 doi:10.20944/preprints202208.0077.v2

Article

Uranium in Waters of the Southern Colorado Plateau: Implications for The Navajo Nation

Kevin D. Webster[a,b,*], Kenneth J. Locey[c], Jon D. Pelletier[d], Jonathan Credo[e], Jani C. Ingram[f] and Barbara A. Klein[a]

[a] Diné College, School of Science, Technology, Engineering and Math, Tsaile, Arizona 86556, USA
[b] Planetary Science Institute, Tucson, Arizona 85719, USA
[c] Center for Quality, Safety and Value Analytics, Rush University Medical Center, Chicago, Illinois 60612, USA
[d] University of Arizona, Department of Geosciences, Tucson, Arizona 85721, USA
[e] University of Arizona, College of Medicine, Tucson, Arizona 85721, USA
[f] Northern Arizona University, Department of Chemistry and Biochemistry, Flagstaff Arizona 86011, USA
* Correspondence: Planetary Science Institute 1700 East Fort Lowell, Suite 106, Tucson, AZ 85719-2395, USA; webster@psi.edu

Abstract: Uranium (U) is enriched in the waters of the southern Colorado Plateau, including waters of the Navajo Nation. The region has naturally occurring U in rocks and a history of U mining which may increase U concentrations in waters. Despite prior research into the concentration of U in the waters of the Navajo Nation, a framework has not been established to understand the variation of U in the region's groundwater. To this end, we examined data from six studies to establish where and why U is likely to be enriched in waters of the southern Colorado Plateau. We show that U concentrations are related to the presence of U-rich rock bodies, elevation, and local aquifer salinity. Additionally, we show that U concentrations in waters downstream from abandoned U mines are higher than in waters that are not downstream from mines, and that the area around mines has an elevated U concentration relative to background U concentrations. Our work can act as a guide for local water withdrawal, regional water remediation and mitigation efforts, and provides a means for understanding the geographical patterns of U concentration in waters of the southern Colorado Plateau.

Keywords: Uranium; Groundwater; Colorado Plateau; Navajo Nation; Chinle Formation

1. Introduction

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 23 September 2022 doi:10.20944/preprints202208.0077.v2

Surface water is scarce on portions of the Colorado Plateau and elevated U in groundwater further complicates water access (Hoover et al., 2017; Credo et al., 2019; Jones et al., 2020). Water scarcity is driven by a low average annual rainfall that is below 20-30 cm per year in some places (Credo et al., 2019; Jones et al., 2020; Ingram et al., 2020). Rainfall in the region is expected to decrease as a result of climate change and groundwater is expected to become more important in the region (Udall and Overpeck, 2017). Enrichments of U in groundwater pose health concerns for people and animals, such as increases in kidney and autoimmune disease prevalence (USDHHS 2013; Hund et al., 2015; Erdei et al., 2019; Rock et al., 2019; Hoover et al., 2020; Ingram et al., 2020; Lister et al., 2021; Nozadi et al., 2022). Despite prior work on elevated U concentrations in the region, a framework for understanding where and why U is likely to be enriched has not yet been established. Such a framework will help improve the well-being of people in the region.

The southern Colorado Plateau is the ancestral land of the Navajo (Diné) people and the current boundaries of the Navajo Nation are located entirely within the region (Figure 1A). Regional U mining began in the 1940s and continued through the 1980s in support of the efforts of the United States during the Cold War (Wenrich et al., 1989). The after-effects of U mining on environmental and public health have resulted in multiple remediation efforts by the US EPA. Currently, approximately 30 % of Diné people lack access to municipal water sources and rely on hauling water to meet their needs. However, water from these unregulated sources has been shown to have U concentrations above the recommended guidelines of 30 μg/L (Credo et al., 2019; Ingram et al., 2020).

U occurs naturally in rocks on Earth and common U bearing rocks include shale and granite (Turekian and Wedepohl, 1961). U tends to dissolve when waters have high Eh and low pH, and is less soluble in waters with low Eh and intermediate pH (Goodwin, 1982). The tailings and materials from U mines are known to contribute to elevated U concentrations in waters through the oxidation of sulfides which decreases the pH (Hoover et al., 2017; Ingram et al., 2020). U also forms complexes with the bicarbonate anion that increase its mobility (Campbell and Ingram, 2014).

More than 1200 mining related features are located in the southern Colorado Plateau (O'Rear, 1966; EPA, 2006). U mining in the region largely focused on the Shinarump Conglomerate Member of the Chinle Formation (Chinle Fm.), and the Salt Wash Member of Morrison Formation (Figure 1B) (Rosenzweig et al., 1954; Evensen, 1958; Sanford 1982). The Shinarump Member is the stratigraphically lowest portion of the Chinle Fm. and tends to be enriched in U compared to other units due to the presence of ancient weathered volcanic debris (Weeks and Garrels, 1959). The presence of similar material also contributes to the presence of U in the Morrison Formation (Morrison Fm.) (Weeks and Garrels, 1959). Prior research has shown that the U concentrations of some waters in the region are related to mine drainage (Hoover et al., 2017). However, U concentrations in the context of regional aquifers or rock units have not been examined.

We gathered data from six published sources to better understand the factors determining the abundance of U in the groundwater of the southern Colorado Plateau. We hypothesized that U concentrations in groundwater should be correlated with regional drainage patterns and the presence of U rich rocks in the region. Additionally, we hypothesized that U mining in the region may influence the concentration of U in groundwater. The results from our work present a framework for understanding the geospatial concentrations of U in groundwater throughout the southern Colorado Plateau.

2. Geological Setting

The Colorado Plateau is bounded on its south, southeast, and southwest by the uplifted Mogollon Rim and in its east by the Southern Rockies (Elston and Young, 1991; Blakey, 2019). Internal regions of uplift in the plateau occur in the Chuska Mountains and in Black Mesa. The major drainages in the basin are the San Juan River, the Colorado River, and the Little Colorado River (Cooley et al., 1969). Rain falling on the western side of the Chuska Mountains either flows north and into the San Juan River or flows south where it eventually enters the Little Colorado River. These regional uplifts and depressions drive the flow of groundwater across the southern Colorado Plateau.

The Colorado Plateau is dominated by four major aquifers, the Coconino-De Chelly aquifer, the Mesaverde aquifer, the Uinta-Animas aquifer, and the Dakota-Glen Canyon aquifer. All four are present in the southern Colorado Plateau but the two most prominent are the Coconino-De Chelly aquifer, and the Dakota-Glen Canyon aquifer. In its southern portion, the Coconino-De Chelly aquifer experiences its highest elevations in the Chuska Mountains, flows south towards the little Colorado River, and discharges through springs in the walls of the Grand Canyon (Robson and Banta, 1995). This flow path roughly traces the elevation gradients in the region (Robson and Banta, 1995). Additionally, solids become dissolved as the water flows across and through the land (Gaillardet et al., 1999; Raymond, 2017), resulting in a pattern of increasing salinity from the Chuska Mountains to the region of discharge near the Grand Canyon (Robson and Banta, 1995). However the highest concentrations of total dissolved solids (TDS) occur in the southeastern portion of the aquifer (Figure 2A). Salinity of the Coconino-De Chelly aquifer can be used as a proxy for the amount of time that water has spent in the aquifer since groundwater tends to increase in salinity the longer it spends in an aquifer (Lakey and Krothe, 1996).

The Coconino-De Chelly aquifer is the surface-most aquifer in the southwest of Colorado Plateau (Figure 1B). In this region, rainwater may infiltrate and percolate through the sediments and rocks of Chinle Fm. into the Coconino-De Chelly aquifer (Johnson and Writ, 2009). Thus, in the south of the Coconino-De Chelly aquifer, the entire Chinle Fm., whose rocks have a median U concentration of 300 ppm., is in hydrological contact with the De Chelly Sandstone (Johnson and Writ, 2009). In places where the colorful Chinle Fm. is not the surface-most unit, the shale-rich formation acts as a barrier between more surficial waters and the Coconino-De Chelly aquifer (Ludington et al., 2007; Robson & Banta, 1995).

The Morrison Fm. is Jurassic in age and hydrologically comprises the Morrison aquifer, an isolated aquifer system within the Dakota-Glen Canyon aquifer system (Robson and Banta, 1995). Several members are recognized within the Morrison Fm., including the uraniferous Salt Wash Member (Rosenzweig et al., 1954; Robson and Banta, 1995). The Salt Wash Member is recognized by light-pink to buff colored sandstone with interbedded green and red mudstones and tends to comprise cliffs (Rosenzweig et al., 1954; Ludington et al., 2007).

