Department of Energy
Washington, DC 20585

May 3, 2019

U.S. Nuclear Regulatory Commission
Attn: Document Control Desk
Deputy Director
Mail Stop T8-F5
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Subject: U.S. Department of Energy Office of Legacy Management Report Entitled Investigation of Non-Mill-Related Water Inputs to the Terrace Alluvium at Shiprock, New Mexico (NRC Docket No. WM-0058)

To Whom It May Concern:

Enclosed, for U.S. Nuclear Regulatory Commission (NRC) review, is a report prepared by the U.S. Department of Energy, Office of Legacy Management (DOE-LM) entitled *Investigation of Non-Mill-Related Water Inputs to the Terrace Alluvium at Shiprock, New Mexico* (LMS/SHP/S14504). Comments previously received from the Navajo Nation Uranium Mill Tailings Remedial Action/Abandoned Mine Lands Department and Navajo Nation Environmental Protection Agency have been incorporated into this report.

This report provides results and interpretation of data collected during the investigation described in the 2015 *Work Plan to Investigate Potential Non-Mill-Related Water Inputs to the Terrace Alluvium at Shiprock, New Mexico*. The objective of this investigation is to better understand the sources of groundwater presently on the terrace area of the Shiprock site, using aqueous chemical and isotopic tracers.

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LMS/SHP/S14504

Investigation of Non-Mill-Related Water Inputs to the Terrace Alluvium at Shiprock, New Mexico

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Abbreviations

AR	activity ratio
$\delta^{2}H_{water}$	delta hydrogen-2 of water
$\delta^{18}O_{sulfate}$	delta oxygen-18 of sulfate
$\delta^{18}O_{water}$	delta oxygen-18 of water
$\delta^{34}S_{sulfate}$	delta sulfur-34 of sulfate
DOE	U.S. Department of Energy
ft	feet
GMWL	global meteoric water line
GNIP	Global Network of Isotopes in Precipitation
H_2S	hydrogen sulfide
mg/L	milligrams per liter
MWL	meteoric water line
pCi/L	picocuries per liter
TU	tritium units
$^{234}U/^{238}U$	uranium-234/uranium-238 activity ratio
UMTRCA	Uranium Mill Tailings Radiation Control Act

Executive Summary

The Shiprock, New Mexico, Uranium Mill Tailings Radiation Control Act 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. The site is managed by the U.S. Department of Energy Office of Legacy Management 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, potentially drying terrace seeps and curtailing surface expression of the groundwater. However, contribution of non-mill anthropogenic water sources may be hindering the dewatering effort, resulting in reduced remedy effectiveness. The objective of this investigation is to identify and differentiate potential non-mill-related water inputs to the shallow terrace groundwater system through the use of aqueous chemical and isotopic tracers.

This report provides results and interpretation of data collected during the investigation described in the 2015 *Work Plan to Investigate Potential Non-Mill-Related Water Inputs to the Terrace Alluvium at Shiprock, New Mexico*. Aqueous chemical and isotopic tracers, such as uranium concentrations and uranium-234/uranium-238 ($^{234}U/^{238}U$) activity ratios, sulfate concentrations and delta sulfur-34 of sulfate ($\delta^{34}S_{sulfate}$) and delta oxygen-18 of sulfate ($\delta^{18}O_{sulfate}$) ratios in sulfate, tritium concentrations, delta hydrogen-2 of water ($\delta^{2}H_{water}$) and delta oxygen-18 of water ($\delta^{18}O_{water}$) ratios in water, and total chlorine concentrations were used in this investigation. The results and interpretation of these data provide a basis for attempting to identify five sources of groundwater recharge to the shallow groundwater system. These sources are (1) water related to the operation of the uranium mill, (2) domestic water use on the terrace, (3) irrigation water, (4) groundwater present on the terrace prior to the mill being in operation, and (5) the infiltration of meteoric water.

The $^{234}U/^{238}U$ activity ratios and $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ data clearly indicate a zone of mill-affected groundwater. However, these data cannot be used to directly determine the original water source. Data from tritium concentrations, $\delta^{2}H_{water}$ and $\delta^{18}O_{water}$ values, and total chlorine detection helped determine potential water sources as follows:

- Water related to the operation of the uranium mill: YES
- Domestic water use on the terrace: YES
- Irrigation water: LIKELY
- Groundwater present on the terrace prior to the mill being in operation: UNLIKELY
- Infiltration of meteoric water: MINIMAL
- Groundwater from flowing artesian well 0648 only exerts a localized terrace influence: MINIMAL

Isotope data alone cannot quantify the amounts of water from these sources. Any additional quantification would require hydrogeologic methods to directly measure precipitation recharge and irrigation losses compared to any past and current water losses from the tailings, along with a better determination of domestic water losses from pipelines. A conclusion of this report is that any groundwater flowing into the area of the terrace containing mill-derived solid-phase uranium and sulfate will become contaminated regardless of origin. Dissolution of mill-derived solid-phase uranium and sulfate will continue for an unknown, extended period of time until the solid phase is exhausted.

1.0 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 Shiprock mill operated from 1954 to 1968. The site is managed by the U.S. Department of Energy (DOE) Office of Legacy Management (LM) and is situated on an alluvial terrace just south of the San Juan River.

As identified in the *Final Draft Work Plan to Investigate Potential Non-Mill-Related Water Inputs to the Terrace Alluvium at Shiprock, New Mexico* (DOE 2015) (the Work Plan), (DOE 2015), the compliance strategy for the terrace is to pump 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. Remedial pumping, focused since 2003 on the swale area, has reduced alluvial groundwater levels in the area of extraction.

The Work Plan proposed an investigation to better understand the source or sources of groundwater that presently exist on the terrace. Potential 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) groundwater present on the terrace prior to the mill being in operation, and (5) infiltration of meteoric water (DOE 2015). The flowing artesian well 0648 is a potential but localized source of groundwater on the terrace. This report presents the aqueous chemical and isotopic data collected during this investigation and provides information on possible mill- and non-mill-related groundwater on the terrace. In addition to water-phase data, this report discusses rock and water interactions that add uncertainty in determining original water sources.

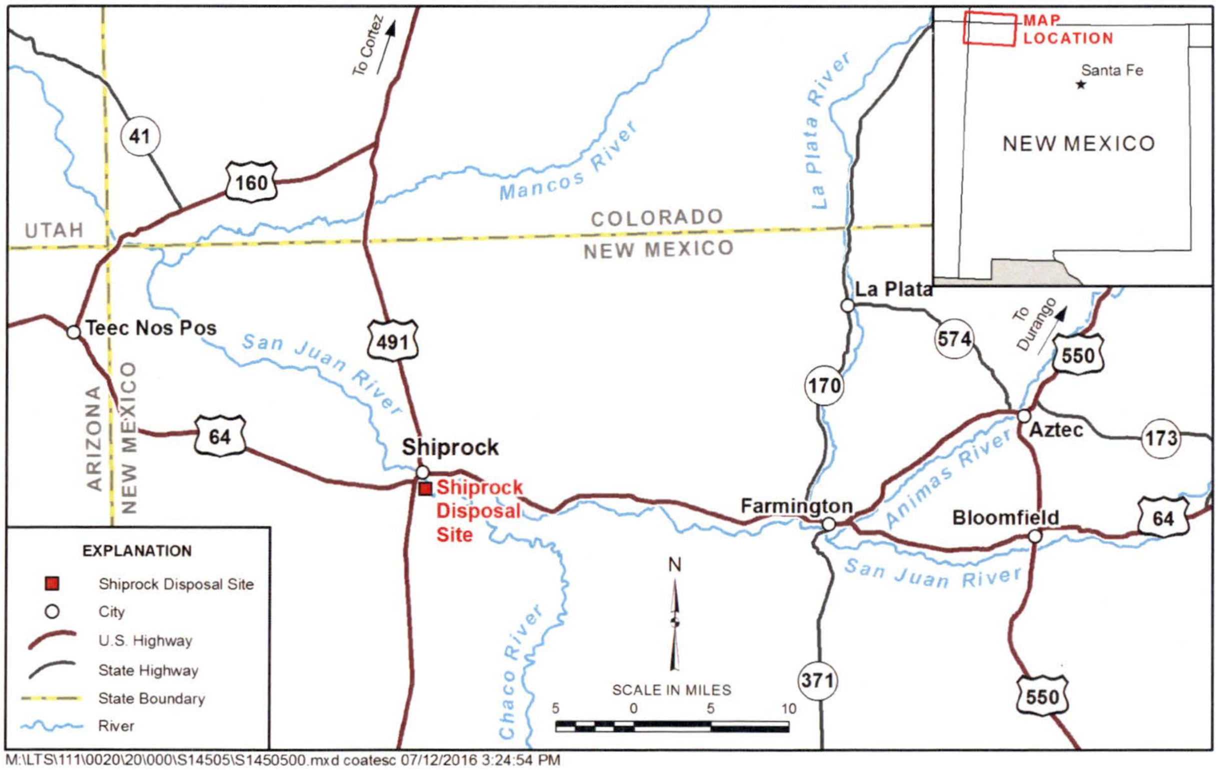

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Figure 1. Shiprock Site Location Regional Setting

2.0 Methods

Beginning in September 2015 and continuing through December 2016, terrace water sampling was conducted in accordance with the associated Work Plan (DOE 2015). Figure 2 shows the sampling locations and site features discussed in this report. Sampling focused on wells located throughout the terrace, with the following exceptions:

- Monitoring well 1154 located in the upper reach of Many Devils Wash, a drainage feature that is incised in the terrace.
- Seeps 0425 and 0426, emanating from the escarpment, are diverted into a common pipe and sampled prior to draining into a sump (combined location referred to as seeps 0425/0426). Thus, terrace-derived water, but the seeps are not located on the terrace.
- Sampling locations FTPIN, FTPOUT, and DTAP represent Farmington Municipal Water Treatment Plant (inflow [FTPIN] and outflow [FTPOUT]) and the Shiprock water distribution network lines from that plant (DTAP). The Farmington Municipal Water Treatment Plant uses water from the Animas River.
- Sampling locations 1214 and 1215 are surface water samples collected from the Evaporation Pond.
- Sampling location 0967 in the San Juan River.

