 57], and likely represent groundwater mixing with deep-earth hydrothermal fluids containing elevated arsenic concentrations [41].

Other groundwater sites with elevated arsenic concentrations do not have a clear source. Near Travertine Falls spring and Travertine Canyon spring, springs B-27-11 10 UNSURV (USGS Site ID 354406113263400, S7 in Fig 4, about 3 km south of Travertine Falls spring) and B-28-12 35 UNSURV (USGS Site ID 354550113313400, S8 in Fig 4, about 9 km west of Travertine Falls spring), have maximum arsenic values of 38 μg/L and 35 μg/L, respectively. Six mineralized breccia pipes with above-background levels of uranium are present on the west rim of Travertine Canyon. Billingsley et al. [58], however, found no obvious relation between locations or alignments of faults and breccia pipes in this area. Wooley Spring (USGS Site ID 365308112472301, S9 in Fig 4) is located north of the Grand Canyon on the Kaibab Indian Reservation and has a maximum arsenic value of 35.8 μg/L. Wooley Spring discharges from the Kayenta Formation of the Glen Canyon Group of Jurassic age, which is present in limited northern parts of the study area [59]. Havasu Spring (USGS Site ID 361303112411200, S10 in Fig 4), the primary source of water for the Havasupai Tribe in Supai Village, is a travertine spring with a maximum observed arsenic concentration of 17 μg/L. Supai Well No. 3 (USGS Site ID 361352112413201, W1 in Fig 4), a 46-m-deep alluvium well located two kilometers downstream of Havasu Spring, has been observed with arsenic values of 5.2 μg/L (2016) and 12 μg/L (1994).

Groundwater in Arizona, like much of the southwestern United States, has elevated arsenic concentrations when compared to the rest of the United States [14]. In drinking-water wells in the southwestern United States, arsenic was found to exceed the MCL more than twice as frequently than in drinking-water wells in the United States as a whole [52]. Primary sources of arsenic in Arizona groundwater include geothermal water and release from volcanic rocks [12, 14]. Water quality data through September 30, 2022 for 2,343 groundwater sites in Arizona outside of the Grand Canyon study area available in NWIS [43] (Fig D in S1 Fig) have a maximum arsenic concentration ranging from < 1 μg/L to 1,400 μg/L, with a median of 4 μg/L. 25% (653) of the Arizona groundwater sites not located in the study area have a maximum arsenic concentration that exceeds the USEPA MCL. The maximum arsenic concentration for all Arizona springs was from the Verde Hot Springs (USGS Site ID 342118111423201; Fig D in S1 Fig) sampled in 1979 (1,400 μg/L), which is classified by Foust et al. [56] as geothermally influenced. Verde Hot Springs is the only spring sampled in Arizona with a higher arsenic concentration than Pumpkin Spring. The maximum arsenic concentration in well samples for all Arizona was taken in 1978 at a 500-ft deep well, C-19-01 28ADC (USGS Site ID 314439112222201), located near the border of Mexico (830 μg/L; Fig D in S1 Fig). Although the Grand Canyon region contains groundwater discharge locations with high levels of arsenic, maximum arsenic concentrations at groundwater sites in the Grand Canyon study area...
are significantly less than maximum arsenic concentrations at other groundwater sites in Arizona (nonparametric Wilcoxon test; p-value \(< 4.0 \times 10^{-12};\) Fig E in S1 Fig).

