

Terrace Geochemistry at the Shiprock, New Mexico, Disposal Site – 17232

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ABSTRACT

The objective of this investigation was to identify and differentiate potential non-mill-related water inputs to a shallow terrace groundwater system through the use of aqueous chemical and isotopic tracers at a former uranium- and vanadium-ore processing facility.

Terrace groundwater in the vicinity of the Shiprock, New Mexico, site is hypothesized to be largely anthropogenic because natural rates of recharge in the terrace are likely insufficient to sustain a continuous water table in the terrace alluvial system, as observed in several analogue terrace locations east of the site and in response to post-mill dewatering efforts across the site. The terrace is composed of alluvial sand and gravel and weathered and unweathered Mancos Shale. Terrace groundwater exists and flows in the alluvium and to a much less extent in the Mancos Shale. Historical data established that in both the terrace and floodplain below the terrace, mill-derived uranium and sulfate is found primarily in the alluvium and the upper portion of the weathered Mancos Shale. Groundwater extraction is being conducted in the vicinity of former mill operations and in washes and seeps to dewater the formation and remove contamination, thus eliminating these exposure pathways and minimizing movement to the floodplain. However, past and present contribution of non-mill anthropogenic water sources may be hindering the dewatering effort, resulting in reduced remedy effectiveness.

Groundwater source signatures can be determined based on chemical and isotopic ratios and are used to help identify and delineate both mill and non-mill water contributions. Aqueous chemical and isotopic tracers, such as $^{234}\text{U}/^{238}\text{U}$ activity ratios and uranium concentrations, $\delta^{34}\text{S}_{\text{sulfate}}$ and sulfate concentrations, tritium concentrations, and $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ are being used in this Phase I study. The aqueous chemical and isotopic analysis has identified areas on the terrace where groundwater is derived from mill-related activities and areas where the groundwater is associated with non-mill activities. A separate field effort of Phase II work will follow, including investigating additional locations for these isotopes and examination of $\delta^{18}\text{O}_{\text{sulfate}}$, $\delta^{34}\text{S}_{\text{sulfate}}$, and chlorofluorocarbon signatures.

INTRODUCTION

The Shiprock, New Mexico, Uranium Mill Tailings Radiation Control Act (UMTRCA) Title I Disposal Site is a former uranium- and vanadium-ore processing facility located in the Navajo Nation adjacent to the San Juan River and the town of Shiprock, New Mexico (Figure 1). The site is managed by the US Department of

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Energy (DOE) Office of Legacy Management (LM) and is situated on an alluvial terrace just south of the San Juan River. The compliance strategy for the terrace is to pump the remaining mill-related water out of the surficial water system (the alluvium and weathered Mancos Shale) and allow this portion of the groundwater system to revert to its original nature, thereby drying the seeps and curtailing surface expression of the groundwater [1]. While most of the east terrace alluvium has been dewatered in response to remedial pumping initiated in 2000, a few locations still exhibit excessive alluvial saturation or persistent seepage from the alluvium. A two-phase investigation is in progress to better understand the origin of groundwater that presently exists on the terrace. Potential historic and present sources of water on the terrace include (1) water related to the operation of the uranium mill, (2) domestic water use on the terrace, (3) irrigation water, (4) pre-mill groundwater, and (5) infiltration of precipitation [2].

METHODS

An initial Phase I of terrace water sampling was conducted in accordance with the associated Work Plan [2], beginning in September 2015 and continuing into February 2016. Figure 1 shows Phase I sampling locations and site features.

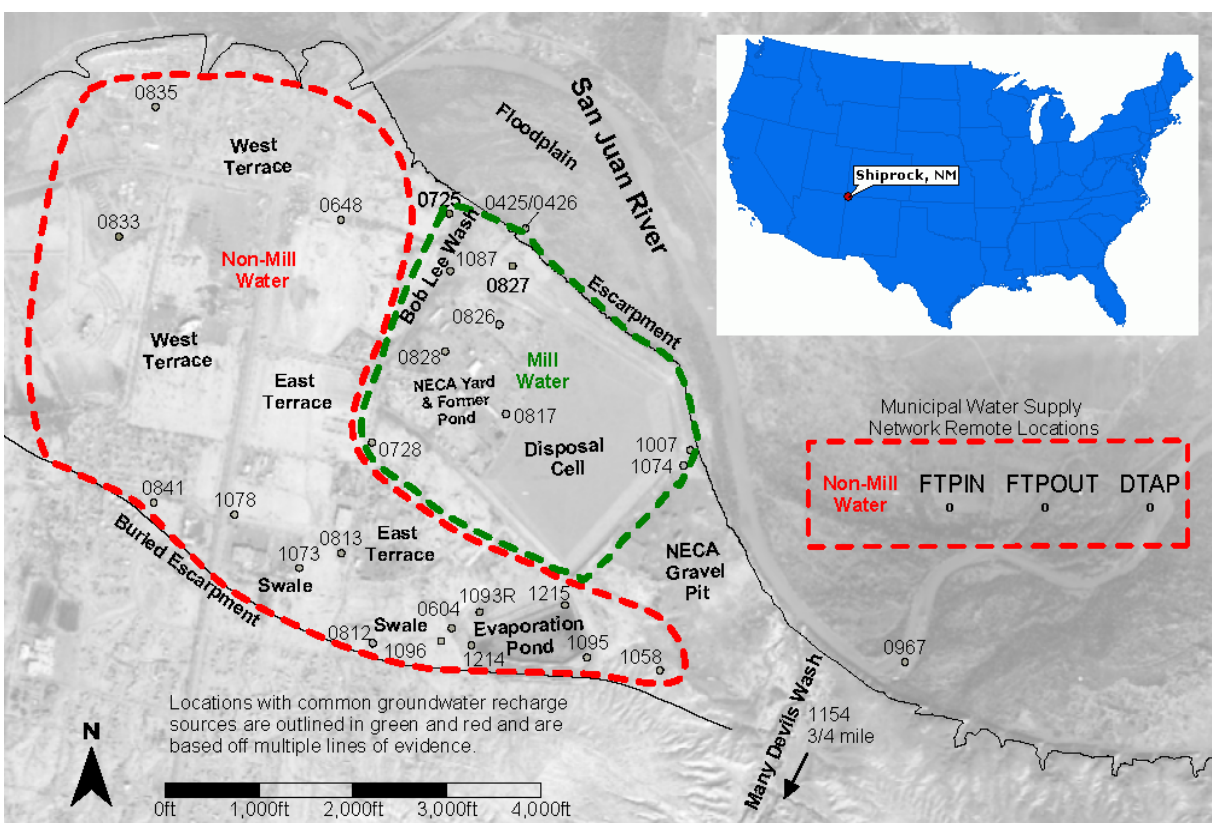


Figure 1. Phase I Sampling Network Locations with Water Source Zones Identified To determine the sources of terrace groundwater the following data were collected:

