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Distribution of uranium and other trace constituents in drainages downstream from reclaimed uranium mines in Cove wash, Arizona

Terri Lynn Lameman Austin

A Professional Project Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Water Resources Hydroscience Concentration

> Water Resources Program The University of New Mexico Albuquerque, New Mexico

> > May 2012

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Committee Approval

The Master of Water Resources Professional Project Proposal of **Terri Lameman Austin** is approved by the committee:

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Abstract

This study examined the distribution of uranium in drainages in Cove wash in northeastern Arizona. The dispersion of uranium from reclaimed mine sites on the Navajo Nation is not well studied in soils, sediment, and water. During the 1950s and 1960s, the Cove mining region produced relative uranium and vanadium ore. Legacy uranium mines in Cove Mesa were reclaimed in phases between the early 1990s to 1998. Following reclamation, however, in 1999, elevated concentrations of uranium were detected in well, seeps and surface water in the watershed, which are above the EPA's MCL (30 μg/L). In August 2011, solid (sediment, soil, and rock), and water (surface and ground) samples were collected down-gradient from reclaimed uranium mines on Cove Mesa and in background areas to determine the distribution and characteristics of uranium and other trace metals. In addition, radiometric surveys were conducted in the study drainage area (4.3 mi^2) . Surface and groundwater samples were analyzed for major cations and anions, trace metals, alkalinity, and ^{18}O . Solid samples were analyzed to determine trace element composition. The results were compared with a 1999 EPA study to determine changes in water chemistry and provide a new baseline value for future investigation. The hypothesis that concentrations of uranium in surface water remain elevated since 1999 was supported. This research provides better understanding of the current distribution of uranium and other trace metals on the Navajo Nation.

INTRODUCTION

The purpose of this study is to examine the distribution of uranium in drainages downstream from former uranium mines located on Cove Mesa in northeastern Arizona (Figure 1). Uranium and vanadium ore were mined from deposits in the Morrison formations. The mines are located on tribal trust lands of the Navajo Nation. Historical mining in the Cove district of the Four Corners region dates back to 1949 (Chenoweth 1967). Most of the uranium mines in Cove were located on the perimeter of steep mesa-like features of the Lukachukai Mountains. Both surface and underground mining was conducted to reach the uranium and vanadium ore deposits (Scarborough 1981). Mining proliferated in 1960 and in 1968 operations ceased. Because the abandoned uranium mines posed significant health and environmental effects to residents of communities (deLemos 2009), mine reclamation in the Cove district began in the early1990s, nearly 35 years after the cessation of mining.

The mobilization of uranium and related constituents from reclaimed mine sites on the Navajo Nation is not well known. In 1999, the United States Environmental Protection Agency (U.S. EPA) collected samples from water sources (e.g. wells, springs, and streams) within Cove Wash watershed in order to provide preliminary screening assessments for further studies. The water samples were analyzed for metals and radionuclides, only. The EPA study detected elevated concentrations of uranium and related metals that in many samples exceeded U.S. EPA maximum contaminant levels (MCL) for drinking water (EPA 2007). The one-time water sampling project was limited in scope, and identified by the U.S. EPA as a preliminary assessment tool. Prior to this sampling event, previous investigation of soils and sediment contamination at mining sites have not be conducted in the Cove mining district. This study provides new baseline values so that changes in the chemistry of soils, sediment, rock, and waters of the Cove area can be identified.

Figure 1**.** Regional map of the study area on the Navajo Nation

The objectives of this study were to: 1) present the geochemical characteristics of surface water, groundwater, surface sediments, rocks and soils in drainages downgradient of reclaimed uranium mines in Cove Mesa, and select domestic wells in Cove; and 2) compare the results of the new data to the historical data to evaluate the hypothesis that concentrations of uranium in the surface water downgradient from reclaimed uranium mines remain elevated.

Waters collected from streams, wells, and seeps exhibit water chemistries that depend on the chemistry of rock units that are in contact with water. Thus, water chemistry data provides important indications about the origins and flow paths of water in groundwater systems. Major ion and trace constituents data can be used to distinguish groundwater from different sources (Langmuir 1997). Trace element, radiochemistry, and isotope data can be used to evaluate the presence of and contributions from mineralized ore bodies in water sources.

BACKGROUND

The Lukachuckai Mountains, located on the Navajo Nation of northeastern Arizona, are the northwestern flank of the Chuska Mountains. Annual precipitation averages 16 inches (in.) higher elevations, and 12 in. in the lowlands areas (NNDWR 2000). The Navajo community of Cove is located in the foothills of the Lukachukai Mountains. The study area is located on Navajo tribal trust lands and within the boundaries of Cove chapter, the local governing district. Current land uses in the Lukachukai Mountains include grazing and farming. The watershed is heavily grazed and serves as seasonal "sheepcamps" for families that transport their livestock into the mountains. Farming occurs in the alluvial valleys at the base of the mountain, downstream from the historic mining area, along the wash.

Cove Wash is an intermittent wash with segments that are perennial. Its headwaters are comprised of seepage springs that originate in the Luckachukai Mountains (Austin 2012). Cove Wash is fed by three main drainages. The wash intersects the Navajo community of Cove of northeastern Arizona. The elevation of the drainage headwaters and the confluence of the drainages are approximately 7,600 feet (ft.) and 6,560 ft., respectively. The project site is in a drainage area of 4.3 square miles $(m²)$ and surrounded by clusters of reclaimed uranium mines

identified as reclaimed mine #NA-302,# NA-312,# NA-313,#NA-315, and #NA-318 (Holiday 2011).

Historical mining activity in northeastern Arizona left a legacy of abandoned mines and waste material between the late 1960s to early 1990s. The uranium deposits in Cove Mesa were discovered in 1949 and further explored by the U.S. Atomic Energy Commission (AEC) in 1950. The mine sites were scattered across the edges of the mesa-like features that the AEC named Mesa I – VII (Chenoweth 1967; Chenoweth and Malan 1973). Although some mining techniques employed stripping and open pits, conventional underground room and pillar methods were commonly used. Waste rock from the adits and shaft were usually removed manually to expose higher grade ore. Ore was extracted and transported offsite to processing mills. Lower grade ores and waste rock were left on site in stockpiles and dumps that extend down the steep hill side and cliffs (USEPA 2007).

In 1960, mining production of U_3O_8 reached its highest of over 400,000 pounds of ore and declined progressively during its last batch of delivery in May 1968. Over the course of 19 years of mining, a total of 724,800 tons of ore $(0.24\% \text{ U}_3\text{O}_8 \text{ and } 1.02\% \text{ V}_2\text{O}_5)$ amounted to 3,483,300 pounds U_3O_8 and 14,730,100 pounds V_2O_5 (Chenoweth and Malan 1973).

In the mid-1990s, the Navajo Nation began reclamation of the abandoned uranium mines on Cove Mesa (Figure 2). All mine portals and adits on the mesa were reclaimed using cut and fill backfilling techniques, land contouring, and18 in. of top soil as the final cover. At mine site NA-312, where the 2011 samples were collected, all the mine-related waste material such as waste ore and structures were backfilled and sealed in the mine portals and adits. However, the mesa division east of the study area still contains inaccessible mine waste-piles slumped on the sides of the mesa cliffs (Holiday 2011).

Figure 2. Location of reclaimed uranium mines on Cove Mesa, Arizona.

Geology

The Lukachukai Mountains are the northwest subdivision of the Chuska Mountains and the northern tip of the Defiance uplift. The Lukachukai Mountains are erosional remnants of sedimentary rocks of Triassic to Tertiary age. The Chuska Sandstone is a thick (3,500 ft.) sandstone unit that covers most of the mountain range (Chenoweth; Chenoweth and Malan 1975; Scarborough 1981) (Figure 3). The Chuska strata were deposited over beveled Mesozoic rocks of the eastward-dipping limb of the Defiance monocline. The Chuska Sandstone is underlain mostly by the Morrison Formation, including the 400 ft. thick Recapture Member. Underlying the Recapture beds is the Salt Wash strata which are exposed continuously around the mountains. The mudstone and claystones of the Salt Wash are units weathered to resistant ledges and cliffs and benches. The cliffs occur along the drainages of the study area that dissect the middle limbs of structural folds (monoclines or steeper limbs of anticlines) (Scarborough 1981). Underlying the Salt Wash beds are the predominately eolian beds of the Bluff Sandstone. The Chinle Formation is present throughout the Lukachukai Mountains and exposed in the many of the valleys.