3. Methods

3.1. Data sources and extraction

We relied on six published data sets to perform the analyses in this study. U concentrations in groundwater were obtained from data published by Credo et al. (2019). Briefly, the dissolved materials in regional waters — including U — were measured from unregulated water sources, namely springs, windmills, water storage tanks, and troughs. The detection limit for U in the samples was 0.047 μg/L. In locations that measured at or below the detection limit, the detection limit was used in the analysis. See Credo et al. (2019) for more information as to how these data were collected.

Characteristics and data regarding the salinity of the Coconino-De Chelly aquifer were obtained from Robson and Banta (1995). These authors identified where the Coconino-De Chelly aquifer is the surface-most aquifer in the region, as well as regions in the Coconino-De Chelly that ranged in concentration of TDS from 0-1 k, 1-3 k, 3-25 k, and > 25 k mg/L (Figure 2A). We extracted these regions from the published maps using the 'countcolors' package in R version 4.2.0 (Figure 2B) (R Core Team, 2022; Weller, 2019). The outlines of the identified collection of points were identified using the 'concaveman' package in R (Figure 2C) (Gombin et al., 2020), and transformed into polygons using the 'sp' package (Figure 2D) (Pebesma and Bivand, 2005). The digital boundary of the polygons generated for the salinity regions within the Coconino-De Chelly aquifer did not exactly correspond with published boundaries since the boundaries of the regions were marked in black and did not correspond to the target color in the image search. To account for the discrepancy, we adjusted the boundaries of the regions of interest by 3 km which approximately corresponded to the missing area.

Information about the locations where the Chinle and Morrison Fms. outcrop were obtained from the keyhole markup language (kml) versions of the geological maps of Arizona and Utah (Ludington et al., 2007). The boundaries of these formations were expanded by 1 km to account for potential imprecision in the plotted boundary of the formation.

Locations of abandoned U mines were obtained from the EPA (2006). Data published by the EPA (2006) and Credo et al. (2019) did not contain elevation data for the abandoned mines and water sources. Elevations for the mines and water sources were obtained by converting the locations of water sources and mines into kml files and uploading them to GPS Visualizer (Schneider, 2019). Water sources located within a particular subsection of the Coconino De-Chelly aquifer or rock unit were identified using the 'sp' package (Pebesma and Bivand, 2005).

Another feature that may influence U concentrations in water sources is the heterogeneity of U concentrations in the rocks. This feature may cause water sources that are downstream from mines to have enriched U concentrations not due to mining, but due to varying U concentrations. To address this, we downloaded aeromagnetic survey data to provide proxy information on the U concentrations at the surface (Hill et al., 2009). Apparent U concentration at a location was recorded in parts per million and tracked as bismuth 214 (Hill et al., 2009). Linear interpolation was used to predict the apparent U concentration at the locations of mines since their locations did not precisely coincide with the measured locations of the aeromagnetic surveys. We limited the analysis of mines and water sources to those in Arizona when analyzing the apparent U concentrations at mines and across the study region.

3.2. Statistical Analyses

We analyzed average U concentrations from 211 water samples. The U concentrations in the water sources on the Navajo Nation were not normally distributed and were log-transformed to better approximate a normal distribution for further analysis. Differences in the U concentrations in water sources in different regions of the Coconino-De Chelly aquifer were assessed using a Kruskal-Wallis rank-sum test followed by a Dunnett's Multiple Comparison test. The relationship between U concentrations and elevation was assessed through linear regression.

Differences between U concentration in waters where the Chinle or Morrison Fm. outcrop and waters from locations where these formations do not outcrop were assessed using Wilcoxon signed-rank tests. Since it was possible that the presence of samples in the Chinle or Morrison Fm. may have influenced the U concentration in regions where one of the formations does not outcrop, waters from locations where the Chinle or Morrison Fm. outcrops were compared against regions where neither formation outcrops.

The presence of mining on U concentrations in water sources was assessed over scales from 1 to 5 km. For individual wells, only mines upstream (i.e., at a higher elevation) from the well were considered. We restricted our analysis to mines upstream from water sources since water and its dissolved load flow downhill. The total number of mines upstream from a water source, the presence of at least one mine upstream from a water source, and the average apparent U concentration of the mines upstream on the U concentrations in samples were assessed through linear regression and Wilcoxon tests, respectively. Importantly, the location of mining features in the EPA dataset exhibits errors of approximately 200 – 300 m (EPA, 2006). Our analysis accounts for potential inaccuracies by allowing for a larger window (≥ 1 km upstream) than the uncertainty present in the location data.

Factors that may influence the U concentration in groundwater are likely correlated. For instance, elevation and the presence of a mine upstream from a well are inherently related because an elevation difference is necessary for the analysis. Additionally, a sample may also exhibit high U concentrations because it was downstream from a mine, but may have simultaneously been located in a U-rich rock formation. To begin understanding the causes between elevated U concentrations and the presence of U-rich rocks in the region, analyses were undertaken where water sources located within the Chinle Fm. were analyzed separately from water sources that were not. Additionally, upstream mining features were limited to those that were present within 2 km to minimize the relationship with elevation.

Multiple linear regression models were used predict U concentrations in water sources across the region and assess colinearities in the predictors of U concentrations. Multiple linear regression models were built using a publicly available online application developed by Rush University Medical Center for reproducible and automated regression analyses (https://rush-regression-workbench.herokuapp.com/). Statistically unimportant features were automatically removed via recursive feature elimination with cross-validation, a machine-learning methodology for identifying the most important features in a statistical model. Predictors used in the multiple linear regression models included the salinity region of Coconino aquifer where a well was located; the elevation of a point; whether a well was located in either the Morrison Fm. or the Chinle Fm.; and the number of mines within 1 and 2 km upstream from a well. Additionally, multiple linear regression models were constructed to predict U concentrations for water sources within the Chinle Fm. using the salinity region of Coconino aquifer, elevation, and the number of mines within 1 and 2 km upstream from a well.

3.3. Data Availability

All figures presented in the manuscript were made using R. All project code and files unique to this manuscript are hosted on GitHub and can be found at (https://github.com/websterkgd/USouthernColoradoPlateau).

4. Results

The U concentration in groundwater of the southern Colorado Plateau exhibited geographical trends (Figure 3). The U concentration in groundwater was related to amount of the TDS in the Coconino-De Chelly aquifer (Kruskal-Wallis rank sum test: $df = 2$, $\chi^2 = 15.9$; $p = 3{\cdot}10^{-4}$) (Figure 4A). The U concentration was not significantly different between regions where TDS ranges from 0 – 1 k mg/L and 1 – 3 k mg/L, but was higher in regions where TDS ranges from 3 – 25 k mg/L (Table 1). Additionally, the elevation (z) of groundwater sampling sites explained 11 % of the variation in U concentrations in the region, with lower elevations tending to have higher U concentrations than higher elevations ([U] = 10^(-0.0013·z + 2.59), $r^2 = 0.11$, $p = 5{\cdot}10^{-7}$) (Figure 4B). The pattern related to elevation was also recovered when the points at the detection limit were removed ([U] = 10^(-0.0009·z + 2.15), $r^2 = 0.09$, $p = 4{\cdot}10^{-5}$). However, the U concentration in groundwater of the Navajo Nation was not higher in regions where the Coconino-De Chelly aquifer is the surface-most aquifer compared to other regions (median $[U]_{Coconino\text{-}De\ Chelly}$ = 3.48 μg/L, $n = 39$; median $[U]_{other}$ = 2.43 μg/L, $n = 172$; Wilcoxon Rank Sum Test: $W = 3666$, $p = 0.36$).

U concentration in waters across the southern Colorado Plateau was influenced by the presence of particular rock formations. Sampling locations in areas where the Chinle Fm. outcrops exhibited higher U concentrations (median $[U]_{Chinle}$ = 6.54 μg/L, $n = 49$) than locations where the Chinle and Morrison Fms. are not present (median $[U]_{no\ Chinle/Morrisonn}$ = 2.26 μg/L, $n = 147$; Wilcoxon Rank Sum Test: $W = 2521$, $p = 0.002$) (Figure 4C). In contrast, U concentrations in areas where the Morrison Fm. outcrops were not statistically different (median $[U]_{Morrison}$ = 1.23 μg/L, $n = 15$) from locations where the Chinle and Morrison Fms. are not present (Wilcoxon Rank Sum Test: W = 1032, $p = 0.69$) (Figure 4D).