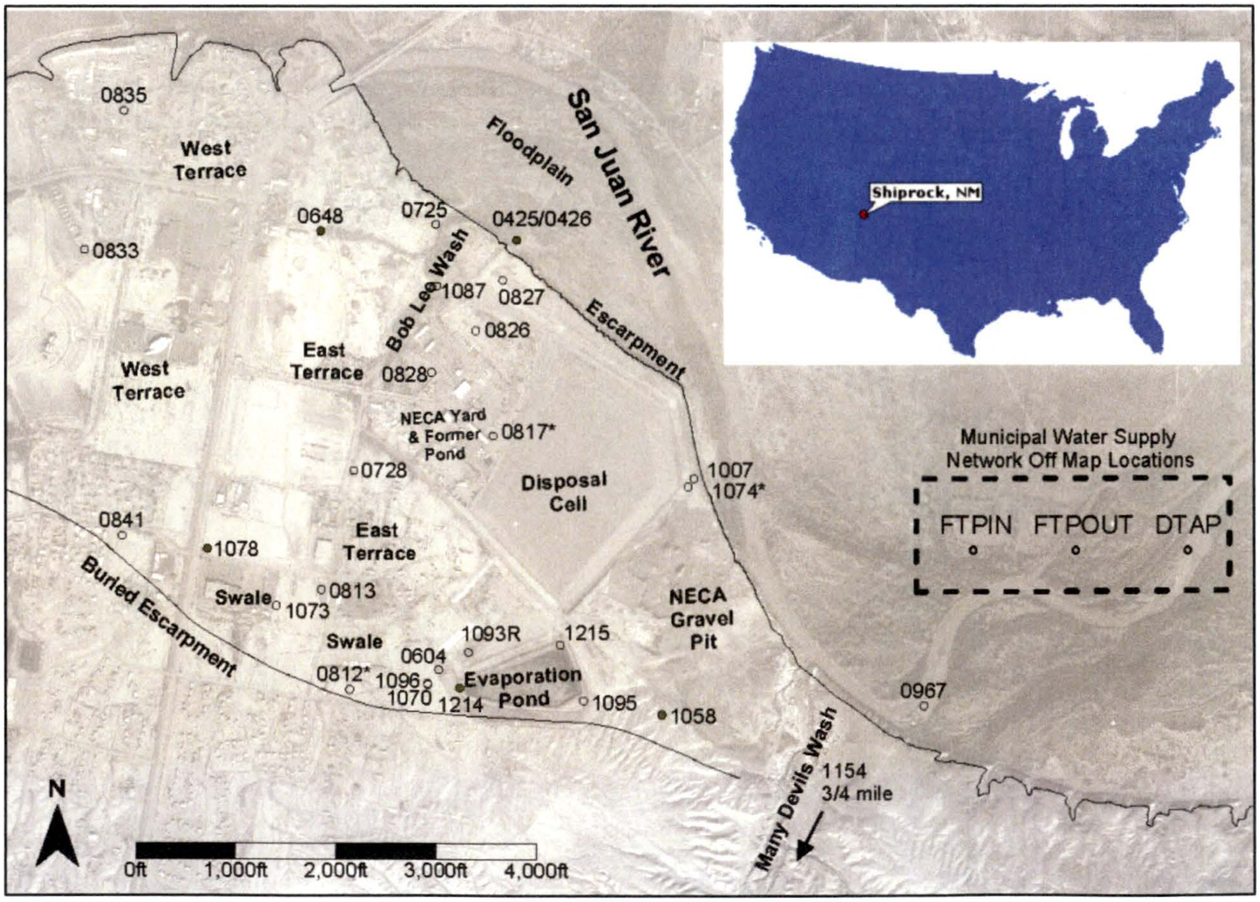

Figure 2. 2015/2016 Investigation Sample Locations and Shiprock Site Features

To help determine the sources of terrace groundwater to these study locations, the following data were collected:

- Uranium-234/uranium-238 ($^{234}U/^{238}U$) activity ratios (ARs) and uranium concentrations
- Delta sulfur-34 ($\delta^{34}S_{sulfate}$) and delta oxygen-18 ($\delta^{18}O_{sulfate}$) values in sulfate concentrations
- Tritium concentrations
- Delta hydrogen-2 ($\delta^{2}H_{water}$) and delta oxygen-18 ($\delta^{18}O_{water}$) values in water
- Total chlorine

The $^{234}U/^{238}U$ ARs and uranium concentrations were measured by GEL Laboratories in Charleston, South Carolina, using method DOE Environmental Measurements Laboratory (EML) HASL-300, U-02-RC (Modified), described at http://www.wipp.energy.gov/namp/.... The $\delta^{34}S_{sulfate}$ $\delta^{18}O_{sulfate}$ values and sulfate concentrations were measured by the U.S. Geological Survey (USGS) Stable Isotope Laboratory in Reston, Virginia, using the method described at https://isotopes.usgs.gov/lab/methods.html. Tritium concentrations were measured by GEL Laboratories in Charleston, South Carolina, using method DOE EML HASL 300, H-02-RC (Modified), described at http://www.wipp.energy.gov/namp/.... Tritium detection limits were 2.5 picocuries per liter (pCi/L) or 0.8 tritium units (TU). These data were selected due to observations in a recent study of the source of water in Many Devils Wash (DOE 2012), which demonstrated that $^{234}U/^{238}U$ ARs, sulfur stable isotopes ($\delta^{34}S_{sulfate}$), and tritium concentrations can be diagnostic of mill-related water. Specifically, the conclusions in DOE 2012 indicated that (1) mill-related uranium had ARs near 1, whereas non-mill-related uranium had values typically greater than 2, (2) mill-related sulfate had $\delta^{34}S_{sulfate}$ values near 0‰, while most non-mill-related sulfate had values less than –20‰, and (3) tritium in mill-related water had an average activity of 76 pCi/L (or 24 TU), while non-mill-related water had tritium activities below 30 pCi/L (mostly below 10 pCi/L or 3.1 TU).

The $\delta^{2}H_{water}$ and $\delta^{18}O_{water}$ values were measured by the USGS Stable Isotope Laboratory in Reston, Virginia, using the method described at https://isotopes.usgs.gov/lab/methods.html. The $\delta^{2}H_{water}$ and $\delta^{18}O_{water}$ values were measured for the possibility of identifying different water sources and past water evaporation. Total chlorine was sampled using a field kit. Total chlorine analyses were completed due to concerns about leakage from buried water supply lines. Total chlorine is a unique indicator of municipal-supply chlorinated water, which would not be found in water samples otherwise.

3.0 Results

Aqueous chemical and isotopic data are presented in Table 1 with interpretative details discussed in Section 4.0 "Data Interpretation." Scaled bubble plot maps for each analysis or isotopic ratio are spatially displayed in Appendix A (Figures A-1 through A-10).

Table 1. Aqueous Chemical and Isotopic Data Used to Assess the Source of Groundwater on the Terrace with Interpretation

Location	$^{234}U/^{238}U$ Ratio	Uranium (mg/L)	2016 $\delta^{34}S_{sulfate}$	2016 $\delta^{18}O_{sulfate}$	2016 Sulfate (mg/L)	2015 $\delta^{34}S_{sulfate}$	2015 Sulfate (mg/L)	Tritium (pCi/L)	Tritium (TU)	Probable Recharge Dates	$\delta^{2}H_{water}$	$\delta^{18}O_{water}$	Total Chlorine (mg/L)
San Juan River Water													
0967	1.65	0.004	3.33	2.08	120	−2.74	280	16.4	5.1	-	−108.73	−14.82	0
Animas River Water													
DTAP	1.40	-	4.52	1.75	120	4.75	-	3.21	1.0	-	−89.56	−11.94	0.68
FTPIN	1.19	-	4.84	1.67	130	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	🟨 -30.45	-2.85	18,000	🟨 −30.65	15,800	8.42	2.6	After 1953	−67.41	−8.39	-
Evaporation Pond													
1214	🟥 1.13	-	-	-	-	🟪 −4.85	-	13.7	4.3	After 1953	−20.52	1.72	-
1215	🟥 1.17	5.7	🟪 -4.63	1.87	70,000	🟪 −5.13	68,000	11.4	3.5	After 1953	−13.92	4.17	0.06
Adjacent to Evaporation Pond													
1093R	🟨 1.45	0.11	🟪 -5.94	-0.36	10,000	🟪 −5.51	6,700	69.8	21.7	After 1953	−75.54	−8.50	0
1095	🟨 1.86	0.043	🟪 0.14	0.6	5,700	🟪 0.22	5,500	49.9	15.5	After 1953	−78.34	−9.13	0
Adjacent to Disposal Cell													
0728	🟥 1.12	0.12	🟨 -18.97	-2.57	6,600	🟨 −15.82	2,800	16.2	5.0	After 1953	−93.81	−12.38	0
0828	🟥 1.00	0.38	🟨 -14.11	-0.13	1,600	🟨 −14.21	1,600	22.2	6.9	After 1953	−83.04	−10.60	0.12
0817*	🟥 0.98	9.18	-	-	13,000	🟪 −1.76	9,730	77.1	23.9	After 1953	−78.01	−8.77	-
0826	🟥 1.09	3.66	🟪 -9.5	-0.65	11,000	🟪 −3.66	13,700	-	-	-	−83.79	−9.38	0.06
1007	🟥 1.12	2.5	🟪 0.61	1.84	13,000	🟪 1.09	13,000	67.1	20.8	After 1953	−79.50	−9.06	0
1074*	🟥 1.13	2.11	-	-	8,500	🟪 −4.75	7,510	63.5	19.7	After 1953	−75.92	−6.95	-
Bob Lee Wash and Seeps from Terrace													
0648	🟨 1.26	0.00011	🟨 11.63	12.36	2,100	🟨 11.91	2,000	2.46	0.8	Prior to 1953	−103.74	−14.04	-
0725	🟥 1.08	0.075	🟪 1.86	6.73	3,200	🟪 6.17	3,000	2.93	0.9	Prior to 1953	−99.21	−13.19	0.14
0827	🟥 1.18	0.8	🟪 -7.87	-0.68	7,900	🟪 −7.74	8,800	66.4	20.6	After 1953	−84.10	−10.48	0
1087	🟥 1.15	0.32	🟪 -5.46	0.84	5,300	🟪 −4.96	4,800	36.6	11.4	After 1953	−81.28	−10.63	0
0425/0426	🟥 1.21	0.45	🟪 -2.09	3.76	4,900	🟪 −5.86	6,100	13.5	4.2	After 1953	−89.76	−11.70	0
Swale													
0604	🟨 3.64	0.074	🟨 -18.47	-3.05	13,000	🟨 −17.00	12,000	32.1	10.0	After 1953	−88.53	−9.50	0
0812*	🟨 2.71	0.138	-	-	-	🟨 −22.77	17,000	6.91	2.1	After 1953	−88.22	−8.15	-
0813	🟨 2.22	0.078	🟨 -10.68	-1.41	9,200	🟨 −10.61	2,800	61.1	19.0	After 1953	−82.74	−8.66	0
0841	🟨 2.46	0.12	🟨 -22.54	-2.56	14,000	🟨 −22.78	14,000	10.9	3.4	After 1953	−84.17	−9.62	0.09
1070	-	0.089	-	-	16,000	-	-	-	-	-	-	-	-
1073	🟨 1.88	0.06	🟨 -19.34	-2.99	11,000	-	12,000	27.9	8.7	After 1953	-85.94	-9.49	0
1078	🟨 2.21	0.12	🟨 -21.54	-3.37	13,000	🟨 −21.66	14,000	9.29	2.9	After 1953	−82.52	−9.36	0
1096	🟨 2.62	0.085	🟨 -21.57	-2.24	16,000	🟨 −21.72	15,000	11.2	3.5	After 1953	−86.01	−9.60	0.09
West Terrace													
0833	🟨 1.56	0.044	🟪 -3.31	2.32	4,100	🟪 −4.52	3,700	19.8	6.1	After 1953	−89.87	−11.54	0
0835	🟨 1.64	0.0031	🟪 3.89	1.21	120	🟪 2.31	120	21.7	6.7	After 1953	−92.58	−12.16	0
East of Disposal Cell													
1058	🟨 2.83	0.0032	🟪 -6.72	-1.06	5,900	🟪 −6.58	5,800	9.67	3.0	After 1953	−96.24	−11.46	0.01

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:

$^{234}U/^{238}U$ ratio and $\delta^{34}S_{sulfate}$ signatures: red = mill related, yellow = non-mill related, and purple = inconclusive

4.0 Data Interpretation

4.1 $^{234}U/^{238}U$ Activity Ratios and Uranium Concentrations

The $^{234}U/^{238}U$ AR data are used to determine the source of uranium in a groundwater sample because the $^{234}U/^{238}U$ AR can distinguish between the uranium derived from weathering of local aquifer minerals and the uranium derived from processing mills (Zielinski et al. 1997). Zielinski et al. (1997) state that most natural groundwater has a $^{234}U/^{238}U$ AR greater than 1.0, with typical values in the range of 1–3, but values in excess of 10 can occur. In contrast, uranium in raffinate, which is the mill-process solution after the majority of the uranium has been removed, 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 uranium ores with ARs slightly above or below 1.0. 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 range of ±0.2 is included to allow for analytical error and potential mixing effects. The raffinate should retain the uranium-isotope composition of the processed ore because neither the rapid, nearly complete dissolution of uranium from crushed ore nor further chemical processing of the leachate will promote any isotopic fractionation (Zielinski et al. 1997). At the Shiprock site, the raffinate in the unlined tailings impoundments would have seeped into the subsurface and flowed towards the San Juan River as anthropogenic groundwater. On this flowpath, some of the uranium from the raffinate would have been lost to the solid phase, either by sorption or precipitation processes.

