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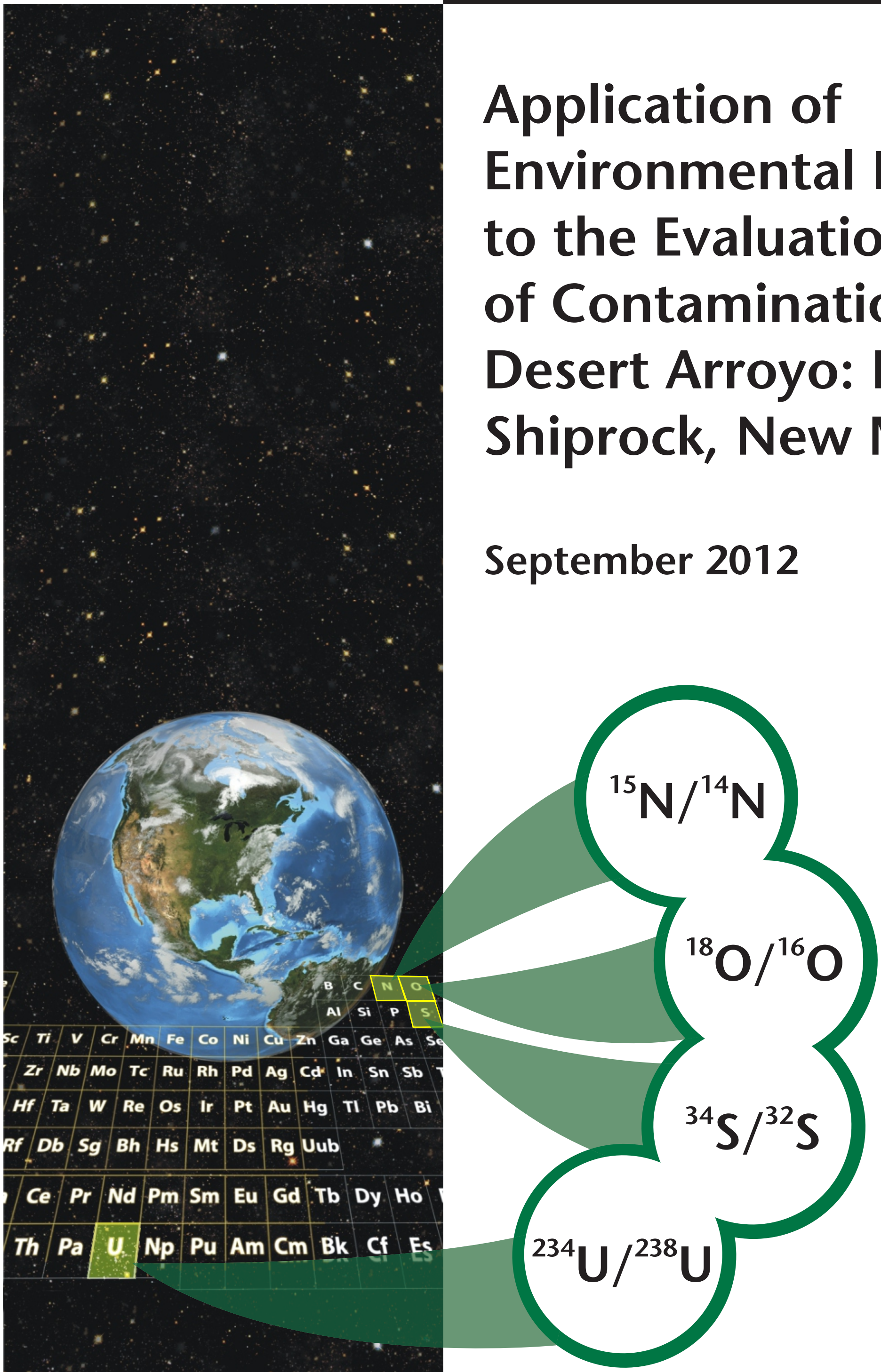
Environmental Sciences Laboratory

Application of Environmental Isotopes to the Evaluation of the Origin of Contamination in a Desert Arroyo: Many Devils Wash, Shiprock, New Mexico

September 2012



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Contents

Figures

Tables

Appendix

Abbreviations

AR	activity ratio
DOE	U.S. Department of Energy
ft	foot
GMWL	global meteoric water line
KPA	kinetic phosphorescence analysis
LM	Office of Legacy Management
LMWL	local meteoric water line
µg/L	micrograms per liter
mL	milliliters
pCi/L	picocuries per liter
VCDT	Vienna Cañon Diablo Troilite (meteorite standard)
VSMOW	Vienna Standard Mean Ocean Water
‰	per mil

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Abstract

Isotopes of hydrogen ($^{2}H/^{1}H$, ^{3}H), nitrogen ($^{15}N/^{14}N$), oxygen ($^{18}O/^{16}O$), sulfur ($^{34}S/^{32}S$), and uranium ($^{234}U/^{238}U$) were determined in groundwater at three desert arroyos near Shiprock, New Mexico. Comparisons were made to groundwater contaminated by a nearby mill site used for processing uranium ores. The $^{34}S/^{32}S$ and $^{234}U/^{238}U$ ratios were useful in distinguishing between mill-related contaminants and contaminants that were leached from the Mancos Shale. The $^{34}S/^{32}S$ and $^{234}U/^{238}U$ signatures are consistent with signatures from major ions and trace elements that indicate the contamination in groundwater in the Many Devils Wash arroyo is derived from the Mancos Shale and not the mill site. Elevated tritium activities are present in groundwater associated with the milling operation because the mill operated in the 1950s and 1960s when elevated tritium levels caused by the atomic bomb testing were present in the water used for milling. The mill site tritium activities exceed tritium activities in Many Devils Wash by about an order of magnitude. Ratios of $^{2}H/^{1}H$, $^{15}N/^{14}N$, and $^{18}O/^{16}O$ were not useful in defining the origin of the contamination; however, these signatures defined two areas of groundwater (upgradient and downgradient) in Many Devils Wash, the arroyo closest to the former uranium mill site. The differences in isotopic signatures observed between these two areas may result from contributions from two different groundwater sources.

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1.0 Introduction

We provide isotopic data ($^2H/^1H$, ^3H, $^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{34}S/^{32}S$, and $^{234}U/^{238}U$) from seepage that occurs in three desert arroyos near Shiprock, New Mexico: (1) Many Devils Wash, (2) Salt Creek Wash, and (3) Upper Eagle Nest (Figure 1). Prior studies suggested that contaminated seepage in Many Devils Wash is derived from a nearby area formerly used for uranium milling (the Shiprock disposal cell), and data were also collected from that area. The former uranium mill was built on a physiographic terrace of the Mancos Shale about 0.5 mile northwest of Many Devils Wash. Contamination from the mill site includes elevated concentrations of nitrate (NO_3), selenium (Se), sulfate (SO_4), and uranium (U) in groundwater in terrace alluvium at the disposal site and in alluvial groundwater in the adjacent floodplain of the San Juan River. Elevated concentrations of these same constituents were measured in groundwater seeping from arroyo walls of Many Devils Wash, which led to the inference that Many Devils Wash contamination was derived from the mill site (DOE 2000). The groundwater compliance strategy for Many Devils Wash is active remediation, for which the U.S. Department of Energy (DOE) Office of Legacy Management (LM) has assumed responsibility.

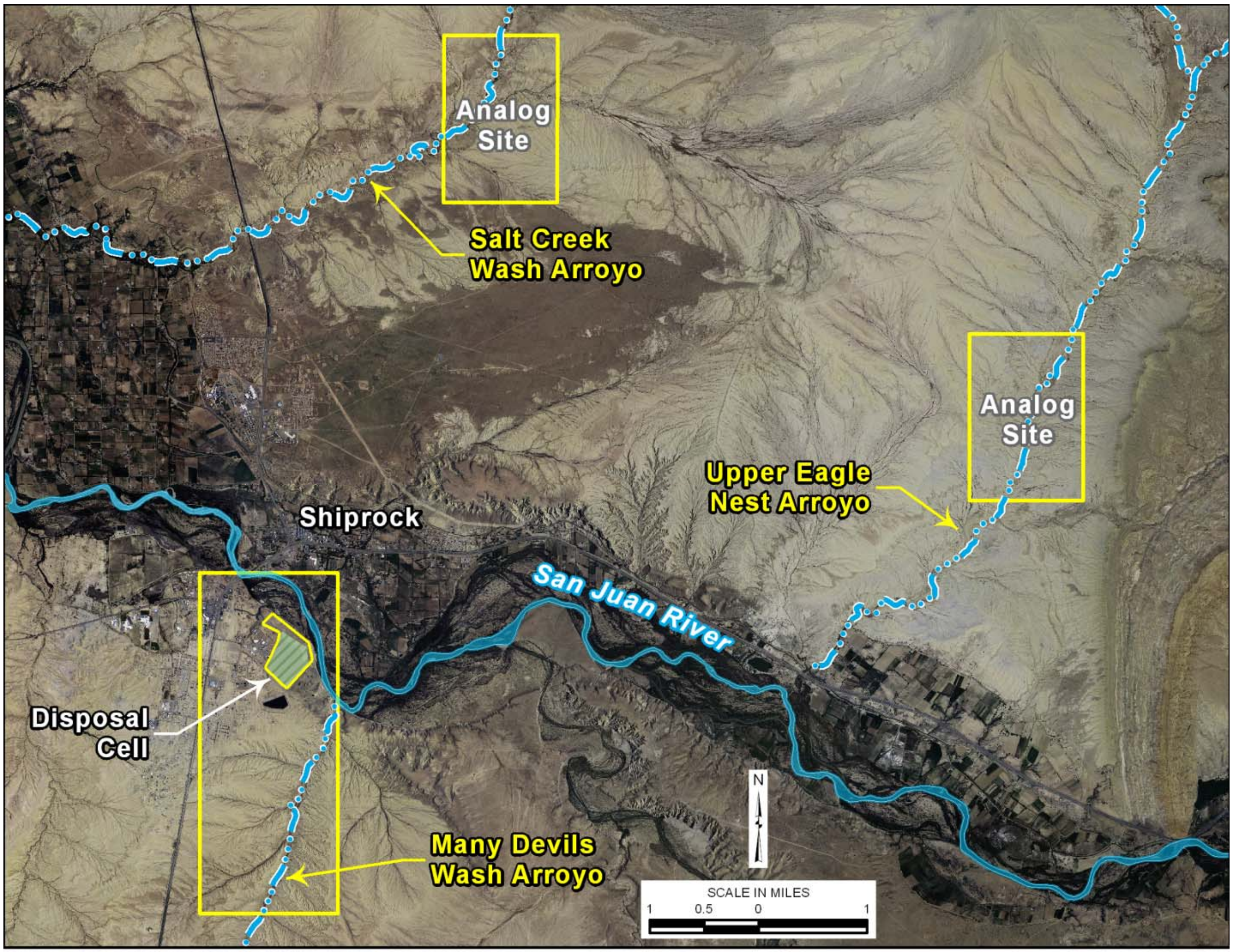

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Figure 1. Locations of Many Devils Wash, Salt Creek Wash, and Upper Eagle Nest arroyos, and the Shiprock uranium mill tailings disposal cell. Outlined areas are shown in more detail on Figure 2.

Several observations suggest that the source of contaminated water seeping into Many Devils Wash arroyo is not derived from the mill site. For example, seeps in Many Devils Wash issue from the east side of the arroyo, which is opposite the mill site. Groundwater flow paths that could cause this paradox are not obvious and seem unlikely. Another inconsistency with a mill site origin of contamination is the U isotope signature. $^{234}U/^{238}U$ activity ratios (ARs) were found to be near secular equilibrium in groundwater at the mill site, but nearly double those values in Many Devils Wash. DOE (2000) considered the higher AR values in Many Devils Wash to be consistent with derivation from the Mancos Shale.

DOE (2000) noted that the Mancos Shale could provide a source of U and other contaminants in groundwater. DOE (2000) provided data on the contaminant composition of Mancos from Butler et al. (1994), who measured elevated concentrations of U in groundwater that had contacted the Mancos Shale and noted that high concentrations of Se and SO_4 from the Mancos Shale caused large-scale diffuse natural contamination in surface water of the Colorado River basin. More recently, elevated concentrations of NO_3, Se, SO_4, and U were measured in seeps issuing from the Mancos Shale throughout much of its depositional basin (Morrison et al. 2012).

Despite these inconsistencies, the evidence refuting a mill site origin for the contamination in Many Devils Wash was considered circumstantial in 2000, and DOE accepted responsibility for its maintenance and remediation (DOE 2000). Remediation efforts in Many Devils Wash included the following:

1. Covering the lower reach of the wash with large-diameter rocks to prevent surface exposure of the contaminated water.
2. Installing a 400 foot (ft) long collection drain to collect contaminated subsurface water.
3. Installing a concrete dam and collection system to collect near-surface contaminated water.

Contaminated water collected from remediation efforts 2 and 3 is pumped to an evaporation pond on the terrace (Figure 2). These efforts have been largely unsuccessful in that most of the rock has been eroded, and the collection drain and dam system have accumulated silt. Maintenance of these systems is costly and may be required often due to flood events that transport large volumes of silt and clay down Many Devils Wash.

Since 2011, new evidence from investigations funded by LM’s Applied Science and Technology program —referred to collectively as the “Origins Project”—prompted a reevaluation of the origin of contamination in Many Devils Wash. In particular, contamination by the same suite of constituents (NO_3, Se, SO_4, and U) was found in the arroyos of Salt Creek Wash and Upper Eagle Nest (the “analog” sites) about 5 miles north and 7 miles northwest, respectively, of the disposal cell (Figure 1). Because they are far removed from, and on the opposite side of, the San Juan River, the analog sites could not have been affected by contamination from the mill site. As part of the Origins Project, eight new wells (1150, 1151, 1153, 1154, 1155, 1156, 1157, and 1159) were installed from August to October 2011 in unconsolidated sediments along the axis of Many Devils Wash (Figure 2). Another aspect of the Origins Project was a multivariate statistical analysis of the groundwater chemical data from these areas, the results of which are presented in a companion report (DOE 2012d).