Average U concentrations were higher at sites downstream from mines compared to others (Table 2). The number of sites downstream from a mine, and the maximum number of mines upstream from a sampling site increased from 2 to 22 as the window of analysis expanded from 1 to 5 km (Table 2). The highest median (Q2) U concentration (9.52 μg/L)

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 23 September 2022 doi:10.20944/preprints202208.0077.v2

occurred if a site was within 2 km of a mine (Figure 5, Table 2), and the maximum difference occurred if at least one mine was present upstream within 3 km of the water source. Additionally, U concentrations in waters increased with the number of mines upstream from a sampling location, although the slope of the relationship decreased from 0.48 to 0.07 $\log_{10}[U]/N_{mines}$ (Table 2).

Within the Chinle Fm., the elevation of sites accounted for 32% of the variation of U concentration in the water source ([U] = 10^(-0.0014·z + 3.04), $r^2 = 0.32$; $p = 2\cdot10^{-5}$) (Figure 6A). Additionally, the presence of a mine within 2 km of a water source did not significantly influence the U concentration of the water source (median $[U]_{mine < 2\ km}$ = 16.5 μg/L, $n = 9$; median $[U]_{no\ mine}$ = 2.87 μg/L, $n = 40$; Wilcoxon Rank Sum Test: W = 253, $p = 0.06$) (Figure 6B). In contrast, elevation only explained 3 % of the U concentration in a water source in locations outside of the Chinle Fm. ([U] = 10^(-0.0009·z + 1.92, $r^2 = 0.03$; $p = 0.008$) (Figure 6C). Additionally, the presence of a mine within 2 km of a water source in locations outside of the Chinle Fm. resulted in statistically greater U concentrations in waters (median $[U]_{mine < 2\ km}$ = 9.39 μg/L, $n = 21$; median $[U]_{no\ mine}$ = 1.61 μg/L, $n = 141$; Wilcoxon Rank Sum Test: $W = 2143$, $p = 0.001$) (Figure 6D).

Multiple linear regression models exhibited varying degrees of explanatory power in explaining the U concentration in water sources, although all were statistically significant ($p < 0.05$). A model of U concentration vs. elevation; the number of mines within one and two kilometers; the salinity of the Coconino De-Chelly Aquifer; and the rock formation was able explain 13 % of the variance in U concentrations. The only significant individual predictor in this model was the presence of the Chinle Fm ($p = 0.001$). The multiple regression model examining water sources within the Chinle Fm. was able to explain 43 % of the variance in U concentration, but only the lowest and highest salinity regions of the Coconino De Chelly Aquifer were predictive of U concentration (0 – 1 k TDS: $p < 0.001$; 3 – 25 k TDS: $p = 0.03$). When all of the salinity regions were removed from the model, the model was able to explain 33 % of the variance in the U concentration and elevation was the most important factor for explaining U concentrations (z: $p < 0.001$).

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 23 September 2022 doi:10.20944/preprints202208.0077.v2

The data from aeromagnetic surveys showed that the Chinle Fm. exhibited higher apparent U than areas outside of the Chinle Fm. within the study region (median $[U_a]_{Chinle}$ = 2.5 ppm, n = 82959; median $[U_a]_{No\ Chinle}$ = 2.1 ppm, n = 267934; Wilcoxon Rank Sum Test: $W = 1.2\cdot10^{10}$, $p < 2.2\cdot10^{-16}$). Mines from the Chinle Fm. showed higher apparent U than areas that were not associated with the Chinle Fm. (median $[U_a]_{mines\ Chinle}$ = 2.6 ppm, n = 292; Wilcoxon Rank Sum Test: $W = 7\cdot10^{7}$, $p < 4\cdot10^{-11}$). Additionally, mines located outside of the Chinle Fm. exhibited higher apparent U concentrations than the study region as a whole (median $[U_a]_{mines\ outside\ Chinle}$ = 2.4 ppm, n = 489; median $[U_a]_{Study\ Region}$ = 2.2 ppm, n = 350893; Wilcoxon Rank Sum Test: $W = 9\cdot10^{7}$, $p = 6\cdot10^{-7}$). However, mines located in the Chinle Fm., did not show higher apparent U concentrations than those located outside of the Chinle Fm. (Wilcoxon Rank Sum Test: W = 75951, p = 0.13). Nor was the average apparent U concentration of the upstream mines a significant factor in predicting the observed U concentration at a water source (Table 2).

5. Discussion

5.1. A regional context for U in groundwater of the southern Colorado Plateau

Concentrations of U in waters of the southern Colorado Plateau are related to elevation, the presence of U-rich rocks in the region, the presence of mines upstream from a water source, and the salinity of the Coconino-De Chelly aquifer. These patterns are consistent with a model whereby U increases in groundwater as groundwater spends more time in contact with a U-rich source and additional inputs of U to regional waters from mining. Similar models have been used to predict the contaminant load of waters in other systems (Jasechko et al., 2017; Frei et al., 2020; Vautier et al., 2021).

5.2. U concentrations in waters and U-rich rocks

Uranium tends to be elevated in water sources that are located in regions where the Chinle Fm. outcrops (Figure 4C). Additionally, elevation is a predictor of U concentration in water sources that are in regions where the Chinle Fm. outcrops (Figure 6A). Furthermore, the water sources located within the Chinle Fm. appear to drive the overall relationship between U concentrations and elevation since elevation was a poor predictor of U concentration if a water source is not located in the Chinle formation (Figure 4B, Figure 6C).

As water flows in an aquifer, including the Coconino-De Chelly aquifer, it accumulates more solids the longer water has spent in the aquifer (Robson and Banta, 1995; Gaillardet et al., 1999; Raymond, 2017). In the upstream portions of the Chinle Fm. and Coconino-De Chelly aquifer, water has had little time to dissolve U and other solids, but downstream portions tend to contain more U and other solids (Figure 4a). Indeed, both elevation and the salinity of the Coconino-de Chelly Aquifer were important, colinear predictors of U concentration in the sampled waters. This finding suggests that elevation and salinity are behaving as proxies for the amount of time water has spent in the aquifer.

The patterns of U in groundwater across the southern Colorado Plateau exhibit globally observed trends in U enrichment in waters and provide context for regional observations. Positive correlations have been observed between U concentrations and salinity in systems in India and Iceland (Nizam et al., 2022; Papageorgiou et al., 2022). Regional work has shown that U concentrations increased in soil effluent from the Chinle region as the soils were exposed to water over longer periods — demonstrating the mobility of U in areas where the Chinle Fm. outcrops (Webber et al., 2021). Our results are also in agreement with work showing that radiation is higher in areas where the Chinle Fm. outcrops than in the surrounding regions (Johnson and Writ, 2009).

In contrast to water sources in the Chinle Fm., water sources within the Morrison Fm. did not show increases in U concentration (Figure 4D). Our observation that groundwaters associated with the Morrison Fm. are not enriched in U agrees with other work yielding similar observations from outcrops of the Morrison Fm. in Colorado where the Salt

Wash Member of the Morrison Fm. is in contact with groundwater (Phoenix, 1959). Low U concentrations in the waters of the Morrison Fm. were attributed to the Eh and pH of groundwater that inhibited the dissolution of U. Additionally, outcrops of the Morrison Fm. are limited in extent in the study region and this may limit the amount of time ground water spends in these units.

Limitations of our study reflect the limitations of available data. First, the depth to the groundwater table in the water sources used in this study is unknown. However, water sources in the region are thought to be sourced by shallow groundwater (Jones et al., 2020). This agrees with our observations that U concentrations tend to be higher in water sources that are located where the Chinle Fm. outcrops. The depth to the water table of each well in the study area potentially contributes to the variation in U concentration in the sampled waters. Velocity of groundwater flow is another source of variation in the data. The velocity of groundwater — especially shallow groundwater — may vary with the inputs to the system over time. Potentially illustrating this variation is that the U concentrations from two springs located near each other show yearly differences (Ingram et al., 2020). This suggests the total amount of water moving through the system in a given year may influence U concentrations. Work in other systems shows that the velocity of the flow of groundwater influences the concentration of dissolved material in groundwater (Lakey and Krothe, 1996). Samples used in our study were collected over a period of years, and flow variability represents a source of variation that we did not control for in our analysis.

5.3. U concentrations in waters and mines

U concentrations in the water sources were higher when a mine was present upstream (Figure 5; Table 2). This result agrees with a study that found elevated U concentrations within 6 km from an abandoned mine (Hoover et al., 2017). When the analyzed water sources were restricted to those that were present within the Chinle Fm., the presence of a mine upstream did not appear to influence the U concentration in the groundwater (Figure 6B). However, if the sampled water source was located outside of the Chinle Fm., the waters tended to show elevated U concentrations if a mine was present upstream (Figure 6D).