The $^{234}U/^{238}U$ AR data are plotted as a function of the concentration of uranium, similar to that in Zielinski et al. (1997), to emphasize that groundwater can contain relatively high concentrations of uranium that may exceed the UMTRCA groundwater standard of 0.044 milligram 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 $^{234}U/^{238}U$ AR values greater than 1.2 but have uranium concentrations 2 to 3 times greater than the UMTRCA groundwater standard (DOE 2012, and Kamp and Morrison 2014). The source of the uranium is the Mancos Shale, which has naturally occurring high levels of uranium.

The plot of the $^{234}U/^{238}U$ AR as a function of the uranium concentration shows that groundwater sampled at locations 0725, 0728, 0817, 0826, 0827, 0828, 1007, 1074, 1087 and evaporation pond sites 1214 and 1215 contains uranium derived from milling operations (Figure 3). 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 (9.18 mg/L), 0826 (3.66 mg/L), 0827 (0.8 mg/L), 1007 (2.5 mg/L), and 1074 (2.11 mg/L). The $^{234}U/^{238}U$ 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. Taken altogether, these groundwater samples identify a current maximum extent where the solid phase still contains mill-related uranium (Figure A-1, with ARs equal or less than 1.2). For the wells with lower uranium concentrations but ARs still less than 1.2, these values may be due to mixing of groundwater sources with and without mill-related uranium or due to equilibrium dissolution of a smaller amount of mill-related uranium on the solid phase.

While the $^{234}U/^{238}U$ ARs are a good indicator of mill-related uranium compared to non-mill sources, these data cannot be used to determine the original groundwater source because of potential rock and water interactions.

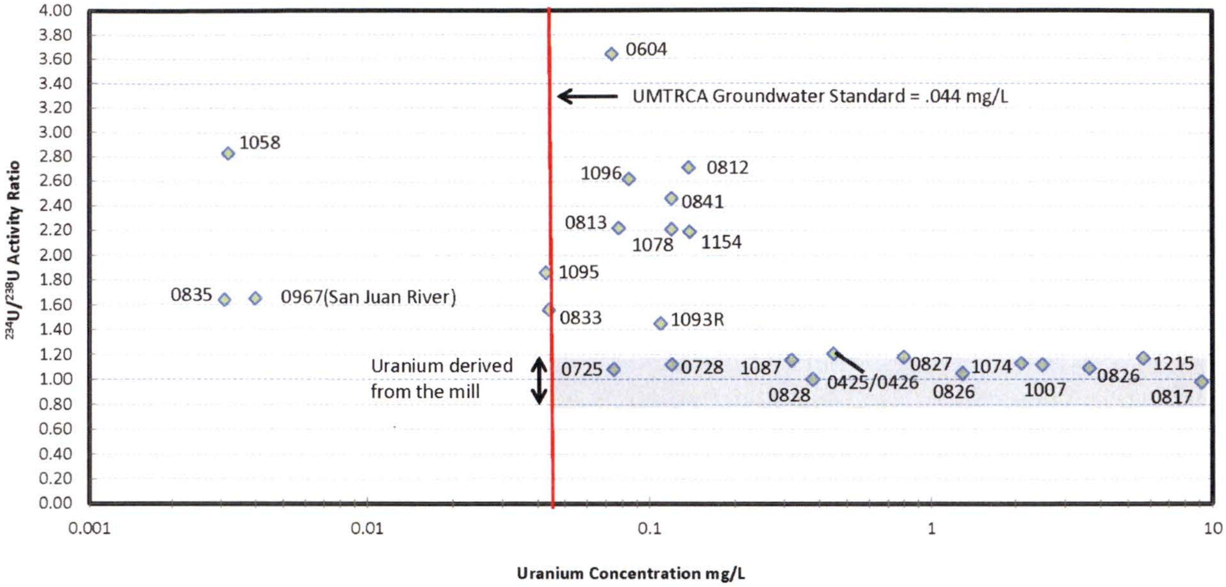

Figure 3. $^{234}U/^{238}U$ Activity–Concentration Plot of Shiprock Groundwater

4.2 $\delta^{34}S_{sulfate}$, $\delta^{18}O_{sulfate}$, and Sulfate Concentrations

In groundwater, the sulfur ($\delta^{34}S_{sulfate}$) and oxygen ($\delta^{18}O_{sulfate}$) compositions in sulfate (SO_4^{2-}) result from the isotopic fractionation of the source elements from chemical and biological processes. As Faure (1986) 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." 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, more-negative $\delta^{34}S_{sulfate}$ values indicate that the sulfate is from the dissolution of a sulfide mineral. The Mancos Shale was deposited in the Cretaceous Sea, and the sulfate contained in the Mancos Shale was formed in the manner just described and has highly negative values of $\delta^{34}S_{sulfate}$ (DOE 2012, and Kamp and Morrison 2014). This is demonstrated by sample 1154 from a monitoring well in the Mancos Shale in Many Devils Wash with a $\delta^{34}S_{sulfate}$ value of –30.45.

Other wells with strongly negative $\delta^{34}S_{sulfate}$ values (<–10 ‰) include all of the swale wells (0604, 0812, 0813, 0841, 1073, 1078, and 1096) and two wells adjacent to the disposal cell (0728 and 0828, Table 1 and Figure 4). The $^{234}U/^{238}U$ AR values for all the swale wells are greater than 1.2 (Table 1 and Figure 1), which along with the strongly negative $\delta^{34}S_{sulfate}$ values, seems to confirm the source of sulfate and uranium in these wells as being from the Mancos Shale. Wells 0728 and 0828 have $^{234}U/^{238}U$ AR values that are indicative of mill-derived uranium and may be in a mixing zone at the edge of the maximum uranium plume extent; thus, the groundwater in these wells could be dissolving mill-related uranium and Mancos Shale-related sulfate.

Besides the Mancos Shale, additional sulfate sources at the Shiprock site are (1) sulfuric acid used in ore processing, (2) dissolution of sulfide minerals in the tailings, (3) San Juan River water, and (4) Animas River water. The resulting tailings pore fluid would be a mix of sulfuric acid and sulfide mineral dissolution with high sulfate concentrations. Thus, the tailings-derived water would contribute the greatest mass of sulfate as either occurring in mill-related groundwater or occurring as precipitated sulfate that can slowly be dissolved. No data on the $\delta^{34}S_{sulfate}$ values for tailings-derived water are available. Sulfuric acid is usually produced from hydrogen sulfide gas recovered from oil and gas production (https://www.sulphurinstitute.org/learnmore/faq.cfm). Faure (1986) states that the $\delta^{34}S_{sulfate}$ values of sulfur in H_2S gas range from –8‰ to +32‰. Unfortunately, the $\delta^{34}S_{sulfate}$ value for sulfuric acid used at the mill is not available; however, based on samples from the tailings cells at the White Mesa Uranium Mill in southwest Utah, a disposal cell at a former uranium mill near Tuba City, Arizona, and sulfuric acid used at the Ambrosia Lake, New Mexico, uranium mill (DOE 2012), the $\delta^{34}S_{sulfate}$ value of the sulfuric acid used at the Shiprock Mill most likely was in the range of –5‰ to +5‰ (Figure 4). The two San Juan River samples with $\delta^{34}S_{sulfate}$ values cover approximately the same range. In Figure 4, the $\delta^{34}S_{sulfate}$ range of –10‰ to +5‰ is highlighted to indicate that results in this range are inconclusive as to original sulfate source. This same range is indicated with the purple shading in Table 1. The inclusion of $\delta^{34}S_{sulfate}$ in the range of –10‰ to –5‰ allows for some source mixing, and the results from Figure 4 and Table 1 highlight the use of $\delta^{34}S_{sulfate}$ as a good indicator of sulfate derived from the Mancos Shale. Wells with sulfate in the –10‰ to +5‰ range could have sulfate derived from sulfuric acid used in ore processing, dissolution of sulfide minerals in the tailings, or smaller amounts of sulfate from river water.

Well 0648 stands out as a non-mill-related sulfate source with a very positive value for $\delta^{34}S_{sulfate}$ at near +12‰. The well is an artesian well with groundwater derived from a deeper formation. This highly positive value for $\delta^{34}S_{sulfate}$ is likely due to gypsum dissolution (Clark and Fritz 1997).

Sulfate concentrations are provided in Table 1. However, waters related to the Mancos Shale (swale category in Table 1) compared to a mill-related source (adjacent to disposal cell in Table 1) based on $^{234}U/^{238}U$ AR values are relatively similar in sulfate concentrations. Thus, sulfate concentrations are not used as a diagnostic for the original sulfate source.

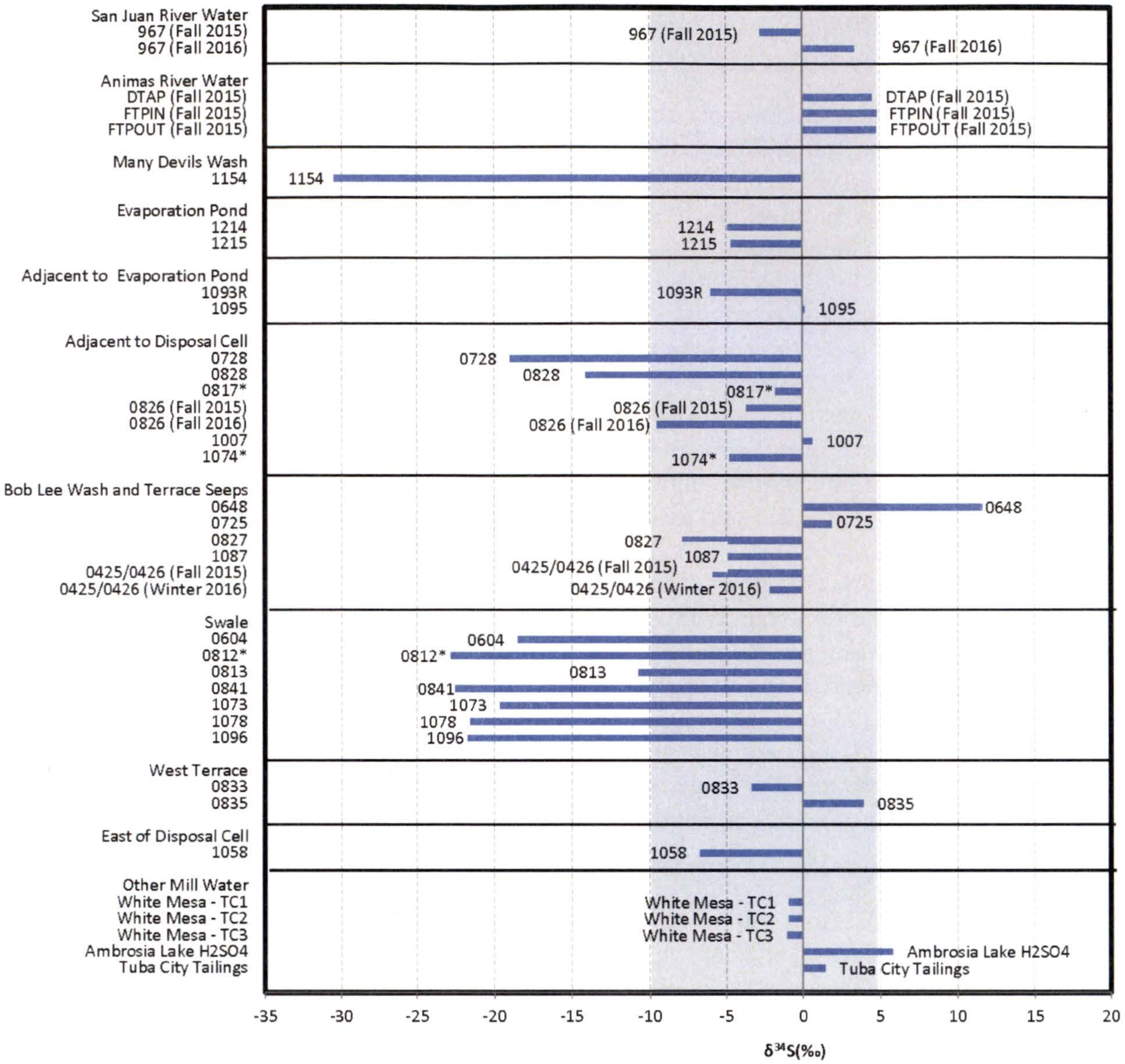

Figure 4. Comparison of $\delta^{34}S_{sulfate}$ Values in Terrace Groundwater (Note: highlighted range is nondefinitive for an exact sulfate source, but is not a Mancos Shale source, and asterisk indicates historical data to assist interpretation.)