Figure 3. Cross section of Lukachuckai Syncline (after Scarborough 1981)

The Morrison Formation is a major source of uranium in the Luckachukai Mountains (Stone 1983). The formation includes the alternating sandstone and siltstone members – Salt Wash, Recapture, Westwater Canyon, and Brushy Basin. The ore-rich Salt Wash member is roughly $0 - 200$ ft. in thickness and occurs $30 - 80$ ft. above the base of the unit. Uranium ore is concentrated in a belt that yielded 99.6% of total uranium and vanadium production in the Lukachukai Mountains (Chenoweth and Malan 1973). The belt trends north and south and lies on the shallow dipping southwest flank of the Chuska syncline. The fine-grained sandstone makes up the lithology of the Salt Wash Member along with lenses of claystone and siltstone . Thin beds of hard limestone also occur in the Salt Wash Member (Chenoweth 1967; Chenoweth and Malan 1975; Scarborough 1981)

Tyuyamunite is a calcium uranium vanandate mineral species that was typically found in the Lukachukai Mountains. Other recovered minerals were corvusite, pascoite, hewettite, matorssite, pyrite and potentially montroseite (Chenoweth and Malan 1975).

Hydrology

Various natural springs discharge at the base of the Chuska Sandstone that feed the perennial reaches of the washes (Cooley *et al*. 1969). Water in the Upper Jurassic rocks occurs mainly in the sandstone units of eolian and fluvial origin. These units are the Entrada, Cow Springs, and Bluff Sandstone, and sandstone beds in the Morrison Formation. The other units of the Upper Jurassic rocks do not produce water and are the confining beds between aquifers (Cooley *et al*. 1969; Stone *et al*. 1983).

Davis *et al.* (1963) published tables of wells and springs surveyed across the Navajo Nation, including those located in Cove chapter. This report describes hand dug wells along the wash with similar well construction of the masonry box. The well depths were reported to be $4 - 4.5$ ft with completion in the alluvium unit.

Previous Environmental Investigations

After completion of mine reclamation, in 1999, the U.S. EPA conducted a water quality study in the Cove mining district (Holiday 2011). The goal of the Abandoned Uranium Mine (AUM) Project was to provide general assessments of radiation sources, and potential exposures from inactive uranium mines on the Navajo Nation. The project sampled commonly-used water sources such as wells, streams, and springs that were in close proximity to abandoned uranium mines. Selection of sampling sites were determined using spatial analysis of wells and surface water bodies in proximity of 1 to 15 miles from uranium mines (USEPA 2007).

Each sample was analyzed for heavy metals and radionuclides and screened for risks if ingested by human (US EPA 2007). Measurements of field parameters including pH, alkalinity, and specific conductance were not done. Chemical analysis of major cations and anions were also not conducted and presented significant information gaps as it limited the interpretation of the source of water, didn't allow chemical speciation that might assist in identifying the source of contaminants, and could not be used in understanding the transport and fate of contaminants in the water. The U.S. EPA report did not provide a description of field and analytical methods, making the comparison of data between constituents problematic. The U.S. EPA recognized that the study was limited and served as a preliminary assessment for further studies. Although the study described in this report is of limited scope it does provide more complete information for interpreting the origin, transport and fate of constituents from the uranium mining region, and provides baseline information for future investigation.

Of the 21 springs, seeps, wells, and streams sampled by EPA within the Cove chapter boundaries, seven waters exceeded the MCLs for arsenic (10.0 μ g/L), uranium (30.0 μ g/L), and the Maximum Contaminant Level Goal for selenium (5.0μg/L). Surface water at the confluence of two main drainages (Area 4) (Figure 4) and further downstream at the confluence of the three drainages exceeded the MCL for uranium and ranged from 51.3 μg/L to 149 μg/L. The seep sampled near mine adit 312 contained concentrations of arsenic (82.8 μg/L), selenium (846 μg/L), vanadium (2550 μg/L) and uranium (879 μg/L). The Ellison well (Figure 3) exhibited uranium concentrations of 34.7 μg/L (EPA 2007). Geochemical characterization of new soil,

sediment, and water sampled collected as part of this study were compared with the results of previous studies conducted by the U.S. EPA.

Figure 4. Location of sites sampled by the U.S. EPA in 1999 (U.S. EPA 2007).

METHODS

The location of reclaimed uranium mines in Cove Wash watershed was retrieved from the Navajo Nation Abandoned Mine Lands (AML) Reclamation Program. The attributes were mapped using ArcGIS 10.0 (ArcInfo) to provide a basis for site selection and to determine the proximity of proposed sampling locations to the reclaimed mines. Previous water quality and spatial data from 1999 were compiled from the *U.S. EPA Navajo Abandoned Uranium Mine Screening Assessment Report*, and were evaluated as part of this study.

Prior to sampling, two field reconnaissance trips were performed in April 2011 and July 2011 with officials of Navajo EPA, Navajo AML, and Arnold Clifford (Geobotanist). The reclaimed mine locations, road conditions to the mine, and verification of the previously U.S. EPA sampled sites (wells, surface water, springs, seeps) were assessed during the reconnaissance to determine whether proposed sampling sites were accessible and if stream flow was present in the drainages. A separate hike along Cove Wash was conducted to locate Well 309 as a possible sample location since it exhibited elevated concentrations of vanadium (20.8 μ g/L) and uranium $(83.7\mu g/L)$; however, the well was not successfully located.

Site Selection

The study site selection was based on the 1999 EPA study and input from the Navajo Nation EPA. It encompassed three previously sampled sites: a uranium mine adit seep (*Cove Mesa 2*), located at the head of the drainage, and near the reclaimed mine NA-312; *Area 4*, which corresponds with the confluence of two main drainages; and *Ellison well*, a domestic well in the Cove community (Figure 5). Five surface water samples were collected in the middle drainage downgradient of reclaimed uranium mines, including Cove Wash, that were not previously sampled by the U.S. EPA. A total of three groundwater samples from wells nearby residential areas in Cove were also sampled. The sampling plan was designed to capture the spatial distribution of uranium in soils, sediment, and water in the flowing drainage downgradient of reclaimed uranium mines NA-302, NA-312, NA-313, NA-315, and NA-318. Sampling was conducted during the monsoon season from August 16 -18, 2011 by field personnel, including Tommy Rock (Navajo EPA), Tanya J. Gallegos (U.S. Geological Survey), and Terri Lameman Austin (University of New Mexico).

Samples with a "W" and "GW" prefix refer to surface water and groundwater samples, respectively. Sample site W01corresponded to the seep spring near reclaimed uranium mine adit NA-312. Site W04 corresponded to the highest location in the drainage that was sampled in this study. Sites W05 and W06 are downstream of W04. Site W03 corresponded to EPA confluence sample Area 4, the confluence of two drainages downstream of the reclaimed mine sites on Cove Mesa. Sample site W07 corresponded to the lowest location (northernmost) of all surface water samples in Cove Wash (just upstream of the bridge). Sample W02 corresponded to the "background" sample from a developed spring, which was presumably undisturbed from mining activity. Sites GW01, GW02, and GW04 are groundwater samples taken from domestic wells approximately 5.6 miles downstream of the reclaimed mines. No wells in the vicinity of the reclaimed uranium mines were found.

Stream sediment samples were collected at sites that corresponded to the surface water sample locations. The soil samples were collected at locations that corresponded to the location of groundwater samples. Rocks, on the ground surface and in outcrops, exhibiting distinct lithology and elevated radiometric measurements were collected. The sampling plan of the solid samples were to characterize soils and sediments from areas: 1) presumed to be undisturbed by mining activity (background); 2) within areas disturbed by mining, as well as 3) rocks exhibiting elevated radiometric readings.