**Groundwater samples near breccia-pipe uranium mines.** Few water-quality data are available from groundwater sites at or near uranium mining areas in the region with which to evaluate potential effects of mining activities on groundwater resources. The Pinenut Mine well (Site W2 in Fig 4) is located north of Grand Canyon on the Pinenut Mine site (Table 1) and is screened in the Mississippian-age Redwall Limestone. Available arsenic concentration data in the Pinenut Well have varied somewhat unpredictably over time, with concentrations before the most recent mining period observed at 6.2 μg/L (2009) and 13.5 μg/L (2012), during mining at 4.1 μg/L (2014), and after mine closure at 11 μg/L (2018). The closest spring to the Pinenut Mine, Willow 1 Spring (S11 in Fig 4), is located 7 km north of the mine and has been monitored by USGS since 2009, owing to its elevated uranium concentrations [8]. Arsenic concentrations at Willow 1 Spring have ranged from 0.6 μg/L to 3.1 μg/L in 26 samples from the site (Table C in S1 Table).

Two wells are regularly sampled by USGS at the Pinyon Plain Mine (formerly known as the Canyon Mine) located south of the Grand Canyon near the town of Tusayan (Table 1). The regional groundwater well at Pinyon Plain Mine (W3 in Fig 4), located on the mine site, is screened in the Redwall–Muav aquifer. In 13 samples collected from the regional well between 2003 and 2022, arsenic concentrations ranged from 0.16 μg/L to 0.5 μg/L (Table C in S1 Table). In 2017, an additional groundwater well was installed adjacent to the mine to monitor the perched groundwater of the Coconino Sandstone. Tillman et al. [8] hypothesized that potential effects from mining activities on groundwater would likely first be observed in the shallow system closest to the mine shaft and ore deposits. Arsenic concentrations in the perched well have decreased in the seven samples from this site, from 4.6 μg/L in 2017 to 0.51 μg/L in 2022 (Table C in S1 Table).

Pigeon Mine, a uranium mine north of Grand Canyon (Table 1), no longer has a well located on site, but a nearby monitoring well was recently installed (2022). Pigeon Canyon Monitoring Well (W5 in Fig 4) is about 4.5 km northeast of the mine site. The well is completed in the Coconino Sandstone aquifer and has a maximum arsenic concentration of 0.9 μg/L. There also are three springs nearby: Pigeon Spring (S12 in Fig 4) is about 2 km east of

Table 1. Breccia pipe mines and proximate groundwater sampling locations discussed in this manuscript.

<table>
<thead>
<tr>
<th>Mine name</th>
<th>Mine history 1</th>
<th>Nearby groundwater sites discussed 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinenut</td>
<td>Mining begun in 1980s, placed on standby in 1989, resumed in 2013, active until 2015 when the mine was closed and reclamation begun.</td>
<td>Pinenut Well (363003112440901); Willow 1 Spring (363357112440801)</td>
</tr>
<tr>
<td>Pinyon Plain</td>
<td>Uranium ore discovered in 1983, shaft completed but mine in standby as of 2022.</td>
<td>Pigeon Plain Mine Regional Well (355308112054101); Pigeon Plain Mine Perched Well (355254112054901)</td>
</tr>
<tr>
<td>Pigeon</td>
<td>In operation between 1985 and 1990</td>
<td>Pigeon Canyon Monitoring Well (364354112291401); Pigeon Spring (364327112303101); Willow Spring 2 (364210112310501); Wildband Spring (364259112303201)</td>
</tr>
<tr>
<td>Orphan Lode</td>
<td>Patented for copper mining in 1906, mining for uranium occurred between 1936 and 1969, subsequently abandoned.</td>
<td>Upper Horn Bedrock Spring (360439112084601); unnamed spring (360449112083701); unnamed spring (36043112083300)</td>
</tr>
<tr>
<td>Grandview 1</td>
<td>Mined for copper between 1893 and 1916, subsequently abandoned.</td>
<td>Miners Spring (360100111582001); Miners Spring at Trail in Hance Canyon (360059111581700); JT Spring (360025111571501); Red Canyon Spring (360020111560401); unnamed spring (360108111592600); unnamed spring (360128111591200)</td>
</tr>
</tbody>
</table>

1. Mine history from U.S. Geological Survey [31].
2. Site name and USGS site identification number.
3. Mined for copper but not uranium.