Since some of the groundwater samples had $\delta^{34}S_{\text{sulfate}}$ values that were similar to the $\delta^{34}S_{\text{sulfate}}$ values of the San Juan River, the Animas River, and that of sulfuric acid thought to be used by the mill, groundwater samples were collected in September 2016 for the analysis of $\delta^{34}S_{\text{sulfate}}$ and $^{18}O_{\text{sulfate}}$ (Figure 5). The resulting groups shown in Figure 5 are consistent with the swale wells showing a unique signature, likely due to the Mancos Shale. The swale well grouping also includes well 0728, which appears to have a mixed mill-related uranium and Mancos Shale-related sulfate signature. Wells west of the disposal cell (0826, 0827, and 0828, Figure 5) show a grouping between the swale wells and the contaminated locations that potentially indicates a mixed sulfate source.

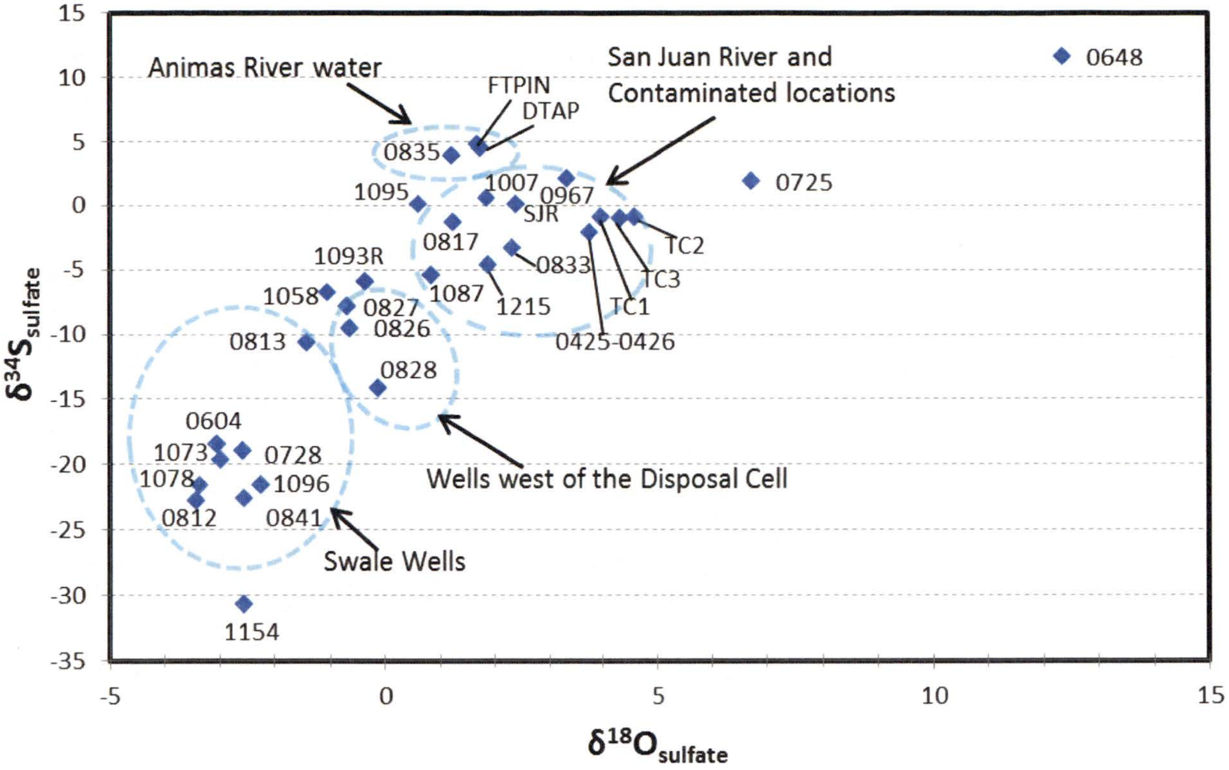

Figure 5. $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ Values in Terrace Groundwater

Similar to the interpretation for the uranium sources based on the $^{234}U/^{238}U$ AR, the $\delta^{34}S_{sulfate}$ and $^{18}O_{sulfate}$ data may indicate potential sulfate sources, mainly as Mancos Shale related or not Mancos Shale related, but these data do not provide information on the original water source. Any groundwater can potentially dissolve sulfate with its associated isotopic signature; thus, tritium, δ^2H_{water} and $\delta^{18}O_{water}$, and total chlorine were measured as indicators that are associated strictly with the incoming groundwater.

4.3 Tritium Concentrations

Tritium (^3H) is an unstable isotope with a relatively short half-life (12.3 years). Tritium is produced naturally in the upper atmosphere at low concentrations, and any precipitation prior to 1953 that may have recharged to groundwater does not have detectable tritium. After 1953, atomic bomb testing contributed excess tritium to the atmosphere. Thus, any precipitation that recharged after 1953 will have detectable tritium (Clark and Fritz 1997).

Tritium concentration data in precipitation collected at the Global Network of Isotopes in Precipitation (GNIP) station in Albuquerque, New Mexico, were obtained from the International Atomic Energy Agency website at http://www-naweb.iaea.org/napc/ih/IHS_resources_gnip.html. These data were accessed in June 2016 and corrected for radioactive decay over the elapsed time between precipitation and groundwater sampling in 2015 (Figure 6).

Tritium units were calculated by dividing the concentration of tritium in picocuries per liter by 3.22 (https://pubs.usgs.gov/ds/751/convFactors.html).

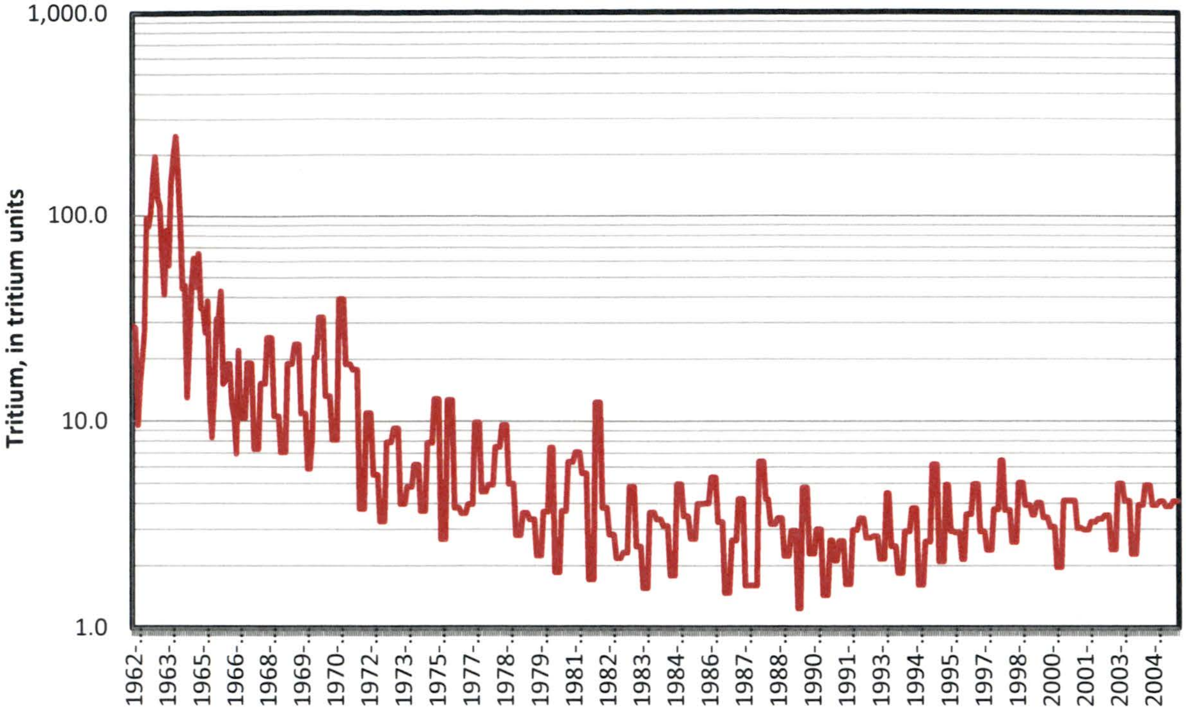

Figure 6. Time-Series Plot of Tritium Concentration in Precipitation Available from the GNIP Station in Albuquerque, New Mexico, 1962–2005

As seen in Figure 6, the interpretation of exact age dates is now difficult due to the relatively flat decay curve from 1971 to the present. Groundwater mixing can also create issues with age dating interpretation. In addition, the tritium values for the Animas River water ranged just above the detection limit (0.8 TU) from 0.9 to 1.5 TU, indicating relatively old water, likely due to baseflow conditions with the majority of the stream flow being groundwater inputs. Thus, the tritium data is used mainly as a prior-to-1953 or after-1953 apparent age identification (Table 1). The term apparent age is used here since mixed groundwater may be derived from waters of different ages. Seven wells do have tritium values above 15 TU (Table 1); thus, the decayed tritium curve (Figure 6) indicates an apparent age of these waters between 1962 and 1972. Six of these wells are near the disposal cell and may have some component of water that was related to water loss through tailings or water used as dust suppression. Two of these six wells (1093R and 1095) are near the evaporation pond and have uranium ARs greater than 1.2. Thus, it is likely that the water source for these wells may have been San Juan River water used for dust suppression. In addition to the tritium values for these wells, the equipotential surface for the groundwater in this area is quite flat (Figure 7), which could create slower groundwater flow rates in this area. The other four wells show uranium ARs near 1, which indicate a mill-related uranium source. However, the water source as water loss through the tailings or water used for dust suppression is unclear. This is due to the possibility that water used for dust suppression could move through areas with a solid-phase source of mill-related uranium. The last well with tritium above 15 TU is well 0813 in the swale area, which does not show a mill-related uranium AR and may be related to water used for dust suppression or is related to precipitation recharge during the 1962–1972 time frame, but in an area with slower groundwater flow rates.