- Uranium-234/uranium-238 ($^{234}\text{U}/^{238}\text{U}$) activity ratios (ARs) and uranium concentrations

- Delta sulfur-34 of sulfate ($\delta^{34}\text{S}_{\text{sulfate}}$) and sulfate concentrations
- Tritium concentrations
- Delta hydrogen-2 ($\delta^2\text{H}_{\text{water}}$) and delta oxygen-18 ($\delta^{18}\text{O}_{\text{water}}$) ratios in water

These data were selected because a recent study of the source of water in Many Devils Wash [3] showed that certain sulfur stable isotopes (in sulfate), tritium concentration, and $^{234}\text{U}/^{238}\text{U}$ ARs are diagnostic of mill-related water. Specifically, milling-derived sulfate had $\delta^{34}\text{S}_{\text{sulfate}}$ values near 0‰, while most non-mill-related sulfate had values less than -20‰ . Mill-derived uranium had an activity ratio near 1, whereas natural uranium had values typically more than 2. Tritium in mill-related water had an average activity of 76 picocuries/liter (pCi/L), while non-mill-related tritium had activities below 30 pCi/L (mostly below 10 pCi/L).

DISCUSSION

Aqueous chemical and isotopic data from the Phase I sampling is presented in Table I for each analysis or isotopic ratio.

The term *mill water* here describes San Juan River water used by the mill when it was in operation from 1954 to 1968 that was contaminated during milling. The term *non-mill water* refers to other water sources on the terrace such as San Juan River water used as dust control during the decommissioning of the mill and as irrigation water on the west terrace, water withdrawn from the Animas River that is treated and used for domestic water and is conveyed through pipes, some of which leak, and the infiltration of precipitation. The $^{234}\text{U}/^{238}\text{U}$ AR is the ultimate arbitrator as to whether water on the terrace is derived from mill or non-mill sources. The other isotopes collected during this study provide additional insight into the source of terrace water but are never used to overrule the $^{234}\text{U}/^{238}\text{U}$ AR mill or non-mill conclusions. Figure 1 also depicts generalized site areas of mill water and non-mill water interpreted from all data. In this study it was not possible to distinguish among the non-mill water sources, so a distinction is made only between mill and non-mill water.

$^{234}\text{U}/^{238}\text{U}$ Activity Ratios and Uranium Concentrations

The $^{234}\text{U}/^{238}\text{U}$ AR data are used in determining the source of uranium in a groundwater sample because the $^{234}\text{U}/^{238}\text{U}$ AR can distinguish between the uranium derived from weathering of local aquifer minerals and the uranium derived from processing mills [4]. Zielinski et al. state that most natural groundwater has a $^{234}\text{U}/^{238}\text{U}$ AR greater than 1.0, with typical values in the range of 1–3, but values in excess of 10 can occur [4]. In contrast, uranium in raffinate contains residual amounts of uranium originally brought into solution by reacting the uranium ore with strong oxidizing solutions of acid or alkali. This uranium is derived from a mixture of materials with ARs above and below 1.0, which presumably has not been exposed to oxidizing conditions. With these considerations, uranium ores that are processed in a mill should have an estimated time-integrated average AR of 1.0 ± 0.2 . The raffinate should retain the uranium-isotope composition of the processed ore because neither the rapid, nearly complete dissolution of uranium from crushed ore or further chemical processing of the leachate will promote any isotopic fractionation [4].

Table I. Chemical and Isotopic Data Used To Assess the Source of Groundwater on the Terrace with Interpretive Groupings and Probable Recharge Dates

Location	²³⁴ U/ ²³⁸ U Ratio	Uranium (mg/L)	δ ³⁴ S _{sulfate}	Sulfate (mg/L)	Tritium (pCi/L)	Tritium (TU)	Probable Recharge Dates	δ ² H _{water}	δ ¹⁸ O _{water}
San Juan River Water									
0967	1.65	0.004	-2.74	280	16.4	5.1		-108.73	-14.82
Animas River Water									
DTAP	1.40	-	4.75	-	3.21	1.0		-89.56	-11.94
FTPIN	1.19	-	4.72	-	4.68	1.5		-90.26	-11.95
FTPOUT	1.38	-	4.79	-	2.84	0.9		-89.15	-11.96
Many Devils Wash, U and SO ₄ from 3/2012 and Tritium from 10/2015									
1154	2.19	0.139	-30.65	15,800	8.42	2.6	Since 1979	-67.41	-8.39
Evaporation Pond									
1214	1.13	-	-4.85	-	13.7	4.3	Since 1971	-20.52	1.72
1215	1.17	5.700	-5.13	68,000	11.4	3.5	Since 1972	-13.92	4.17
Adjacent to the Evaporation Pond									
1093R	1.45	0.110	-5.51	6,700	69.8	21.7	1962–1971	-75.54	-8.50
1095	1.86	0.043	0.22	5,500	49.9	15.5	1962–1971	-78.34	-9.13
Adjacent to the Disposal Cell									
0817*	0.98	9.180	-1.76	9,730	77.1	23.9	1962–1971	-78.01	-8.77
0826*	1.09	3.660	-3.66	13,700	-	-		-83.79	-9.38
1007	1.12	2.500	1.09	13,000	67.1	20.8	1962–1971	-79.50	-9.06
1074*	1.13	2.110	-4.75	7,510	63.5	19.7	1962–1971	-75.92	-6.95
Swale									
0604	3.64	0.074	-17.00	12,000	32.1	10.0	1966–1969	-88.53	-9.50
0812*	2.71	0.138	-22.77	17,000	6.91	2.1	Since 1982	-88.22	-8.15
0813	2.22	0.078	-10.61	2,800	61.1	19.0	1962–1971	-82.74	-8.66
0841	2.46	0.120	-22.78	14,000	10.9	3.4	Since 1972	-84.17	-9.62
1078	2.21	0.120	-21.66	14,000	9.29	2.9	Since 1975	-82.52	-9.36
1096	2.62	0.085	-21.72	15,000	11.2	3.5	Since 1972	-86.01	-9.60
Bob Lee Wash									
0648	-	-	11.91	-	2.46	0.8	Prior 1953	-103.74	-14.04
0725	1.08	0.075	3.91	3,000	2.93	0.9	Prior 1953	-99.21	-13.19
1087	1.15	0.320	-4.96	4,800	36.6	11.4	Since 1965	-81.28	-10.63
Alluvium									
0827	1.18	0.800	-7.74	8,800	66.4	20.6	1962–1971	-84.10	-10.48
0833	1.56	0.044	-4.52	3,700	19.8	6.1	Since 1969	-89.87	-11.54
0835	1.64	0.0031	2.31	120	21.7	6.7	Since 1969	-92.58	-12.16
Alluvium and Mancos Shale									
0728	1.12	0.120	-15.82	2,800	16.2	5.0	1969–1972	-93.81	-12.38
0828	1.00	0.380	-14.21	1,600	22.2	6.9	Since 1966	-83.04	-10.60
East of the Disposal Cell									
1058	2.83	0.0032	-6.58	5,800	9.67	3.0	Since 1979	-96.24	-11.46
Seeps from Terrace									
0425/0426	1.21	0.450	-5.86	6,100	13.5	4.2	Since 1971	-89.76	-11.70