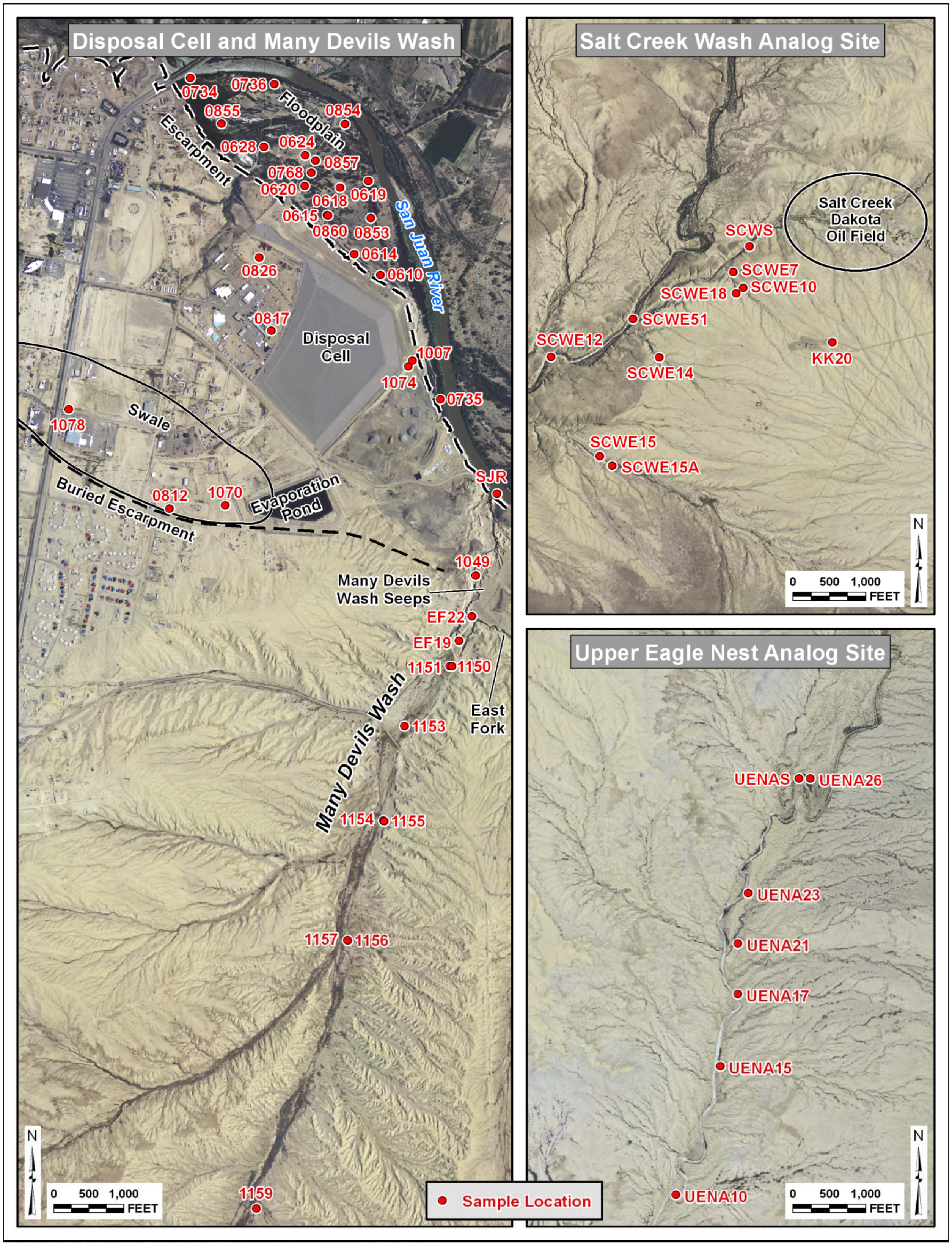

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Figure 2. Location maps for disposal cell, Many Devils Wash, Salt Creek Wash, and Upper Eagle Nest. Map locations are shown in Figure 1.

The purpose of this study is to evaluate the use of environmental isotopes toward enhancing the understanding the origins of groundwater contamination in the Many Devils Wash area. In particular, isotopic signatures that could be used to distinguish groundwater sources were investigated. To evaluate possible sources of groundwater contamination in Many Devils Wash, the isotopic chemistry of groundwater near the disposal cell and at the analog sites is also addressed in this study.

1.1 Site Descriptions

The LM uranium mill tailings disposal cell was built on a physiographic terrace elevated about 60 to 70 ft above the floodplain of the San Juan River and is separated from the floodplain by a steep escarpment (Figure 2). The mill operated from 1954 through 1968 and processed about 1.5 million tons of uranium ore. DOE (2000) estimated that the mill used about 1 billion gallons of water. Much of this water was placed in unlined ponds, and a portion infiltrated the subsurface. DOE decommissioned the site by stabilizing the mill tailings and other milling waste in an engineered disposal cell at the same location as the former mill. Decommissioning was completed in 1986. A comprehensive groundwater investigation was conducted in 1998 and 1999, and DOE detailed the results in the *Final Site Observational Work Plan for the Shiprock, New Mexico, UMTRA Project Site* (DOE 2000).

About 10 to 35 ft of terrace alluvium, composed of sand and gravel, underlie the disposal cell. The Mancos Shale Formation underlies the terrace alluvium. The Mancos Shale is composed predominantly of dark gray shale with occasional siltstone, bentonite, and dolomite beds. The near-surface portion of the Mancos is weathered, as manifested by a color change from the dark gray shale of competent, unweathered shales to light yellowish-gray shades of weathered beds. Chemically, the weathered portion is characterized by a loss of organic carbon, the oxidation of pyrite, and increases in iron oxide minerals and gypsum.

South of the disposal cell, the terrace alluvium is overlain by 50 to 60 ft of loess. The alluvium contains gravel and sand layers that filled ancestral channels of the San Juan River that are shown by a bedrock elevation map (DOE 2005). The terrace alluvium is absent south of a buried Mancos Shale escarpment defined by borehole data (DOE 2005). A predominant paleochannel, called the “swale,” abuts and is subparallel to the buried escarpment (Figure 2). Groundwater in the swale has elevated concentrations of the same suite of contaminants (NO_3, Se, SO_4, and U) as the tailings (DOE 2012a). Because of the presence of this suite of contaminants, DOE accepted responsibility for the maintenance and remediation of groundwater in the terrace alluvium.

Groundwater in the terrace alluvium was postulated to be derived solely from anthropogenic sources, dominantly the tailings operations, with possible contributions from irrigation and leaking municipal piping systems (DOE 2000). The uranium milling operation hosted tailings ponds, raffinate ponds, ore piles, and separation facilities, all of which may have contributed contamination to groundwater. Because these sources had different chemical compositions, the resulting groundwater concentrations depended on the locations of the various inputs (DOE 2000). Another potential source of contamination to the terrace sediments is from groundwater interaction with Mancos Shale.

A uranium plume underlies the disposal cell and extends into the floodplain. The highest-concentration portions of the U plume are in the terrace alluvium and weathered Mancos close to the disposal cell, on the floodplain adjacent to the escarpment just north of the disposal cell, and in a zone traversing the floodplain in a line trending northward from the disposal cell (Figure 3a). SO_4 and NO_3 are more concentrated in the swale area and Many Devils Wash than near the disposal cell (Figures 3b and 3c). There is no hydraulic continuity between the terrace and floodplain alluvial systems; thus, contamination of the floodplain resulted from flow from the tailings area through the Mancos Shale. Flow through the Mancos is evident from the presence of localized seeps of contaminated groundwater that daylight along the escarpment. The seep discharge, as well as discharge directly to the alluvium, occurs along bedding planes and subvertical fractures in the Mancos shale beds. All floodplain wells used in this study are screened in alluvium and are close to the escarpment.

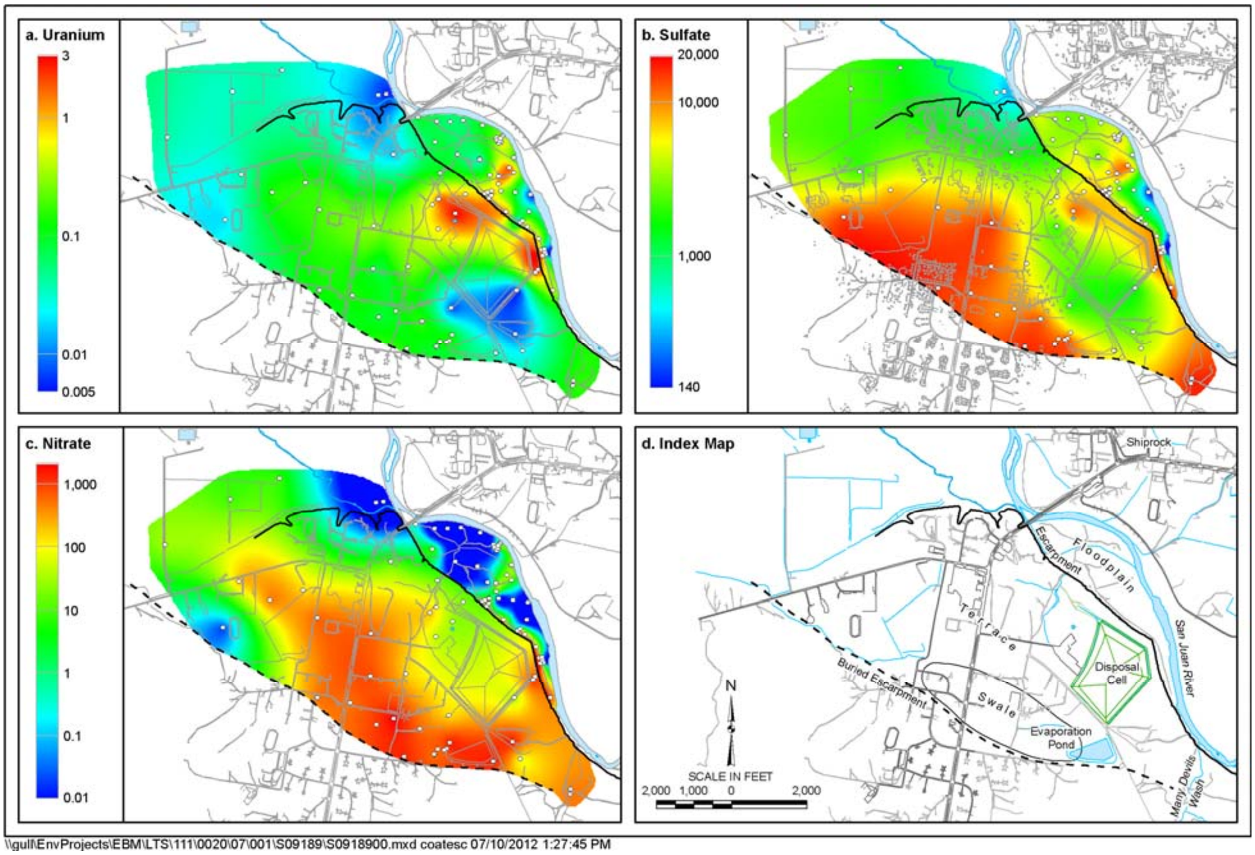

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Figure 3. Concentrations of (a) U, (b) SO_4, and (c) NO_3 in groundwater at the Shiprock site. Concentrations in milligrams per liter; data are the most recent from 2010 and 2011.

An extraction system began operation in 2003 and is still active. Contaminated groundwater is extracted from nine wells and two collection trenches on the terrace, and from two wells and two collection trenches on the floodplain. As of January 2012, 26.6 million gallons of contaminated groundwater had been extracted from the terrace, and 74 million gallons had been extracted from the floodplain (DOE 2012a). The extracted water is evaporated in a 10-acre pond on the terrace (Figure 2).

The lowermost reach of the Many Devils Wash arroyo is within 0.5 mile southeast of the disposal cell. Contaminated groundwater seeps to the ground surface along a 400 ft section of the southeast wall of the arroyo (Figure 2). The arroyo cuts through 20 to 30 ft of steep-walled loess deposits. At the base of the loess is as much as 3 ft of gravelly alluvium, which is underlain by weathered Mancos Shale (DOE 2011a). Surface water in Many Devils Wash has a light yellow to deep red color imparted by dissolved constituents. The origin of the color is unknown, but the color is not due to iron. It may be derived from dissolved organic carbon (Morrison et al. 2012); however, dialysis tests indicate that the molecules are less than 1,000 molecular weight, a size too small to be humic acid. Results from laboratory tests conducted to determine the cause of the coloration are reported separately (DOE 2012c).

The Salt Creek Wash and Upper Eagle Nest analog sites are geologically similar to the Many Devils Wash site. Both analog sites have arroyo channels that cut through loess and weathered Mancos Shale. Seeps issue from bedding plane partings and joints in the Mancos. Surface water has a deep red color in Salt Creek Wash arroyo and a light yellow color in Upper Eagle Nest arroyo, colors that are similar to the colors of surface water observed in Many Devils Wash arroyo.

1.2 Chemical Signatures

Chemical signatures of the groundwater in Many Devils Wash, tailings, the swale, the floodplain (near the escarpment), and the analog sites were compared using traditional chemical plotting tools (e.g., Piper and Stiff diagrams) and multivariate statistical methods. DOE reported the results of the chemical signatures in a companion report titled *Multivariate Statistical Analysis of Water Chemistry in Evaluating the Origin of Contamination in Many Devils Wash, Shiprock, New Mexico* (DOE 2012d). Briefly, groundwater samples from Many Devils Wash, the swale, and the analog sites have chemical signatures that are distinct from the tailings and floodplain samples.

Figure 4 compares cation (Ca, K, Mg, and Na) distributions in Many Devils Wash to those in the swale, tailings, and floodplain samples. The samples from Many Devils Wash and the swale differ from those in the tailings and floodplain areas. The swale and Many Devils Wash samples have higher sodium concentrations, and lower potassium concentrations, than samples from the tailings and floodplains areas. The variations observed in the chemical signatures are interpreted as being derived from two independent sources: (1) interaction with the Mancos Shale, and (2) tailings fluids (DOE 2012d). The current study uses groundwater signatures derived from environmental isotopes to independently investigate the groundwater origins.