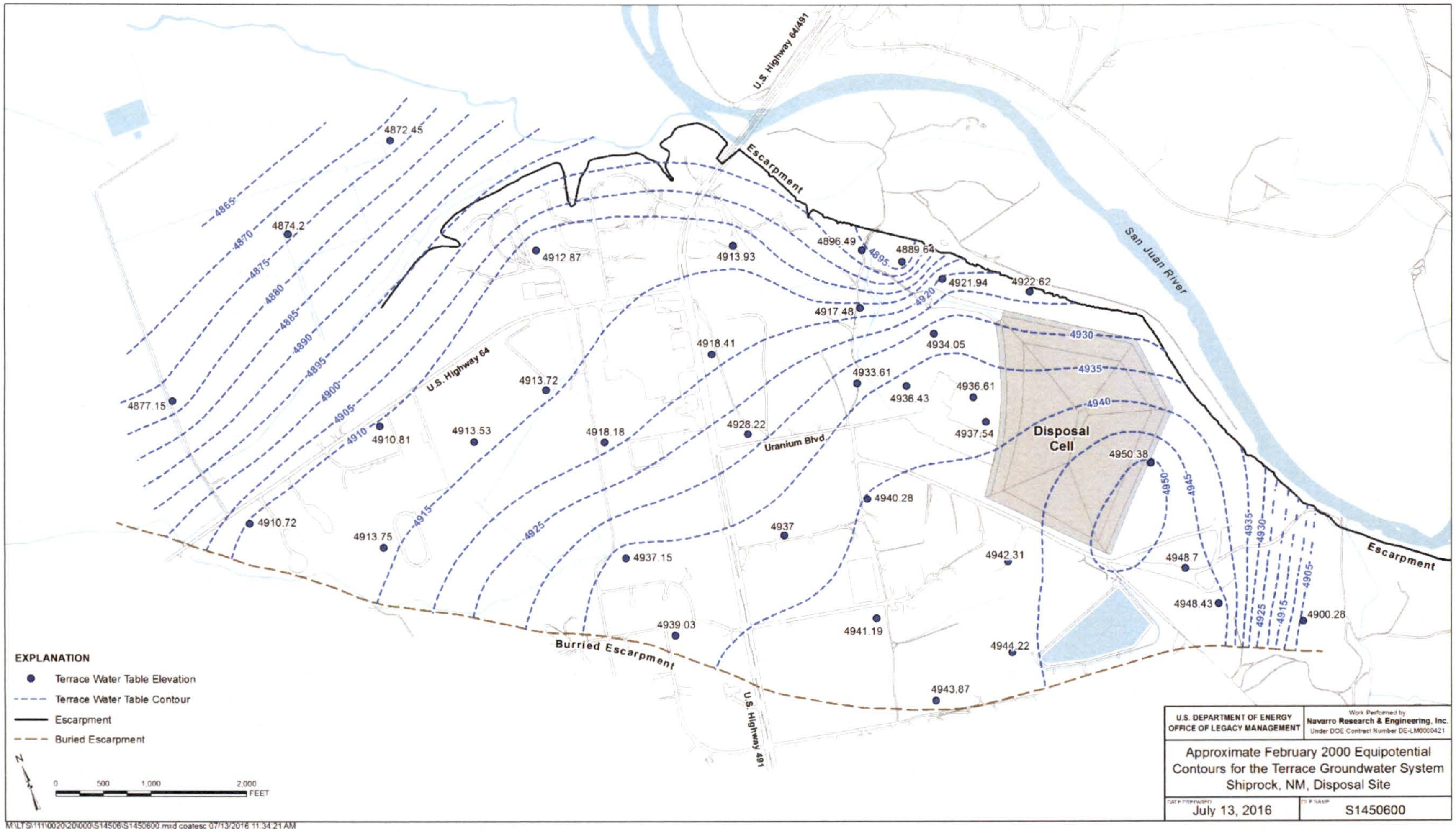

Figure 7. Equipotential Surface for the Terrace Groundwater System in 2000

Overall, since all but two samples (0648 and 0725) 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. Well 0648 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 well 0648 cannot be present-day precipitation, water from leaking pipelines, or mill-related water, and we can logically conclude that this artesian well contains groundwater from a deeper, older source that is not mill related. Well 0725 has a tritium value just above the detection limit, which indicates that the source of groundwater to this well could be groundwater from well 0648 as it flows down Bob Lee Wash and perhaps mixes with small amounts of other water sources.

4.4 δ^2H_{water} and $\delta^{18}O_{water}$

δ^2H_{water} and $\delta^{18}O_{water}$ values are useful in identifying groundwater sources because these isotopes are part of the water molecule and do not interact with the solid phase. In general, δ^2H_{water} and $\delta^{18}O_{water}$ values are more negative with colder temperatures, thus creating changes in these isotopes with elevation and season. For groundwater recharge, the seasonal changes tend to be averaged out to give δ^2H_{water} and $\delta^{18}O_{water}$ values that are representative of recharge elevations and the local climate.

Worldwide, δ^2H_{water} and $\delta^{18}O_{water}$ values plot on a straight line called the global meteoric water line (GMWL, Craig 1961). Local areas sometimes have meteoric water lines (MWLs) that are parallel, but slightly offset from the GMWL, such as data from the arid zone in Nevada (Nevada MWL, Welch and Preissler 1986). Both the GMWL and the Nevada MWL for δ^2H_{water} and $\delta^{18}O_{water}$ values are plotted in Figure 8 along with all the Shiprock samples. Wells 0648 and 0725 are specifically labeled in Figure 8 because both of these wells had tritium values at or near the detection limit. Thus, the water source to these wells is likely much older and probably not related to current river sources or recent recharge. Of all the groundwater samples, well 0648 is the most isotopically depleted (Table 1 and Figure 8), which indicates that the water in this well is from a different source than the rest of the terrace wells. In fact, well 0648 is a flowing artesian well screened very deep in the Jurassic Morrison Formation. Water from well 0648 flows into Bob Lee Wash, and well 0725 is adjacent to the Bob Lee Wash drainage downstream from well 0648 and, thus, is likely recharged to some degree by this water.

Because the San Juan River and the Animas River have headwaters at much higher elevations, they likely have variations in δ^2H_{water} and $\delta^{18}O_{water}$ values that are not represented by the single sampling event values listed in Table 1. The San Juan River sample was collected on 9/24/2015, and the Animas River Samples (DTAP, FTPIN, and FTPOUT) were collected on 10/22/2015. The δ^2H_{water} and $\delta^{18}O_{water}$ values for the San Juan and Animas river samples are plotted in Figure 8, but the potential seasonal variability of the δ^2H_{water} and $\delta^{18}O_{water}$ values is unknown. This variability could potentially be quite large due to different water sources throughout the year, such as baseflow conditions in the winter from groundwater discharge compared to snowmelt runoff in the spring.

A key point in interpreting δ^2H_{water} and $\delta^{18}O_{water}$ data is that evaporation results in a deviation from the meteoric water line along a line with a lower slope (Clark and Fritz 1997). An approximate evaporation line for the Shiprock samples can be drawn with the evaporation pond samples being one end member and the San Juan River sample being the other end member (Figure 8). Half of the samples plot below the Nevada MWL and all of the samples plot below the GMWL, indicating water sources that have experienced some evaporation before or during recharge to the groundwater. Sample 1154 from a monitoring well in Many Devils Wash plots on the Nevada MWL and is probably most representative of the δ^2H_{water} and $\delta^{18}O_{water}$ values in local recharge without any evaporation. All of the other groundwater samples plot quite close to the evaporation trend line that connects the San Juan River water samples with the evaporation pond samples.

While the δ^2H_{water} and $\delta^{18}O_{water}$ data are inconclusive for exact original source waters due to potential seasonal variations in the river water, the data plot around the evaporation trend line and generally between monitoring well 1154 in Many Devils Wash and the San Juan River water (Figure 8). This suggests that groundwater on the terrace has undergone some evaporation and is derived from a combination of Animas River water, San Juan River water, or precipitation recharge (Figure 8).

4.5 Total Chlorine Concentrations

Total chlorine concentrations were used to identify possible leakage from pipes supplying domestic water. Chlorine is added to water in water treatment plants to kill potentially harmful microorganisms. Free chlorine is the term used to describe hypochlorous acid and hypochlorite, which form when chlorine is added to water. These are the compounds that kill microorganisms. Total chlorine is the sum of free chlorine and combined chlorine, which is the chlorine that reacts with ammonia and other nitrogen compounds and is less effective in disinfection. Concentrations of total chlorine and free chlorine should be greater in water derived from a water treatment plant relative to water from other sources. Measurable amounts of total chlorine were detected in the DTAP sample and wells 0725, 0826, 0828, 0841, 1058, and 1096. Any detection of total chlorine is direct evidence of domestic water as one source of groundwater recharge on the terrace. However, other groundwater sources are a possibility, and the detection of total chlorine cannot be used to quantify volumes. The lack of total chlorine cannot rule out domestic water sources, as total chlorine is quickly consumed by reactions in the subsurface. For example, at one location (0728), a leaking line has been confirmed and recently fixed by the local water authority, but that sample did not show any detection of total chlorine.

No clear patterns can be identified in Table 1 for total chlorine, likely due to the scattered nature of domestic water pipeline leaks. However, well 0828 illustrates the fact that $^{234}U/^{238}U$ ARs near 1.0 do not necessarily indicate a mill-water source. What $^{234}U/^{238}U$ ARs near 1.0 do indicate is a mill-related uranium source. Thus, this report specifically discussed the uranium source as being separate from the water source. As a result, total chlorine data can indicate a water source that has at least some component of domestic water, but the overall evaluation of the geochemistry refers back to solid-phase interaction, such as the $^{234}U/^{238}U$ ARs.

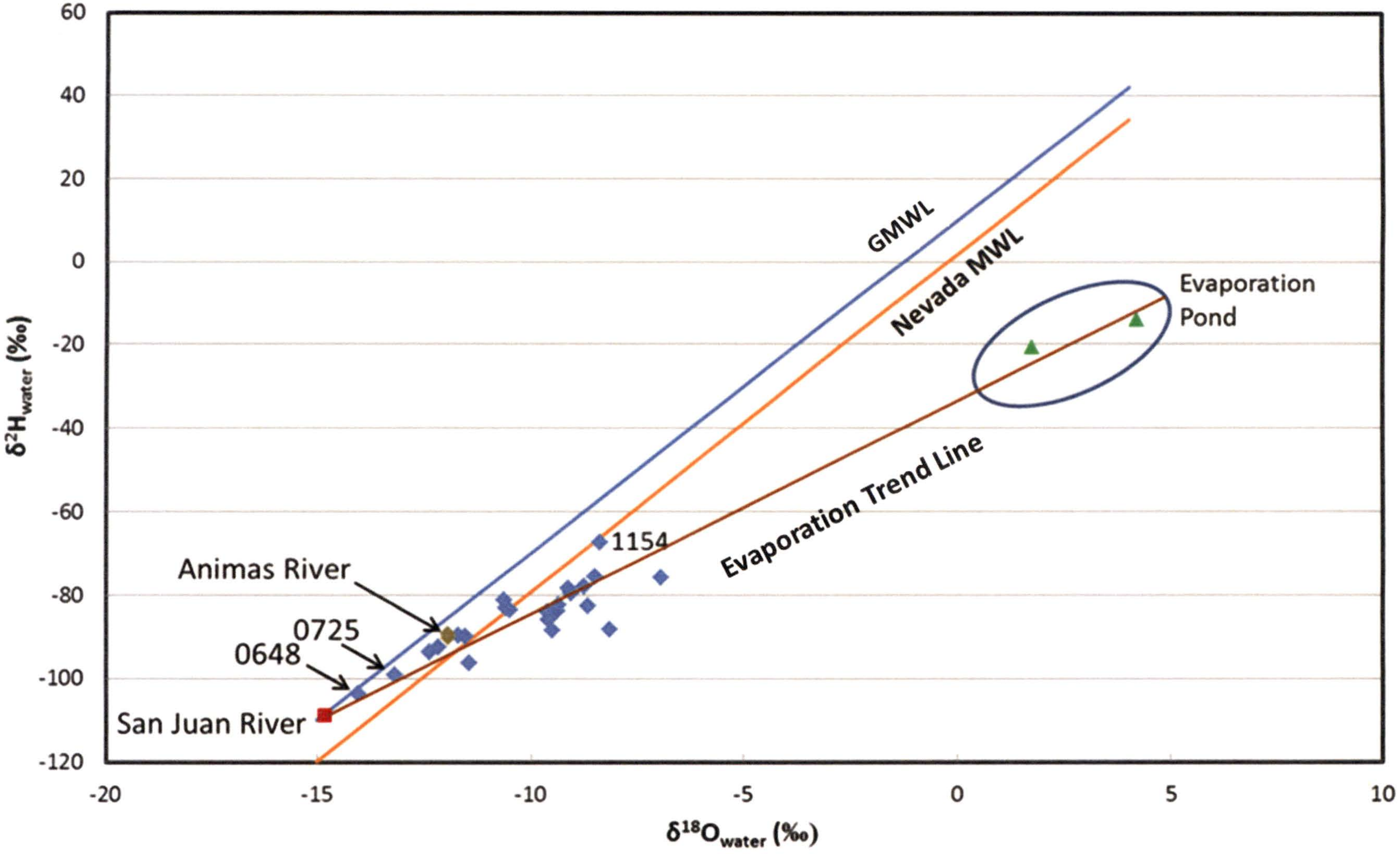

Figure 8. δ^2H_{water} and $\delta^{18}O_{water}$ Composition of Collected Samples

5.0 Summary and Conclusions

The objective of this investigation is to better understand the sources of groundwater that presently exist on the terrace. Potential 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) groundwater present on the terrace prior to the mill being in operation, and (5) infiltration of meteoric water. This objective was addressed with water sampling and analyses for $^{234}U/^{238}U$ activity ratios and uranium concentrations, $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ values and sulfate concentrations, tritium concentrations, $\delta^{2}H_{water}$ and $\delta^{18}O_{water}$ values, and total chlorine.