In areas where the Chinle Fm. outcrops, U concentrations from water sources from locations with a mining feature present upstream were statistically indistinguishable from those locations without a mining feature upstream. There are two likely explanations for this finding. First, U concentrations in these water sources are likely high because of interactions with U-rich material, and interactions with material from mines may not sufficiently increase U concentrations. This is potentially supported by our observation that the average apparent U concentration at mining sites within the Chinle Fm. was not higher than the Chinle Fm. as a whole. Second, our result may be a false negative. The median U concentration of 16.5 μg/L from sites with a mine upstream was the highest observed for any subgroup examined, and the p-value of 0.06 was near statistical significance; a likely consequence of small sample size. Future work on the ratio of $^{234}U/^{238}U$ of waters in the region where the Chinle Fm. outcrops may help determine the influence of a mine by assessing how long water from a water source has been in the aquifer (Johnson and Writ, 2009; Campbell and Ingram, 2014).

The increased U concentration in water sources downstream from a mine in locations where the Chinle Fm. does not outcrop yields itself to a few explanations. First, tailings or material from a mine may enter water from these locations. It is known that such materials influence U concentrations in waters (Winde, 2010; Hoover et al., 2017). However, apparent U concentrations from mining sites outside of the Chinle Fm. were also elevated compared to the surrounding regions. The increased U concentrations in these areas may represent natural heterogeneity in the rocks and thereby drive increased U concentrations in waters downstream, but could also be elevated because human disturbance has exposed or covered the ground surface with U rich material thereby increasing the measurements.

5.4. Implications for well placement and remediation

Our findings have implications for the ongoing remediation and mitigation of U in groundwater in the region. If possible, new water sources should not be installed in areas that are downstream from mines or located within the Chinle Fm. Further, residents should be taught to recognize the locations where the Chinle Fm. outcrops and to avoid using water from such locations, if possible. Additionally, remediation and or mitigation efforts of U in water sources should first be targeted to water sources in downstream regions where the Chinle Fm. outcrops since it is likely to be found at greater concentrations in these areas.

6. Conclusions

U concentrations in waters of the southern Colorado Plateau are related to elevation, locations where the Chinle Fm. outcrops, the presence of mines upstream from water sources, and the salinity of the Coconino-De Chelly aquifer. These relationships can be explained by the regional flow paths of groundwater, and additional interactions with U-rich material from mines. This work provides insight into elevated U concentrations in groundwater of the southwestern Colorado Plateau and begins the work of parsing natural contributions to increased U concentrations in the region and anthropogenic inputs. Our findings provide a basis for public education programs and for helping others understand which unregulated water sources are at risk for elevated U concentrations.

Several directions for future work exist. Future studies should assess the depth to the water table and more closely monitor the U concentrations in water sources over time to better understand possible temporal fluctuations in elements of concern. Additionally, forward modeling of groundwater flow may yield greater insight into variations in U across the region. Future regional assessments of U may analyze the stable isotopic concentration of U in water sources to better understand the flow paths and how much time water has spent in the aquifer.

Competing Interests

The authors declare no competing interests.

Acknowledgments

Funding for this work was provided by the NSF TCUP TEA-Center Grant [2054903] to K.D.W., and by the National Institute of Environmental Health Sciences, Grant [P50 ES026089] to J.C.I. K.D.W. thanks F.T. Boyd for discussions that led to the development of this project; J.T. Lennon for an introduction to geospatial data analysis using R; and the Delafield Public Library.

References

Blakey, R.C., 2019. Chapter 7: Pennsylvanian-Jurassic sedimentary basins of the Colorado Plateau and Southern Rocky Mountains, in Miall, A.D., (Ed.), The Sedimentary Basins of the United States and Canada. Elsevier 315-367. https://doi.org/10.1016/B978-0-444-63895-3.00007-3.

Campbell, N.R., Ingram, J.C., 2014. 4 - Characterization of $^{234}U/^{238}U$ activity ratios and potential inorganic uranium complexation species in unregulated water sources in the southwest region of the Navajo Reservation. In Ahuja, S. (Ed). Water Reclamation and Sustainability. Elsevier 77-94.

Cooley, M.E., Harshbarger, J.W., Akers, J.P., Hardt, W.F., 1969. Regional hydrogeology of the Navajo and Hopi Indian Reservations, Arizona, New Mexico, and Utah. United States Geological Survey Professional Paper 521-A. https://pubs.usgs.gov/pp/0521a/report.pdf

Credo, J., Torkelson, J., Rock, T., Ingram, J.C., 2019. Quantification of elemental contaminants in unregulated water across Western Navajo Nation. International Journal of Environmental Research and Public Health 16, 2727. https://doi.org/10.3390/ijerph16152727

Elston, D.P., Young, R.A., 1991. Cretacous-Eocene (Laramide) landscape development and Oligocene-Pliocene drainage of transition zone and Colorado Plateau, Arizona. Journal of Geophysical Research 96 (B7), 12389-12406. https://doi.org/10.1029/90JB01978

Environmental Protection Agency (EPA), 2006. Uranium Location and Database Compilation. Office of Radiation & Indoor Air Radiation Protection Division (6608J). Washington, DC, USA

Environmental Protection Agency (EPA). 2018 Navajo Nation: Cleaning Up Abandoned Uranium Mines. *Providing Safe Drinking Water in Areas with Abandoned Uranium Mines.* https://www.epa.gov/navajo-nation-uranium-cleanup/providing-safe-drinking-water-areas-abandoned-uranium-mines

Evensen, G.G., 1958. The Shinarump Member of the Chinle Formation, in Anderson, R.Y., Harshbarger, J.W. (Eds.), Black Mesa Basin (Norteastern Arizona). New Mexico Geological Society 9th Annual Fall Field Conferece Guidebook, p. 95 – 97

Erdei, E., Shuey, C., Pacheco, B., Cajero, M., Lewis, J., Rubin, R.I., 2019. Elevated autoimmunity in residents living near abandoned uranium mine sites on the Navajo Nation. *Journal of Autoimmunity* 99, 15-23. https://doi.org/10.1016/j.jaut.2019.01.006

Frei, R.J., Abbott, B.W., Dupas, R., Gu, S., Gruau, G., Thomas, Z., Kolbe, T., Aquilina, L., Labasque, T., Laverman, A., Fovet, O., Moatar, F., Pinay, G., 2020. Predicting nutrient incontinence in the Anthropocene at watershed scales. Frontiers in Environmental Science 7, 200. https://doi.org/10.3389/fenvs.2019.00200

Gaillardet, J., Dupré, B., Allègre, C.J., 1999. Geochemistry of large river suspended sediments: silicate weathering or recycling tracer? Geochimica et Cosmochimica Acta 63 (23-24), 4037-4051. https://doi.org/10.1016/S0016-7037(99)00307-5

Goodwin, B. 1982. Calculated uranium solubility in groundwater: implications for nuclear fuel waste disposal. Canadian Journal of Chemistry 60, 1759-1766. https://doi.org/10.1139/v82-241

Gombin, J., Vaidyanathan, R., Agafonkin, V., 2020. _concaveman: A Very Fast 2D Concave Hull Algorithm_. https://CRAN.R-project.org/package=concaveman

Jasechko, S., Perrone, D., Befus, K.M., Bayani Cardenas, M., Ferguson, G., Gleeson, T., Luijendijk, E., McDonnell, J.J., Taylor, R.G., Wada, Y., Kirchner, J.W., 2017. Global aquifers dominated by fossil groundwaters but wells vulnerable to modern contamination. Nature Geoscience 10, 425–429. https://doi.org/10.1038/ngeo2943

Johnson, R.H., Writ, L., 2009. Geochemical analyses of rock, sediment, and water from the region in and around the Tuba City Landfill, Tuba City, Arizona. U.S. Geological Survey Open-File Report 2009-1020.

Hill, P.L., Kucks, R.P., Ravat, D., 2019. Aeromagnetic and aeroradiometric data for the conterminous United States and Alaska from the National Uranium Resource Evaluation (NURE) Program of the U.S. Department of Energy. United States Geological Survey Open-File Report 2009-1129.