"SS", "S", and "RK" prefix refer to surface sediment, soil, and rock samples, respectively. Sample SS01 corresponds to the soil collected at the seep near mine adit NA-312. SS02 and SS03 correspond to the sediments collected at the head of the drainage near reclaimed mine adit NA-312. SS04 is a composite of sediment samples collected 50ft. downgradient of the reclaimed adit NA-312. SS05 corresponds to the background sample collected upgradient of mine NA-312. SS06 corresponds to the stream-sediment collected in the drainage at the confluence. SS07correponds to the stream-sediment sample collected at the highest reach of the drainage, where water sample W04 was collected. SS08 was collected in the drainage between SS07 and SS09 where no water was present. SS09 corresponds to the location where water sample W05 was collected. SS10 was the stream-sediment sample that corresponds to the location of water sample W06. SS11 was the stream-sediment sampled that corresponds to the location of water

sample W07. SS12 corresponds to stream-sediment collected in a dry drainage upstream of the confluence. RK01 corresponds to a sandstone rock sample downgradient of mine NA-312. RK02 – L and RK02 –R are split samples of the same rock collected immediately downgradient of reclaimed mine adit NA-312 and appeared as ore or waste-rock. RK03 is a sample from a distinct sandstone lens located upgradient of mine NA-312. RK04 is rock sample from a red sandstone outcrop (inside an alcove) adjacent to the drainage near water sample W06. Sample RK05 corresponds to the rock specimen collected from a distinct red sandstone outcrop, and upslope of the confluence water sample (W03). S01 and S02 correspond to the surface soil collected upgradient and downgradient to Joe well, respectively. S03 and S04 correspond with surface soil collected upgradient and downgradient of PHS 7-3065 well, respectively. S05 and S06 correspond with surface soil collected in the wash downgradient and upgradient of Ellison well, respectively.

Figure 5. Location of samples collected during this study in 2011

FIELD METHODS

Water sampling

Water samples were analyzed for major ions, trace elements, alkalinity, and ^{18}O isotope. Sampling protocols adhered to the methods described in the USGS report by Alpine *et al.* (2010). Each water sample was collected in high density polyethylene Nalgene bottles. All samples were filtered in the field using 0.45 micron pore size filters connected to new dedicated silicone tubing and a Geotech Geopump™ peristaltic pump. New nitrile gloves were worn during each sample collection to avoid cross contamination. Samples analyzed for major ions, trace metals, and uranium isotopic ratios were acidified with 2-mL of Ultrex nitric acid. Samples analyzed for major anions and alkalinity were filtered without acidification. Samples analyzed for 18 O were collected with without acidification in a clear glass bottles with a baked polyseal cap. Duplicate samples and field blanks were collected for surface water and groundwater sets. The blanks contained deionized water and were collected and processed similarly to other water samples. All bottles from each sample were then bagged together in clean plastic bags and labeled. The samples were preserved in coolers filled with ice prior to lab analysis.

The surface water samples were collected by submerging the bottles either in the center of the drainage where sufficient flow was present or in ponded areas where flow was low. Streamflow of the drainage was discontinuous and reemerged as isolated shallow water pools. Flow discharge measurements were not collected since the stream flow was discontinuous and consisted of isolated shallow water pools. The seep sample (W01) near the mine was sampled as close to the point of discharge. Sampling techniques for the well samples (GW01, GW02, and GW04) were modified from the USGS sampling procedures described in Alpine *et al.* (2010). Groundwater samples were collected after purging the wells for at least 1 to 2 minutes, before the well was pumped dry. No water level readings were not taken since the wells were encased by a stone masonry box. Background (W02) water quality was determined by sampling from a developed spring that was presumably undisturbed by historical mining activity.

Quality control and quality assurance measures that were performed throughout field sampling included the: use of the USGS field and laboratory protocols, calibration of instruments prior to collecting field measurements, collection of field sample blank, record keeping, establishment of a chain-of-custody, and review of analytical results. The sample processing site was conducted under an outdoor shelter at the Cove chapter house in order to reduce the impact of dust, wind, and sun on the samples. Log books were maintained for recording field measurements, site descriptions, and geographic position system (GPS) coordinates. Photographs were also taken for each site.

Sediment, soil, and rock sampling

Twenty – six stream sediment, soil, and rock samples were collected in the Cove study area (Figure 5). Soil and stream-sediment sampling techniques followed protocols described by in Alpine *et al.* [Chapter B] (2010). Eleven stream sediment samples were collected from transects of wet and dry drainages, and corresponded with locations of surface water samples. Six soil samples were collected at the three groundwater samples sites at depths of $0 - 2$ in. Five rock samples were collected from the ground surface or outcrop units that exhibited unique lithologic features and/or elevated radiological readings. Background samples (BK-01 and BK-02) were collected upgradient from the reclaimed mine sites.

Prior to sampling, a plastic trowel was conditioned by digging it in soil nearby the sampling location and wiped clean with a clean paper towel. The trowel was used to excavate $0 - 5$ in. depths of soil and $2 - 4.5$ lb. of soil was placed in a plastic bag. For each soil and streamsediment samples, organic material including plants, roots, and leaves and pebbles (> 1 in. diameter) were removed so that the sample consisted only of mineral matter. Where water was present, sediments from the drainage were collected in areas of fine-grained deposits. The sediments were also collected downstream of the water sampling sites in order to not increase any turbidity. The sediment samples were allowed to sit for up to five minutes so that the coarser particles could settle. The rock specimens, located on the ground in the drainage area and in the outcrops, that exceeded background gamma radiation $(6 \mu R/hr)$ were collected. The rock sample from an outcrop were fragmented with a rock hammer, as needed. All solid samples were placed in separate plastic bags and labeled accordingly.

Radiation survey

Gamma radiation measurements were collected at each sample site with a Ludlum Model 19 microR meter. The reported units of the gamma measurements were in microrads $(\mu R)/$ hour (h). MicroR readings were taken on the ground surface. Additional measurements were made along the drainage at locations between sample sites. The walking surveys provided rapid assessments of radioactivity in drainages and anomalies in exposed rock units. The Ludlum microR meters are useful instruments often used by health physicist to obtain measurements of radiation. The μ R/h readings are usually compared with the average radioactivity (3.2 μ R/h) of rock or soil sources (Alpine *et al*. 2010). Prior to sampling activities, the microR meter was calibrated by the USGS personnel.

ANALYTICAL METHODS

Waters

Field measurements of water temperature, dissolved-oxygen (DO) concentration, specific electrical conductance (SC), pH, and reduction-oxidation potential were collected with a calibrated multi-probe instrument in order to preserve the sample integrity and ensure data accuracy. The probe was rinsed with pure deionized water in between samples. Field measurements of alkalinity was conducted at the processing site and performed using incremental titrations to a pH endpoint of 4.5 using a standardized sulfuric acid solution (0.160 normality) and a calibrated hand-held titrator. Field parameters were measured in accordance with standard USGS protocols described in the USGS Investigations Report (Alpine *et al*. 2010 (Chapter C)).

Trace elements, dissolve uranium, major ions, alkalinity, and ¹⁸O were determined by the USGS Center Energy Resources Science Center Lab personnel in Denver, Colorado. Filtered and acidified samples were submitted for analyses of major ions, trace elements, and dissolved uranium using an ELAN® DRC II Quadrupole inductively coupled plasma–mass spectrometry (ICP – MS). ICP-MS was selected due to its superior detection capability compared to the inductively coupled plasma-atomic emission spectrometry (ICP-AES). This method also requires no preparation of the water samples for. Acidified (HNO₃) samples were submitted for analyses of major cations by ICP –AES. Non-acidified samples were submitted for analyses of major

anions by ion chromatography (IC). Filtered and non-acidified samples were analyzed for carbonate alkalinity through a Mantech, Automax 73 Alkalinity Titrator. Alkalinity measurements were also completed by titrations in the field to a pH of 4.5 with sulfuric acid. For this report, the field alkalinity measurements were used.

A duplicate set of (filtered and acidified) water samples were sent to the Northern Arizona University (NAU) Laboratory to analyze uranium concentrations. Ketterer (2011) reported the calibration procedures using 5 μg/L of Ir internal standard to the samples and blanks. No extra preparation or sample dilution was required for measurement of uranium concentrations with a Thermo X Series II quadrupole ICP – MS. A Peltier-cooled, glass horn-shaped chamber and self-aspirating FEP Teflon concentric nebulizer was used in combination with the ICP – MS. The ICP – MS was operated in peak-hopping mode and uranium concentration swere measured with 3 runs of 300 sweeps each (Ketterer 2011).

Soils, sediment, and rock

Sediment and rock samples were prepared for laboratory analyses according to protocols described by Alpine *et al*. (2010). The samples were air dried between 20 – 25 °C inside a dust hood to minimize particulate dispersion. The samples were passed through a stainless steel sieve with an 80-mesh opening. The sieved sampled was split into two parts; one part was preserved and archived and the other part was pulverized to ≤ 100 – mesh. The ≤ 100 -mesh portion of soils, stream sediment, and rock, were further split into two parts, one part was preserved and archived. The other part was submitted to a contract laboratory for analysis of elemental composition.