The $^{234}U/^{238}U$ activity ratios identify the areas where uranium in the groundwater is mill related compared to naturally occurring (non-mill-related, or non-mill-affected, Figure 9). The determination of mill-related versus non-mill-related sulfate (Figure 4 and Figure 5) matches the data for $^{234}U/^{238}U$ activity ratios, albeit with a bit more uncertainty in the interpretations. While the $^{234}U/^{238}U$ activity ratios and the $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ values can identify mill-related sources of uranium and sulfate in the groundwater, other isotopes were used for specific water sources because uranium and sulfate can be dissolved from the solid phase and are not indicators of the original water source. Tritium data indicate water sources that are mainly post-1953. The $\delta^{2}H_{water}$ and $\delta^{18}O_{water}$ data indicate a minimal amount of water related to local precipitation, and the total chlorine identifies wells that have some water source due to domestic water pipeline leaks.

Evidence presented in this report suggests that the majority of groundwater recharge at the Shiprock site occurred during or after the mill was in operation. A similar conclusion was reached by Robertson et al. (2016) based on their analysis of chlorofluorocarbons (CFCs) in groundwater collected from 12 wells throughout the terrace. They stated that "at least some fraction of water has recharged since the 1940s and that at least some wells (0813, 0817, 0824, and 0833) have a substantial fraction of water that is composed of younger (post-Mill water)." The original source waters can be summarized as follows:

- Water related to the operation of the uranium mill: YES
- Domestic water use on the terrace: YES
- Irrigation water: LIKELY
- Groundwater present on the terrace prior to the mill being in operation: UNLIKELY
- Infiltration of meteoric water: MINIMAL
- Groundwater from flowing artesian well 0648 only exerts a localized terrace influence: MINIMAL

Water related to the operation of the mill includes tailings drainage and dust-suppression water. Both include the higher tritium values due to recharge during the period of mill operations seen in six well samples. However, the separation of the two sources is unclear, due to the possibility of dust-suppression water moving through zones with uranium contamination on the solid phase. Leakage from pipelines that carry domestic water was clearly determined by the detection of total chlorine in several wells. Irrigation water from the San Juan River is difficult to distinguish from Animas River, but a loss of irrigation water to the underlying groundwater is a logical water source, especially on the west terrace; water from the San Juan River was and continues to be used to irrigate fields. Any groundwater that was present on the terrace prior to milling operations would not contain any tritium. Given the detection of tritium in all shallow groundwater samples, a terrace groundwater source prior to milling either did not exist or has been replaced by more recent water sources (post-1953). Based on the $\delta^{2}H_{water}$ and $\delta^{18}O_{water}$ values in a Many Devils Wash spring sample, post-1953 meteoric water on the terrace appears to be minimal, but this does not preclude mixing between precipitation recharge and other water sources. Additional data on $\delta^{2}H_{water}$ and $\delta^{18}O_{water}$ values for local groundwater recharge compared to the seasonal range of $\delta^{2}H_{water}$ and $\delta^{18}O_{water}$ values in the San Juan and Animas rivers would be necessary to better identify the infiltration of meteoric water.

A conclusion of this report is that any groundwater flowing into the area of the terrace containing mill-derived solid-phase uranium and sulfate (mill-affected, Figure 9) will become contaminated regardless of origin. Dissolution of mill-derived solid-phase uranium and sulfate will continue for an unknown, extended period of time until the solid phase is exhausted. On the basis of the groundwater isotope data in this report, the main water sources flowing as groundwater in the mill-affected area are water related to the operation of the mill (tailings fluid loss and dust-suppression water), leakage of domestic water from pipelines (Animas River water), irrigation water (San Juan River water), and possibly some infiltration of meteoric water. Isotope data alone cannot quantify the amounts of water from these sources. Any additional quantification would require hydrogeologic methods to directly measure precipitation recharge and irrigation losses compared to any current water losses from the tailings, along with a better determination of domestic water losses from pipelines.

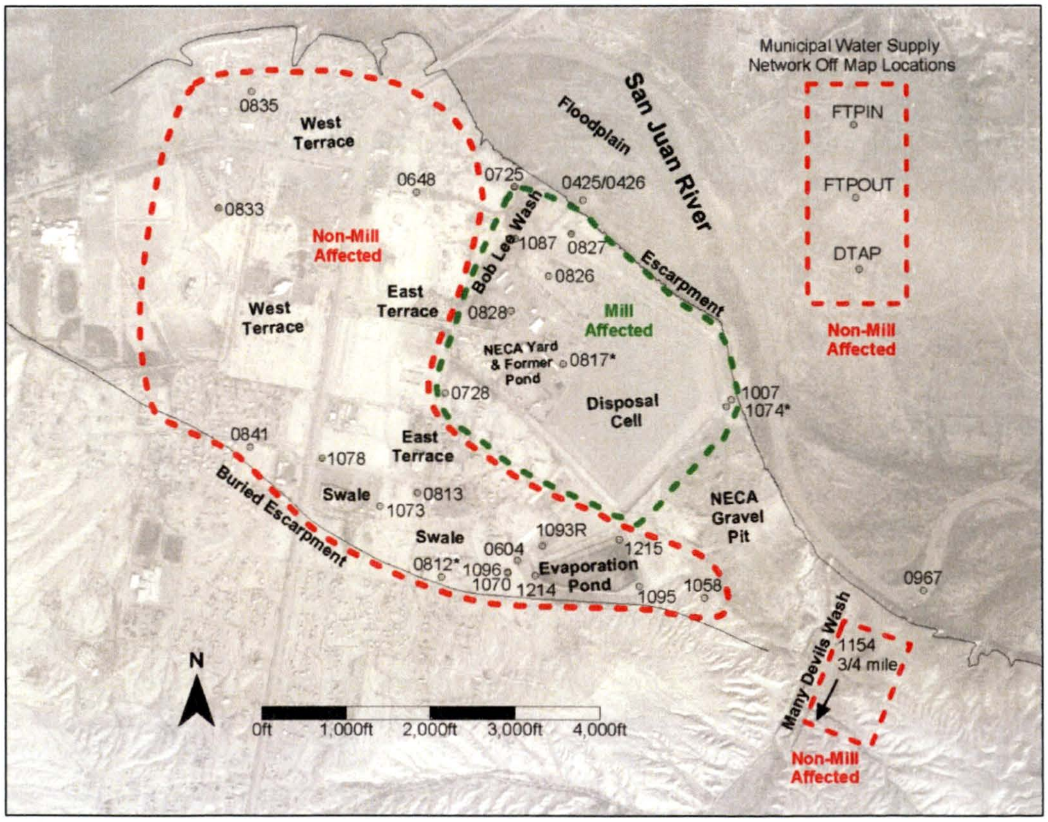

Figure 9. Mill- and Non-Mill-Affected Groundwater Interpretative Map with All Sampling Locations (Note: all sampling locations included; however, 0967, 1214, 1215, DTAP, FTPIN, and FTPOUT are surface water sample locations considered in the groundwater interpretations.)

6.0 References

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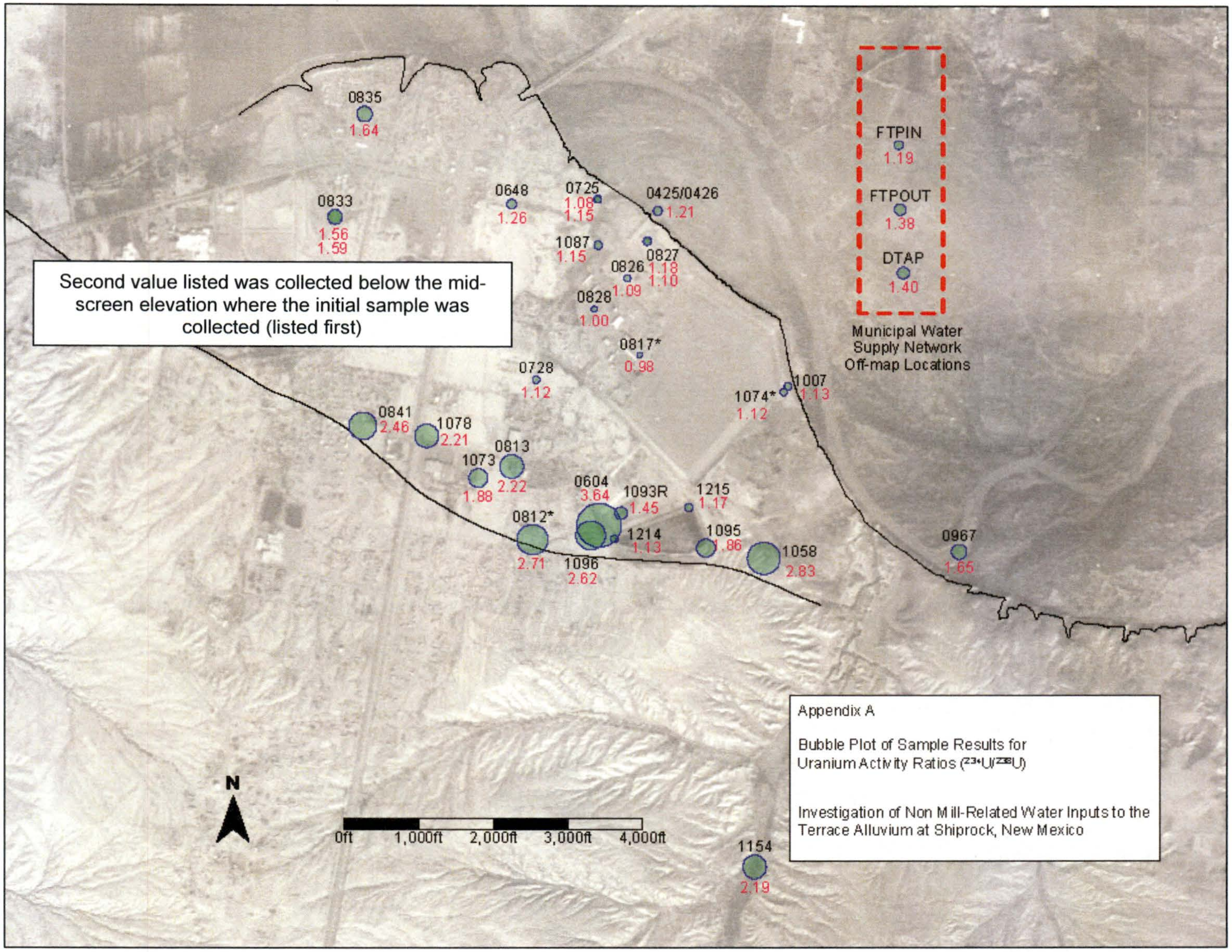
Appendix A