Hoover, J., Gonzales, M., Shuey, C., Barney, Y., Lewis, J., 2017. Elevated arsenic and uranium concentrations in unregulated water sources on the Navajo Nation, USA. Exposure and Health 9, 113-124. https://doi.org/10.1007/s12403-016-0226-6

Hoover, J.H., Coker, E., Barney, Y., Shuey, C., Lewis, J., 2018. Spatial clustering of metal and metalloid mixtures in unregulated water sources on the Navajo Nation – Arizona, New Mexico, and Utah, USA. Science of the Total Environment 633, 1667-1678. https://doi.org/10.1016/j.scitotenv.2018.02.288

Hoover, J.H., Erdei, E., Begay, D., Gonzales, M., NBCS Study Team, Jarrett, J.M., Cheng, P.Y., Lewis, J., 2020. Exposure to uranium and co-occurring metals among pregnant Navajo women. Environ Res. 190 (109943). https://doi.org/0.1016/j.envres.2020.109943

Hund, L., Bedrick, E.J., Miller, C., Huerta, G., Nez, T., Ramone, S., Shuey, C., Cajero, M., Lewis, J., 2015. A Bayesian framework for estimating disease risk due to exposure to uranium mine and mill waste on the Navajo Nation. Royal Statistical Society 178 (4), 1069-1091. https://doi.org/10.1111/rssa.12099

Ingram, J.C., Jones, L., Credo, J., Rock, T., 2020. Uranium and arsenic unregulated water issues on Navajo lands. Journal of Vacuum Science and Technology A 38. 031003. https://doi.org/10.1116/1.5142283

Jones, L., Credo, J., Parnell, R., Ingram, J.C., 2020. Dissolved uranium and arsenic in unregulated groundwater sources – Western Navajo Nation. Journal of Contemporary Water Research and Education 169, 27-43

Lakey, B., Krothe, N.C., 1996. Stable isotopic variation of storm discharge from a perennial karst spring, Indiana. Water Resources Research 32 (3), 721-731.

Lister, A., Froyum, J,. Credo, J., Ingram, J.C., 2021. Determination of uranium in sheep hearts from the Navajo Nation. Journal of Veterinary Medicine and Animal Science 4 (1), 1055.

Ludington, S., Moring, B. C., Miller, R. J., Stone, P. A., Bookstrom, A. A., Bedford, D. R., Evans, J. G., Haxel, G. A., Nutt, C. J., Flyn, K. S., Hopkins, M. J., 2007. *Preliminary integrated geologic map databases for the United States* Western States: California, Nevada, Arizona, Washington, Oregon, Idaho, and Utah. Version 1.3 USGS Open File Report 2005-1305.

Nizam, S., Dutta, S., Sen, I.S., 2022. Geogenic controls on the high levels of uranium in alluvial aquifers of the Ganga Basin. Applied Geochemistry 143, 105374. https://doi.org/10.1016/j.apgeochem.2022.105374

Nozadi, S.S., Li, L., Luo, L., MacKenzie, D., Erdei, E., Du, R., Roman, C.W., Hoover, J., O'Donald, E., Burnette, C., Lewis, J., 2022. Prenatal metal exposures and infants' developmental outcomes in a Navajo population. International Journal of Environmental Research and Public Health 19 (45). https://doi.org/10.3390/ijerph19010425

O'Rear, W.B., 1966. Summary and chronology of the domestic uranium program: U.S. Atomic Energy Commission. Technical Memorandum TM-182, p. 50.

Papageorgiou, F., McDermott, F., Van Acken, D., 2022. Uranium in groundwaters: Insights from the Leinster granite, SE Ireland. Applied Geochemistry 139, 105236. https://doi.org/10.1016/j.apgeochem.2022.105236

Pebesma, E.J., Bivand, R.S., 2005. Classes and methods for spatial data in R. R News 5 (2), https://cran.r-project.org/doc/Rnews/

Phoenix, D., 1959. Part 4. Occurrence and chemical character of groundwater in the Morrison Formation. In (R.M. Garrels and E.S. Larsen 3d, Ed.) Geochemistry and Mineralogy of the Colorado Plateau Uranium Ores. United States Geological Survey Professional Paper 320

R Core Team, 2022. R: A Language and Environment for Statistical Computing. Vienna, Austria. https://www.R-project.org/

Robson, S.G., and E.R. Banta. 1995. Ground Water Atlas of the United States, Arizona, Colorado, New Mexico, Utah. U.S. Geological Survey. HA 730-C

Rock, T., Camplain, R., Teufel-Shone, N.I., Ingram, J.C., 2019. Traditional sheep consumption by Navajo People in Cameron, Arizona. International Journal of Environmental Research and Public Health 16, 4195. https://doi.org/10.3390/ijerph16214195

Rosenzweig, A., Gruner, J.W., Gardiner, L., 1954. Widespread occurrence and character of uranite in the Triassic and Jurassic sediments of the Colorado Plateau. Economic Geology 49, 351-361.

Sanford, R.F., 1982. Preliminary model of regional Mesozoic groundwater flow and uranium deposition in the Colorado Plateau. Geology 10, 348-352.

Schneider, A. 2019. GPS Visualizer. https://www.gpsvisualizer.com/elevation

Turekian, T., and Wedepohl, H., 1961. Distribution of the elements in some major units of the earth's crust. Geological Society of America Bulletin 72, 175-192.

United States Department of Health and Human Services (USDHHS), 2013. Toxicological profile for Uranium. Agency for Toxic Substances and Disease Registry: Atlanta, GA, USA, 2013.

Udall, B., Overpeck, J., 2017. The twenty-first century Colorado River hot drought and implications for the future. Water Resources Research 53 (3), 2404-2418. https://doi.org/10.1002/2016WR019638

Vautier, C., Kolbe, T., Babey, T., Marçais, J., Abbott, B.W., Laverman, A.M., Thomas, Z., Aquilina, L., Pinay, G., de Dreuzy, J.-R., 2021. What do we need to predict groundwater nitrate recovery trajectories? Science of the Total Environment 788, 147661. https://doi.org/10.1016/j.scitotenv.2021.147661

Webber, Z.R., Webber, K.G.I., Rock, T., St. Clair, I., Thompson, C., Groenwald, S., Aanderud, Z., Carling, G.T., Frei, R.J., Abbott, B.W., 2021. Diné citizen science: Phytoremediation of uranium and arsenic in the Navajo Nation. *Science of the Total Environment* 794, 148665. https://doi.org/10.1016/j.scitotenv.2021.148665

Weeks, A.D., Garrels, R.M., 1959. Part 1. Geologic setting of the Colorado Plateau ores. In (R.M. Garrels and E.S. Larsen 3d, Ed.) Geochemistry and Mineralogy of the Colorado Plateau Uranium Ores. United States Geological Survey Professional Paper 320

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 23 September 2022 doi:10.20944/preprints202208.0077.v2

Weller, H., 2019. countcolors: Locates and Counts Pixels Within Color Range(s) in Images. https://CRAN.R-project.org/package=countcolors

Wenrich, K.J., Chenoweth, W.L., Finch, W.E., Scarbourough, R.B., 1989. Uranium in Arizona in geological evolution of Arizona, in Jenny, J.P., Reynold, S.J. (Eds.), Arizona Geological Society Digest 17, pp. 259-794.

Winde, D., 2010. Uranium pollution of the Wonderfonteinspruit, 1997-2008 part 1: Uranium toxicity, regional background and mining-related sources of uranium pollution. Water SA 36 (3), 239-256.