After crushing and sieving, the solid samples digested with a 4 -acid mixture of nitric, perchloric, hydrochloric, and hydrofluoric, according to procedures described by Taggart (2005). The digested samples were heated to 110°C to dryness and redissolved with nitric acid. The resulting liquid was analyzed by ICP – MS and ICP – AES. The data of total elemental analysis is reported in parts per million (ppm) or as a percentage of the solid-phase total.

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RESULTS

Surface water

Water samples were collected and include 6 surface water samples, 1 seep, and 3 wells. The parameters measured in the field were pH, temperature, specific conductivity, dissolved oxygen, alkalinity, and redox potential (Table 1). Analytes including major ions, trace elements, alkalinity, uranium isotopes, and 18 O were measured in the lab. The water quality results were compared with the 1999 US EPA data.

Surface water samples were collected from five locations within the drainage outlined in Figure 4 (W03, W04, W05, W06, and W07) and a background spring. These surface drainage waters are near neutral pH (7.35 to 8.04). Dissolved oxygen varied from 4.95 mg/L at the drainage inside the alcove (W06) to 8.04 mg/L at the lowest point sampled downstream of the confluence point in Cove Wash (W07). The redox potential ranged from 106.2 mV in the drainage sample (W05) to 122.6 mV downstream in Cove Wash (W07).

Specific conductivity of the surface waters in the drainage ranged from 606 μ S/cm at the lowest sampled point in Cove Wash to 831μ S/cm at the uppermost sample point in the drainage (Figure 6). The specific conductivity of the surface waters in the drainage decreased as water flowed down-gradient. Specific conductance is a measure of the water to conduct an electric current, and is an indirect indicator of total dissolved solids (TDS). The decrease in specific conductance with distance downstream might reflect processes of evaporation, infiltration, or greater chemical weathering of the rock units in the higher points sampled.

Figure 6. Specific conductivity of seep spring and surface waters sampled along drainage versus distance from the seep

A trilinear diagram of major anions and cations shows that most surface waters are of the calcium-magnesium-bicarbonate type (Figure 7). Of the surface water samples, calcium was the most abundant cation followed by sodium, magnesium, and potassium. Sulfate was the most abundant anion followed by chloride. Concentration of nitrate was less than the minimum reporting limit (0.08 mg/L NO_3) in all of the surface water and seep samples. The uppermost point sampled in the drainage (W04) had the highest concentrations of calcium (99.9 mg/L), sodium (72.4 mg/L), chloride (27.7 mg/L) and sulfate (49.9mg/L), consistent with the higher values of specific conductance. The lowest point sampled downstream of the confluence (W07) in Cove drainage (W07) had the lowest contribution of both cations and anions, consistent with the lowest values of specific conductance. Low major-ion concentrations may indicate higher contributions from local recharge and shorter residential time with the aquifer rock. Also, a monsoonal rain event occurred late in the afternoon the day prior to sampling this site.

Table 1.Physical properties and chemical analyses of water samples from selected seep, spring, and surface water, Cove area, northeastern Arizona, 2011.

Alt., altitude; ft, feet; WGS 84 datum for latitude and longitude; °C, degrees Celsius; SC., specific conductance; μS/cm, microsiemens per centimeter; DO, dissolved oxygen; mg/L, milligram per liter; Alk., alkalinity; mV, millivolts;

mg/L, milligram per liter; μg/L, microgram per liter

Figure 7. Trilinear diagram of major ion composition of the seep, surface water, groundwater, and background spring, Cove, Arizona.

The seep sample (W01) has significantly different solution chemistry than the stream water. It had a slightly alkaline pH of 8.15. Dissolved oxygen of the seep had the lowest value of 5.26 mg/L. Redox potential was 78.8 mV which is significantly lower than the surface samples and indicative of a less oxidizing water than the surface water samples. The seep contains mostly sodium –potassium – sulfate type water (Figure 7), which indicates it is discharging from different water bearing zone, and possibly recharging through rocks that contain sulfide (Deutsch 1997). The seep sample showed sodium as the dominant cation, followed by calcium, potassium, and magnesium. The seep is evidently enriched in sulfate. The seep had the highest specific conductance value of 1487 μS/cm.

The results of the trace element analyses are shown in Table 2. The surface water analysis barium ranged from 263μg/L to 309 μg/L, lithium ranged from 43μg/L to 85.6 μg/L, manganese ranged from 28.4μg/L to 681μg/L, and strontium ranged from 1120μg/L to 2210μg/L. Arsenic concentrations in the surface waters were below the MCL (10.0 μg/L) except for the middle reach of the drainage which was 25.5 μg/L. Vanadium concentrations $(5.3\mu g/L)$ to $20.1\mu g/L$) increased with distance from the seep to the lowest reach in Cove Wash (Figure 8). Molybdenum increased from the highest reach to the drainage inside the alcove (W06) to 18.9 μ g/L and significantly decreased to 3.6 μ g/L in Cove Wash. Concentrations of antimony, cadmium, cobalt, copper, selenium, and silver were less than the minimum reporting limit in nearly all of the surface water and seep samples.

Uranium concentrations for all surface waters samples exceeded the MCL $(30.0 \mu g/L)$. The values widely ranged from 54.4 μg/L (W07) in the lowest reach in Cove Wash to 208μg/L (W03) at the confluence of the two drainages (Figure 9). Sample W07 was sampled the day after a thunderstorm which may have diluted water in the wash resulting in lower concentrations of some constituents. Nonetheless, the presence of elevated concentrations of uranium in the drainages suggests a source is contributing to the uranium load in the stream.

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Table 2. Chemical analyses of water samples from selected seep, spring, and surface water, Cove area, northeastern Arizona, 2011.

μg/L, microgram per liter; <, less than detection limit

μg/L, microgram per liter; <, less than the detection limit; USGS, US Geological Survey results; NAU, Northern Arizona University lab results; Avg., average of USGS and NAU values

Figure 8. Concentrations of vanadium in water samples versus distance from seep

Figure 9. Concentrations of uranium in water samples versus distance from seep

Several elements after often associated with uranium minerals including arsenic, molybdenum, and vanadium. Crossplots of these elements versus uranium concentration in the surface water samples were generated to determine if there are correlations that might indicate their origin (Figure 10). The plots indicate that no apparent correlation of uranium with arsenic, molybdenum and vanadium can be discerned.

Figure 10. Plots showing correlation of uranium with arsenic, molybdenum, and vanadium.

The seep sample (W01) yielded the highest concentrations for arsenic (48.1 μ g/L), cadium (1.1) μg/L), copper (0.98 μg/L), lithium (345 μg/L), molybdenum (763 μg/L), selenium (1210 μg/L), strontium (5390 μg/L), uranium (1550 μg/L), and vanadium (2030 μg/L). The cuase of these elevated concentrations is not known. The major ion chemistry of this seep sis significantly different than the other surface or groundwaters in the watershed (Figure 7) which suggests it is from a substantially different source. Further study of this and other seeps springs in the basin would help understand the hydrology and geochemistry of the basin.

Groundwater

Water chemistry samples were collected for the Joe well, PHS 7-3065 well, and Allison well (GW01, GW02, GW03, respectively) to provide a geochemical baseline of the aquifer. The variations of the groundwater chemistry are affected by the different lithologies of the bedrock units and by mineralization. The Ellison well (GW04) was part of the 1999 EPA study and measured uranium concentrations (34.73μg/L) that exceeded the MCL. The Ellison well was categorized as "more at risk" if ingested by humans according to the US EPA study (EPA 2007). Historically, these wells were used by the community for domestic and livestock purposes since homes in the remote area of Cove were not served by a public water system until two decades ago. In 2006, Navajo EPA and US EPA issued a health advisory for the Ellison well. The Joe well and PHS 7-3065 well are presently used by the local community as a water source for livestock. During the 1930s to 1940s, the Civilian Conservation Corp. manually developed many shallow wells across the Navajo Nation for domestic water supply. There were no available records of these wells to determine the total depth, lithology, and the aquifer the wells were developed; however, an investigation in 1954 by Cooley *et al.* (1954) measured similar hand dug wells in the local area. The completed aquifer of these other hand dug wells were generally recorded as the alluvial aquifer with wells depths reported as $4.0 - 4.5$ ft, and static water levels as $2.1 - 3.3$ ft. However, this information was not available for the Joe well, the PHS 7-3065 well, or the Allison well.