Sample Results Bubble Maps



Second value listed was collected below the mid-screen elevation where the initial sample was collected (listed first)

Appendix A

Bubble Plot of Sample Results for Uranium Activity Ratios ($^{234}U/^{238}U$)

Investigation of Non Mill-Related Water Inputs to the Terrace Alluvium at Shiprock, New Mexico

Figure A-1. Bubble Plot of 2015 Sample Results for Uranium Activity Ratios ($^{234}U/^{238}U$)

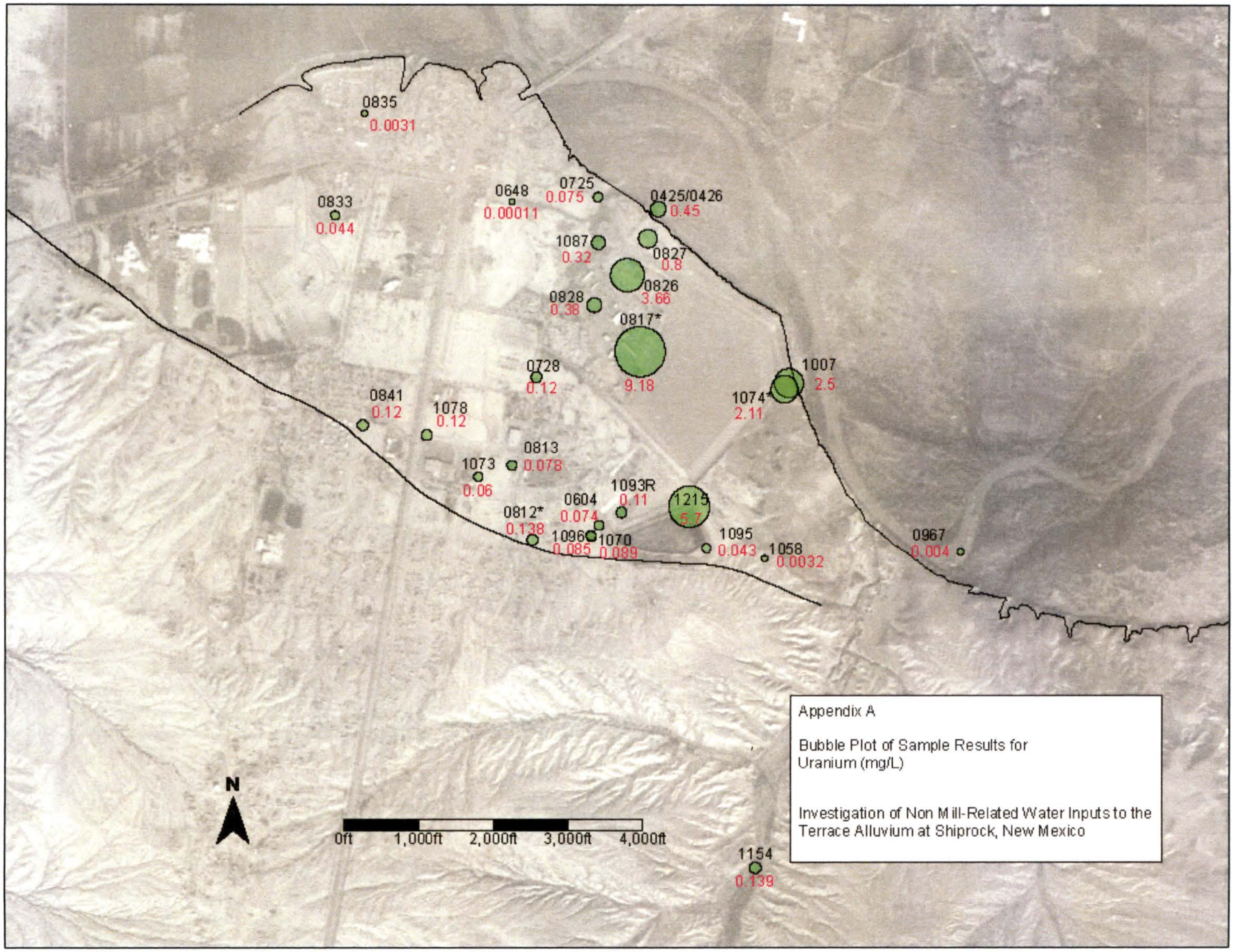


Figure A-2. Bubble Plot of 2015 Sample Results for Uranium (mg/L)