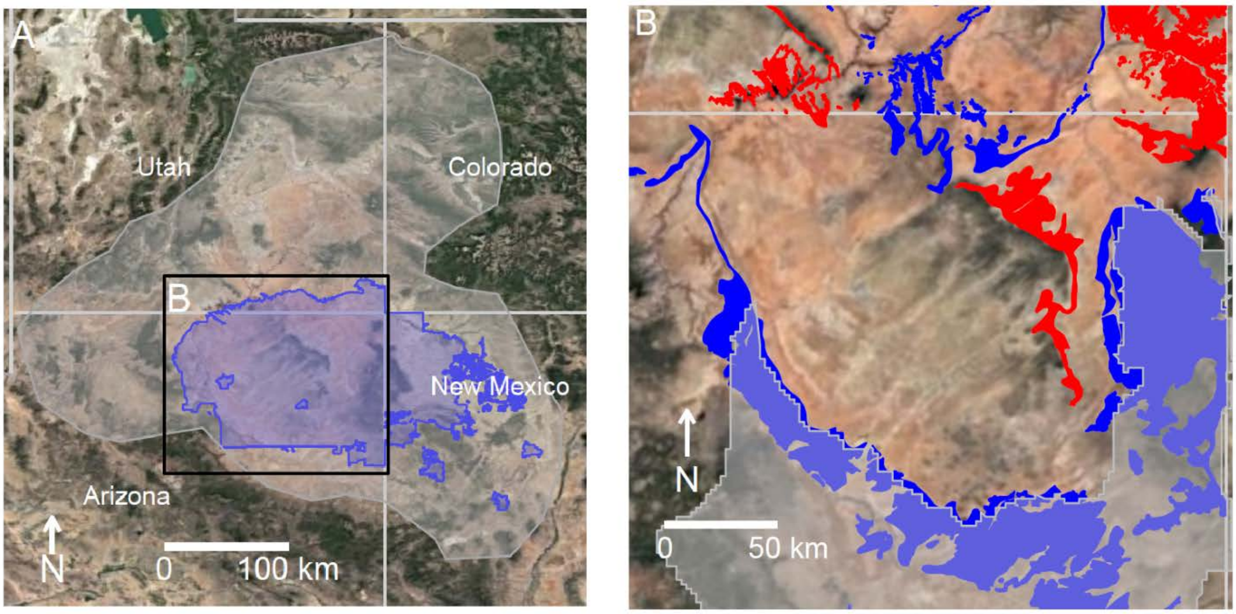

Figure 1: A) The location of the Colorado Plateau shaded in gray within the mountain-west region of the United States. Note the presence of the Navajo Nation and Hopi Reservation (blue) within the Colorado Plateau. B) The location of

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 23 September 2022 doi:10.20944/preprints202208.0077.v2

the study area showing the presence of the Chinle Formation (blue), Morrison Formation (red), and the area where the Coconino-De Chelly aquifer is the surface-most aquifer (gray). Satellite imagery from Google Earth.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 23 September 2022 doi:10.20944/preprints202208.0077.v2

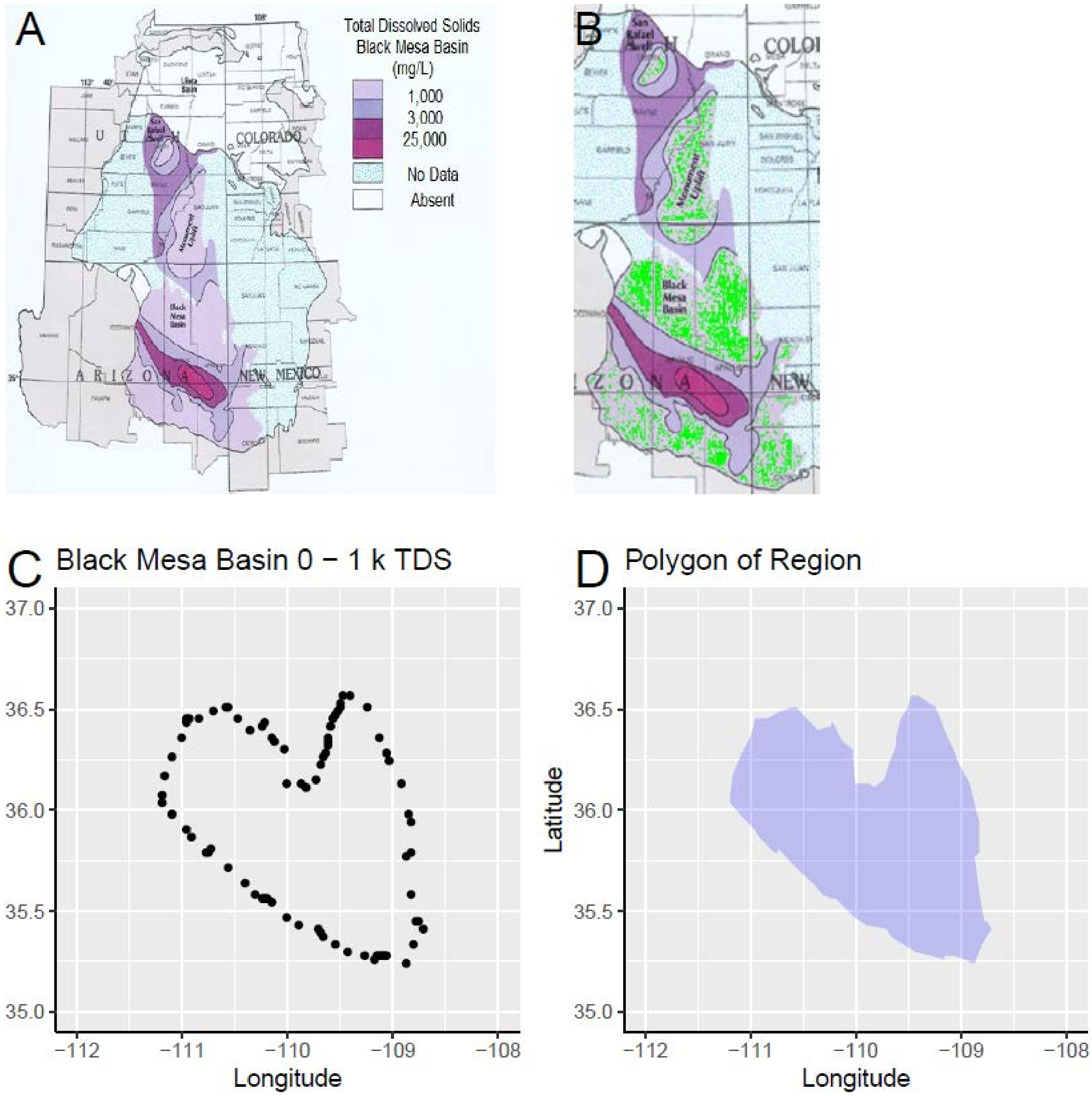

Figure 2: A) The regions of total dissolved solids in the Coconino-De Chelly aquifer from Robson and Banta (1995). B) A particular region with the aquifer was converted into a digital format depending on the color in the figure. C) Outlines of the identified regions were then obtained, and finally converted into polygons (D) for later analysis.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 23 September 2022 doi:10.20944/preprints202208.0077.v2