The field measurements and major ions analyzed for the three wells are listed in Table 3.The groundwater is near neutral pH (7.36 to 7.37). Dissolved oxygen ranged from 4.54 mg/L in the Joe well to 6.58 mg/L in the Ellison well. Redox potential widely ranged from 74.2 mV in the PHS 7-3065 well to 151.4 mV in the Ellison well. The trilinear diagram illustrates consistency of the major ion composition of the well samples (Figure 7). Sodium is the most abundant cation followed by calcium, magnesium, and potassium. Sulfate is the most abundant anion followed by chloride. Specific conductance values ranged from 1051 μS/cm in the PHS 7-3065 well to 1398 μS/cm in the Joe well. The high levels of specific conductance might suggest leaching of salts accumulated through evapotranspiration during infiltration events. The Joe well had the slightly higher specific conductance and greater contributions to the water composition from magnesium, sodium, chloride, and sulfate than other wells.

Table 3. Physical properties and chemical analyses of water samples from selected wells, Cove area, northeastern Arizona, 2011.

ft, feet; WGS 84 Datum for Latitude and Longitude; °C, degrees Celsius; ft, feet; Spec. cond., specific conductance; μS/cm, microsiemens per centimeter; DO, dissolved oxygen; mg/L, milligram per liter; Alk., alkalinity; mV, millivolts;

μg/L, microgram per liter; <, less than the detection limit

Overall the trace elements in the groundwater samples were low compared to the U.S. EPA drinking water standard, except for uranium. Uranium concentrations in the Ellison well was reported as 68.7 μg/L, and exceeded the MCL (30μg/L). The Ellison well (GW04) also yielded the highest concentration of cadmium (125μg/L), lithium (131 μg/L), manganese (43.3μg/L), strontium (1760μg/L), and zinc (214 μg/L) (Table 4). The Joe well (GW01) yielded the highest concentrations of selenium (29.0 μg/L) and vanadium (28.4μg/L). Arsenic concentrations varied narrowly from 5.30 μg/L in the PHS well to 7.90 μg/L in the Joe well Barium varied from 61.5 in the Joe well to 125 μg/L in the Ellison well. Cadmium concentration in the Joe well was 0.02 and below minimum reporting limits for the other two wells. Cesium concentrations ranged narrowly from 0.12 to 0.13 μg/L. Copper ranged from 0.60 to 6.30 μg/L. Lithium ranged from 58.3 μg/L in the PHS well to 131 μg/L in the Ellison Well. The MCL of arsenic (10μg/L) was not exceeded by the groundwater samples. Concentrations of antimony, and molybdenum were less than minimum reporting limits of 0.3 μ g/L and 2.0 μ g/L, respectively, in all three of the wells sampled.

Table 4. Physical properties and chemical analyses of water samples from selected wells, Cove area, northeastern Arizona, 2011.

| μ g/L, microgram per liter, \sim , less triam the detection limit | | | | | | | | | | | | | |
|---|------------------------|------|-------------|--------|-------------|-------------|-------------|-------------|-------------|-------------|--------|-------------|-------------|
| Sample | | | As | Ba | Cd | Сe | Co | Cu | | Mo | Mn | Pb | Rb |
| ID | Sample site | pН | $(\mu q/L)$ | (µg/L) | $(\mu g/L)$ | (µg/L) | $(\mu g/L)$ | $(\mu g/L)$ |
| GW01 | Joe Well | 7.36 | 7.90 | 61.5 | 0.02 | 0.12 | < 0.02 | 0.60 | 91.7 | < 2.0 | ~10 | < 0.05 | 0.31 |
| GW02 | PHS 7-3065 well | 7.37 | 5.30 | 90.6 | < 0.02 | 0.12 | < 0.02 | 0.63 | 58.3 | < 2.0 | <10 | 2.06 | 0.52 |
| GW04 | Ellison well | 7.36 | 6.50 | 125 | < 0.02 | 0.13 | 0.24 | 6.30 | 131 | < 2.0 | 43.3 | 2.04 | 1.10 |

microgram per liter; < less than the detection limit

μg/L, microgram per liter; <, less than the detection limit; USGS, US Geological Survey Lab results; NAU, Northern Arizona University Lab results; Avg, average of USGS and NAU values

Oxygen isotopes

Stable isotope ratios of oxygen (${}^{18}O: {}^{16}O$) were measured and reported as $\delta {}^{18}O$, in units of parts per thousand $\binom{0}{0}$. The vapor pressure of water containing the lighter isotopes of oxygen $\binom{16}{0}$ is greater than that of water containing the heavier isotope, (^{18}O) . Therefore, ^{16}O evaporates slightly faster than 18 O. Of the surface water samples, the values of 18 O measured does not show an apparent trend with distance from the seep; however, the lowest value of $\delta^{18}O$ was measured in the highest sampled location in the drainage (W04), and the highest value of $\delta^{18}O$ corresponded with the sample collected in the lowest sampling location in Cove Wash (W07). Sample W07 was the surface water collected at the lowest elevation and enriched in the heavy isotope species. Surface water sample W05 collected downstream of W04 measured abrupt changes in the concentrations of ¹⁶O. The lowest value of δ^{18} O of all the water samples was measured in the seep (W01) and appears to be depleted in the heavy isotope species which suggests that is it meteoric water of recent origin (Figure 13).

Figure 11. Plot of ¹⁸O values of all water samples versus distance from seep.

Comparison of 2011 data with previous dataset

Chemical constituents analyzed from 3 water samples (W01, W03, GW04) were compared with the results obtained in a previous study conducted by the U.S. EPA (2007) (Table 6). Samples were collected from three previously sampled locations (Cove Mesa, Area 4, and Ellison well) for the basis of comparing datasets. Previously sampled locations were field verified with Navajo EPA officials and GPS coordinates provided in the dataset. Nine constituents (arsenic, barium, copper, iron, manganese, selenium, vanadium, zinc, and uranium) were evaluated in both datasets. No major ions were analyzed in the EPA study, which limited interpretation of the data.

The seep sample (W01) was compared with the EPA sample identified as Cove Mesa 2. The following constituents increased in concentration between 1999 to 2011: barium (from 55.0 to 75.3μg/L), copper (from 0 to 0.98 μg/L), selenium (from 846 to 1210 μg/L), vanadium (from 255 to 2030μg/L), zinc (from 3.8 to 5.0 μg/L) and uranium (from 879.0 to 1550 μg/L). Arsenic concentrations decreased from 82.8 μg/L in 1999 to 48.1μg/L in 2011, as well as iron (from189 to $\langle 20\mu g/L \rangle$, and manganese (from 5.60 to $\langle 20.0\mu g/L \rangle$.

Table 5. Data of constituents comparing 1999 EPA data with data collected in 2011.

| Table 5. Data of constituents comparing 1999 EPA data with data collected in 2011. | | | | | | | | | | | | | | | | | | | |
|--|-----------------|------|---------------------|----|-----------|----------|--------------|-------------|------------------------------|------|------|----------|--------------|-----|----------------|-----|-------|-------|-------|
| | | | | | | | | | | | | | | | | | | | |
| units expressed as $\mu q/L$; shaded cells indicate U.S. EPA (1999) data; unshaded cells indicate the 2011 data | | | | | | | | | | | | | | | | | | | |
| Sample | | | | | | | | | | | | | | | | | | | |
| ID | Sample location | As | As | Ba | Ba | Сu | Cu | Fe | Fe | Mn | Mn | Se | Se | V | v | Zn | Zn | U | U |
| W01 | Seep water | 82.8 | 48.1 | | 55.1 75.3 | Ω | 0.98 | 189 | ≤ 20.0 5.60 ≤ 10.0 | | | 846 | 1210 | 255 | 2030 | 3.8 | 5.00 | 879.0 | 1550 |
| W03 | Confluence area | | $7.40 \le 0.02$ 203 | | 125 | Ω | | 0.24 40.9 | 45.1 | 15.1 | 43.3 | Ω | 2.00 | | 38.3 13.2 6.10 | | 214 | 149.0 | 231.0 |
| GW04 | Ellison well | 6.30 | 5.80 131 | | | 307 52.4 | < 0.02 279 | | < 20.0 72.5 | | 73.3 | Ω | < 1.0 11.4 | | 19.3 | 196 | < 3.0 | 34.70 | 68.7 |

units expressed as μg/L; shaded cells indicate U.S. EPA (1999) data; unshaded cells indicate the 2011 data

The surface water sample (W03) was compared with EPA sample identified as Area 4 collected at the confluence of two drainages. The following constituents increased in concentration between 1999 to 2011: iron (from 40.9 to 45.1 μg/L), manganese (from 15.1 to 43.3 μg/L), selenium (from 0 to 2.0 μg/L), zinc (from 6.10 to 214 μg/L) and uranium (from 149 to 231 μg/L). Concentrations of arsenic, barium, and vanadium decreased in 2011.