Abbreviations: - = no data, * = historical data to assist interpretation, mg/L = milligrams per liter, TU = tritium unit

Color coding of data identified below and discussed in subsequent isotope subsections:

²³⁴U/²³⁸U ratio and δ³⁴S_{sulfate} signatures: red = mill related, yellow = non-mill related, and purple = non-definitive.

δ²H_{water} and δ¹⁸O_{water} signatures: Group 1 = gray, Group 2 = brown, Group 3 = blue, and Group 4 = green.

The $^{234}\text{U}/^{238}\text{U}$ AR data are plotted in Figure 2 as a function of the concentration of uranium to emphasize that groundwater can contain relatively high concentrations of uranium that may exceed the UMTRCA groundwater standard of 0.044 milligrams per liter (mg/L) but be derived from non-mill or natural sources. For example, groundwater samples collected from Eagle Nest Arroyo and Salt Wash Creek, which are near the Shiprock UMTRCA site but not in hydraulic connection with the site, have $^{234}\text{U}/^{238}\text{U}$ AR values greater than 1.2 but have uranium concentrations 2 to 3 times greater than the UMTRCA groundwater standard. The source of the uranium is the Mancos Shale, which has naturally occurring high levels of uranium.

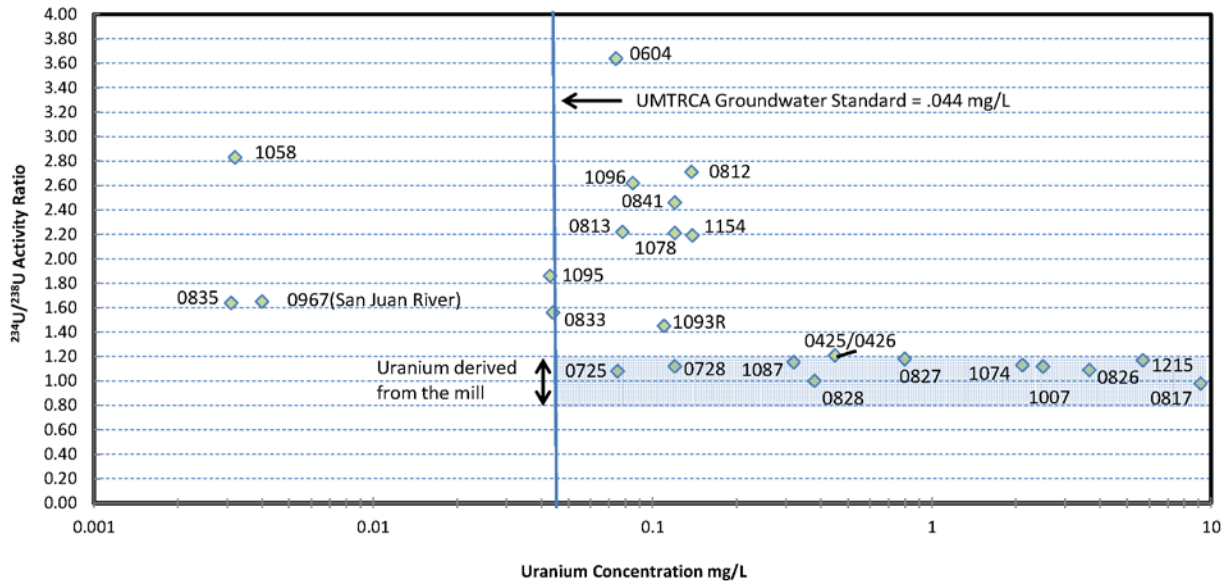


Figure 2. $^{234}\text{U}/^{238}\text{U}$ Activity-Concentration Plot of Shiprock Groundwater

The plot of the $^{234}\text{U}/^{238}\text{U}$ AR versus uranium concentration shows that groundwater sampled at locations 0725, 0728, 0817, 0826, 0827, 0828, 1007, 1074, 1087, and evaporation pond site 1215 contains uranium derived from milling operations (Figure 2). Wells 0725, 0728, 0828, sump 1087, and seeps 0425 and 0426 have uranium ARs that indicate a mill source of uranium, but the uranium concentrations are relatively low: 0.075, 0.120, 0.380, 0.320, and 0.450 mg/L, respectively, relative to those of wells 0817, 0827, 1007, and 1074 (Table I). This may be a result of uranium attenuation as mill water flowed away from the former mill site. Uranium attenuation, or the loss of uranium from groundwater, can occur from a variety of physical and chemical processes. Physical processes include advection, diffusion, and dispersion. Chemical processes include adsorption to the weathered Mancos Shale and precipitation of uranium minerals such as coffinite (USiO_4) and uraninite (UO_2).