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the mine site, Willow Spring 2 (S13 in Fig 4) is about 1.5 km southwest of the mine site, and Wildband Spring (S14 in Fig 4) is about 2.2 km southeast of the mine site. Pigeon Spring has been sampled by USGS quarterly since 2016 because of high (>50 μg/L) uranium concentrations at the site. These high uranium concentrations, however, do not appear to be caused by nearby mining activities [60]. Arsenic concentrations from 32 samples at Pigeon Spring between 2012 and 2022 ranged from 0.3 μg/L to 2.2 μg/L (Table C in S1 Table). Arsenic values also are low at Willow Spring 2 and Wildband Spring, with maximum concentrations of 0.73 μg/L and 1 μg/L, respectively (Table C in S1 Table).

Orphan Lode Mine, commonly referred to as Orphan Mine, is an abandoned uranium mine on the South Rim of Grand Canyon (Table 1). Groundwater emerges in the Horn Creek drainage at the base of bedrock cliffs near the Redwall-Muav Limestone contact about 500 m down gradient of the Orphan Mine. Groundwater at the Upper Horn Bedrock Spring (S21 in Fig 4) has elevated uranium (as high as 293 μg/L) and arsenic concentrations mostly ranging from 5.3 to 10 μg/L with a single high arsenic value of 24.2 μg/L in March 2019. Groundwater infiltrates into alluvial material below these sites and re-emerges at two springs lower in the drainage (S22 and S23 in Fig 4) with lower values of uranium (7.2 to 39.3 μg/L) and arsenic (<2.5 to 7.7 μg/L). Investigation of evolution of the water using an extensive suite of geochemical tracers for Horn Creek groundwaters is the subject of another study [61].

Although not a uranium mine, the abandoned Grandview Mine (also referred to as Last Chance Mine) is a former breccia pipe copper mine on the South Rim of Grand Canyon (Table 1). The majority of the Grandview breccia pipe was located in the Redwall Limestone and the ore deposit was noted to contain substantial arsenic concentrations [62]. Nearby Miners Spring (S15 in Fig 4) and Miners Spring at Trail in Hance Canyon (S16 in Fig 4) are located about 0.6 km southeast of the mine and discharge from the Redwall-Muav aquifer. Arsenic results from six samples at Miners Spring between 2000 and 2016 range from 17 μg/L to 19.3 μg/L, and one available sample at Miners Spring at Trail in Hance Canyon in 1981 had a value of 20 μg/L. Alter et al. [62] concluded that, although north-trending fractures may preclude groundwater movement from Grandview Mine to Miners Spring, they may be hydraulically connected based on their proximity. Two other springs to the southeast of Grandview Mine, JT Spring (S17 in Fig 4) about 3.5 km southeast of the mine and Red Canyon Spring (S18 in Fig 4) about 5 km southeast of the mine, also discharge from the Redwall-Muav aquifer and have arsenic concentrations that exceed the MCL (maximum arsenic values of 14.4 μg/L and 17 μg/L, respectively). About 1.5 km to the west of Grandview Mine, two unnamed Redwall-Muav aquifer springs (S19, S20 in Fig 4) have maximum arsenic concentrations of 4.8 μg/L and 1.6 μg/L, respectively.

Conceptual models of possible breccia-pipe uranium mining effects on arsenic in groundwater

Arsenic concentrations elevated with respect to drinking water benchmarks are present in groundwater at some sites in the Grand Canyon region. With the exception of a few groundwater samples from the Pinenut Mine well and springs near the abandoned Orphan Mine, however, there is no observational evidence that groundwater at or near current or former breccia-pipe uranium mine sites is elevated in arsenic concentrations. This is especially apparent when comparing relative arsenic concentrations in groundwater near mine sites to naturally occurring arsenic from travertine springs in other parts of the study area. Because of substantial uncertainty about the rate and direction of groundwater flow in the area, however, lack of evidence of groundwater contamination at sites sampled to date does not exclude the possibility of contamination at future times or currently unmonitored locations. In this
section, we present conceptual models of possible impacts of breccia-pipe uranium mining activities on arsenic concentrations in groundwater and discuss the likelihood of different pathways of contamination.