The Ellison well (GW04) was compared with EPA sample identified as Ellison well collected in Cove. The following constituents increased in concentration from 1999 to 2011: barium (131 to 307μg/L), manganese (72.5 to 73.3 μg/L), vanadium (11.4 to 19.3 μg/L), and uranium (34.7 to 68.7 μg/L). Concentrations decreased in arsenic (7.4 to 5.8μg/L), copper (52.4 to <0.02 μg/L) iron (279 to $\langle 20.0 \,\mu g/L \rangle$, and zinc (196 to $\langle 3.0 \mu g/L \rangle$) between 1999 to 2011.

Over the past 11 years, concentrations of uranium have increased in the seep spring, confluence, and Ellison well. The concentrations have exceeded the EPA MCL of uranium (30μg/L), which applies to drinking water. We use this number because during the sampling event, livestock grazing in and alongside the drainages was observed and evident that they are drinking from possibly the same source we sampled in the streams. This poses a health concern for the livestock that are ingesting water containing elevated levels of uranium, particularly, since most Navajo people consume the meat and organ parts of the animals. Additionally, farming also occurs in the lowland areas, downstream of the main confluence of the three drainages, and water source for irrigation has primarily been from developed springs and runoff from the streams. Whether the community is utilizing the same source derived from the confluence area is uncertain but should be of concern.

Sediment, Soil, and Rock

Eleven stream sediment samples, 7 soil samples, and 5 rock samples were collected in the drainage area, and mine site NA-312 (Figure 14). All samples were analyzed by ICP–AES and ICP–MS after acid digestion.

Measurements of aluminum oxide (Al_2O_3) , iron oxide (Fe_2O_3) , magnesium oxide (MgO) , potassium oxide (K_2O) , arsenic, beryllium, cesium, molybdenum, antimony, and thallium showed little variation among the soil, sediment, and rock samples (Table 8). The concentrations of Al_2O_3 ranged from 4.47% to 7.76% with sample RK04 as an outlier of 9.86%. The concentrations of Fe₂O₃ ranged from 0.74% to 2.08%. The concentrations of MgO ranged from 0.16 % to 1.27 %. The concentration of K_2O ranged from 1.87 % to 3.33%. Arsenic concentrations ranged from 1.87 ppm to 4.36 ppm with one outlier in sample RK02-L (6.89 ppm). Beryllium concentrations ranged from 0.43 ppm to 1.34 ppm. Cesium concentration ranged from 1.21 ppm to 4.73 ppm. Concentrations of molybdenum ranged from 0.22 ppm to 1.60 ppm, with one outlier in sample SS01 (2.46 ppm). Antimony concentrations ranged from 0.28ppm to 0.54 ppm, with two major outliers (RK02-R and RK02-L).

For most of the stream sediment and soil samples there was little variation in the trace element concentrations (Table 8). Copper concentrations in the stream-sediment samples in the drainages ranged from 6.92 ppm to 10.6 ppm. Soils collected upgradient and downgradient of the three groundwater samples ranged from 8.04 ppm to 12.0 ppm. Concentration of copper in the rock samples ranged from 6.19 ppm to 14.7 ppm. Strontium concentrations in stream-sediment samples ranged from 83.1-210 ppm. Soils collected upgradient and downgradient of the groundwater samples ranged from 112- 450 ppm strontium. Six rock samples were collected in the drainage, and with two exceptions, showed little variation in their major and minor element compositions (Tables 7 and 8). Rock samples from the drainage areas contained 82.7- 493 ppm of strontium. Vanadium concentrations in sediment and soil samples ranged from 32.8-94.5 ppm and 24.2 -37.6 ppm, respectively. Concentrations of vanadium in the rock samples varied from 11.1 to 18100 ppm. Uranium concentrations in the sediment and soil samples ranged from 1.23- 1.66 ppm and 2.00-13.2 ppm, respectively. Uranium concentrations in the rock samples varied from 0.97 ppm to 35000 ppm; compared to background soil and stream samples that exhibited

uranium concentration ranging from 1.51 to 1.82 ppm U. Lead concentrations in the sediment and soil samples ranged from 10.0-13.0 ppm and 10.4-15.6 ppm, respectively. Rock samples from the drainage areas varied from 8.90 ppm to 445 ppm of lead. The very high concentrations of lead were measured in rock sample, RK02-L, which also contained the highest concentrations of strontium (493 ppm), barium (2990 ppm), vanadium (18,100 ppm), and uranium (35,000 ppm). In contrast, RK02-R contained lower concentrations of trace element of the split sample. Rock samples RK02-L and RK02-R are splits of the same rock sample and collected at the uppermost part of the drainage just 50 ft. downstream of mine NA-312. The rock sample displayed distinct lithologic characteristics similar to ore or waste-rock that was collected on the ground surface. The total gamma reading of this rock was 1200 μR/h. Rock sample RK04 collected from a distinct red sandstone unit (inside an alcove) adjacent to the drainage contained the majority of the lowest concentrations of trace elements mentioned above. RK04 was collected downgradient of water sample W06 and the gamma reading of this rock was 11 μ R/h.

The highest concentration of uranium in the stream-sediment samples was found at a 100 ft. transect below the reclaimed adit NA-312 (SS04) Sediment sample SS04, the closest sample downgradient to the reclaimed mine NA 3-012, also contained the highest concentrations of chromium (13.4 ppm), copper (10.6 ppm), lead (13.0), uranium (10.0 ppm), and vanadium (82.5ppm). The lowest concentrations of uranium and vanadium in the stream-sediment samples were measured at the location near the confluence (SS06) where water sample W03 was sampled and contained the highest concentration of uranium.

Compared with the rest of the sediment samples, the sediment sample collected at the seep (SS01) contained the highest amounts of trace elements – arsenic (5.16 ppm), chromium (14.5 ppm), gallium (6.95 ppm), lithium (17 ppm), rubidium (62.7 ppm), uranium (18.2 ppm), vanadium (94.5 ppm), and zinc (18.6 ppm). This was consistent with the water sample that exhibited high concentrations of trace-elements including arsenic, lithium, vanadium, and uranium. This sediment sample was dark and mucky.

The soil samples are represented by surface soils collected at $0 - 2$ in. depths near the three wells that were sampled. Samples S01 and S02 correspond with surface soil at the high point and low point adjacent to Joe well, respectively. Samples S03 an S04 correspond with surface soil adjacent and upgradient of PHS 7-3065 well and stream sediment, in a wash, downgradient of PHS-3065 well. Samples S05 and S06 correspond with surface soil, in the Wash, downgradient and upgradient of the Ellison well, respectively. The trace elements concentrations of the soil samples fell in a narrow range for arsenic \setminus (2.12 to 3.41 ppm), cobalt (2.63 to 4.23 ppm), molybdenum (0.30 to 0.57 ppm) and uranium (1.23 to 1.66 ppm). Chromium concentrations varied from 10.7 to 21 ppm; copper ranged from 8.04 to 12 ppm; lithium ranged from 10.5 to 16.4 ppm; manganese ranged from 236 to 335 ppm; lead concentrations ranged from 10.4 to 15.6 ppm; rubidium concentrations ranged from 54.5 to 73.2; vanadium concentrations ranged from 24.2 to 37.6 ppm; and concentrations of zinc ranged from 14.9 to 25.0 ppm. Concentrations of cadium were reported at undetected values. Concentration of bismuth also reported undetected values, except for sample S03.

Generally, the concentration of trace elements in the soil and sediment samples in the Cove Wash watershed appear to be closely to crustal abundance values for soils in the western U.S, specifically for arsenic (2ppm), cadmium (0.18 ppm), cobalt (25 ppm), copper (60 ppm), molybdenum (2 ppm), nickel (80 ppm), lead (16 ppm), vanadium (150 ppm), and zinc (70 ppm) (Smith and Logsdon 1999).

Figure 12. Locations of stream, soil, and rock sample sites, Cove, Arizona.