The $^{234}\text{U}/^{238}\text{U}$ ARs for wells located in the swale (0604, 0812, 0813, 0841, 1078, and 1096), wells located adjacent to the evaporation pond (1093R and 1095), wells located farthest west of the disposal cell (0833 and 0835), and well 1058 located east of the disposal cell indicate a non-mill source of uranium.

$\delta^{34}\text{S}_{\text{sulfate}}$ and Sulfate Concentrations

In groundwater, the sulfur ($\delta^{34}\text{S}_{\text{sulfate}}$) and oxygen ($\delta^{18}\text{O}_{\text{sulfate}}$) compositions in sulfate (SO_4^{2-}) result from the isotopic fractionation of the source elements from chemical and biological processes. As Faure states, "The most important cause for variations in the isotopic composition of sulfur in nature is the reduction of sulfate ions by anaerobic bacteria such as *Desulfovibrio desulfuricans* which live in sediment deposited in the oceans and in lakes. These bacteria split oxygen from sulfate ions and excrete H_2S which is enriched in ^{32}S relative to the sulfate." [5] Under reducing conditions, the hydrogen sulfide (H_2S) can react with elements such as iron to form metallic sulfides, which precipitate from solution. When subsequently exposed to the atmosphere during erosion, these metallic sulfides are oxidized to sulfate, and the sulfur atom retains the isotopic signature it had in the metallic sulfide. Therefore, negative $\delta^{34}\text{S}_{\text{sulfate}}$ values indicate that the sulfate was created from the dissolution of a sulfide mineral in which the H_2S originated from reduction of sulfate by anaerobic bacteria. The Mancos Shale was deposited in the Cretaceous Sea, and the sulfate contained within was formed in the manner just described and has highly negative values of $\delta^{34}\text{S}_{\text{sulfate}}$.

A comparison of the $\delta^{34}\text{S}_{\text{sulfate}}$ values in groundwater with those in sulfuric acid can assist in identifying the source of sulfate in groundwater. Sulfuric acid, used in ore processing, is usually produced from hydrogen sulfide gas recovered from oil and gas production (<http://www.sulphurinstitute.org/learnmore/faq.cfm>). Faure states that the $\delta^{34}\text{S}_{\text{sulfate}}$ values of sulfur in H_2S gas range from -8‰ to $+32\text{‰}$ [5]. While the $\delta^{34}\text{S}_{\text{sulfate}}$ value for sulfuric acid used at the mill is not available; comparison of $\delta^{34}\text{S}_{\text{sulfate}}$ samples collected from wells surrounding the Shiprock Site (0817, 0826, 1007, and 1074), and off-site locations that used the same milling process (White Mesa Uranium Mill, Utah; Tuba City, Arizona UMTRCA site, and Ambrosia Lake, New Mexico UMTRCA site) indicate that the $\delta^{34}\text{S}_{\text{sulfate}}$ value of the sulfuric acid used at the Shiprock Mill most likely was in the range of -5‰ to $+5\text{‰}$ (Figure 3).

Plots of $\delta^{34}\text{S}_{\text{sulfate}}$ show that groundwater in wells adjacent to the disposal cell, 0817, 0826, 1007, 1074, and 1087 and evaporation pond sites 1214 and 1215 most likely have sulfate derived from sulfuric acid used in the milling process and support the interpretation of the $^{234}\text{U}/^{238}\text{U}$ AR data of mill-derived water as a source of sulfate and uranium at these wells (Figure 3). Wells 1093R and 1095 are extraction wells located adjacent to the evaporation pond. Well 1093R has a $\delta^{34}\text{S}_{\text{sulfate}}$ value indicating a non-mill source of sulfate and supports the interpretation of the $^{234}\text{U}/^{238}\text{U}$ AR data of non-mill water as a source of uranium to this well. Well 1095 has a $\delta^{34}\text{S}_{\text{sulfate}}$ value indicating a mill source of sulfate and a $^{234}\text{U}/^{238}\text{U}$ AR that indicates a non-mill source of uranium. The reason for the different source signatures with respect to sulfate and uranium is not known.