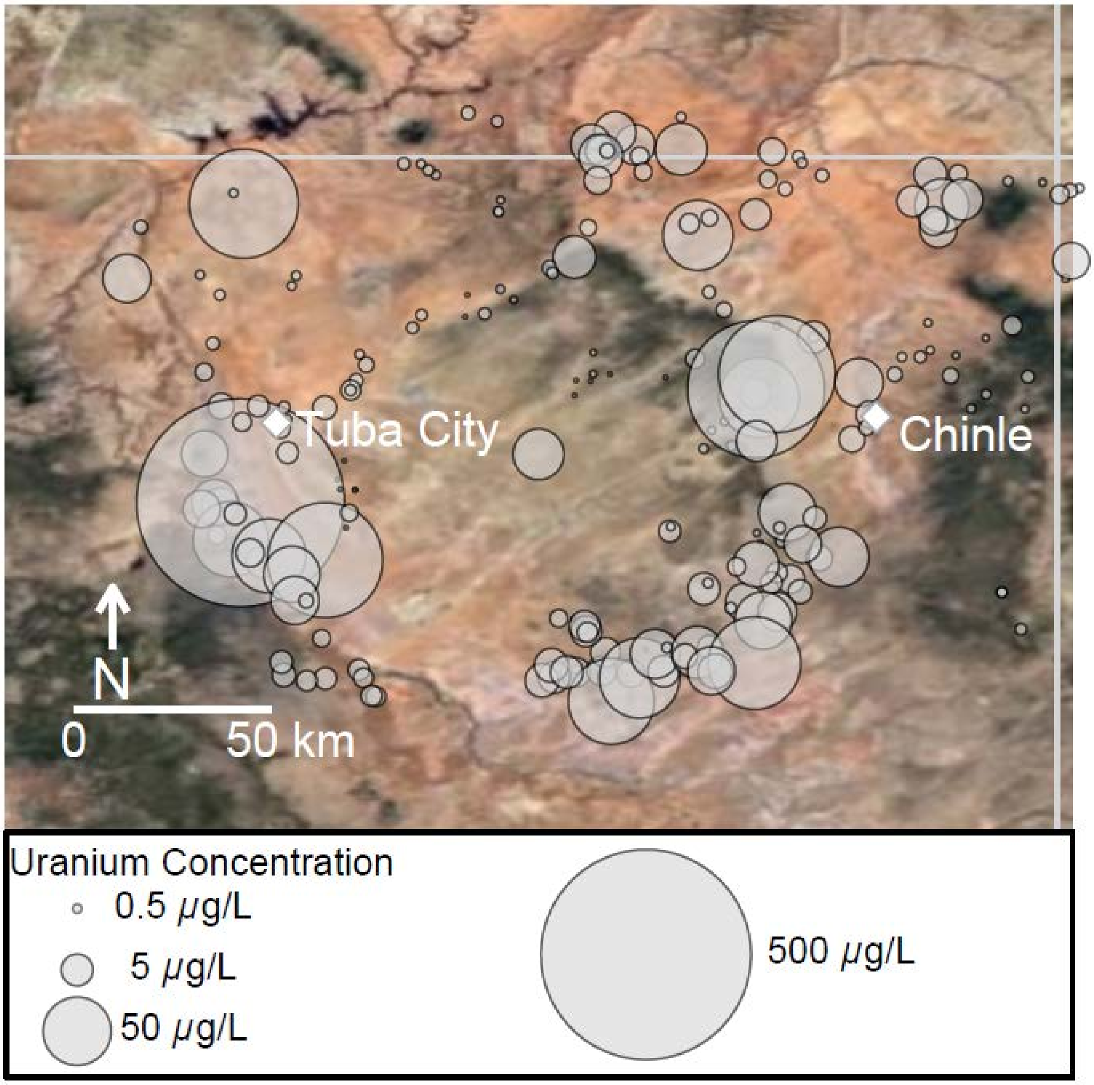

Figure 3: Visual representation of the concentration of uranium (U) concentration in unregulated water sources across the study region. The range of U concentration in the samples is from 0.047 μg/L to 490 μg/L. The towns of Chinle and Tuba City are shown for reference. Satellite imagery from Google Earth.

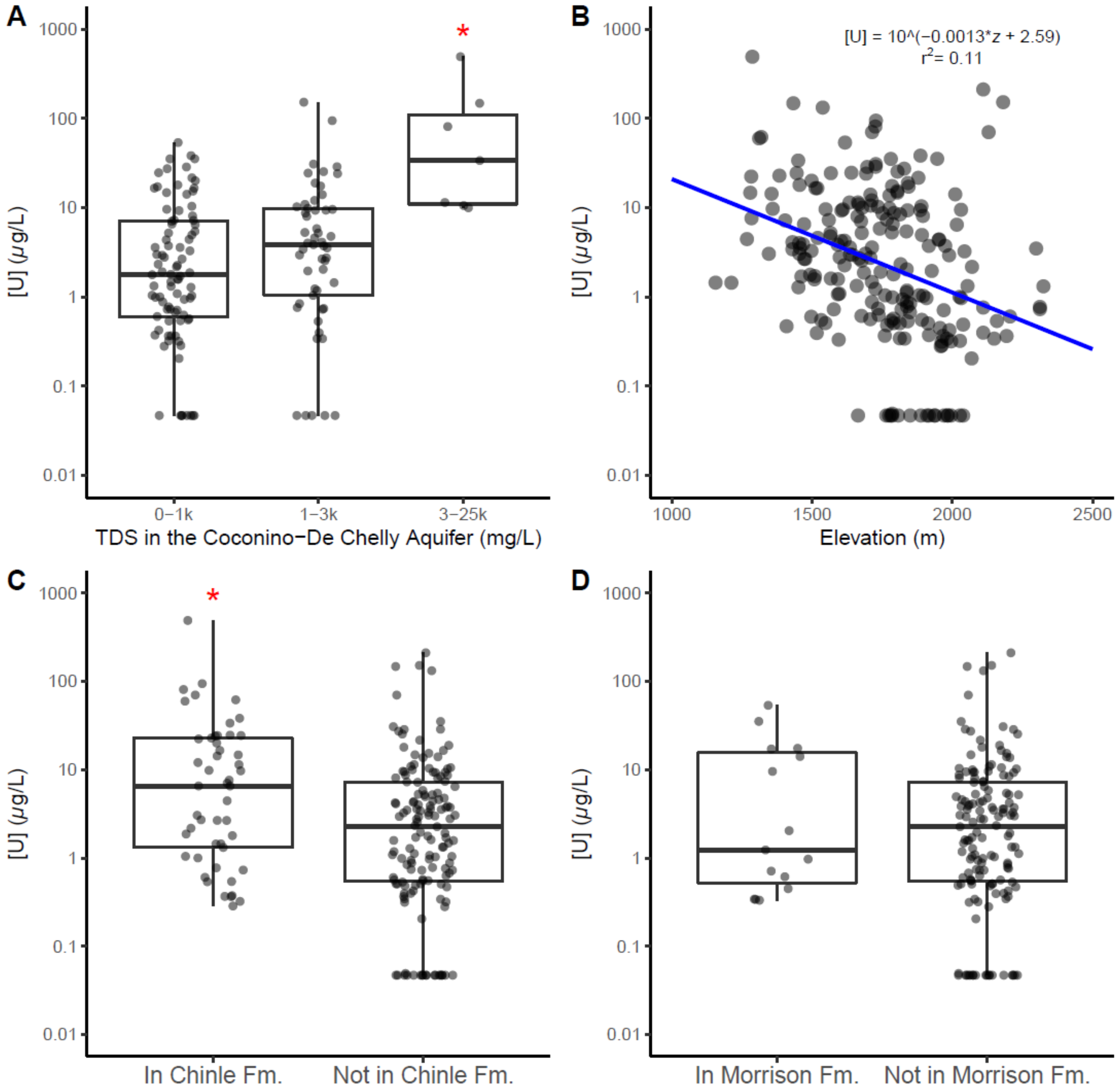

Figure 4: A) Boxplots showing the relationship between U concentrations in groundwater and Total Dissolved Solids region in the Coconino-De Chelly aquifer. The asterisk indicates that significantly higher U concentrations were observed in regions of the Coconino-De Chelly aquifer where TDS ranges from 3 – 25k mg/L. B) U concentrations in groundwater plotted against elevation. C) Boxplots showing the relationship between U concentrations in groundwater and whether a water source is located in a location where the Chinle Formation outcrops. The asterisk indicates that significantly higher U concentrations were observed in regions where the Chinle Formation outcrops. D) Boxplots

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 23 September 2022 doi:10.20944/preprints202208.0077.v2

showing the relationship between U concentrations in groundwater and whether a water source is located in a location where the Morrison Formation outcrops. Note that U concentrations are always expressed on a log_{10} axis.