1.3 Isotopic Systematics

1.3.1 Sulfur

Sulfur forms four stable isotopes: ^{32}S, ^{33}S, ^{34}S, and ^{36}S. Their natural abundances are approximately 95.02, 0.75, 4.21, and 0.02 percent, respectively (Faure 1977). In groundwater systems, several important chemical and biological processes result in fractionation between ^{34}S and ^{32}S that can be used to help interpret the origin of dissolved sulfur-bearing species. Biochemical reduction of SO_4 to sulfide in groundwater typically results in fractionation of 20 to 40 per mil (‰) (Clark and Fritz 1997). Oxidation of sulfide results in fractionations of about

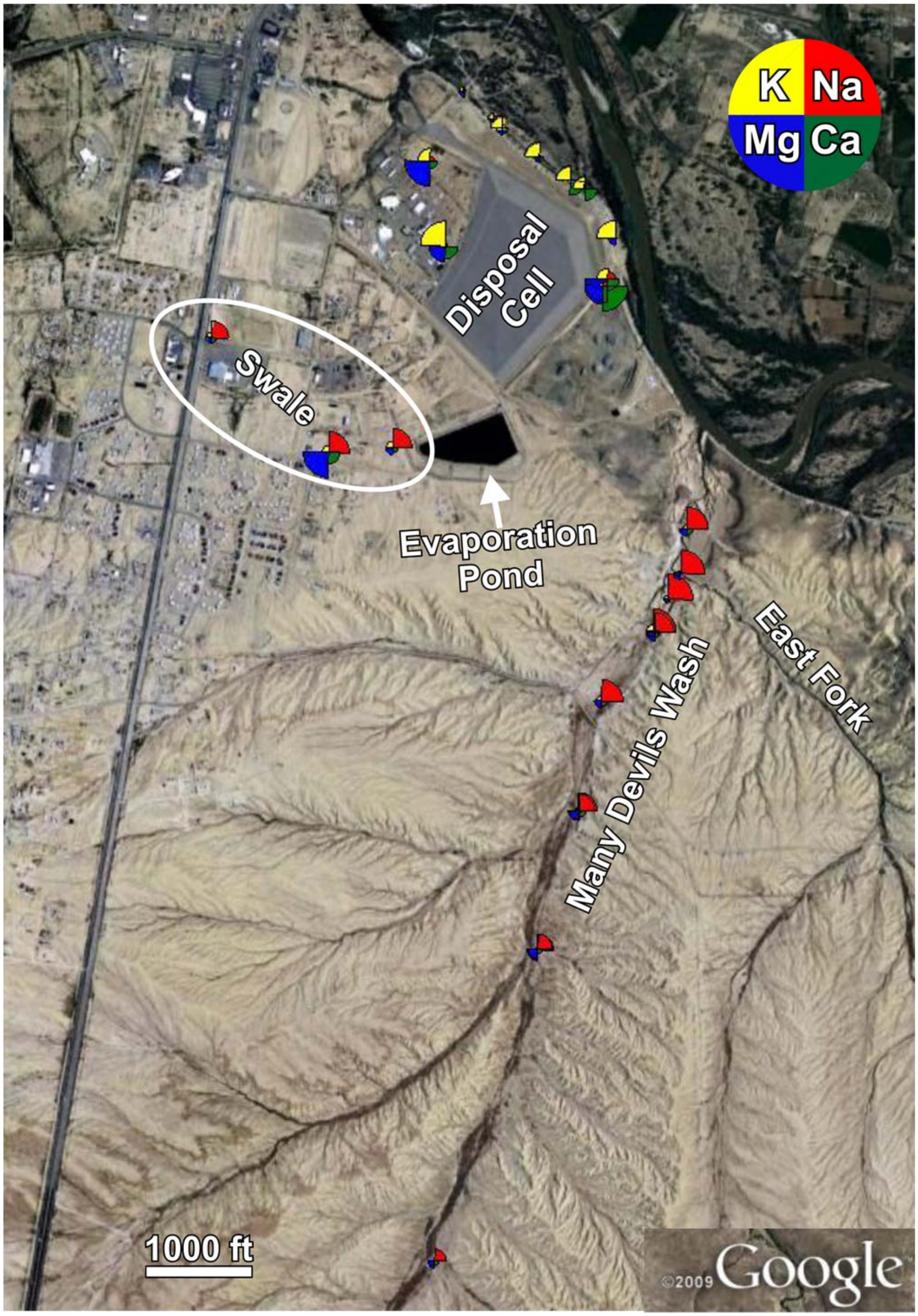

Figure 4. Starburst plot of cations at the Shiprock mill site, Many Devils Wash, the swale, and the floodplain escarpment wells. The radius of each "wedge" on the symbols indicates the relative proportion of this component to all other samples on the map.

5 ‰. Both reduction and oxidation favor the transfer of the lighter ^{32}S atom into the product phase due to the lower energy required for bond cleavage. Thus, products of both oxidation and reduction are enriched in ^{32}S and have lower δ^{34}S signatures.

Sulfur isotope ratios can be used as groundwater tracers if two or more groundwater sources have measurably different ratios. In a study of groundwater contamination from a uranium mill in the Ambrosia Lake, New Mexico, uranium district, Ries (1982) determined that δ^{34}S-SO_4 could be used to distinguish SO_4 derived from uranium milling operations from naturally occurring SO_4. Like Ries's study, our study's purpose was to use groundwater tracers, such as sulfur isotopes, to differentiate between tailings-derived and naturally occurring contamination in groundwater near the uranium milling site at Shiprock.

1.3.2 Uranium

Three U isotopes occur naturally in groundwater systems: ^{234}U, ^{235}U, and ^{238}U. All three are radioactive. Their half-lives are 2.45×10^5, 7.037×10^8, and 4.468×10^9 years, respectively (Weigel 1986). ^{235}U and ^{238}U have no parent nuclides and have been decreasing in abundance on earth since its formation about 4.5 billion years ago. Approximately 99.275 percent of the mass of natural U is ^{238}U, 0.72 percent is ^{235}U, and only 0.005 percent is ^{234}U (Weigel 1986). ^{234}U is a daughter of ^{238}U, following decay of short-lived nuclides ^{234}Th and ^{234}Pa (Figure 5). Because of its relatively short half-life, ^{234}U emplaced during formation of the earth has since decayed, and all ^{234}U present today was formed by decay of ^{238}U. In a closed system that contains ^{238}U, ingrowth of ^{234}U will occur until the activities of ^{234}U and ^{238}U are identical. The condition of equivalency of ^{234}U and ^{238}U activities is called "secular equilibrium" and takes about 1 million years to achieve.

$^{238}\text{U}\ (\alpha,\ t_{1/2} = 4.468 \text{ x } 10^9 \text{ yr}) \rightarrow$

$^{234}\text{Th}\ (\beta,\ t_{1/2} = 24.1 \text{ da}) \rightarrow$

$^{234}\text{Pa}\ (\beta,\ t_{1/2} = 1.18 \text{ min}) \rightarrow$

$^{234}\text{U}\ (\alpha,\ t_{1/2} = 2.45 \text{ x } 10^5 \text{ yr}) \rightarrow$

$^{230}\text{Th}\ (\alpha,\ t_{1/2} = 7.5 \text{ x } 10^4 \text{ yr})$

Figure 5. Decay of ^{238}U through ^{230}Th. Types of decay (α, β) and half-lives ($t_{1/2}$) are shown.

^{234}U activity often exceeds ^{238}U activity in groundwater systems, a discovery that Osmond and Cowart (1976) credit to Cherdyntsev et al. (1955). The mass difference between the two isotopes is small, and fractionation based on mass, such as what occurs with many light stable isotopes (e.g., ^{18}O/^{16}O), does not occur with the U isotopes. The increased abundance of ^{234}U in groundwater is instead caused by its radiogenic properties. The ^{234}U/^{238}U AR is often used to express the degree of disequilibrium. The AR value for seawater is nearly constant at 1.15. AR values in groundwater commonly exceed 1.0 and often exceed 2.0 (Osmond and Cowart 1976).

The enrichment of ^{234}U in groundwater is often explained by the recoil of ^{234}Th following the emission of alpha particles from mineral-bound ^{238}U, and the subsequent decay of ^{234}Th to ^{234}U. Where the recoil results in a termination in a mineral grain, the crystal lattice is disrupted and the daughter ^{234}U atom is more susceptible to leaching by pore fluids than is ^{238}U. An increase in oxidation state of the ^{234}U atoms during alpha decay can further increase susceptibility to leaching (Petit et al. 1985). Although these radiogenic and chemical mechanisms are widely cited as the cause of high AR values in groundwater, relatively few direct measurements of these processes have been documented. Two key experimental studies documenting these effects are summarized as follows:

- Kigoshi (1971) may have been the first to unequivocally demonstrate the effects of alpha recoil to transfer ^{234}Th from mineral grains to water. He conducted a set of experiments using powdered zircon ($ZrSiO_4$) suspended in water and observed a systematic increase in ^{234}Th activity in the water over a period of 40 days. Kigoshi (1971) used geometrical calculations to estimate a recoil range of 550 angstroms.
- A novel study by Fleischer (1980) used ^{235}U as a proxy for ^{234}U. ^{235}U is produced by alpha decay of ^{239}Pu. Samples of quartz, orthoclase, muscovite, and obsidian were juxtaposed with a ^{239}Pu source for 28 days. The minerals were then leached in acidic and basic solutions. Because ^{235}U is fissionable, its distribution and concentration in the minerals and the leach solutions was determined at low levels using fission track counting methods following exposure to a neutron flux. Results indicated that alpha recoil caused ejection of ^{235}U atoms into adjacent minerals, where they were susceptible to leaching. The chemical composition and pH of the leach solutions made little difference to the degree of leaching.

1.3.3 Water Isotopes (^{18}O and ^{2}H)

Oxygen is the most abundant element in the earth's crust and is composed of three naturally occurring stable isotopes, ^{18}O, ^{17}O, and ^{16}O. ^{16}O is the dominant isotope, with an abundance of 99.756 percent, and ^{18}O constitutes 0.205 percent (Faure 1977). There are two naturally occurring stable isotopes of hydrogen: ^{1}H, with an abundance of 99.985 percent, and ^{2}H, which is also called deuterium (D). Because oxygen and hydrogen form the water molecule, their isotopic signatures have been used to help track the migration and evolution of water masses in the atmosphere and lithosphere. The ratio $^{18}O/^{16}O$, together with the ratio $^{2}H/^{1}H$, has been used extensively to track water movement in the hydrologic cycle and interpret the origin of groundwater sources. The $\delta^{18}O$ and δD values change due to fractionation when water evaporates and condenses. Fractionation occurs during evaporation because bonds with ^{16}O are weaker than those with ^{18}O, resulting in a higher vapor pressure for ^{16}O and preferential release of ^{16}O into the vapor phase (Clark and Fritz 1997). Similarly, H_2O has a higher vapor pressure than does D_2O, and D is enriched in the liquid phase.

Craig (1961) plotted $\delta^{18}O$ versus δD of natural meteoric water samples collected worldwide and discovered that most fall on a straight line, later called the global meteoric water line (GMWL). The $\delta^{18}O$ and δD values of meteoric water are tied to the movement of atmospheric water masses that originate over the ocean and move inland, precipitating water along the route. The $\delta^{18}O$ and δD signature of the initial water mass is imposed by evaporation at the ocean surface. As the water mass moves inland, the first water to condense and fall to the ground surface has $\delta^{18}O$ and δD values that are similar to those found in ocean water, but the residual cloud mass is enriched in the lighter isotopes. Further precipitation results in meteoric water with progressively lighter isotopic signatures, a process that can be modeled by Rayleigh fractionation. Thus, the $\delta^{18}O$ and δD signature of a groundwater sample can sometimes be used to differentiate the source of the water. For example, water that is derived from a high elevation could have a characteristic $\delta^{18}O$ and δD signature different from a lower-elevation source. The $\delta^{18}O$ and δD signatures of groundwater are often enriched relative to values in precipitation due to fractionation effects of evaporation and transpiration during infiltration.

The GMWL averages the variation observed locally at sampling stations around the globe. Meteoric water precipitating in localized areas may deviate significantly from the GMWL, and isotope hydrologists encourage the use of local meteoric water lines (LMWL) to improve interpretation of local water sources. An LMWL for the Colorado Plateau compiled by Kendall and Coplen (2001) was used in this study.

1.3.4 Nitrogen

Nitrogen-14 is the most abundant isotope of nitrogen in the natural environment. Another stable isotope of nitrogen, ^{15}N, has an abundance of 0.366 percent. The ratio of $^{15}N/^{14}N$ is often measured in groundwater and sediments to help interpret the fate and transport of dissolved NO_3 and ammonium (NH_4). Nitrogen is a biologically active element in the shallow earth where processes of oxidative nitrification (production of NO_3 from NH_4 or nitrite [NO_2]) and reductive denitrification (production of NO_2 or diatomic nitrogen from NO_3) often occur. Nitrogen release from bedrock, particularly organic-rich marine shale, has been found to be an important source of nitrogen to groundwater (Holloway and Dahlgren 2002). Using $\delta^{15}N$ as an investigation tool, McMahon et al. (1999) found that electron donors in the Pierre Shale, a Mancos Shale stratigraphic equivalent, were able to denitrify some of the NO_3 in groundwater contacting it. Garvin (2012) used $\delta^{15}N$ and $\delta^{18}O$ of dissolved NO_3 ($\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3) to conclude that NO_3 in Many Devils Wash is derived from nitrification of NH_4 in the Mancos Shale and that the resultant NO_3 is being denitrified.

Because of the use of ammonia gas and nitric acid (Merritt 1971), the uranium milling process was a source of NH_4 and NO_3 to the terrace groundwater system at Shiprock. The $\delta^{15}N$ values of the ammonia gas, and the $\delta^{15}N$ and $\delta^{18}O$ values of the nitric acid used in the milling are unknown.

1.3.5 Tritium

Tritium (^3H) is a radioactive isotope of hydrogen with a half-life of 12.26 years. It is produced in the upper atmosphere (Faure 1977). ^3H combines with atmospheric oxygen to form water molecules, becoming part of the hydrologic cycle. High concentrations of ^3H were introduced into the atmosphere during atomic bomb testing mostly in the period from 1954 to 1963. Several thousand picocuries per liter (pCi/L) have been measured in rainfall in the 1960s as a result of bomb testing. This "bomb spike" ^3H has been used in many hydrologic studies to determine approximate ages of groundwater. Although there are many complications due to the heterogeneous nature of groundwater systems, Clark and Fritz (1997) provide some general guidelines for interpreting ^3H concentrations:

- ^3H concentrations less than 3 pCi/L are submodern (i.e., recharged prior to 1952).
- ^3H concentrations from 16 to 48 pCi/L are modern (i.e., less than about 10 years).
- ^3H concentrations greater than 97 pCi/L have significant bomb spike and probably recharged in the 1960s or 1970s.
- ^3H concentrations greater than 160 pCi/L are dominantly composed of 1960s bomb-spike recharge.