**During mining operations**

During active mining, waste rock and ore are often piled at land surface within the fenced mining compound (Fig 2). Metals, including arsenic, will be readily leached from these materials when contacted by water [15], but mobilization of contaminated water offsite is unlikely, owing to the design of mine sites to drain internally to a lined retention pond (Fig 2). Dust may be blown from onsite materials to offsite areas where precipitation and runoff may mobilize available metals [63]. Transport from land surface downward to groundwater near mine sites, however, is unlikely during near-future time periods, owing to groundwater depth (>300 m to the C-aquifer near Pinyon Plain Mine) and lack of evidence of recent groundwater recharge (Pinyon Plain Mine wells have radiocarbon ages that indicate the mean age of the water is greater than 10,000 years old [64]). A recent investigation by Solder et al. [64] did reveal 8 of 47 groundwater sites in the area south of Grand Canyon with average mean groundwater age less than 500 years, and higher values of tritium, suggesting possible recent recharge that may indicate the potential for land-surface-to-groundwater transport on a decadal to centuries scale. Of these sites, only Horn Creek Alluvial Spring was near a former uranium mine and the rest were not located along likely groundwater flow paths near current or proposed uranium mines or known mineralized breccia pipes. Samples from all other groundwater sites in the region indicate average mean groundwater ages of thousands to tens of thousands of years [64]. Runoff generated from substantial rainfall near mine sites may encounter preferential groundwater recharge pathways (e.g., geologic faults) as it flows away from the mine, but these recharge events, if they occur at all, are likely to be infrequent and short-lived in the semi-arid study area.

At the mine sites, perched groundwater enters the mine shaft when the aquifer units are encountered during shaft construction, with the amount and duration of groundwater flow into the shaft varying by mine location (e.g., [65]). Groundwater entering the shaft will likely become highly enriched in metal concentrations. Total arsenic concentrations as high as 1,090 μg/L were reported from the sump at Hermit Mine [66] and have been reported as high as 299 μg/L in the shaft at Pinyon Plain Mine, which has yet to begin mining uranium [65]. Historically, and at the two current mine sites in the region (Pinyon Plain Mine and Arizona 1), excess water in mine shafts is managed by pumping water from the shaft to land surface where it is stored in containment ponds and evaporated (Fig 2), thus minimizing further infiltration or movement offsite during active mining operations.

As long as water entering the mine shaft is not permitted to accumulate, the mine site is adequately graded to eliminate offsite runoff, and the containment pond liner remains impermeable, metals contamination of groundwater, including arsenic, appears unlikely during normal active mining operations.

**Post mine closure and reclamation**

Reclamation and monitoring requirements of breccia-pipe mining sites have changed over time, from essentially abandonment of the Orphan Mine [28] to more recent requirements of 30-year post-mining groundwater monitoring at the Pinyon Plain Mine [67]. Most modern breccia-pipe uranium mines in the region are required to seal off water-bearing geologic units in the mine shaft, seal the shaft at land surface, and clean and re-grade surface features at the
mine, among other activities (e.g., [68, 69]). Mine operators also are permitted to place any remaining waste rock back in the shaft before sealing at land surface (e.g., [68]).