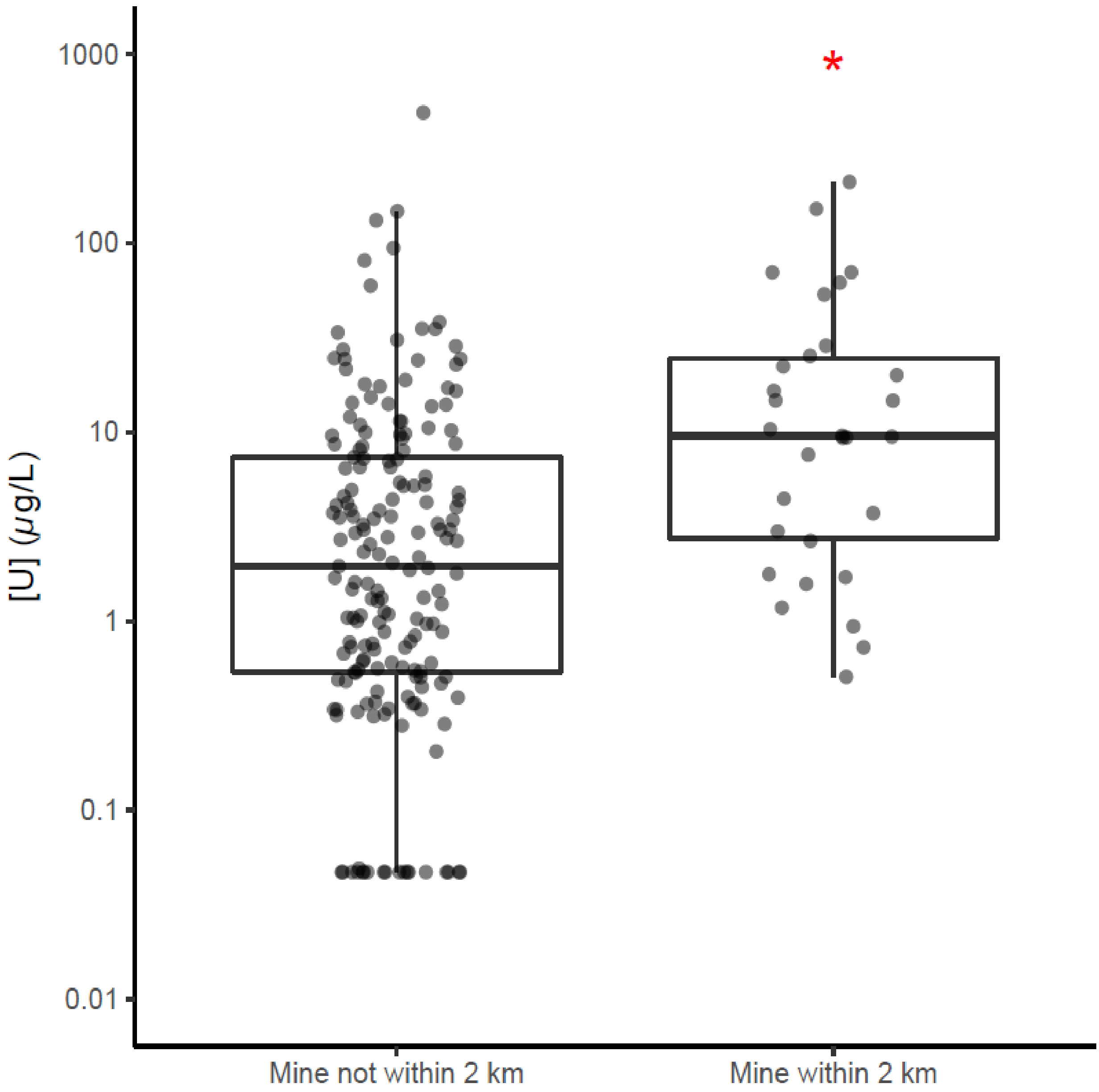

Figure 5: Boxplots showing the relationship between U concentrations in groundwater and whether a mine is located upstream and within 2 km of the water source. The asterisk indicates that significantly higher U concentrations were

 doi:10.20944/preprints202208.0077.v2

observed in sources that were within 2 km and downstream from a mine. Note that U concentrations are expressed on a log_{10} axis.

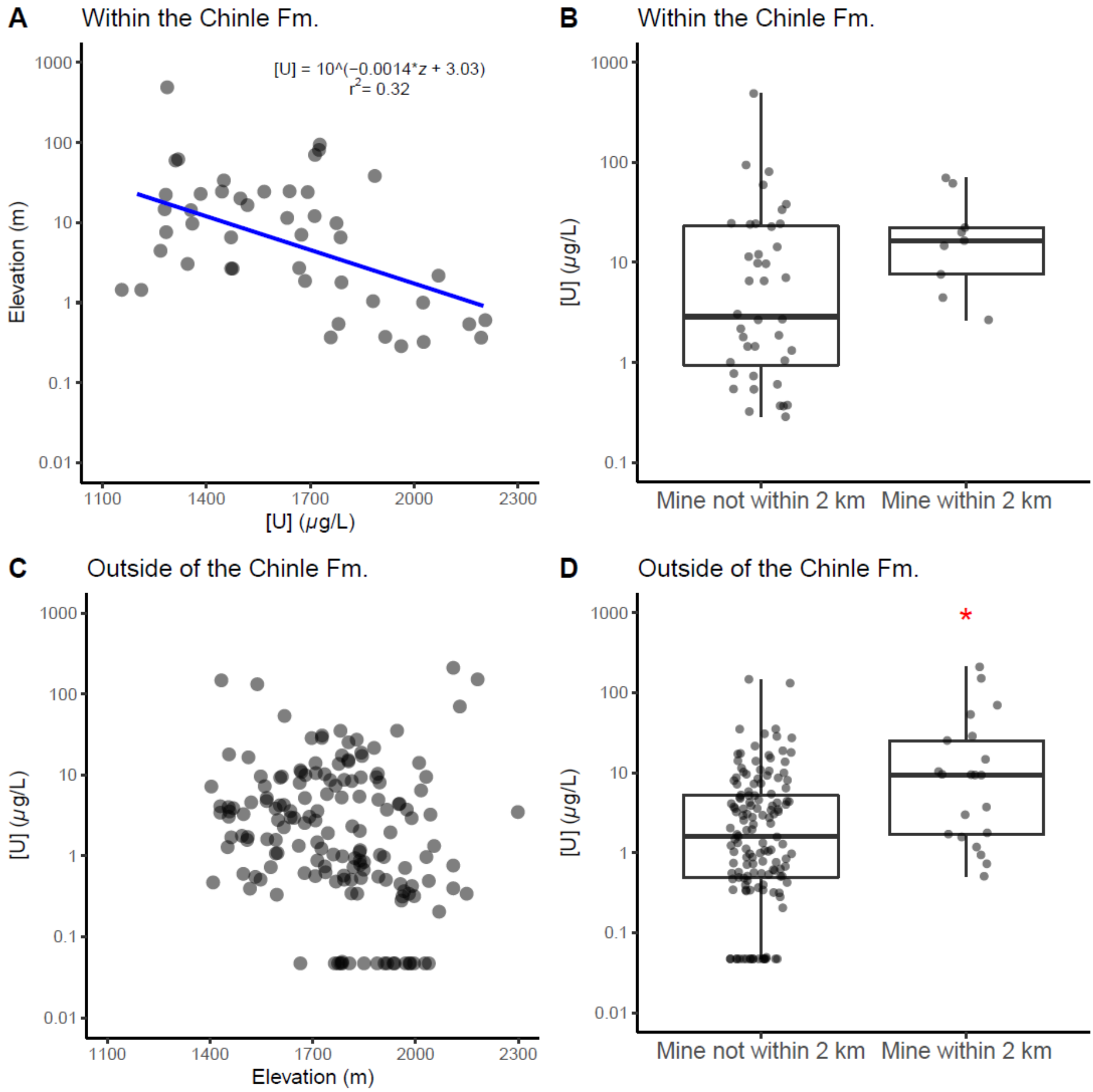

Figure 6: A) Within the Chinle Fm., the elevation of sample locations is an important predictor of the U concentration in a water source. B) Samples obtained from locations that were within 2 km of a mine within the Chinle Formation were statistically indistinguishable from those that were not in the vicinity of a mine. C) The elevation of sample locations is not an important predictor of the U concentration in a water source in locations outside of the Chinle Fm.

D) Samples obtained from locations that were within 2 km of a mine outside of the Chinle Formation exhibited statistically greater U concentrations compared to those that were not in the vicinity of a mine. Note that U concentrations are always expressed on a log_{10} axis.

 doi:10.20944/preprints202208.0077.v2

Table 1: Medians and sample sizes of water samples from different salinity regions in the Coconino-De Chelly aquifer.

TDS (mg/L)	Q1, Q2, Q3 [U] (μg/L)	No. of samples	*p:* Dunnetts's MC 0 – 1 k vs…
0 – 1 k	0.57, 2.17, 6.49	81	---
1 – 3 k	1.00, 4.01, 10.0	48	0.23
3 – 25 k	11.0, 33.7, 109	7	$4 \cdot 10^{-5}$

Table 2: Statistical relationships between average U concentrations and upstream mines

Distance to a mine	No. of sites with a mine upstream	Max. no. of mines upstream from a sample site	Wilcoxon rank-sum ($Q2[U]_{mine}$, $Q2[U]_{no\ mine}$) (W, p)	Linear Regression $\log_{10}[U]$ vs. $N_{mines\ upstream}$ (slope, r^2, p)	Linear Regression $\log_{10}[U]$ vs. $Q2[U_a]_{mines\ upstream}$ (slope, r^2, p)
1 km	13	2	(9.47 μg/L, 2.29 μg/L) (3978, $4 \cdot 10^{-5}$)	(0.48, 0.04, 0.003)	(-0.03, $7 \cdot 10^{-4}$, 0.094)
2 km	30	6	(9.52 μg/L, 1.95 μg/L) (1920, 0.003)	(0.20, 0.05, 0.0004)	(0.03, 0.002, 0.81)
3 km	41	10	(9.39 μg/L, 1.65 μg/L) (5180, $1 \cdot 10^{-6}$)	(0.13, 0.06, 0.0002)	(0.02, $6 \cdot 10^{-4}$, 0.89)
4 km	50	20	(9.31 μg/L, 1.58 μg/L) (5799, $3 \cdot 10^{-6}$)	(0.08, 0.06, 0.0003)	(0.18, 0.06, 0.09)
5 km	56	22	(7.49 μg/L, 1.45 μg/L) (6221, $2 \cdot 10^{-6}$)	(0.07, 0.07, 0.0001)	(0.14, 0.04, 0.14)