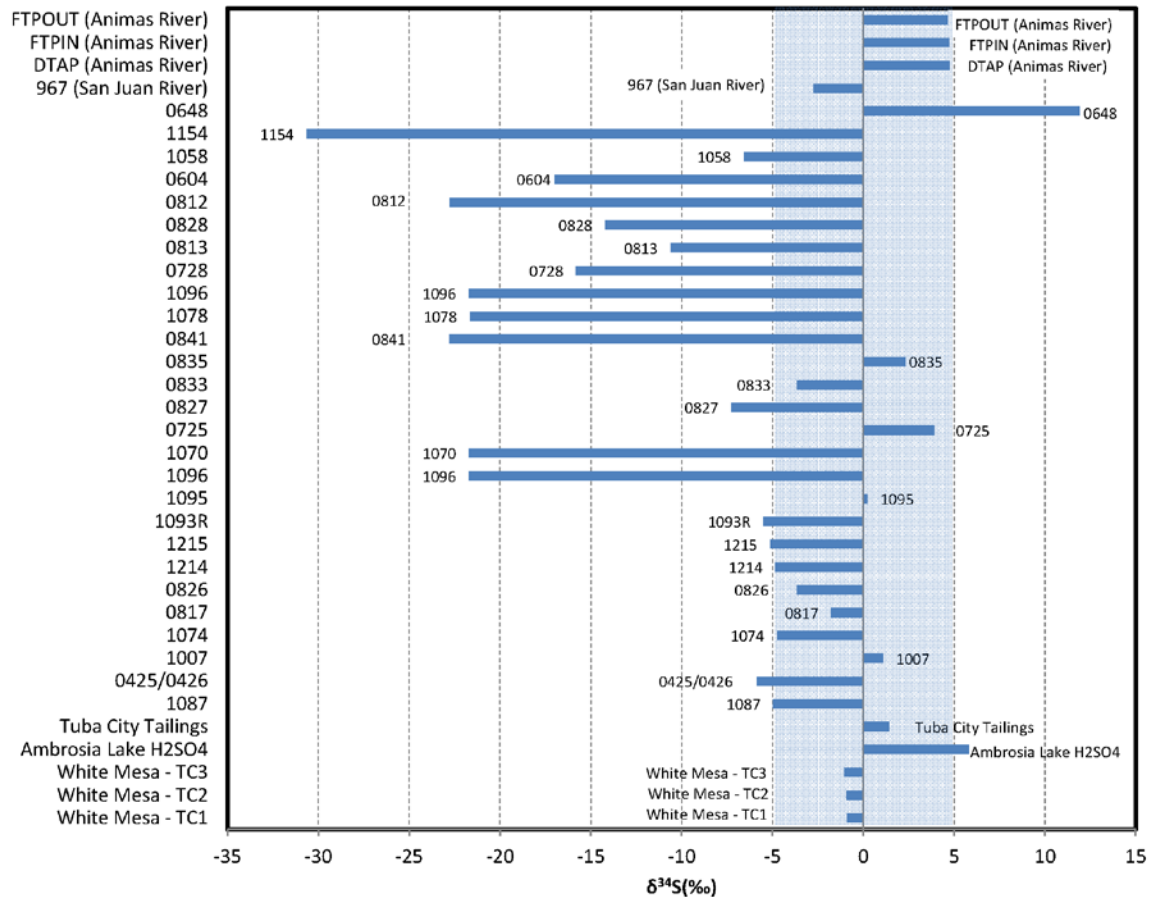


Figure 3. Comparison of $\delta^{34}\text{S}_{\text{sulfate}}$ Values in Terrace Groundwater and Other Former Mill Sites (the likely value of the sulfuric acid used at the Shiprock Mill is shown in the blue shaded range)

Swale wells 0604, 0812, 0813, 0841, 1070, 1078, and 1096 and well 1058 have $\delta^{34}\text{S}_{\text{sulfate}}$ values less than -5‰ , indicating that the source of sulfate is probably the Mancos Shale. This supports the interpretation of the $^{234}\text{U}/^{238}\text{U}$ ARs that the groundwater at these wells is not mill related.

Well 0725 has a $\delta^{34}\text{S}_{\text{sulfate}}$ value that is within the range of $\delta^{34}\text{S}_{\text{sulfate}}$ values thought to be representative of sulfate derived from sulfuric acid used in the milling process but is also within the $\delta^{34}\text{S}_{\text{sulfate}}$ values of the treated water network, including the DTAP, FTPIN, and FTPOUT locations. This indicates that the source of sulfate at this well could be the sulfuric acid used at the mill or Animas River water that has made its way to the terrace alluvium or a mixture of both sources.

The $\delta^{34}\text{S}_{\text{sulfate}}$ values of wells 0833 and 0835, on the western area of the terrace, indicate a non-mill source of sulfate but different sources for each well. The $\delta^{34}\text{S}_{\text{sulfate}}$ value of well 0833 falls within the range thought to be representative of the sulfuric acid used by the mill but is also close to that of San Juan River water and is consistent with the $^{234}\text{U}/^{238}\text{U}$ ARs that indicate a non-mill source of water, most likely derived from San Juan River water used as irrigation water. The $\delta^{34}\text{S}_{\text{sulfate}}$ value of well 0835 also is within the range thought to be representative of

the sulfuric acid used by the mill but also matches that of DTAP. Therefore, sulfate at this well could be derived from Animas River water used for municipal water supply that entered the subsurface through leaks in the distribution pipes. Similar to the case for well 0833, this interpretation is consistent with the $^{234}\text{U}/^{238}\text{U}$ ARs that indicate a non-mill source of water. The $^{234}\text{U}/^{238}\text{U}$ ARs lend support to the interpretation of the $\delta^{34}\text{S}_{\text{sulfate}}$ values that the source of sulfate at these wells is non-mill related with sulfate at well 0833 more influenced by San Juan River water and sulfate at well 0835 more influenced by Animas River water. The interpretation that the source of sulfate at wells 0725, 0833, and 0835 may be Animas River or San Juan River water is based on only one sulfur isotope sample collected from each source. To verify the conclusions, additional samples should be collected from the San Juan River and the Animas River over a range of flows to determine the amount of variation that can occur in the value of $\delta^{34}\text{S}_{\text{sulfate}}$.

Wells 0728, 0827, and 0828 are located in the area on the terrace in which the $^{234}\text{U}/^{238}\text{U}$ ARs indicate a mill source of uranium but have large negative values of $\delta^{34}\text{S}_{\text{sulfate}}$, indicating a non-mill source of sulfate, likely derived from the Mancos Shale. These wells are screened across the alluvium and Mancos Shale contact, which likely explains the contradiction between the $^{234}\text{U}/^{238}\text{U}$ AR and $\delta^{34}\text{S}_{\text{sulfate}}$ mill and non-mill source designations. The $\delta^{34}\text{S}_{\text{sulfate}}$ value for seeps 0425 and 0426 is -5.85‰ , which is very close to the range of $\delta^{34}\text{S}_{\text{sulfate}}$ values thought to be representative of sulfuric acid used by the mill and is consistent with the $^{234}\text{U}/^{238}\text{U}$ ARs that indicate a mill source of uranium. So it is plausible that the source of sulfate in this seep is mill water. Well 0648 has the most positive $\delta^{34}\text{S}_{\text{sulfate}}$ value, which indicates the source of sulfate to this well must be other than the Mancos Shale, sulfuric acid from the mill, or water from the San Juan and Animas Rivers.

Well 1154 in the upper parts of Many Devils Wash had the most negative $\delta^{34}\text{S}_{\text{sulfate}}$ value and, along with the $^{234}\text{U}/^{238}\text{U}$ AR, clearly indicates that the groundwater at this location has not been affected by the mill. Therefore, the uranium and sulfate at well 1154 is naturally occurring and is most likely derived from the Mancos Shale.

The $\delta^{34}\text{S}_{\text{sulfate}}$ values of samples collected from the San Juan River and Animas River are within the range thought to be representative of sulfuric acid used by the mill. This makes distinguishing between a mill or non-mill source of sulfate for groundwater samples that have $\delta^{34}\text{S}_{\text{sulfate}}$ values within this range difficult. The analysis of groundwater samples for $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{18}\text{O}_{\text{sulfate}}$ may provide a greater degree of separation among samples derived from different sources and thus better distinguish between a mill and non-mill source of sulfate. It is recommended that the analysis of this isotopic pair be done on samples collected during Phase 2 sampling.

Tritium Concentrations

Tritium (^3H) is an unstable isotope with a relatively short half-life (12.3 years), making it an excellent indicator of when recent groundwater recharge occurred, that is, the date at which water infiltrated into the ground. Because of this rapid decay, water that entered the subsurface prior to 1953 would today contain no detectable tritium.