These guidelines were published in 1997, and subsequent ^{3}H decay results in a value of 69 pCi/L for the year 2012 for groundwater composed dominantly of bomb-spike recharge (compared to 160 pCi/L for 1997).

2.0 Methods

2.1 Sampling

Groundwater from seeps was collected from hand-dug holes. Water was pumped from the holes with a peristaltic pump until it reached a steady flow rate; in all cases, the seep samples represented flowing groundwater. Flow from most seeps was estimated to be less than 1 gallon per minute. Shallow wells (EF-19, EF-22, 0826, and 1049) were sampled with a peristaltic pump. Wells that were too deep to be sampled with a peristaltic pump (0817 and 1074) were sampled with a downhole bladder pump. In some deep wells (1007, 1150, 1154, 1156, and 1159), the water column was too short for a bladder pump to be used, so these wells were sampled with a bailer. Wells 1070 and 1078 have downhole pumps installed as part of a groundwater extraction system and are equipped with sampling spigots. Samples were collected from the spigots after purging several liters of water. Samples of San Juan River water were collected by dipping containers into the river at a location about 150 ft upstream of Many Devils Wash.

Samples for isotopic analyses were field-filtered through 0.45-micrometer in-line filters, using a low-flow peristaltic pump. Samples were collected in Nalgene bottles: 1 liter for U isotopes, 1 liter for ^{3}H, 1 liter for sulfur isotopes, and 125 milliliters (mL) for chemical U. A 125 mL sample for analysis of nitrogen isotopes was collected in an amber Nalgene bottle, and 40 mL was collected in a glass bottle for analysis of ^{18}O and D in water. Water was limited in some wells. For this reason, sample volumes from those wells were smaller than usual. In well 1159, only 500 mL was collected for sulfur isotopes, and only 500 mL was collected for U isotopes. In well 0812, no U isotope sample was collected, and only 500 mL was collected for sulfur isotope analysis. In well 1007, only 500 mL was collected for U isotopes, and only 500 mL was collected for sulfur isotopes. Because the samples had relatively high concentrations of U and SO_4, the lower volumes of these samples did not affect the results. The pH of the samples analyzed for nitrogen isotopes was adjusted to between 10 and 12 with pellets of NaOH. The pH of the samples collected for analysis of U isotopes and chemical U was adjusted to about 2, using concentrated nitric acid. All pH adjustments were made in the field shortly after sample collection, and all samples were kept on ice or refrigerated prior to analysis.

2.2 Analysis

Chemical U concentrations were determined by laser-induced kinetic phosphorescence analysis (KPA) using a Chemchek (Richland, Washington) KPA-11 at LM’s Environmental Sciences Laboratory (Grand Junction, Colorado). Samples were analyzed for ^{234}U, ^{235}U, and ^{238}U by GEL Laboratories (Charleston, South Carolina). A spike of ^{232}U was added, and the sample was evaporated to dryness. The residue was redissolved, purified using anion exchange resins, and filtered. The filter was counted in an alpha spectrometer using count times sufficient to achieve a detection of 0.1 pCi/L for each U isotope. Total chemical U concentrations determined from alpha spectrometry analyses were consistent with those determined by KPA.

^{3}H was enriched and analyzed by GEL Laboratories. Samples were distilled and then enriched by electrolysis at 5 ^{o}C over a 2-week period (Morton et al. 2009). Enriched samples were analyzed by liquid-scintillation using count times adequate to achieve a detection of 2.5 pCi/L ^{3}H.

Stable isotopes of hydrogen, oxygen, nitrogen, and sulfur were analyzed at the U.S. Geological Survey Stable Isotope Laboratory (Reston, Virginia). The sulfur isotopic composition was determined on dissolved SO_4 by precipitating it as barium sulfate, converting it to sulfur dioxide, and analyzing it by mass spectrometry. To determine the oxygen isotopic composition of dissolved SO_4, the barium sulfate was converted to carbon monoxide and then analyzed by mass spectrometry. Nitrogen and oxygen isotopes were measured on dissolved NO_3 by bacterial conversion to nitrous oxide and subsequent analysis by mass spectrometry. Oxygen and hydrogen isotopic activities in water were determined by equilibration with carbon dioxide and hydrogen, respectively, and subsequent analysis by mass spectrometry. Concentrations of ^{18}O and D were calculated from activities as described by Sofer and Gat (1972) and Horita et al. (1993).

Stable isotope data are reported as ‰ deviations from widely used standards: nitrate nitrogen as δ^{15}N relative to N_2 in air, nitrate oxygen as δ^{18}O relative to Vienna Standard Mean Ocean Water (VSMOW), SO_4 sulfur as δ^{34}S relative to troilite in the Cañon Diablo Meteorite standard (VCDT), SO_4 oxygen as δ^{18}O relative to VSMOW, water deuterium as δD relative to VSMOW, and water oxygen as δ^{18}O relative to VSMOW.

3.0 Results and Discussion

Environmental isotopes are often used in studies of contaminated groundwater to help evaluate groundwater flow and decipher the origin of the contamination source. In this study, we use an assortment of environmental isotopes (^{2}H/^{1}H, ^{3}H, ^{15}N/^{14}N, ^{18}O/^{16}O, ^{34}S/^{32}S, and ^{234}U/^{238}U) to evaluate the origin of groundwater contamination near Shiprock, New Mexico. Results of each isotope are discussed individually. A complete set of data is provided in Table 1.

3.1 Sulfur

Results of sulfur isotopic analyses of SO_4 in groundwater samples collected in March 2012 are shown in Figure 6. The samples from Many Devils Wash were depleted in ^{34}S, with δ^{34}S values in SO_4 (δ^{34}S-SO_4) ranging from -31.1 to -24.4 ‰. SO_4 in samples from the analog sites at Salt Creek Wash and Upper Eagle Nest and the swale were also depleted in δ^{34}S-SO_4 but less so than at Many Devils Wash. In contrast, SO_4 in the tailings samples was relatively enriched in ^{34}S, with δ^{34}S-SO_4 values approaching 0 ‰. Values of δ^{34}S-SO_4 from samples collected at 10 locations (one from Many Devils Wash, six from Salt Creek Wash, two from Upper Eagle Nest, and one from the tailings area) in September 2011 each showed values similar to the earlier results (values are not shown in Figure 6). San Juan River samples had δ^{34}S-SO_4 values of 0.07 and 2.2 ‰ in September 2011 and March 2012, respectively (values are not shown on Figure 6).

Table 1. Analytical Results

ID	**Group**	**Sample Date**	**NO_3 (mg/L)**	**SO_4 (mg/L)**	**U (µg/L)**	**^{234}U (pCi/L)**	**^{238}U (pCi/L)**	**AR**	**$\delta^{34}S$-SO_4 (VCDT)**	**$\delta^{18}O$-SO_4 (VSMOW)**	**$\delta^{18}O$-H_2O (VSMOW)**	**δD-H_2O (VSMOW)**	**$\delta^{15}N$-NO_3 (Air N_2)**	**$\delta^{18}O$-NO_3 (VSMOW)**	**^3H-H_2O (pCi/L)**
610	FP Qal	2/13/2001			2,103	729	707	1.03							
614		2/13/2001			2,106	745	708	1.05							
615		2/14/2001			2,956	1,030	994	1.04							
618		2/13/2001			859	299	289	1.03							
619		2/14/2001			931	337	313	1.08							
620		2/14/2001			794	301	267	1.13							
624		2/14/2001			886	324	298	1.09							
628		2/12/2001			36	12.5	12.4	1.01							
734		2/13/2001			142	65.9	47.9	1.38							
735		2/13/2001			66	29.9	22.3	1.34							
736		2/13/2001			339	137	114	1.20							
768		6/14/2000			1,014	383	341	1.12							
853		2/14/2001			148	62	50	1.23							
854		2/13/2001			3,956	1520	1330	1.14							
855		2/13/2001			74	25	25	1.00							
857		2/13/2001			253	97	85	1.13							
860	FP Km	2/15/2001			11.60	9.4	3.9	2.41							
812	Swale	4/14/2011	5,900	16,100	138	123	45.4	2.71			-8.20	-89.22			6.91
		3/23/2012	6,670	17,000	144				-22.77	-3.43	-8.15	-88.22	6.53	1.99	
1070		3/21/2012	2,900	15,700	82.9	79.7	29	2.75	-21.71	-2.52	-9.02	-83.83	6.64	0.99	28.1
1078		3/21/2012	2,850	14,600	129	91.7	42	2.18	-22.20	-2.83	-9.25	-86.07	7.41	4.32	12.4
817	Tailings	4/14/2011	2,970	8,110	11,800	3960	4070	0.97			-9.11	-78.94			62.1
		8/31/2011	2,550	9,730	9,180	2670	2730	0.98	-1.76	1.16	-8.77	-78.01	10.34	8.76	77.1
		12/8/2011	2,590	10,700	8,210										53.1
		3/22/2012	2,750	11,100	9,280	2800	2780	1.01	-1.29	1.25	-8.83	-79.24	12.01	7.68	
826		3/22/2012	812	13,700	3,660	1180	1080	1.09	-3.66	0.57	-9.38	-83.79	28.64	16.81	
1007		3/23/2012	2,360	13,300	2,480	994	882	1.13	0.99	1.64	-8.70	-80.62	11.94	7.34	87.7
1074		3/23/2012	5,330	7,510	2,110	877	775	1.13	-4.75	-0.01	-6.95	-75.92	6.16	5.46	63.5

Table 1 (continued). Analytical Results

ID	Group	Sample Date	NO_3 (mg/L)	SO_4 (mg/L)	U (µg/L)	^{234}U (pCi/L)	^{238}U (pCi/L)	AR	$\delta^{34}S$-SO_4 (VCDT)	$\delta^{18}O$-SO_4 (VSMOW)	$\delta^{18}O$-H_2O (VSMOW)	δD-H_2O (VSMOW)	$\delta^{15}N$-NO_3 (Air N_2)	$\delta^{18}O$-NO_3 (VSMOW)	^3H-H_2O (pCi/L)
1049	MDW	3/21/2012	2,270	17,500	154	127	52.4	2.42	-27.13	-2.60	-8.37	-75.44	10.13	5.49	3.81
1150		12/7/2011	2,760	17,400	139										3.59
		3/21/2012	2,660	17,800	158	110	43.7	2.52	-25.88	-2.19	-8.63	-77.53	8.65	4.83	
1151		12/7/2011	1,680	16,300	123										3.47
1154		12/8/2011	1,400	15,500	102										4.73
		3/22/2012	1,390	15,800	139	88.5	40.4	2.19	-30.66	-2.55	-8.29	-69.45	13.61	7.56	
1156		12/7/2011	1,290	15,100	104										4.29
		3/22/2012	1,250	15,000	150	93.9	43.7	2.15	-30.89	-2.41	-8.32	-68.88	13.76	7.47	
1157		12/7/2011	1,210	14,800	124										3.53
1159		3/22/2012	860	11,900	106	77.6	31.7	2.45	-31.14	-2.15	-8.30	-65.59	14.31	8	
EF-19		3/21/2012	3,180	17,500	156	115	45.9	2.51	-24.43	-2.05	-8.75	-80.73	8.37	4.62	
EF-22		12/2/2010	3,190	22,600	174	139	57	2.44							
		4/14/2011	2,570	17,200	139	124	50.3	2.47			-8.35	-75.76			4.84
		9/2/2011	2,720	19,200	139	138	61.4	2.25	-26.60	-2.40	-8.50	-76.52	8.56	5.94	4.35
		12/7/2011	2,840	19,200	187										6.42
		3/21/2012	2,590	18,100	188	115	47.6	2.42	-26.51	-2.43	-8.66	-76.92	9.32	5.17	
SCW12	SCW	4/13/2011	6,180	86,000	550	516	211	2.45			10.41	-2.45			
SCW51		4/13/2011	2,270	23,400	126	186	77.1	2.41			-6.49	-70.34			
SCWE10		4/13/2011	1,490	17,800	182	144	72.6	1.98			-7.22	-73.33			
		9/1/2011	1,160	17,200	138	125	59.7	2.09	-19.95	1.24	-8.78	-79.88	12.40	9.51	6.88
		12/6/2011	1,540	21,100	154										5.29
		3/20/2012	1,120	18,300	155	95.3	45.1	2.11	-19.86	1.63	-9.34	-83.86	10.69	7.99	<2.86
SCWE14		4/13/2011	2,010	15,200	150	183	60	3.05			-6.28	-67.19			
		9/1/2011	2,160	18,300	155	181	63.1	2.87	-21.95	0.84	-5.47	-63.87	11.10	11.56	4.06
		12/6/2011	2,100	16,200	156										4.8
		3/20/2012	2,340	21,500	209	261	91.6	2.85	-22.06	1.12	-5.40	-67.08	11.05	9.53	13.3
SCWE15		4/13/2011	1,450	15,600	138	119	54.9	2.17			-6.68	-57.37			
SCWE15A		9/1/2011	1,720	12,300	127	108	52.6	2.05	-22.48	-1.94	-7.12	-60.13	14.85	9.73	8.28
		3/20/2012	1,520	10,800	140	87.8	43.9	2.00	-22.69	-2.26	-7.10	-60.45	15.95	9.35	8.73