Table 6. Chemical properties of soil, sediment, and rock samples, Cove, Arizona.

| | | ft, feet; WGS 1984 datum for latitude and longitude; µR/hr, microR/hr radioactivity measurement unit; --, no measurement taken | | | | |
|---------------------|-----------------------|--|--------------------------------------|----------|--------------------|----------------|
| Sample ID | Sample type | Site description | Altitude (f ^t) | | Latitude Longitude | µR/hr |
| S01 | Soil | Surface soil at high point adjacent to Joe Well | 6222 | 36.57957 | -109.20980 | $\overline{7}$ |
| S ₀₂ | Soil | Surface soil at low point adjacent to Joe Well | 6210 | 36.57980 | -109.20980 | 6 |
| S ₀₃ | Soil | Surface soil adjacent to and upgradient of PHS 7-3065 | 6221 | 36.57853 | -109.20933 | 7 |
| S ₀₄ | Soil | Stream sediment downgradient of PHS 7-3065 in wash | 6208 | 36.57822 | -109.20930 | 7 |
| S ₀₅ | Soil | Surface soil sample downgradient of Ellison Well (in wash) | 6230 | 36.57908 | -109.22569 | 6 |
| S ₀₆ | Soil | Surface soil sample upgradient of Ellison Well (in wash) | 6251 | 36.57877 | -109.22535 | 5 |
| SS01 | | Sediment Soil at Seep | 7514 | 36.51074 | -109.23538 | 13 |
| SS02 | | Sediment Sediment at head of drainage | 7343 | 36.51177 | -109.23366 | 40 |
| SS03 | | Sediment Stream sedment | 7356 | 36.51197 | -109.23341 | 24 |
| SS04 | | Sediment 100-transect below reclaimed adit | 7445 | 36.51144 | -109.23452 | -- |
| SS05 | | Sediment Background upstream of mine 312 | 7547 | 36.51107 | -109.23638 | 9 |
| SS06 | | Sediment Sediment at Confluence Area 4 at W03 | 6576 | 36.54133 | -109.23005 | 9 |
| SS07 | | Sediment Sediment from drainage at W04 | 6770 | 36.52985 | -109.23636 | 19 |
| SS08 | | Sediment Sediment midpoint of drainage (no water) | 6797 | 36.52936 | -109.23640 | 20 |
| SS09 | | Sediment Sediment from drainage at W05 | 6852 | 36.53166 | -109.23558 | 12 |
| SS10 | | Sediment Sediment from drainage at W06 | 6820 | 36.53377 | -109.23440 | 9 |
| SS11 | | Sediment Sediment sample from drainage at W07 | 6446 | 36.55633 | -109.22185 | 5 |
| SS12 | | Sediment Sediment from dry drainage upstream of confluence | 6638 | 36.54147 | -109.23136 | 6 |
| RK01 | Rock | Rock | 7399 | 36.51143 | 109.23395 | 36 |
| RK02-R | Rock | Hot rock at head of drainage (right side) | 7399 | 36.51186 | -109.23355 | 1200 |
| RK02-L | Rock | Hot rock at head of drainage (left side) | 7349 | 36.51186 | -109.23355 | 1200 |
| RK03 | Rock | Red-gray-yellow lens upgradient of mine 312 | 7888 | 36.51530 | -109.23775 | $\overline{7}$ |
| RK04 | Rock | Red rock adjacent to drainage | 6785 | 36.53496 | -109.23316 | 11 |
| RK05 | Rock | Red Rock adjacent to drainage, upslope of confluence | 6633 | 36.54139 | -109.22998 | 3 |

ft, feet; WGS 1984 datum for latitude and longitude; μR/hr, microR/hr radioactivity measurement unit; --, no measurement taken

Table 7. Chemical properties of soil, sediment, and rock samples, Cove, Arizona – Continued.

| Sample ID | Sample type | Al ₂ 03 %wt | Ba ppm | CaO %wt | Fe ₂ O ₃ %wt | K_2O %wt | MgO %wt | Na ₂ O %wt | $P2$ O5 %wt | SiO ₂ %wt | SO ₃ %wt | Sr ppm | TiO ₂ %wt |
|---------------------|-----------------------|---------------------------|-----------|------------|---------------------------------------|---------------|------------|--------------------------|----------------|-------------------------|------------------------|-----------|-------------------------|
| S ₀₁ | Soil | 6.24 | 586 | 1.37 | 1.25 | 2.35 | 0.59 | 1.12 | 0.07 | 72.5 | 0.02 | 126 | 0.20 |
| S ₀₂ | Soil | 4.47 | 902 | 7.88 | 1.18 | 1.87 | 1.38 | 0.73 | 0.05 | 66.2 | 0.05 | 450 | 0.17 |
| S03 | Soil | 6.62 | 611 | 1.81 | 1.48 | 2.44 | 0.86 | 1.01 | 0.10 | 70.7 | 0.03 | 152 | 0.21 |
| S ₀₄ | Soil | 6.52 | 730 | 4.95 | 1.83 | 2.31 | 1.40 | 0.94 | 0.09 | 68.0 | 0.06 | 315 | 0.26 |
| S05 | Soil | 5.37 | 602 | 2.61 | 1.25 | 2.00 | 0.92 | 1.05 | 0.05 | 72.2 | 0.06 | 121 | 0.16 |
| S ₀₆ | Soil | 7.76 | 601 | 1.82 | 1.89 | 2.55 | 1.02 | 0.92 | 0.09 | 70.7 | 0.02 | 112 | 0.25 |
| SS01 | Sediment | 6.08 | 559 | 3.52 | 1.52 | 2.36 | 0.92 | 0.74 | 0.07 | 66.2 | 0.07 | 210 | 0.17 |
| SS02 | Sediment | 5.56 | 464 | 1.87 | 1.62 | 2.09 | 0.91 | 0.58 | 0.06 | 65.8 | < 0.02 | 117 | 0.17 |
| SS03 | Sediment | 5.56 | 448 | 1.77 | 1.46 | 2.10 | 0.82 | 0.64 | 0.06 | 66.3 | < 0.02 | 114 | 0.18 |
| SS04 | Sediment | 7.13 | 508 | 2.59 | 1.89 | 2.54 | 1.21 | 0.75 | 0.08 | 66.7 | 0.02 | 133 | 0.19 |
| SS05 | Sediment | 6.96 | 537 | 2.00 | 2.08 | 2.48 | 1.05 | 0.77 | 0.08 | 64.2 | 0.03 | 132 | 0.22 |
| SS06 | Sediment | 4.89 | 448 | 0.98 | 0.93 | 1.99 | 0.59 | 0.64 | 0.04 | 68.2 | 0.02 | 83.1 | 0.13 |
| SS07 | Sediment | 5.70 | 467 | 1.35 | 1.11 | 2.10 | 0.80 | 0.79 | 0.05 | 70.1 | 0.03 | 90.9 | 0.14 |
| SS08 | Sediment | 4.74 | 494 | 1.08 | 1.21 | 1.93 | 0.60 | 0.61 | 0.05 | 66.4 | < 0.02 | 82.3 | 0.16 |
| SS09 | Sediment | 5.58 | 453 | 1.61 | 1.15 | 2.18 | 0.84 | 0.66 | 0.06 | 70.2 | < 0.02 | 84.6 | 0.14 |
| SS10 | Sediment | 5.51 | 514 | 1.46 | 1.12 | 2.09 | 0.78 | 0.72 | 0.05 | 70.6 | < 0.02 | 90.1 | 0.14 |
| SS11 | Sediment | 4.67 | 629 | 1.56 | 1.36 | 1.82 | 0.63 | 0.59 | 0.05 | 66.2 | 0.02 | 91.4 | 0.19 |
| SS12 | Sediment | 5.60 | 520 | 1.11 | 1.16 | 2.09 | 0.71 | 0.71 | 0.04 | 67.3 | < 0.02 | 85.3 | 0.15 |
| RK01 | Rock | 3.11 | 185 | 12.7 | 1.17 | 1.15 | 0.75 | 0.16 | 0.04 | 50.8 | < 0.05 | 77.0 | 0.10 |
| RK02-R | Rock | 5.85 | 516 | 7.97 | 2.06 | 1.82 | 1.93 | 0.26 | 0.04 | 57.3 | < 0.05 | 140 | 0.08 |
| RK02-L | Rock | 5.30 | 2990 | 7.31 | 1.34 | 2.19 | 1.82 | 0.24 | 0.05 | 61.2 | 0.08 | 493 | 0.09 |
| RK03 | Rock | 9.86 | 366 | 1.64 | 3.22 | 3.33 | 1.50 | 0.30 | 0.07 | 61.0 | < 0.05 | 119 | 0.29 |
| RK04 | Rock | 6.41 | 437 | 1.64 | 0.74 | 2.31 | 0.85 | 0.99 | 0.04 | 70.0 | < 0.05 | 82.7 | 0.08 |
| RK05 | Rock | 7.66 | 423 | 6.19 | 1.97 | 2.24 | 3.64 | 1.27 | 0.12 | 73.0 | < 0.05 | 150 | 0.25 |

%wt., weight percent; ppm, parts per million;

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Table 8. Chemical properties of soil, sediment, and rock samples, Cove, Arizona. – Continued.

ppm, parts per million

Table 8. Chemical properties of soil, sediment, and rock samples, Cove, Arizona. – Continued.