Tritium decays exponentially according to the radioactive decay equation [6]

$$A = A_0 2^{-t/T} \quad (1)$$

where

A = tritium activity at present (tritium unit [TU], where 1 tritium unit or TU is 1 tritium atom per 10^{18} hydrogen atoms); A_0 = initial tritium activity (TU); T = half-life (years); and t = elapsed time (years).

A time-series plot of the tritium data from the Global Network of Isotopes in Precipitation (GNIP) station in Albuquerque, New Mexico, along with a time-series plot of the data corrected for radioactive decay over the elapsed time between precipitation and groundwater sampling in 2015, is shown in Figure 4. The theoretical amount of tritium remaining in the 2015 groundwater system was calculated using Equation (1). Tritium units were calculated by dividing the concentration of tritium in picocuries per liter by 3.22 (<http://pubs.usgs.gov/ds/751/convFactors.html>).

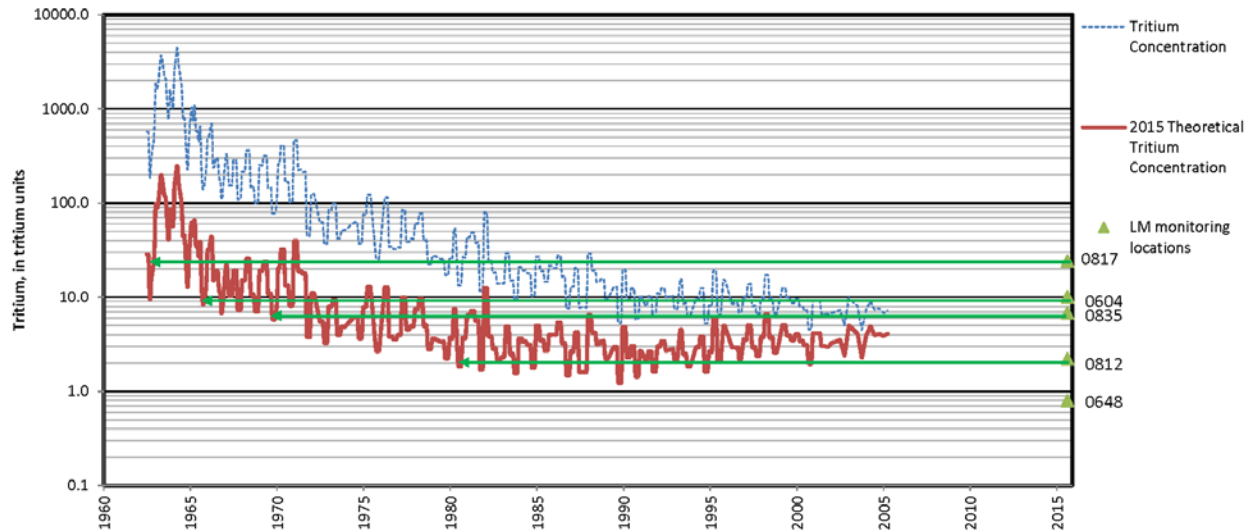


Figure 4. Time-Series Plot of Tritium Concentration in Precipitation Available from the GNIP Station in Albuquerque, New Mexico, 1962–2005 (accessed June 2016 from http://www-naweb.iaea.org/naweb/ih/IHS_resources_gnip.html)

The date of groundwater recharge using tritium data only provides a semiquantitative value because the multiple peaks in the tritium content of precipitation can indicate multiple possible years of recharge. Because all but two samples have measurable amounts of tritium, most groundwater on the terrace infiltrated after 1953 because any tritium that infiltrated into groundwater prior to 1953 would have decayed to concentrations below the detection levels. The dates of groundwater recharge vary, due to the likely multiple years of recharge. Therefore, dates are assigned as occurring since a probable date in Table I. For example, well 0604 has a corrected tritium concentration of 10.0 TU. Corrected values of 10.0 TU were measured in 1966, 1967, 1968, and several years between

1969 and 1982, so water could have infiltrated into the groundwater sampled by well 0604 in any one or more of those years, but not before the mid-1960s, which is consistent with milling operations.

Well 0648, which is a flowing artesian well screened very deep in the Jurassic Morrison Formation, has a tritium value at the detection limit, indicating that groundwater in this well was recharged prior to 1953. This indicates that groundwater recharge to this well cannot include present-day precipitation, water from leaks in the distribution pipes, or mill-related water. Well 0725 has a tritium value just above the detection limit, which indicates that the source of water to this well could be a mixture of water flowing from well 0648 and water from the mill, perhaps early in its operation. Water from well 0648 discharges to ground surface, runs off to Bob Lee Wash and infiltrates the subsurface in the vicinity of well 0725. The interpretation that some groundwater at well 0725 is derived from the mill is supported by the $^{234}\text{U}/^{238}\text{U}$ AR and $\delta^{34}\text{S}_{\text{sulfate}}$ values.

Wells 0833 and 0835 have similar tritium values, indicating that groundwater recharge could have occurred between 1969 and 2003. This indicates that there is a similar source of water at these sites, most likely water from either the Animas River or San Juan River or precipitation. Animas River and/or San Juan River water as a source of groundwater recharge to these wells is supported by the $\delta^{34}\text{S}_{\text{sulfate}}$ values, which suggest that these two waters are a source of sulfate in the groundwater at these wells. The $^{234}\text{U}/^{238}\text{U}$ ARs for these two wells indicate non-mill water as the source of uranium. Seeps 0425 and 0426 have a tritium value similar to that of wells 0833 and 0835 wells, but both the $^{234}\text{U}/^{238}\text{U}$ ARs and the $\delta^{34}\text{S}_{\text{sulfate}}$ value suggest mill water as the source of uranium and sulfate to the seep. The mill ceased operation in 1968, but the site was not cleaned up for more than a decade after mill closure. So perhaps the source of water to the seep is mill water that infiltrated into the ground after mill closure but prior to cleanup. Well 0728 has a tritium value similar to that of wells 0833 and 0835 and seeps 0425 and 0426, but identifying the source of water to this well is somewhat ambiguous. The $^{234}\text{U}/^{238}\text{U}$ AR indicates a mill source of uranium, but the source of sulfate based on the $\delta^{34}\text{S}_{\text{sulfate}}$ value could be interpreted as being non-mill water. The use of $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values as described in the following section may provide clarification on the source of groundwater recharge to well 0728.