Table 1 (continued). Analytical Results

ID	Group	Sample Date	NO_3 (mg/L)	SO_4 (mg/L)	U (µg/L)	^{234}U (pCi/L)	^{238}U (pCi/L)	AR	$\delta^{34}S$-SO_4 (VCDT)	$\delta^{18}O$-SO_4 (VSMOW)	$\delta^{18}O$-H_2O (VSMOW)	δD-H_2O (VSMOW)	$\delta^{15}N$-NO_3 (Air N_2)	$\delta^{18}O$-NO_3 (VSMOW)	^3H-H_2O (pCi/L)
SCWE18	SCW	4/13/2011	900	16,900	106	101	40	2.53			-9.97	-86.84			
		9/1/2011	1,130	18,200	94	92.1	39	2.36	-19.92	1.85	-9.84	-85.95	7.89	6.58	3.95
		12/6/2011	731	15,800	93										<2.85
		3/20/2012	599	15,100	99	80.8	33.2	2.43	-19.46	2.73	-10.90	-90.94	8.45	5.96	<2.75
SCWE7		4/13/2011	2,060	17,700	133	146	53.4	2.73			-7.68	-78.05			
		9/1/2011	1,980	18,700	126	136	52.6	2.59	-20.31	1.78	-8.03	-78.83	5.39	6.44	<3.81
		12/6/2011	1,760	19,800	134										<2.83
		3/20/2012	1,670	20,200	145	134	50.8	2.64	-20.39	2.11	-8.50	-82.14	6.98	6.58	<2.76
SCWS		12/7/2010	3,610	23,800	160	150	53.3	2.81							
		4/13/2011	3,600	23,500	120	197	68.4	2.88			-5.20	-65.80			
		9/1/2011	2,340	20,900	106	145	43.2	3.36	-20.94	1.87	-7.24	-75.39	6.63	5.93	<4.28
		12/7/2011	2,180	20,500	114										<2.94
		3/20/2012	2,050	20,000	142	153	45.2	3.38	-21.34	2.27	-7.96	-79.70	5.72	5.34	<2.55
KK20	Other	4/14/2011	<0.5	513	<40	<0.094	<0.088	<1.07			-13.72	-101.80			<3.41
		8/31/2011	<0.5	376	<40	0.285	<0.075	<3.82			-13.64	-99.41	-17.66	9.29	<2.85
		12/6/2011	<0.5	416	<40										<2.64
SJR		4/14/2011	2	159	<1.7	1.39	0.905	1.54			-11.60	-89.27			23.6
		9/2/2011	1.2	106	<1.3	0.818	0.618	1.32	0.07	2.41	-11.79	-87.55	8.19	3.61	20
		12/7/2011	1.8	148	<1.4										18.3
		3/21/2012	2	131	<1.5	0.52	0.49	1.06	2.21	3.20	-12.39	-92.72	8.13	0.85	
UENA10	UEN	4/12/2011	4,690	63,900	359	329	156	2.11			6.01	-23.73			
UENA15		4/12/2011	1,590	34,600	130	98.8	47.3	2.09			-1.72	-48.24			
UENA17		4/12/2011	1,320	38,900	52	79.9	37.6	2.13			-4.62	-57.37			
UENA21		3/24/2011			51										
		4/12/2011	838	11,900	58	38.6	19.9	1.94			-9.48	-76.57			
		9/1/2011	862	12,800	51	38.5	20.4	1.89	-19.71	-1.85	-9.53	-75.76	11.04	6.87	7.7
		12/6/2011	849	12,600	55										9.29
		3/20/2012	877	13,300	51	46.2	22.9	2.02	-19.92	-1.83	-9.50	-75.95	11.69	6.12	
UENA23		4/12/2011	832	11,700	45	34.5	17.1	2.02			-9.20	-76.24			
UENA26		4/12/2011	1,050	14,600	41	31.5	16.3	1.93			-5.20	-62.31			10.1

Table 1 (continued). Analytical Results

ID	Group	Sample Date	NO_3 (mg/L)	SO_4 (mg/L)	U (µg/L)	^{234}U (pCi/L)	^{238}U (pCi/L)	AR	$\delta^{34}S$-SO_4 (VCDT)	$\delta^{18}O$-SO_4 (VSMOW)	$\delta^{18}O$-H_2O (VSMOW)	δD-H_2O (VSMOW)	$\delta^{15}N$-NO_3 (Air N_2)	$\delta^{18}O$-NO_3 (VSMOW)	^3H-H_2O (pCi/L)
UENAS	UEN	12/2/2010	1,070	12,800	53	31.3	14.7	2.13							
		9/2/2011	849	11,900	44	32.2	16.1	2.00	-20.46	-1.76	-9.63	-76.82	10.83	6.12	7.75
		12/6/2011	826	11,800	41										4.89
		3/20/2012	838	12,100	38	30.7	15.1	2.03	-20.52	-1.78	-9.63	-76.79	11.39	5.92	

FP = floodplain
Km = Mancos Shale
MDW = Many Devils Wash
Qal = Alluvium
SCW = Salt Creek Wash
UEN = Upper Eagle Nest
SJR = San Juan River

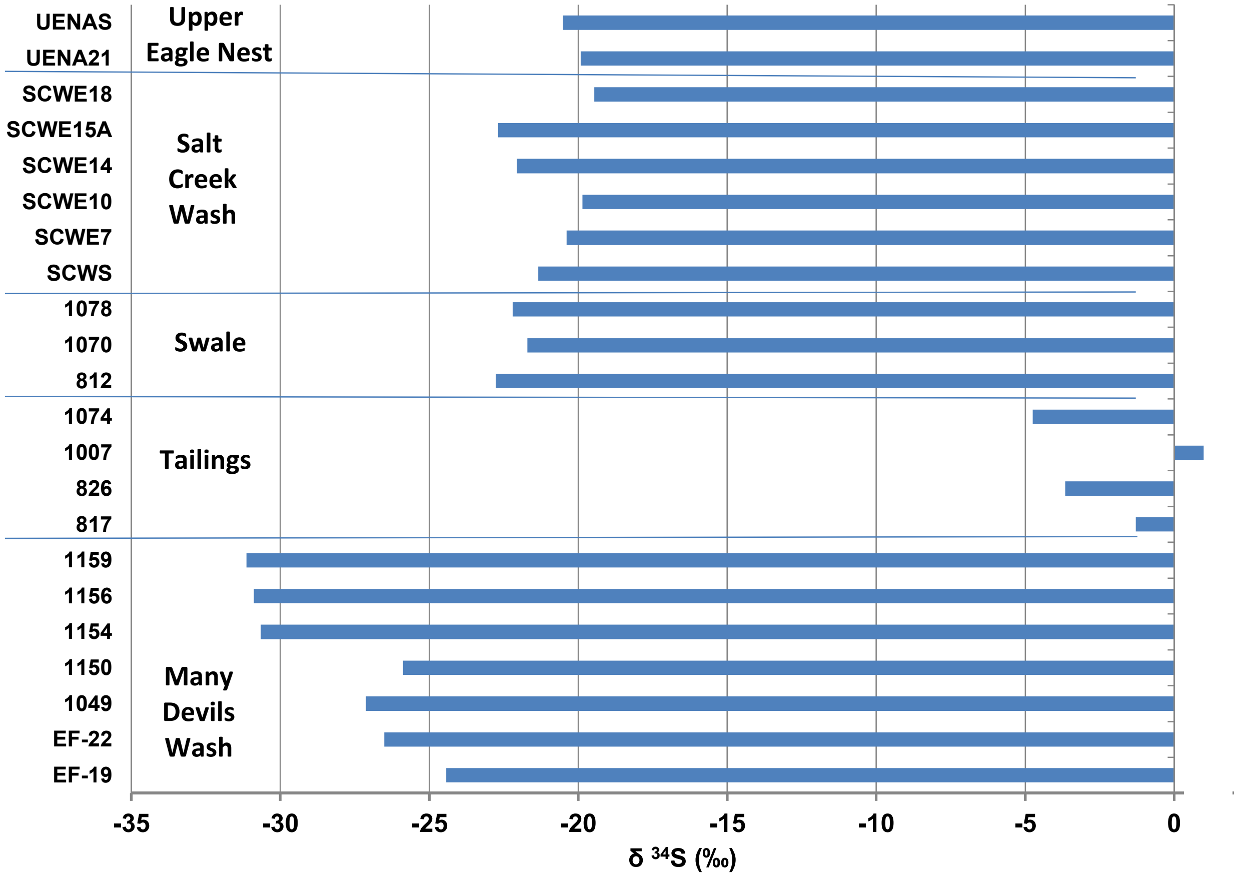

Figure 6. $\delta^{34}S$ (‰) values in groundwater samples collected in March 2012.

The distinct difference between $\delta^{34}S$-SO_4 values in groundwater at the analog sites and those from the tailings offers possibilities for using sulfur isotope signatures to help determine the origin of the SO_4 in the groundwater. Many Devils Wash and the swale have depleted $\delta^{34}S$ signatures, suggesting that SO_4 in the groundwater at these locations has a source similar to that at the analog sites, with little or no contribution from the mill. Substantial amounts of concentrated sulfuric acid were used in the milling operation to leach U from the ores (Quinn undated). From these results, it would be expected that the SO_4 in groundwater contaminated by a uranium mill would have a $\delta^{34}S$-SO_4 value of about 0 ‰, whereas SO_4 from groundwater interaction with Mancos Shale would be less than -17 ‰. The depleted values in groundwater samples from Many Devils Wash indicate that the source of the SO_4 is from leaching of Mancos Shale rather than the mill site.

SO_4 concentrations in groundwater near the mill site are dominated by the contribution from the milling process and typically exceed 10,000 milligrams per liter (mg/L). At the analog sites, the SO_4 is derived by leaching of gypsum and possibly other SO_4 minerals in the Mancos Shale (DOE 2011b), and groundwater concentrations of SO_4 typically range from about 12,000 to 20,000 mg/L.

To further investigate the origin of the SO_4, an effort was made to determine $\delta^{34}S$ values for sulfuric acid used in the milling operation. In addition to the $\delta^{34}S$ values shown in Figure 6 that likely reflect the sulfuric acid signature at the Shiprock mill, we compiled additional unpublished values from the LM database and from published literature for other uranium mill sites (Figure 7). A mill at the Ambrosia Lake uranium mining district used sulfuric acid to dissolve the ores, resulting in concentrations of SO_4 of more than 38,000 mg/L in the tailings ponds (Ries 1982). A sample of the sulfuric acid used at the mill analyzed by Ries (1982) had a $\delta^{34}S$ value of 5.8 ‰ ("H2SO4" on Figure 7); the sulfuric acid was manufactured from elemental sulfur obtained from sour H2S gas. The SO_4 in water samples collected from two tailings ponds at Ambrosia Lake had $\delta^{34}S$ values of -1.1 and 3.7 ‰ (Pond 1 and Pond 3 on Figure 7). Five additional samples were collected by Ries (1982) from shallow alluvium near the mill ponds. The $\delta^{34}S$-SO_4 values of these mill-related samples, designated by a "P" prefix on Figure 7, range from -1.9 to 6.0 ‰.

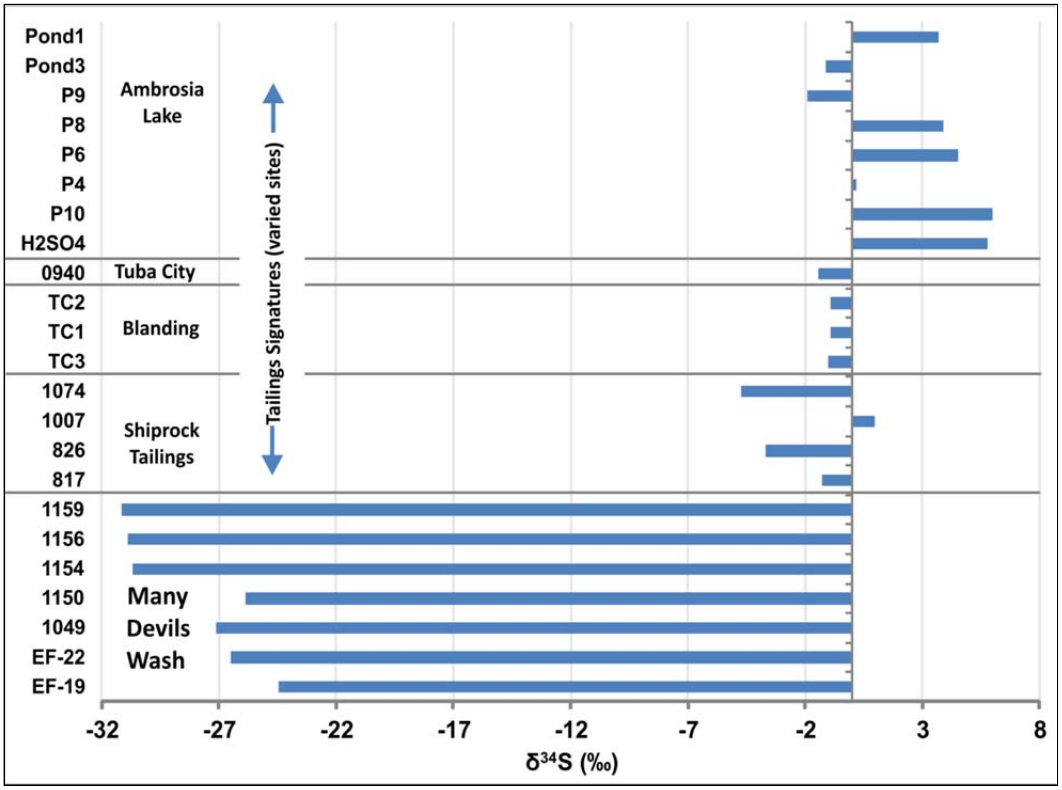

Figure 7. Comparison of $\delta^{34}S$-SO_4 (‰) signatures. March 2012 Many Devils Wash groundwater samples with mill tailings $\delta^{34}S$-SO_4 signatures from Ambrosia Lake (Ries 1982), Blanding (Hurst and Solomon 2008), Shiprock, and Tuba City (Appendix A) uranium milling sites.

$\delta^{34}S$ was determined on SO_4 from a former uranium mill near Tuba City, Arizona (data in Appendix A; well data are in DOE 2010). The uranium mill tailings at the Tuba City site were stabilized in a disposal cell at the mill site. In February 2012, groundwater was sampled from well 0940 located hydraulically downgradient and within 50 ft of the disposal cell. Well 0940 was selected because it had the highest SO_4 concentration (6,490 mg/L) of any groundwater samples; the $\delta^{34}S$- SO_4 value of -1.43 ‰ is used to represent the SO_4 signature from the tailings (Figure 7). Sixteen additional wells in the plume from Tuba City sampled in February 2012 had $\delta^{34}S$- SO_4 values ranging from -5.56 to 4.01 ‰ with a mean of -1.36 ‰ (not shown on Figure 7; see Appendix A). Hurst and Solomon (2008) collected three samples from tailings effluent at an operating uranium mill at Blanding, Utah. These tailings effluent samples ("TC" prefix on Figure 7) had δ^{34}S values of -1.04, -0.93, and -0.89 ‰.

The δ^{34}S-SO_4 values in samples representative of the SO_4 derived from milling at Ambrosia Lake, Blanding, and Tuba City combined with the samples representative of tailings at Shiprock (817, 826, 1007, and 1074) suggest that uranium milling imparts a characteristic δ^{34}S-SO_4 signature ranging from about -5 to +5 ‰. From these data, it appears that δ^{34}S-SO_4 signatures in tailings are similar to those of H_2SO_4 despite the occurrence of reduced sulfides in the ores that likely had negative δ^{34}S values. The mill-related H_2SO_4 must dominate over the smaller contribution from the ore sulfides.