Mineralized breccia pipes are highly heterogeneous, containing both ore grade material and other rocks. Mine waste rock, although not high enough in uranium to be classified as ore, may contain elevated levels of arsenic and other metals and trace elements. Even low-grade waste material remaining at land surface may leach metals, including arsenic, when in contact with precipitation or runoff. Carver [70] analyzed stream sediments near the Hack Canyon Mine Complex (Fig 1) and found a large increase in arsenic just below the mine (1,460 to 2,000 mg/kg) compared with upstream sediments (1.2 to 11.5 mg/kg), although farther downstream concentrations were reduced to near background levels (0.97 to 8.9 mg/kg). Otton et al. [15] analyzed sediment samples and performed leachates on material from reclaimed uranium mines in the Grand Canyon region. Of the 212 sediment samples analyzed, arsenic concentrations in 25 were greater than 100 mg/kg, and in 8 were greater than 1,000 mg/kg. Leachate experiments on sediment samples indicated high solubility of arsenic over short periods of time, with concentrations increasing by orders of magnitude over a time interval of hours. For example, an ore sample from Hack Mine with 3,210 mg/kg arsenic produced an arsenic concentration in water of 2,020 μg/L when leached for 1 hour with simulated rainwater, a concentration of 13,800 μg/L after 24 hours, and 36,400 μg/L after more than 24 hours (with 300 mg/L bicarbonate added). Leachate concentrations from mine waste material also were heterogeneous (ranging from 3.8 to 799 μg/L), where some samples with lower arsenic concentrations in the sediment had higher concentrations in the leachate, which may be related to how the arsenic is bound to the sediment samples.

As previously discussed, however, leached metals from waste materials at land surface would need to transit a deep unsaturated zone to reach even the perched groundwater system in the region, and any runoff from these materials away from the mine site, although it may encounter preferential groundwater recharge pathways as it flows away from the mine, would likely be infrequent and short-lived in the semi-arid study area. An improperly sealed shaft at land surface could allow meteoric water to contact waste rock and mine workings. As described by Alter et al. [62], mining activity creates substantial open spaces and, if stormwater infiltration were to occur, sulfate mineral suites that are highly soluble in acidic water will cause the downward movement of metals.

After mining activities have ceased and the mine site has been reclaimed, any groundwater entering the shaft would no longer be pumped to the surface for evaporation. Although modern clean closure practices require the sealing of groundwater-bearing units in the shaft, there is no available long-term observational evidence of the effectiveness of this practice for eliminating water entering the post-reclamation shaft. Additionally, historical breccia-pipe uranium mining in the region likely did not include such shaft-sealing requirements. Water entering the shaft at a post-reclamation mine site would contact enriched metal concentrations in waste rock in the shaft or mine workings in the breccia pipe, altering the chemistry of the water. If water moves from the shaft to groundwater near the mine, highly enriched water may be transported to the surrounding aquifer. Bern et al. [42] conducted laboratory experiments simulating the evolution of native groundwater interacting with breccia pipe uranium mine ore material and moving away from the mine. Batch experiments were performed to simulate contact of groundwater with uranium-rich and sulfide-rich ore material, movement of this mine water downgradient into an anoxic then an oxic environment, and then water-rock interactions along groundwater-flow paths in sedimentary rock aquifer material. Results showed an increase of one to three orders of magnitude in arsenic concentrations for groundwater in contact with ore samples, with mostly decreasing concentrations during the change from reducing to oxidizing conditions, and further reductions in arsenic concentrations during contact with
sedimentary rock material. After long-term contact with most sedimentary rock material, arsenic concentrations had returned to nearly the original natural groundwater conditions, with the exception of Redwall Limestone in contact with uranium-rich ore material and Coconino Sandstone in contact with both ore materials, which remained substantially elevated (as high as 224 μg/L) relative to drinking water benchmarks. These experiments show that metals can be released during groundwater contact with ore material and arsenic concentrations may be attenuated by oxidizing water conditions and contact with many sedimentary rock units, but that arsenic concentrations may remain elevated in groundwater in conditions that occur in the perched Coconino Sandstone aquifer and the upper portions of the regional Redwall-Muav aquifer. Arsenic concentrations that may be mobilized from mining sites in either the perched or regional aquifers, however, will likely be decreased through mixing with native groundwater along flow paths.