Well 1154, located within Many Devils Wash, has a probable recharge date of 1979 to present and supports the interpretation of the $^{234}\text{U}/^{238}\text{U}$ ARs and $\delta^{34}\text{S}_{\text{sulfate}}$ values that indicates groundwater recharge at this well is not mill related and is most likely modern precipitation. Well 1058, located on the eastern side of the disposal cell about halfway between the disposal cell and Many Devils Wash, has a probable recharge date of 1979 to present. The source of groundwater to this well could be San Juan River water that was applied to a Navajo Engineering and Construction Authority (NECA) gravel pit operating in the area between about 1970 and 2009 to suppress dust during surface remediation or precipitation.

Wells 0812, 0841, 1078, and 1096 are located in the area of the terrace referred to as the swale and have probable recharge dates of early to mid-1970s to present, except for well 0812, which has a probable recharge date of 1982 or later. This indicates precipitation as the likely source of groundwater recharge, but it also

corresponds to the time in which San Juan River water was sprayed as dust control in the area in and around the NECA gravel pit east of the disposal cell. Surface runoff across much of the gravel pit flows to the southwest, which could infiltrate and continue in that direction as groundwater. Wells 0604 and 0813 have recharge dates older than the other swale wells, with groundwater recharge potentially occurring in the early 1960s to early 1970s. The reason for this is not known at this time. Tritium age dates suggest groundwater recharge occurred in the early 1960s for wells adjacent to the disposal cell. These include wells 0817, 1007, and 1074. These dates correspond to when San Juan River water was being used by the mill. Wells 0827, 0828, and sump 1087 have probable recharge dates of the early to mid-1960s suggesting mill-contaminated process waters is a plausible source of groundwater recharge to these wells. Extraction wells at locations 1093R and 1095 adjacent to the current evaporation pond and south of the former evaporation ponds under the disposal cell have probable recharge dates from the 1960s.

$\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$

The $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values are useful in identifying sources of groundwater recharge and can support the interpretations of the isotopic data discussed in the previous three sections. Data were compared to the global [7] and arid-zone [8] meteoric water lines, and four distinct groupings of water samples were identified (Figure 5 and Table I).

The global meteoric water line is based on $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values collected in precipitation from locations around the world. The arid-zone meteoric water line is based on $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values collected in precipitation from arid areas such as that of the study area.

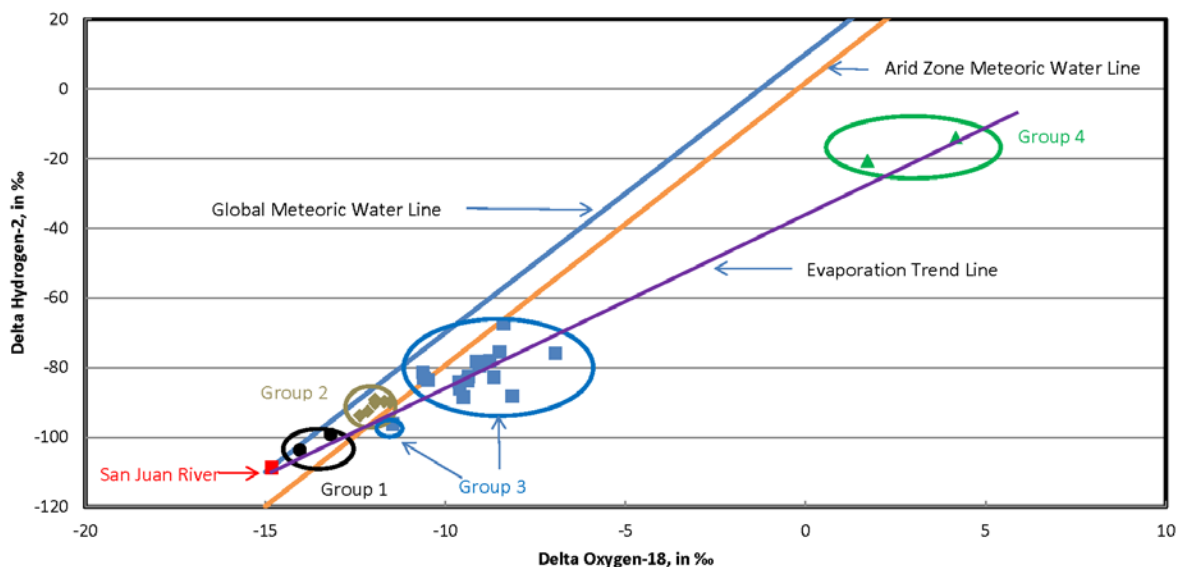


Figure 5. $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ Composition of Terrace Groundwater

The samples from the two Group 1 wells, 0648 (artesian well) and 0725, are the least isotopically enriched of all samples, which indicates that the water in these wells is recharged from a source area at a temperature lower than that of the site, perhaps a high-elevation source, or that recharge occurred when the climate was

cooler than it is today. This interpretation is consistent with the tritium value that indicates groundwater recharge at well 0648 occurred prior to 1953 and is not derived from recent precipitation or anthropogenic sources on the terrace. Water from well 0648 flows into Bob Lee Wash and infiltrates the subsurface in the vicinity of well 0725. Groundwater sampled from well 0725 is slightly isotopically enriched relative to well 0648; this can result from evaporation as water from well 0648 flows down the Bob Lee Wash drainage. The $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values in well 0725 can also result from the mixing of water from well 0648 with mill water since the $^{234}\text{U}/^{238}\text{U}$ AR and $\delta^{34}\text{S}_{\text{sulfate}}$ value indicate a mill source of uranium and sulfate in groundwater at this well.

The $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values for Group 2 plot between the Global Meteoric Water Line and the Arid-Zone Meteoric Line. The isotopic enrichment and deviation from the Global Meteoric Water Line indicate more localized and lower elevation recharge, which would be subject to isotopic enrichment through evaporation as precipitation infiltrates into the ground and percolates to the water table. The source of the groundwater recharge, however, may or may not be precipitation. Group 2 includes locations FTPIN and FTPOUT, which are samples from a water treatment plant in Farmington, New Mexico, that treats water withdrawn from the Animas River. Following treatment, water is conveyed to the Shiprock terrace and was sampled locally at the location labeled DTAP.