Groundwater at the Salt Creek Wash and Upper Eagle Nest analog sites migrates through weathered Mancos Shale, and SO_4 is derived from dissolution of SO_4 minerals indigenous to the weathered Mancos. Unweathered Mancos contains sulfide minerals, mainly pyrite, that oxidize to SO_4 during weathering. Partings and veinlets filled with gypsum are common in the weathered Mancos Shale, and its dissolution contributes SO_4 to groundwater migrating through the Mancos. Tuttle et al. (2007) analyzed δ^{34}S-SO_4 values from 49 shale and Mancos-derived soil samples collected near Montrose, Colorado, and Hanksville, Utah (Figure 8). δ^{34}S values in these samples ranged from -27.1 to -15.1 ‰ with a mean of -21.5 ‰. Sixteen samples that contained visible gypsum had a mean δ^{34}S-SO_4 value of -21.0 ‰.

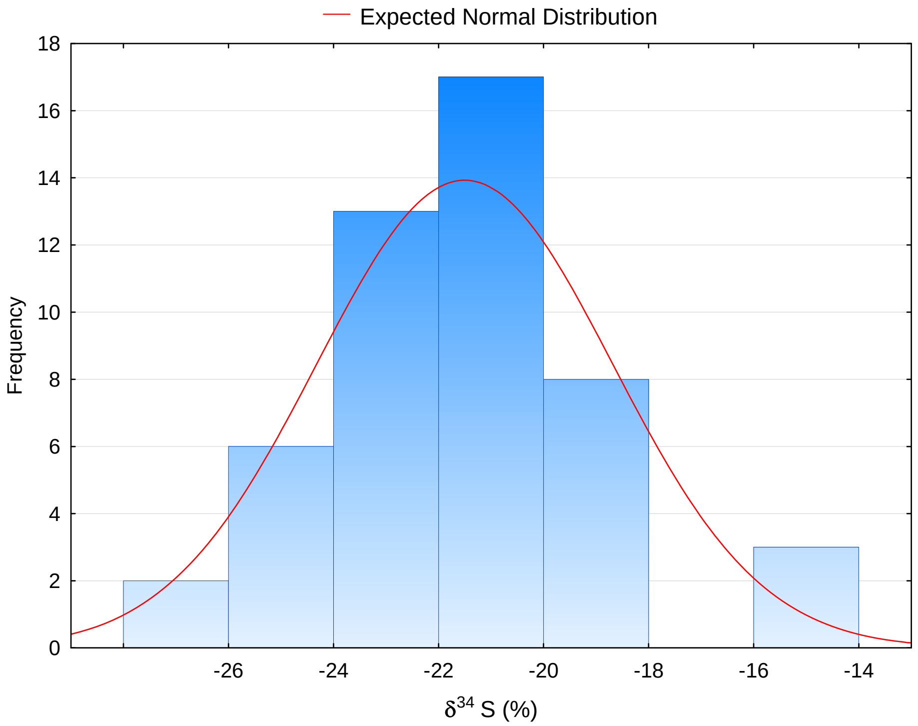

Figure 8. Histogram of δ^{34}S-SO_4 (‰) in SO_4 released by water leaching of solid phase Mancos Shale samples collected near Montrose, Colorado, and Hanksville, Utah. Data from Tuttle et al. (2007).

The δ^{34}S-SO_4 results of the solid samples indicate that Mancos Shale contains SO_4 minerals with δ^{34}S-SO_4 values that are significantly depleted relative to the SO_4 signature of about 0 ‰ observed for mill-derived SO_4. The depleted δ^{34}S signature of the Mancos is probably an artifact of the wholesale oxidation of ^{34}S-depleted sulfide minerals. Sulfide minerals commonly have depleted δ^{34}S values resulting from bacterial SO_4 reduction. Fractionation during bacterial mediated SO_4 reduction favors partitioning of ^{32}S into the product sulfide phase with fractionation factors that typically range from about 20 to 40 ‰ (Clarke and Fritz 1997).

3.2 Uranium

Most of the AR values from the March 2012 sampling of Many Devils Wash, Salt Creek Wash, Upper Eagle Nest, and the swale area are between 2 and 3 (Figure 9). In contrast, the tailings samples had AR values of about 1.0, indicating that they are nearly at secular equilibrium. The secular equilibrium values for the tailings are explained in terms of the ore-forming processes and subsequent milling of the ores. Ores processed at the Shiprock mill were from the Chinle and Morrison Formations of the Triassic and Jurassic geologic periods, respectively. The ores likely formed millions of years ago, possibly at or shortly after the time of sediment deposition. Thus, ^{238}U has had ample time for ingrowth to ^{234}U, and secular equilibrium exists in the ore bodies. Concentrated acids and bases were used to release U from the ores, resulting in complete dissolution of the U ore minerals. Thus, the milling process would not fractionate ^{238}U from ^{234}U, resulting in post-milling AR values that are also near secular equilibrium. All four wells that were sampled to represent mill tailings water had AR values near 1 (Figure 9).

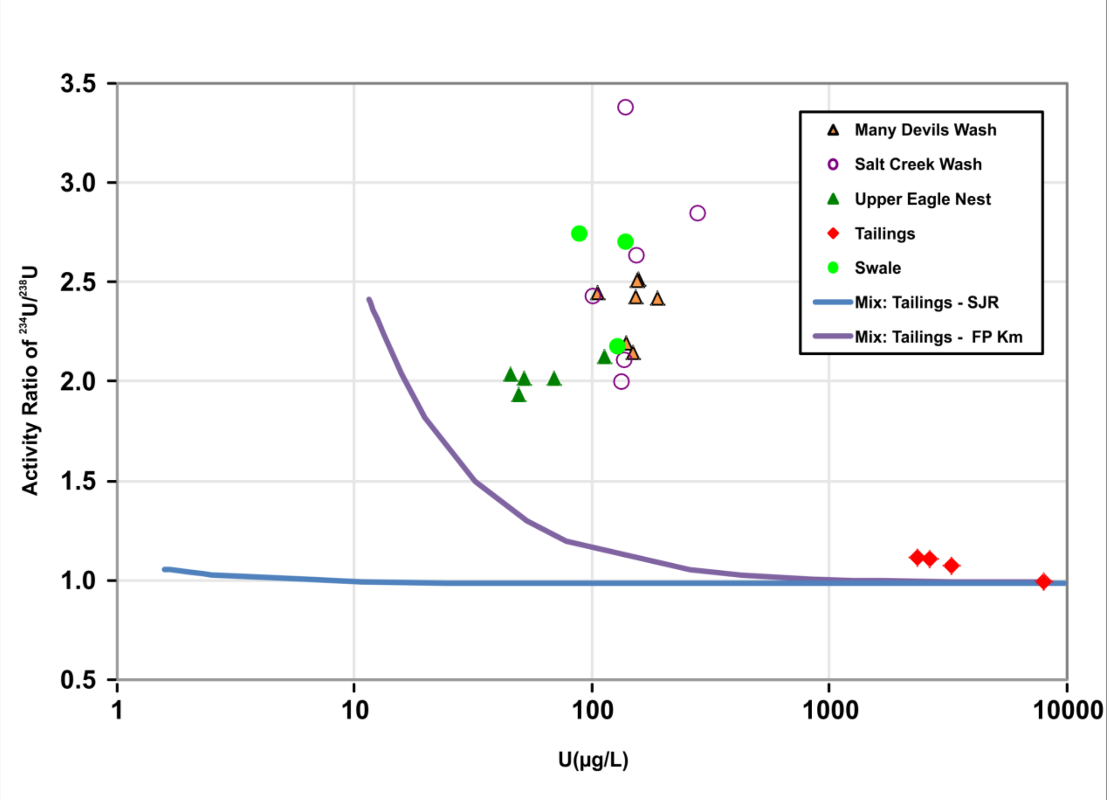

Figure 9. AR and U concentration results for March 2012. Mixing curves are explained on Figure 10.

The U concentrations and AR values of the samples from Many Devils Wash, Salt Creek Wash, Upper Eagle Nest, and the swale are consistent with signatures found in Mancos Shale groundwater seeps in a regional study that covered much of the Mancos depositional basin (DOE 2011b, Morrison et al. 2012). Many of the AR values found in shale seeps in the regional study were higher than 2, and the age of the water feeding some of the seeps was determined to be young (less than about 20 years) based on field relationships. These observations suggest that the U was leached from secondary minerals deposited in the Mancos Shale that had developed elevated AR values by alpha recoil during regional uplift and weathering (DOE 2011b). The signatures shown in Figure 9 for Many Devils Wash, Salt Creek Wash, Upper Eagle Nest, and the swale are consistent with U contributed from leaching of Mancos Shale.

U isotopes were not analyzed on groundwater samples from the Shiprock floodplain in March 2012; however, data are available from samples collected in February 2001 (Figure 10). Based on geologic observation and a conceptualization of groundwater flow paths, the mill-related contamination in terrace groundwater flows through fractured Mancos shale and enters the floodplain alluvium along the escarpment (DOE 2012b). AR values for most of the samples displayed on Figure 10 are near the secular equilibrium value of 1.0, consistent with an origin from the mill tailings. The U concentration and AR signatures in floodplain alluvium are distinct from Many Devils Wash and the analog sites, as can be seen by comparing Figures 9 and 10.

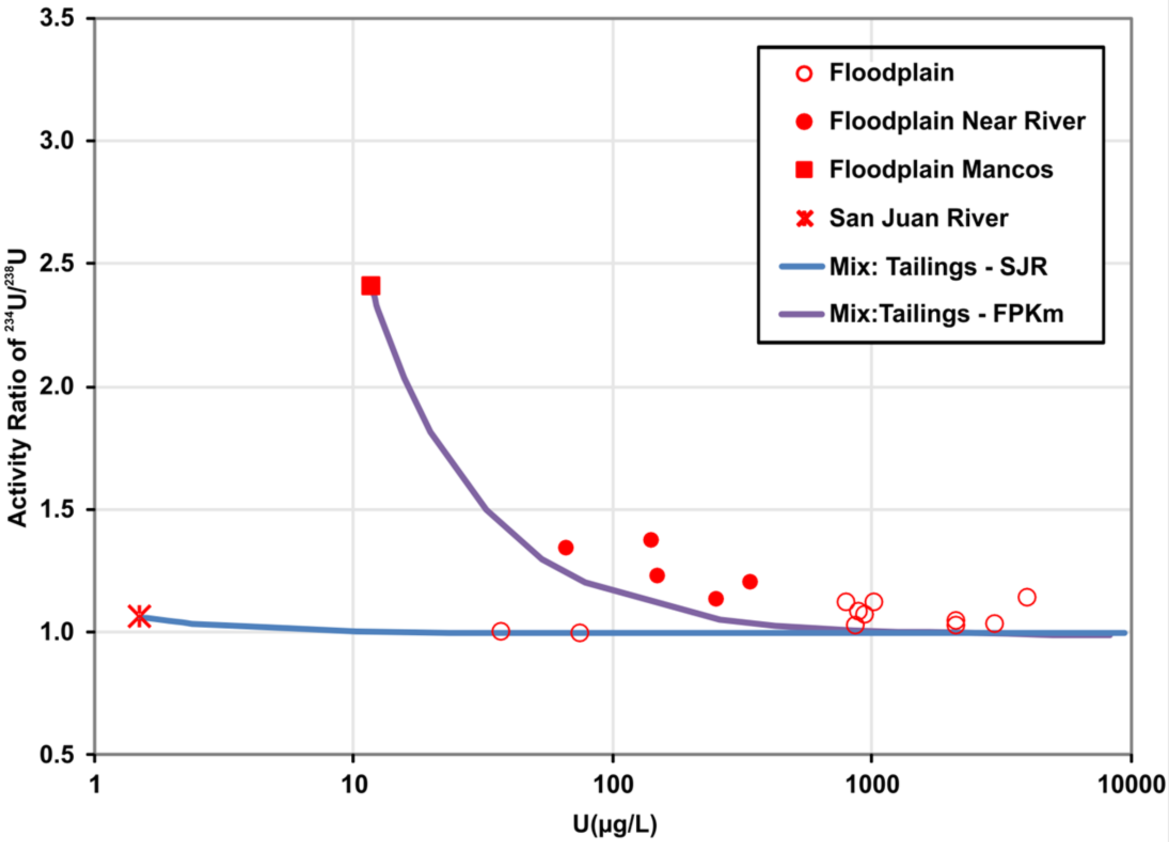

Figure 10. AR and U concentration results from the Shiprock floodplain, February 2001 (both filled and open red circles are floodplain samples; see text for discussion). Curves show calculated mixing of tailings pore water with San Juan River (SJR) water and with Mancos Shale groundwater from a floodplain well (FPKm). The same mixing curves are shown on Figure 9.

Some samples, depicted as closed red circles on Figure 10, have higher AR values that range from 1.13 to 1.38. The samples with these higher AR values are from wells near the San Juan River and may have had more interaction with river water. However, simple mixing of tailings water with San Juan River water will not produce these higher AR signatures, as indicated by the "SJR" mixing line on Figure 10. Because the tailings water has much higher U concentrations, the tailings AR values dominate the mixture until more than 99 percent of the mixture is San Juan River water. Interaction with Mancos Shale can explain the higher AR values measured in the near river samples. A groundwater sample was collected from a floodplain well ("FP Km" on Figure 10) at a depth of 86 ft, which is 72 ft below the upper contact of the Mancos Shale. This Mancos groundwater sample had a U concentration of 11.6 micrograms per liter (µg/L) and an AR value of 2.41. Mixtures of tailings water with Mancos-derived groundwater could produce U isotopic signatures similar to the near river floodplain values (solid red circles), as indicated by mixing curve "FPKm" on Figure 10.

In summary, U isotopic values in tailings groundwater are near the secular equilibrium values derived from the ores. The U in groundwater at Many Devils Wash, the swale, and the analog sites is derived from leaching of Mancos Shale and does not reflect a tailings source. U in groundwater on the floodplain is mostly derived from the tailings; however, floodplain groundwater near the San Juan River may have leached some U from the Mancos Shale.

3.3 Water Isotopes (^{18}O and D)

In Figure 11, values of δ^{18}O and δD for the samples collected for this study in 2011 and in March 2012 and floodplain samples collected by Garvin (2012) in 2010 are compared to the LMWL for the Colorado Plateau compiled by Kendall and Coplen (2001). Three samples collected from greater than 1,000 ft depths in the Morrison and Dakota Formations (denoted as "Deep" in Figure 11) in the Shiprock area had the most depleted δ^{18}O and δD signatures and plot near the LMWL. The San Juan River sample was slightly more enriched than the deep samples and also fell on the LMWL.