There are currently no data that indicate elevated arsenic concentrations in groundwater that originated at breccia-pipe uranium mines are moving away from reclaimed uranium mines in the region. Groundwater flow paths are slow in most of the areas near mines, however, meaning possible elevated metals concentrations may take decades or more to reach spring discharge locations. Eliminating water from entering reclaimed mine shafts could help reduce or prevent transport of mine-contaminated water to surrounding groundwater, but the effectiveness of shaft-sealing practices has not been evaluated through observational data. Also, although modern breccia-pipe uranium mines are required to prevent water from entering the shaft, it is unclear if previously reclaimed or abandoned mines in the region all had this same requirement. Although the Pinyon Plain Mine Aquifer Protection Permit [67] requires monitoring of groundwater quality in the perched aquifer downgradient of the mine site for 30 years post-closure, mining has yet to begin at the site (2022), meaning information from these groundwater monitoring data will not be available for decades to come. Installation of monitoring wells and monitoring of groundwater quality in perched groundwater near a previously reclaimed uranium mine in the region could provide valuable data on the effectiveness of current and historical clean-closure practices.

**Summary and conclusions**

The Grand Canyon area hosts some of the highest-grade uranium deposits in the United States. Since the 20-year withdrawal of federal land from future uranium mining near Grand Canyon began in 2012, the USGS has collected environmental data and published investigations to provide information to decision makers who will determine if the mining withdrawal should be eliminated, extended, or made permanent. Although potential uranium contamination of water resources from mining activities is a concern, arsenic contamination may potentially be a greater risk to human populations in the area. This study presents an assessment of arsenic in groundwater in the Grand Canyon area. Analytical results were available for 652 samples collected from 230 groundwater sites (182 springs and 48 wells) between June 1, 1977, and September 30, 2022. About 88% (202) of the groundwater sites had a maximum arsenic concentration below the drinking water benchmark of 10 μg/L, with all but 3 of the 28 sites with exceedances having a maximum arsenic concentration <40 μg/L. Elevated concentrations in most high-arsenic groundwater sites in the study area are likely influenced by natural geothermal sources. Groundwater data available from near former or current uranium mines are sparse. Maximum arsenic concentrations exceed the MCL in springs near Orphan Lode Mine and the regional groundwater well at Pinenut Mine, but it is unclear if these exceedances are a result of past mining activities. Potential pathways of groundwater contamination from uranium mines were evaluated to elucidate conditions under which elevated concentrations of
arsenic might be expected to become mobilized from breccia-pipe uranium mining activities. If water enters the shaft at a post-reclamation mine site, it will likely contact enriched metal concentrations in waste rock or mine workings in the breccia pipe and may transport elevated arsenic concentrations into surrounding perched groundwater, although these concentrations may be attenuated by contact with sedimentary rock units and dilution with native groundwater. Modern breccia-pipe uranium mines are required to seal water bearing geologic units prior to mine closure, but the effectiveness of shaft-sealing practices has not been evaluated through observational data. Monitoring perched groundwater near a previously reclaimed uranium mine could provide valuable data on the effectiveness of clean-closure practices to protect groundwater resources.

Supporting information

S1 Fig. A. Boxplots comparing absolute difference in arsenic concentration between environmental and replicate groundwater samples in the Grand Canyon study area for different ranges of arsenic concentration. B. Relation between maximum arsenic concentration at a groundwater site and select water-quality properties and constituents for all sites (top group) and only sites with maximum arsenic concentrations greater than the maximum contaminant level (MCL) of 10 μg/L (bottom group). C. Relation between maximum arsenic concentration and uranium concentrations at all groundwater sites at which both results were available. D. Map of the maximum arsenic concentration observed at 2,343 groundwater sites in the State of Arizona outside the Grand Canyon study area. E. Boxplots comparing the distributions of maximum arsenic concentrations at groundwater sites in the Grand Canyon study area and groundwater sites in the rest of Arizona.

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