Radioactivity survey

Radioactivity measurements (microR) were performed at the reclaimed uranium mine site NA-312 and the drainages downgradient (Figure 15). In addition, measurements were collected at the well sites. MicroR measurements of the stream sediment immediately downgradient of mine site NA-312 ranged from 24 to 40 μR/h, and was higher than background (6μR/h). The radiological measurement of the surface soil at the seep was 13 μR/h. Rock sample RK01 collected downgradient of the reclaimed mine NA-312 appeared as mine waste or ore rock and contained a reading of 36 μR/h. Split rock samples RK-02-R and RK-02-L of the same rock, collected further downgradient of the mine site, had an anomalously high reading of 1200 μR/h. This rock resembled mine waste rock or ore rock. Steam sediment site upstream of the mine site exhibited a reading of 9 μR/h. In the drainages where water samples were collected, readings ranged from 9 to 20 μR/h. The measurement of the confluence of the two drainages was 9 μR/h. The radiological measurement downstream in Cove Wash at water sample site W07 was 5 μR/h. MicroR readings of soil sediments at the Joe well were $6 - 7 \mu R/h$. The readings of soil sediment at the PHS well was 7 μ R/h, and the soil sediments at the Ellison well was $5 - 6 \mu$ R/h.

Figure 13. Location of radiological surveys with μR/h reading, Cove, Arizona.

Summary and Conclusion

This study has presented new information of the composition of water, soil, and sediment that was not available prior to this study. This study represents a snapshot of the study area in 2011 and presents a new baseline in which it can be compared with future observations and investigations. This study also observed the changes that have occurred at three locations previously sampled by the U.S. EPA. The EPA study was the only published data available for the Cove area and it reflects a preliminary baseline in 1999. No statement can be made about the uncertainty associated with the EPA reported data; however, it was utilized for the basis of comparison of trace metals in this study.

There were no distinct patterns of trace-element concentrations of the surface water and sources for uranium, arsenic, molybdenum, and vanadium. Concentrations of arsenic and molybdenum were relatively low for surface water and groundwater samples in the study area. This finding was consistent with low concentrations of arsenic and molybdenum in the stream-sediment sample and soil samples. Overall, there was little variation of select trace-elements in the soils and stream-sediment samples; however, the rock samples (RK-02-L and RK-02-R) collected immediately downgradient of the reclaimed mine sites exhibited the highest concentration of trace-elements.

The evaluation of the data has shown the following:

- The surface water samples collected in the drainages ranged from 63.8 μ g/L to 231 μ g/L, and exceeded the MCL for uranium. With respect to background, the surface water samples exhibited high concentrations of lithium (43.0 to 85.6 μ g/L), manganese (28.4 to $681\mu g/L$), and strontium (1120 to 2210 $\mu g/L$). Three surface water samples also exhibited high levels of vanadium (12.7 to 20.1 μg/L) compared to background.
- Concentrations of uranium did not correlate with arsenic, molybdenum, and vanadium, which are often present in uranium minerals.
- The water chemistry of the seep sample is distinct from the surface water chemistry. It exhibited high concentrations of uranium (1550 μg/L), arsenic (48.1μg/L), cadium (1.1 μg/L), copper (0.98 μg/L), lithium (345 μg/L), molybdenum (763 μg/L), selenium (1210

 μ g/L), strontium (5390 μ g/L), and vanadium (2030 μ g/L) with respect to the surface water samples.

- The Joe well (GW01) yielded the highest concentrations of selenium $(24.5\mu g/L)$ and vanadium (28.4μg/L) of the three groundwater samples. The Ellison well (GW04) yielded the highest concentration of cadmium (125μg/L), lithium (131 μg/L), manganese (43.3μg/L), strontium (1760μg/L), zinc (214 μg/L), and uranium (68.7μg/L) of the three wells. Uranium concentrations in the Ellison well exceeded the MCL of 30μg/L. The MCL of arsenic (10μg/L) was not exceeded by the three groundwater samples.
- Analyses of the sediment samples showed that sample SS04, the closest sample to the reclaimed U mine, contained the highest concentration of certain trace elements (Co, Cu, Cr, Pb, U and V).
- Stream-sediment sample (SS06) collected near the confluence contained the lowest concentrations of uranium and vanadium and was not consistent with the surface water sample (W03) collected nearby which contained the highest concentrations of uranium.
- There was little variation of select trace-elements (Al_2O_3) , Fe_2O_3 , MgO , K_2O , As, Be, Cs, Mo, Sb, and Tl) in the soil and sediment samples, and this was also consistent with the relatively low concentrations of arsenic and molybdenum in the surface water and groundwater samples.
- Of all sediment samples, the seep sample (SS01) contained the highest concentrations of trace elements – As, Cr, Ga, Li, Rb, U, V, and Zn; and was consistent with the water sample that exhibited the highest concentrations of certain trace-elements.
- Comparison with the 1999 EPA data has determined that over the past 11 years the samples of the: seep exhibited increased concentrations in barium, copper, selenium, vanadium, zinc, and uranium; surface water at the confluence of two drainages exhibited increased concentrations in iron, manganese, selenium, zinc, and uranium; Ellison well exhibited an increased concentrations in barium, manganese, vanadium, and uranium. Uranium concentrations continue to exceed the EPA MCL $(30 \mu g/L)$ at these samples sites.

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- The confluence area is heavily grazed by livestock, and the consumption of the water that is elevated in uranium poses a health concern. Farming also occurs in the alluvial valleys downstream of the confluence and identifying the water source the community utilizes for irrigation is also of other concern.
- MicroR readings of the stream sediment immediately downgradient of mine site NA-312 exceeded background (6μR/h), and varied from from $24 - 40$ μR/h. The microR readings taken as the remaining sample sites were generally low compared to background.

Recommendations

A drawback of this project was the timing constraint and the limited set of water, soils, stream sediments, and rock samples collected and analyzed for the site. The scope of work and tight schedule for this report precluded a detailed analysis and integration of the analytical results of the solid (soil, sediment, and rock) samples. Additional samples collected further upstream of the highest sampled point in the drainage and downstream of the lowest sampled point in the drainage could provide further insight. Collection of solid samples of mine waste in the other mesa division and around other reclaimed and un-reclaimed uranium mining areas could also assist with further interpretation. A more thorough and advanced analysis of the solid phase chemistry with respect to the solution phase in Cove Mesa is necessary to further understand the processes that control the distribution and mobilization of uranium in this area. Further, it is important to determine the primary source of water that was observed in the drainages, and whether it is derived from groundwater or from runoff. Future investigations that may facilitate this understanding could include:

- Collect additional water and sediment samples of the entire drainage, including the upper reaches between the sampling points and the reclaimed mine site NA-NA-312; the two major umsampled drainages of Cove Wash, located east and west of the drainage sampled during this study
- Collect solid samples from the mine waste pile(s) located on the other mesa division east of the mine NA-312
- Thoroughly evaluate the 2011 data of the soils, sediment, and rock samples, and then use those results to interpret the rock – water interactions, and the aqueous geochemistry of uranium and other constituents in the water
- Establish "true" background concentrations of surface water and groundwater samples by evaluating pre and post mining data and whether the water source was disturbed by past mining activity.
- Further interpret the ²³⁴U/²³⁸U activity ratios (AR) to interpret uranium concentrations and to determine if it is possible to distinguish whether the uranium is anthropogenic or naturally derived
- Thoroughly evaluate the oxygen isotopic data to provide insight on possible sources of groundwater recharge and hydrogeologic interactions affecting groundwater along the flow path.
- Obtain and leach solid samples such as waste rock and ore samples to determine the availability of trace elements and geochemical signatures of source rocks
- Evaluate water chemistry data of streams within and adjacent to Cove chapter, which is routinely monitored and collected by the Navajo EPA;
- Evaluate water chemistry and soil chemistry data collected, at seeps and springs in the watershed to understand groundwater hydrology and chemistry.
- Understand the well construction to identify source of groundwater

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