Samples collected by Garvin (2012) from floodplain wells near the escarpment had δ^{18}O and δD signatures close to that of the San Juan River, indicating that the groundwater in this area is mostly derived from incursion of river water into the floodplain alluvium (Figure 11). A mixing calculation indicates that a ratio of about 20 parts tailings water to 80 parts San Juan River water will produce this isotopic signature. U concentration data were used to further validate the mixing ratio. Using a reasonable U concentration for the incoming tailings water of 10,000 µg/L, the 20 percent tailings mixture would result in a U concentration of 2,000 µg/L, which is a reasonable value for the floodplain groundwater.

Many of the data from the Salt Creek Wash analog site fall near a linear trend that intersects the LMWL near the Dakota/Morrison groundwater and San Juan River water values. Because it is located hydraulically upgradient and is far removed from the San Juan River, Salt Creek Wash groundwater could not be influenced by river water. However, groundwater in the Dakota Sandstone is artesian in the Salt Creek Wash area and affords a possible source for the Mancos seeps. Groundwater may seep to the surface through natural fractures. Numerous oil and gas wells have been drilled into the Dakota Sandstone in that area (the Salt Creek Dakota Oil Field, Figure 2) and, if compromised, could provide conduits for Dakota groundwater. Another possible source of water for the seeps is local infiltration from meteoric water.

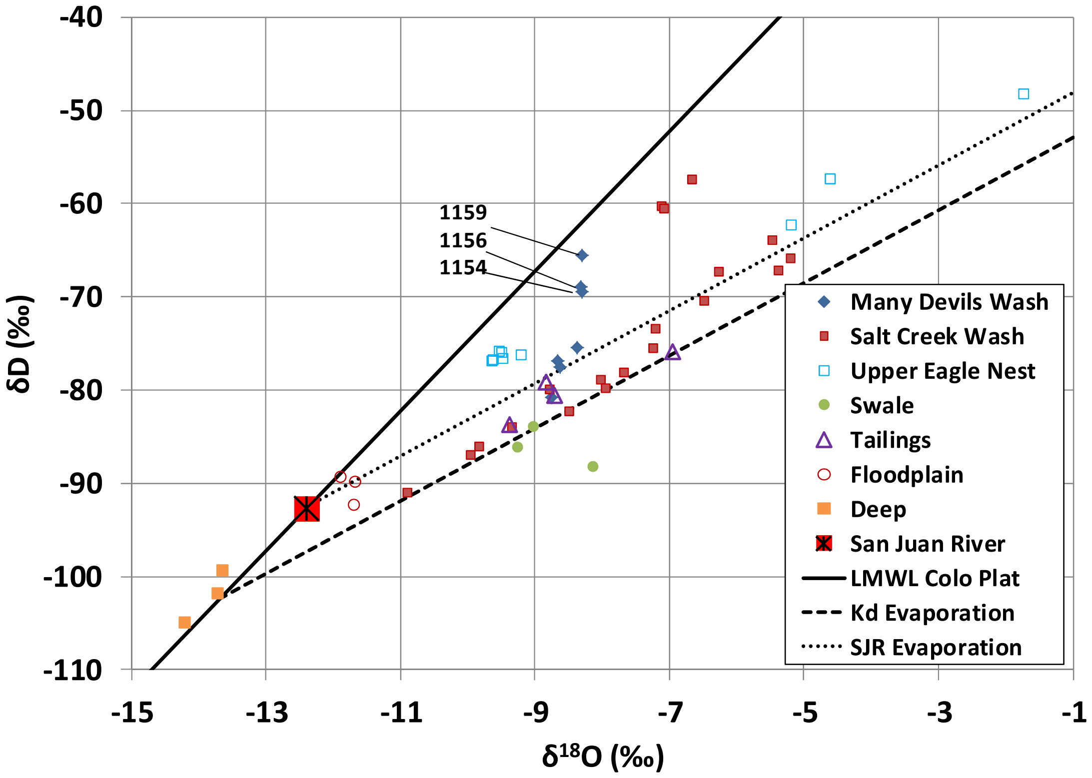

Figure 11. $\delta^{18}O$ versus δD results for 2011 and 2012.
Floodplain results are from Garvin (2012). "Deep" wells are in the Morrison and Dakota Formations.
Evaporation trends for San Juan River (SJR) and "Deep" water are drawn for zero humidity.

The LMWL does not necessarily depict the isotopic composition of infiltration water. Infiltration water is commonly enriched in $\delta^{18}O$ and δD due to fractionation from evaporation and transpiration. Thus, although much of the Salt Creek Wash data fall on a linear trend characteristic of evaporation, it is not possible to determine from $\delta^{18}O$ and δD data alone if the source of water is deep Dakota water or local infiltration. Evaporation of seep water may occur from recent exposure to the atmosphere in the seepage area. During the 2011 investigation, a few samples of seep water were collected from pools adjacent to seeps, and some evaporation may have occurred prior to sample collection (Morrison et al. 2012). Three Salt Creek Wash data points are enriched in δD, with values ranging from -60.1 to -57.4 ‰, relative to the main trend (Figure 11). The three enriched values are from locations SCWE15 and SCWE15A, which are in a separate tributary and may be fed by a separate water source.

$\delta^{18}O$ and δD values of samples from Upper Eagle Nest also fall along a lineation characteristic of evaporation but are enriched relative to those from Salt Creek Wash (Figure 11). The most enriched sample from Upper Eagle Nest ($\delta^{18}O$ = -1.7 ‰) had an anomalously high specific conductivity value, confirming the influence of evaporation on this sample.

Samples from Many Devils Wash had a narrow range of $\delta^{18}O$ values, but δD varied widely from -80.7 to -65.6 ‰ (Figure 11), suggesting that D is being added to or removed from the water. There are few known mechanisms that can explain changes in δD without changes in $\delta^{18}O$. Saturation with hydrogen sulfide gas has been shown to affect such a change in δD and would be possible if the water came up from depth, but there is no evidence for such a mechanism. Another possibility is that more than one source of water contributes to the groundwater system in Many Devils Wash. The most depleted $\delta^{18}O$ and δD samples were collected from the Many Devils Wash seep area (wells 1049 and EF-22) and about 1,000 ft upgradient of the seeps (EF-19). The three most enriched values (δD ranging from -69.5 to -65.6 ‰) were collected from wells 1154, 1156, and 1159, which are located farther to the south and are hydraulically upgradient of the other sampling points in Many Devils Wash (Figure 11).

The tailings data occupy a small area on the δD-versus-$\delta^{18}O$ plot and overlap values from Many Devils Wash and Salt Creek Wash (Figure 11). The uranium mill used San Juan River water, and the tailings water likely had δD-versus-$\delta^{18}O$ signatures similar to river water until it was enriched from evaporation in the mill ponds.

Although the δD-versus-$\delta^{18}O$ signatures provide information about the origin of the water samples collected for this study, various interpretations are possible, and the results, taken by themselves, are insufficient to differentiate individual water sources.

3.4 Nitrogen

Garvin (2012) interpreted $\delta^{18}O$ in dissolved NO_3 ($\delta^{18}O$-NO_3) values in samples from Many Devils Wash to indicate that nitrification of NH_4 derived from the Mancos Shale was most likely the source of NO_3 in groundwater at Many Devils Wash. This inference is based on results documented in several published papers that suggest NO_3 that is formed by nitrification of NH_4 obtains up to two oxygen atoms from the water phase and one oxygen atom from atmospheric O_2 (the "2:1 rule"). The following is a summary of the research most often cited as supporting the 2:1 rule.

Using suspensions of *Nitrobacter agilis* to oxidize NO_2 to NO_3 in $H_2{}^{18}O$, Aleem et al. (1965), Kumar et al. (1983), and Hollocher (1984) separately concluded that the third oxygen atom is derived from water. In the nitrification of NH_4 to NO_2 using suspensions of *Nitrosomonas europaea* with $H_2{}^{18}O$, Andersson and Hooper (1983) found that the NO_2 obtained one oxygen atom from water and one from O_2. Using a single incubation test containing forest floor soils, Mayer et al. (2001) determined that up to two of the oxygen atoms in NO_3 formed from nitrification of soil NH_4 are derived from the water phase. The Mayer et al. (2001) results support the 2:1 rule; however, in a second test, they found that significantly less than two oxygen atoms were derived from the water, presumably because this system was NH_4-limited and proceeded via a different biological pathway. These research efforts suggest a significant contribution of oxygen atoms to the product phases of nitrification, and show that $\delta^{18}O$-NO_3 formed by nitrification commonly ranges from +2 to +14 ‰.

Garvin (2012) applied the 2:1 rule for his data from Many Devils Wash by calculating values of $\delta^{18}O$-NO_3 assuming that the $\delta^{18}O$ of the water that nitrified NH_4 from the Mancos Shale was the same as that measured in the water samples. The differences between the observed $\delta^{18}O$-NO_3 values and the calculated values are provided in Table 2. The differences are all positive values and are within a range typical of nitrification processes reported by other authors. Garvin (2012) suggests that the higher values of observed $\delta^{18}O$-NO_3 are caused by rate-limited nitrification of rock NH_4 leading to a higher proportion of atmospheric O_2 in the NO_3.

Table 2. $\delta^{18}O\text{-}NO_3$ Values in Many Devils Wash Samples and Calculated by the 2:1 Rule. Modified from Garvin (2012). Samples from "This Study" were collected in March 2012.

Sample Number	Reference	Observed $\delta^{18}O\text{-}H_2O$ (‰)	Observed $\delta^{18}O\text{-}NO_3$ (‰)	Calculated $\delta^{18}O\text{-}NO_3$ (‰)	Difference[a] (‰)
EF-13	Garvin (2012)	-8.60	5.48	1.93	3.55
EF-19	Garvin (2012)	-8.83	4.84	1.78	3.06
EF-23	Garvin (2012)	-8.19	7.07	2.21	4.87
EF-24	Garvin (2012)	-8.66	4.52	1.89	2.63
EF-6	Garvin (2012)	-8.59	3.77	1.94	1.83
EF-17	Garvin (2012)	-8.78	4.34	1.81	2.52
Seep	Garvin (2012)	-8.71	5.09	1.86	3.23
1049	Garvin (2012)	-8.60	5.96	1.93	4.03
EF-19	This Study	-8.75	4.62	1.83	2.79
EF-22	This Study	-8.66	5.17	1.89	3.28
1049	This Study	-8.37	5.49	2.09	3.40
1150	This Study	-8.63	4.83	1.91	2.92
1154	This Study	-8.29	7.56	2.14	5.42
1156	This Study	-8.32	7.47	2.12	5.35
1159	This Study	-8.30	8.00	2.13	5.87

[a] Observed $\delta^{18}O\text{-}NO_3$ minus calculated $\delta^{18}O\text{-}NO_3$

The differences from the 2:1 rule measured in our study (Table 2) are similar to those measured by Garvin with a few that are slightly higher (the highest values, those more than 5 ‰, are from the southernmost wells). Although none of the experimental data for $\delta^{18}O\text{-}NO_3$ in the literature are from rock NH_4, it seems plausible that nitrification of rock NH_4 would also obey the 2:1 rule. Thus, it can be stated that the $\delta^{18}O\text{-}NO_3$ signatures in Many Devils Wash are consistent with current knowledge of the nitrification processes.

To help determine if the $\delta^{18}O\text{-}NO_3$ signatures from Many Devils Wash are unique, the 2:1 rule was applied in the same manner to the other samples collected for this study, and the differences are plotted on Figure 12. Other than one outlier from the tailings, the results from Salt Creek Wash, the swale, the tailings, and Upper Eagle Nest are within the same general range as those from Many Devils Wash. Thus, the $\delta^{18}O\text{-}NO_3$ signatures do not appear to be useful in distinguishing among the sample populations.

$\delta^{15}N\text{-}NO_3$ values were collected to provide an additional signature of the contaminated water in Many Devils Wash. On a plot of $\delta^{15}N\text{-}NO_3$ versus $\delta^{18}O\text{-}NO_3$, samples from some populations occur together, whereas others are spread out (Figure 13). Many Devils Wash samples occur in two clusters along a lineament developed by Garvin (2012) as the best fit to his Many Devils Wash data (Figure 13). Salt Creek Wash samples are scattered and are enriched in $\delta^{18}O\text{-}NO_3$ relative to the lineament. Upper Eagle Nest samples form a group near the Many Devils Wash samples. Several of the tailings samples have $\delta^{15}N\text{-}NO_3$ values similar to those at Many Devils Wash, Upper Eagles Nest, and Salt Creek Wash, but others vary considerably. Floodplain samples are highly variable and are separated from other populations. The swale samples had similar $\delta^{15}N\text{-}NO_3$ values but depleted and variable $\delta^{18}O\text{-}NO_3$ values. Three samples collected from the San Juan River have similar $\delta^{15}N\text{-}NO_3$ values but variable $\delta^{18}O\text{-}NO_3$ values (Figure 13). These results indicate that the $\delta^{15}N\text{-}NO_3$ and $\delta^{15}N\text{-}\delta^{18}O$ data have limited value in determining the origin of Many Devils Wash seepage water.