Wells 0728, 0833, and 0835 are located near an area on the terrace where pipes conveying water from FTPOUT are suspected to be the source of groundwater in the terrace alluvium in these areas. At one location (0728), a leaking line has since been confirmed and recently fixed by the local water authority, while the other locations (0833 and 0835) are in residential areas where irrigation using municipal water likely occurs and leaks may exist. The $^{234}\text{U}/^{238}\text{U}$ ARs and $\delta^{34}\text{S}_{\text{sulfate}}$ values at wells 0833 and 0835 indicate a non-mill source of uranium and sulfate to these wells, and tritium values indicate groundwater recharge occurred after the mill ceased operation. Therefore, groundwater recharge to these wells is most likely derived from a combination of municipal water and precipitation.

The $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values for Group 3 plot on or below the Arid-Zone Meteoric Line and indicate a greater degree of evaporation than that in the Group 1 and Group 2 wells. Well 1154, located in the upper part of Many Devils Wash, plots on the Arid-Zone Meteoric Line, which indicates that the source of groundwater recharge to Many Devils Wash is precipitation. A similar conclusion regarding the source of groundwater recharge at well 1154 was reached by Robertson et al. [9]. That the groundwater recharge at this well is not mill-related water is supported by the $^{234}\text{U}/^{238}\text{U}$ AR and $\delta^{34}\text{S}_{\text{sulfate}}$ values.

Other Group 3 wells (0604, 0812, 0813, 0817, 0826, 0841, 1007, 1058, 1074, 1093R, and 1095) all plot below the Arid-Zone Meteoric Line, and this could indicate precipitation as the source of groundwater recharge. However, several lines of evidence suggest that, similar to the wells in Group 2, precipitation may not be the source of groundwater recharge to these wells. A trend line through the $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values of Group 3 water samples to the $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values of the San Juan River can be drawn and indicates an evaporative signature because the slope is lower than the meteoric water line [10]. This is an indication that San Juan

River water, used as the source of water to the mill while it was in operation from 1954–1968 and in the NECA gravel pit as a dust suppressant from 1970 to 2009, in addition to precipitation, is a possible source of groundwater recharge. Similar to precipitation, any San Juan River water from the tailings cell or the NECA gravel pit that infiltrated into the ground would evaporate to some degree. As a result, water remaining in the ground would become isotopically enriched; that is, it would contain greater concentrations of the $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ isotopes relative to the water originally withdrawn from the San Juan River.

Although the $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values of the San Juan River will undoubtedly vary both seasonally and year-to-year and, thus, plot on different positions on the global meteoric line, evidence indicating that San Juan River water is a source of groundwater recharge to Group 3 wells is that (1) seepage from the tailings pile was observed in 1960 in the vicinity of the wells where the disposal cell was later located [11,12], (2) the $^{234}\text{U}/^{238}\text{U}$ AR and $\delta^{34}\text{S}_{\text{sulfate}}$ values of groundwater at wells 0817, 0826, 1007, and 1074 indicate that the source of uranium and sulfate is mill-derived water, (3) the $^{234}\text{U}/^{238}\text{U}$ AR and $\delta^{34}\text{S}_{\text{sulfate}}$ values of groundwater at wells 0725, 0728, and seeps 0425 and 0426 indicate that the source of uranium and sulfate is a combination of mill-derived water and municipal water used on the terrace, and (4) tritium age dates for wells adjacent to the disposal cell, 0817, 0827, 1007, and 1074, indicate groundwater recharge occurred during the early 1960s when the mill was operating. Samples need to be collected over a range of San Juan River flows to establish the expected variation of these isotopes. Two lines of evidence indicate that the tritium concentration in the San Juan River is similar to that in precipitation. The $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values of the San Juan River sample plot directly on the Global Meteoric Water Line, so it is reasonable to assume that if those two isotopes in the San Juan River are similar to those in precipitation, tritium values would be similar as well. Second, corrected tritium concentration values ranged between 2 and 6 TU from 1998 to 2005 and have been somewhat consistent. Assuming that this consistency extends to 2015, the tritium concentration of the San Juan River sample collected in 2015 falls within this range.

Although wells 1093R and 1095 are included in Group 3 and have low concentrations of uranium and $^{234}\text{U}/^{238}\text{U}$ ARs that indicate a non-mill source of uranium, the probable groundwater recharge date indicates that recharge occurred during the 1960s. Wells 0827 and 0828 and sump 1087 plot close to one another near the Arid-Zone Meteoric Line and are located west of the disposal cell in the NECA yard near a former mill-related pond. The NECA pond was present from the mid-1970s to about 1984 and was presumably constructed to hold surface-water drainage from the NECA buildings area [1]. Additionally, prior to the mid-1970s there was a pond in this area that held contaminated mill process waters [1]. The $^{234}\text{U}/^{238}\text{U}$ ARs and tritium age dates indicating that groundwater recharge occurred since the mid-1960s support the interpretation of mill-derived water at these wells. Initially, water from the San Juan River was the likely water source, followed by NECA activities sourced by Animas River water: both may have infiltrated into the ground and were possible sources of groundwater recharge to these three well locations.

The $\delta^2\text{H}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{water}}$ values for Group 4 (evaporation pond locations 1214 and 1215) plot well below the Arid-Zone Meteoric Line and represent the most

isotopically enriched water samples collected. The extreme evaporation that these samples have undergone is a result of water in the evaporation pond being constantly exposed to the atmosphere.

CONCLUSIONS

The aqueous chemical and isotopic analysis has identified areas on the terrace where groundwater is derived from mill-related activities and areas where the groundwater is associated with non-mill activities (Figure 1).

In addition to precipitation recharge, other non-mill anthropogenic recharge sources also contribute to the terrace flow system. Anthropogenic recharge is primarily derived from leaking municipal water lines and irrigation activities.

To better define sources of groundwater recharge on the terrace, sampling in the Phase 2 study will include the collection of the chemical and isotopic tracers used in this study from local precipitation and the San Juan and Animas Rivers at different flows and seasons, and from the mouth of Bob Lee Wash. Additional isotopic data collection could include that of chlorofluorocarbons and $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{18}\text{O}_{\text{sulfate}}$ in select wells.

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