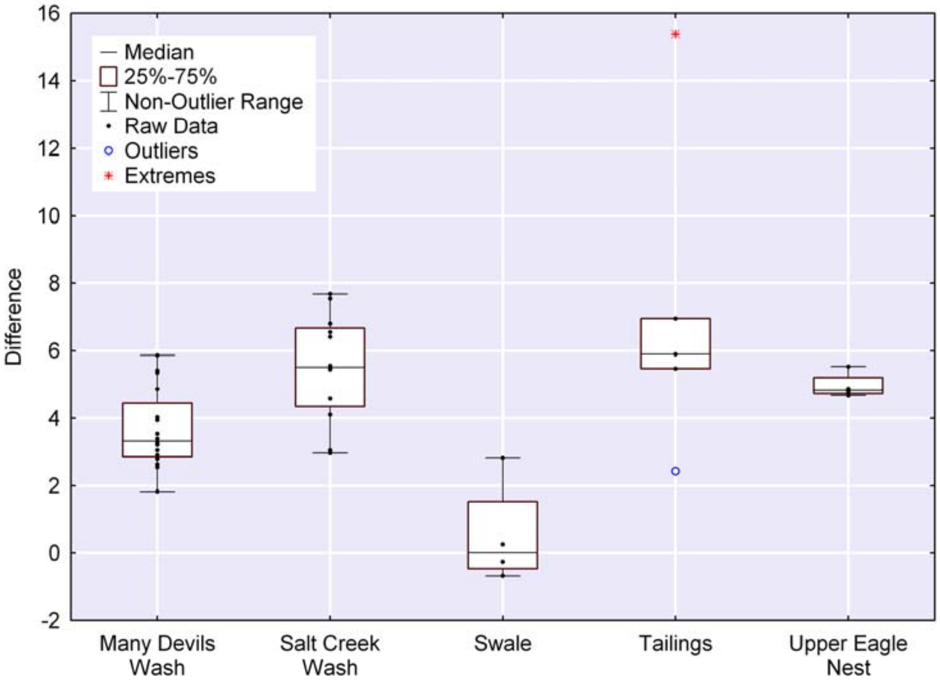

Figure 12. Distributions of differences in ‰ between observed and calculated $\delta^{18}O\text{-}NO_3$ by population.

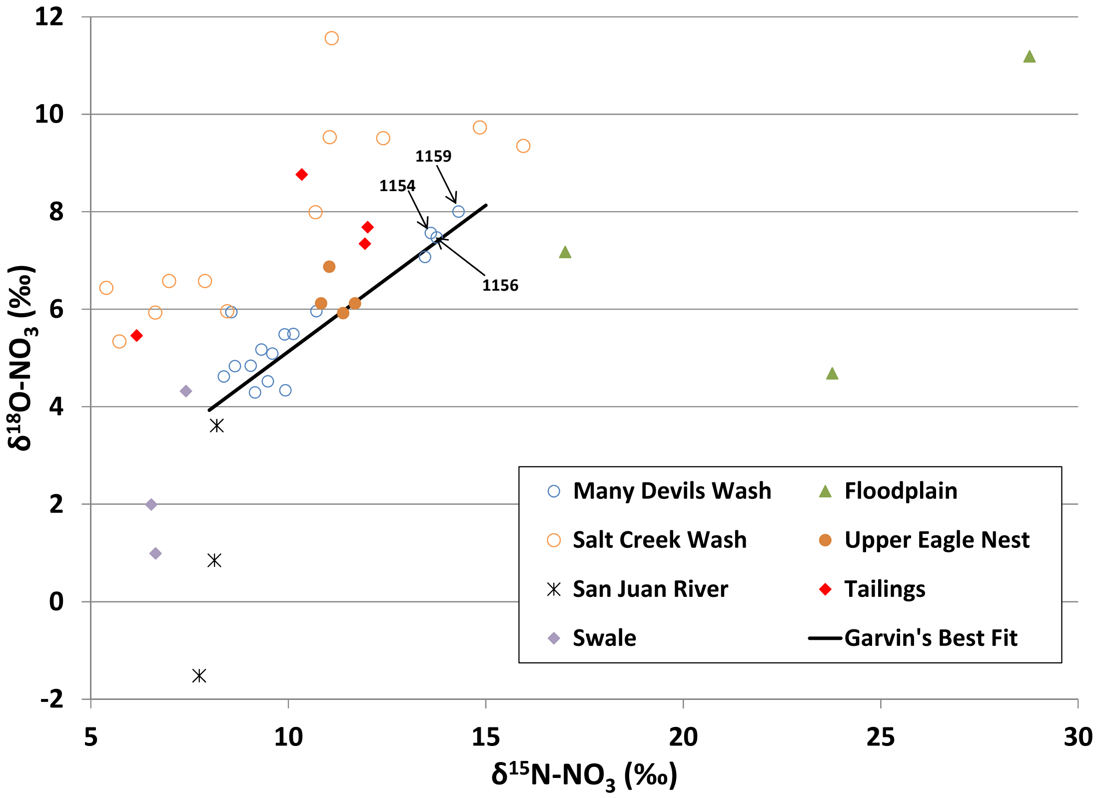

Figure 13. $\delta^{15}N$ versus $\delta^{18}O$ in dissolved NO_3. Floodplain data and some data from Many Devils Wash and San Juan River are from Garvin (2012). Garvin's (2012) best-fit line to his data from Many Devils Wash is shown.

Garvin (2012) used δ^{15}N-NO_3 and δ^{18}O-NO_3 values to provide an isotopic signature for interpreting nitrogen cycling. Denitrification causes an increase both the δ^{15}N-NO_3 and the δ^{18}O-NO_3 in the residual groundwater. Literature references provided by Garvin (2012) indicate that loss of NO_3 from denitrification commonly produces a slope of about 0.5 on a δ^{15}N-NO_3 versus δ^{18}O-NO_3 plot. Garvin's (2012) data had a similar slope of 0.6, suggesting that denitrification was active. Garvin's best-fit line matches well with our March 2012 data (Figure 13). An assessment of denitrification using this approach assumes that a mass of water progressively loses its NO_3 through denitrification, with the δ^{15}N-NO_3 and δ^{18}O-NO_3 of the residual fraction continually enriching, a process that is described by Rayleigh fractionation.

In a groundwater system, loss of NO_3 and increasing δ^{15}N-NO_3 should occur as the groundwater mass moves down the hydraulic gradient. In contrast, the data from Many Devils Wash have an opposite trend. The heaviest δ^{15}N-NO_3 and δ^{18}O-NO_3 signatures in Many Devils Wash are in hydraulically upgradient wells 1154, 1156, and 1159 (Figure 13). Thus, denitrification via Rayleigh fractionation does not accurately depict the observed trend in δ^{15}N-NO_3 and δ^{18}O-NO_3.

3.5 Tritium

^{3}H activities measured in samples collected from the San Juan River at a single location in April 2011, December 2011, and March 2012 were 23.6, 18.3, and 19.9 pCi/L, respectively. The March 2012 value is plotted on Figure 14 and was considered to represent the ^{3}H activity in precipitation in the Shiprock area caused by cosmogenic effects.

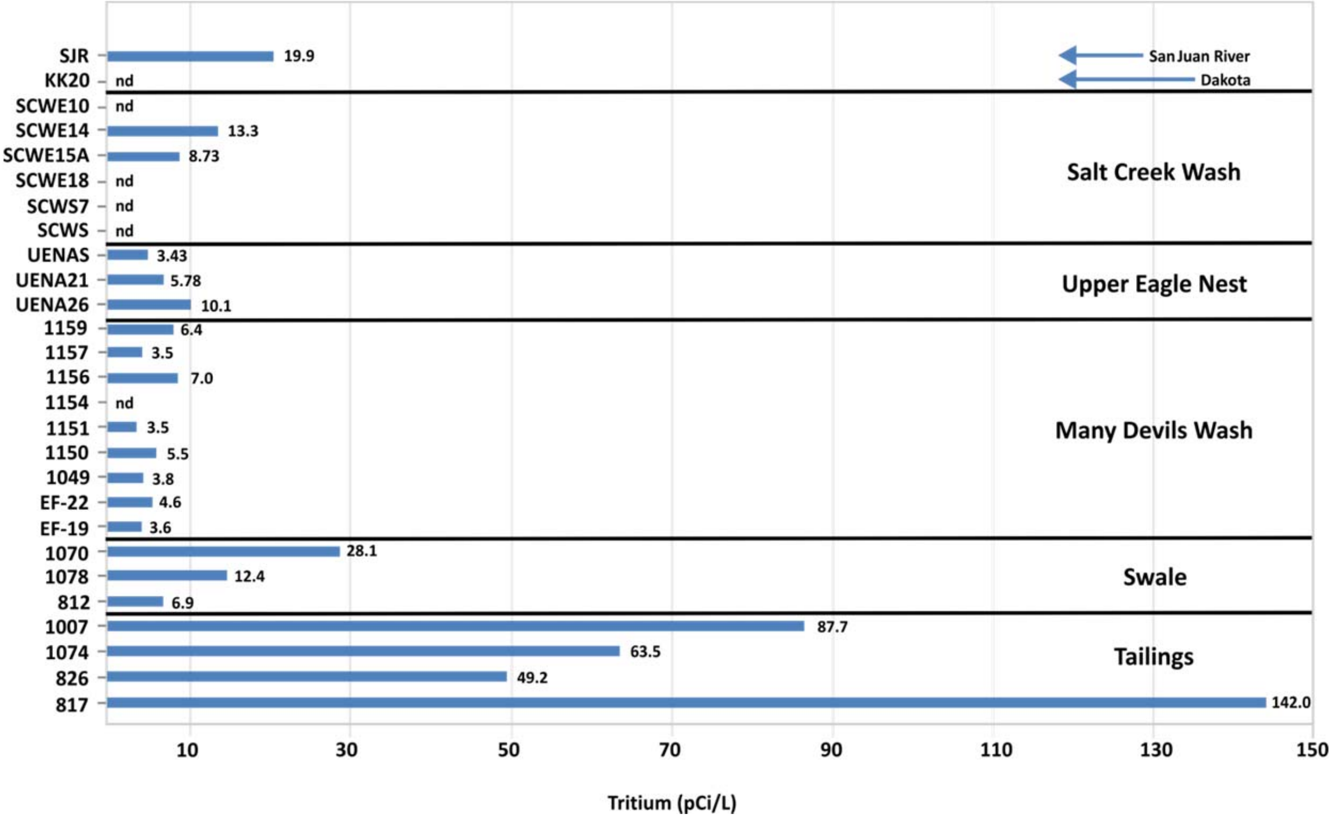

Figure 14. Tritium results. nd = not detected.

The ^3H activity was less than the detection limit (about 2.5 pCi/L) in the deep sample collected from the Dakota Formation in the Salt Creek Wash area. Four samples collected from seeps in Salt Creek Wash also had ^3H activities less than the detection limit (Figure 14). These seeps may be fed from deep groundwater. The two samples from Salt Creek Wash (SCWE14 and SCWE15A) that had detectable ^3H were collected from seeps in a tributary separated from the other sample locations and may have had a different source of water, possibly recent infiltration. ^3H activity ranged from 3.43 to 10.1 pCi/L in the three samples collected from seeps at Upper Eagle Nest. These seeps may contain a mixture of deep groundwater and recent recharge.

The four tailings samples had ^3H activities that greatly exceeded the San Juan River values (Figure 14). After accounting for subsequent decay to the year 2012, the tailings values are consistent with ^3H activities that Clark and Fritz (1997) considered to be "dominantly 1960s recharge." The mill operated from 1954 to 1968, and the tailings water likely reflects a bomb-spike value resulting from the use of surface water in the milling process.

The samples from Many Devils Wash are all low in ^3H. Activities range from nondetect (less than about 2.5 pCi/L) to 7.0 pCi/L (Figure 14). Artesian conditions are present in the deep subsurface in the project area, as evidenced by a well completed at 1,860 ft in the Morrison Formation, which has had a nearly constant flow of about 64 gallons per minute to the mill site area since its installation in 1961. The Gallup Sandstone is present at a depth of about 550 ft along the Many Devils Wash axis, and groundwater in the Gallup is likely artesian. The low ^3H activities in groundwater in Many Devils Wash provide evidence that the wash may be fed by a deep groundwater source. Another possibility is that the wash is fed by meteoric water with travel times exceeding 30 years.

^3H activities in the swale samples ranged from 6.9 to 28.1 pCi/L. The swale values are consistent with a mixture of recent infiltration and deep groundwater. The highest ^3H value (28.1 pCi/L) is higher than the San Juan River values and may reflect a component of bomb-spike water, possibly from the tailings area. The ^3H activities in the swale groundwater could also be derived from meteoric water with travel times of several decades.

4.0 Conclusions

Environmental isotopes were used to fingerprint groundwater in Many Devils Wash and make comparisons with groundwater at the nearby Shiprock mill site and two analog sites. Based on distance and hydraulic gradients, we conclude that groundwater at the analog sites could not have been affected from contaminants from the Shiprock mill site. The groundwater at the analog sites has contaminant concentrations similar to those in Many Devils Wash. Isotopic results indicate that the contaminants in Many Devils Wash, the swale, and the analog sites are likely derived from interaction with the Mancos Shale and that contaminants from the tailings disposal cell likely feed the shallow alluvium near the mill site and were transported by groundwater to the floodplain. The isotopic results are consistent with a multivariate analysis of chemical concentration data conducted in a companion study (DOE 2012d).

The $\delta^{34}S$-SO_4 and the uranium AR values were the most diagnostic isotopic parameters for distinguishing Mancos-related contamination from mill-related contamination. The Mancos-derived SO_4 values were depleted in $\delta^{34}S$, with most values less than -20 ‰, whereas milling-derived SO_4 had $\delta^{34}S$ values near 0 ‰. Milling-derived U has an AR near the secular equilibrium value of 1, whereas Mancos-derived U had higher AR values that were typically more than 2.

Several isotopic signatures defined two distinct groups of samples collected from groundwater in Many Devils Wash: southern upgradient wells (1154, 1156, and 1159) and northern downgradient wells. With one exception, samples collected from the upgradient wells were more enriched in δD than those collected from the downgradient wells. Also, the $\delta^{15}N$ and $\delta^{18}O$ values of dissolved nitrate were enriched, and the $\delta^{34}S$ values of dissolved SO_4 were slightly depleted, in the upgradient wells. A possible explanation of these isotopic signatures is the occurrence of separate water sources for the upgradient and downgradient groundwater.

^3H activities in the tailings far exceeded those in all other groundwater samples. The high ^3H activity in the tailings results from bomb-spike water used in the milling process. Where mill tailings sites used surface water, the ^3H signatures are useful in tracking mill-related groundwater contamination.

5.0 Acknowledgments

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Appendix A

Unpublished Sulfur Isotope Data Sampled February 14 and 15, 2012 from the Tuba City, Arizona, Disposal Cell

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Table A–1. Unpublished Sulfur Isotope Data Sampled from the Tuba City, Arizona, Disposal Cell

Well	**SO_4 (mg/L)**	**$\delta^{34}S$ ‰**
0262	1850	3.2
0263	2840	1.68
0265	1120	-3.28
0267	2990	0.78
0268	363	-3.22
0275	2200	-2.15
0286	2850	-1.62
0287	1670	-4.61
0906	2060	-4.04
0908	2620	-0.94
0934	2800	-2.58
0935	2350	-2.21
0938	2420	-3.41
0940	6490	-1.43
0941	1390	-5.56
0942	2990	4.01
1131	1760	2.27

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