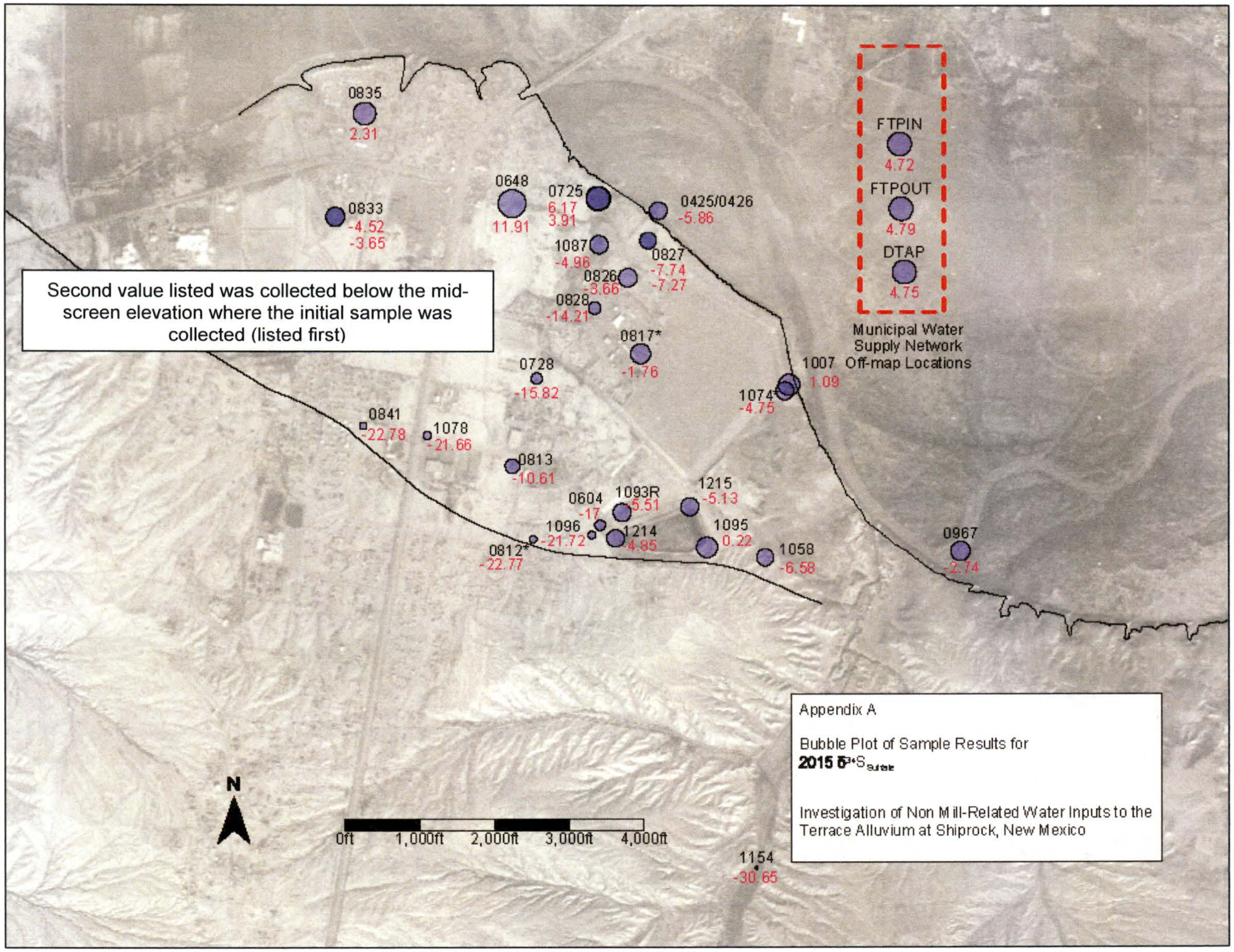


Figure A-3. Bubble Plot of 2015 Sample Results for $\delta^{34}S_{sulfate}$

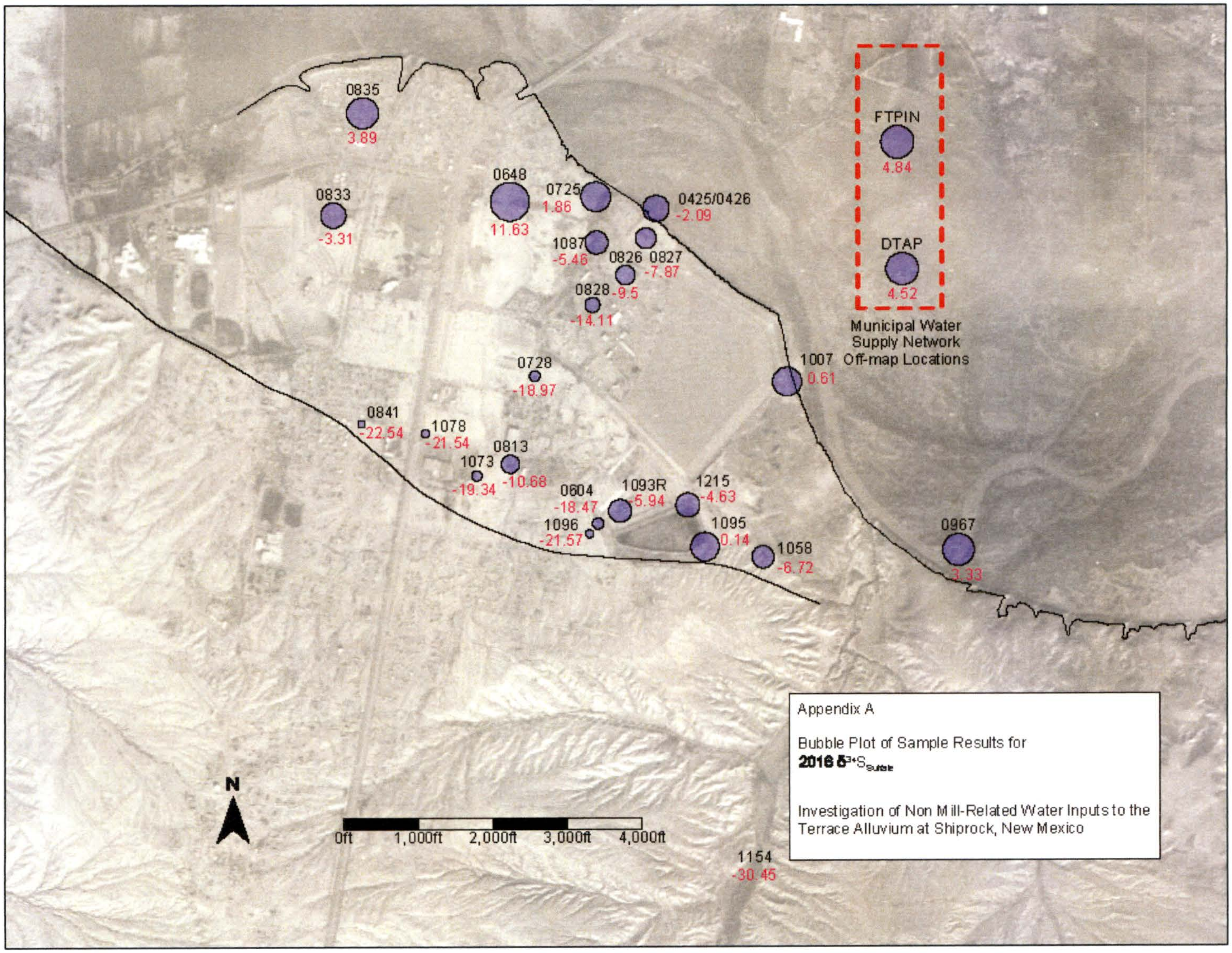


Figure A-4. Bubble Plot of 2016 Sample Results for $\delta^{34}S_{sulfate}$

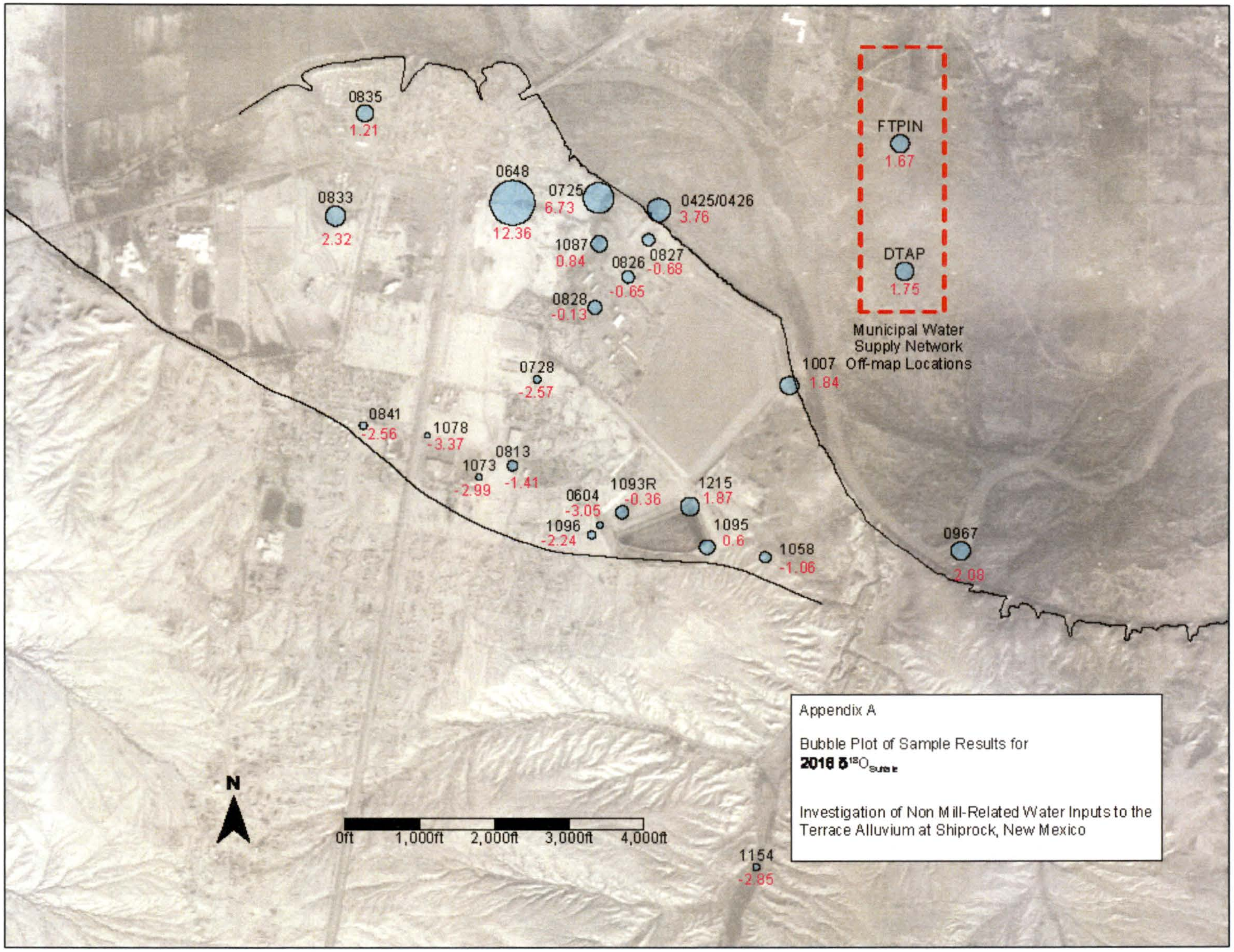


Figure A-5. Bubble Plot of 2016 Sample Results for $\delta^{18}O_{sulfate}$

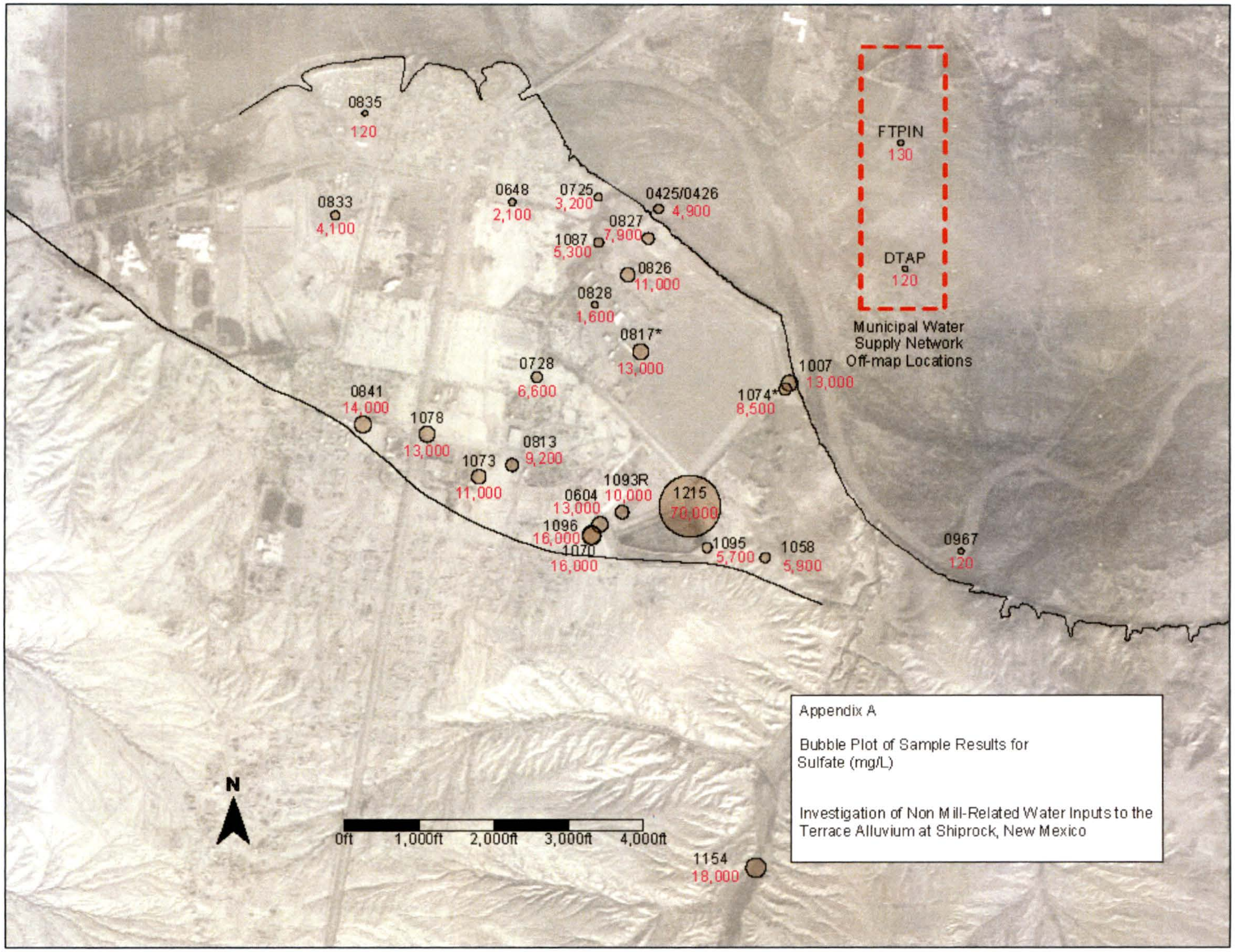


Figure A-6. Bubble Plot of 2015 Sample Results for Sulfate (mg/L)

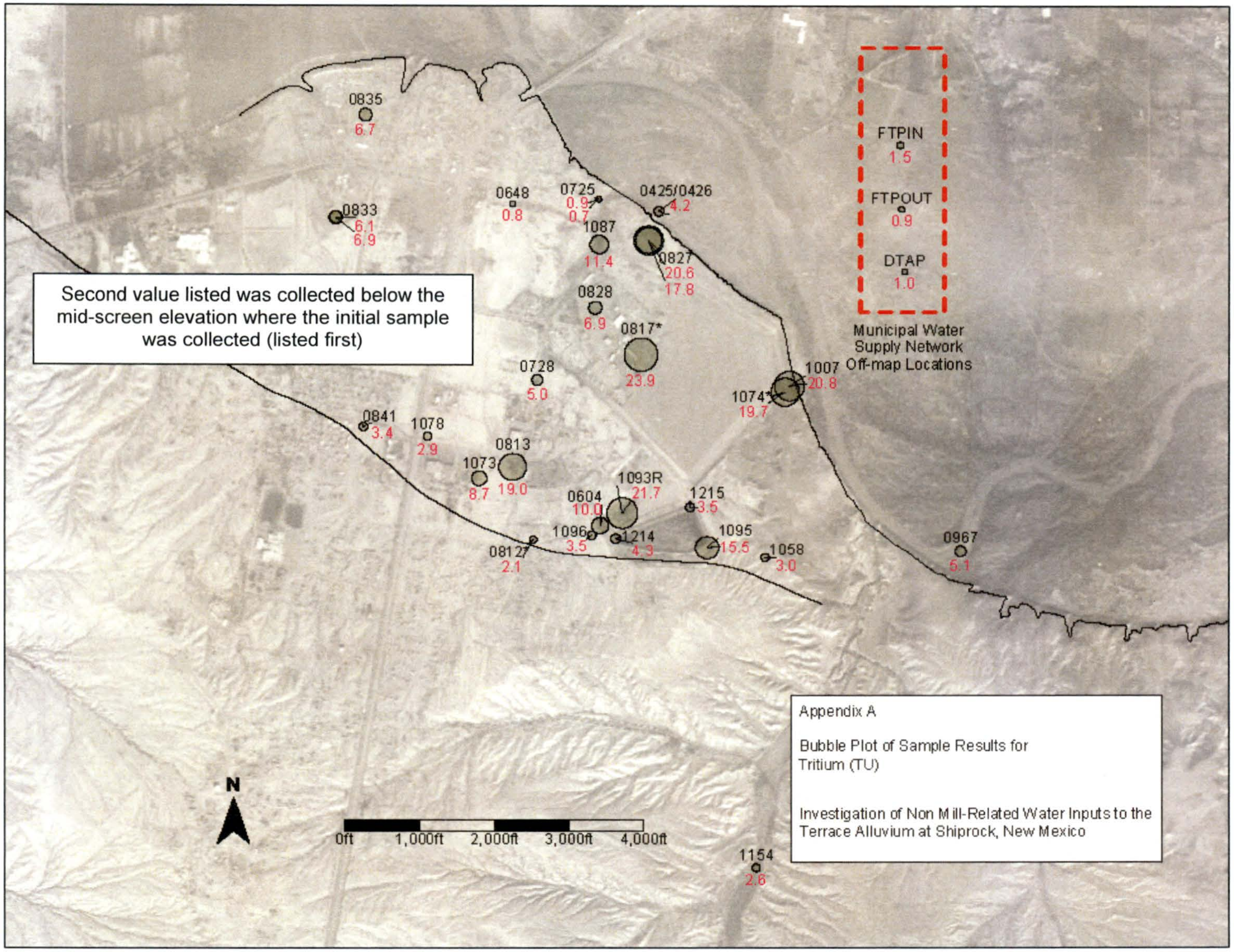
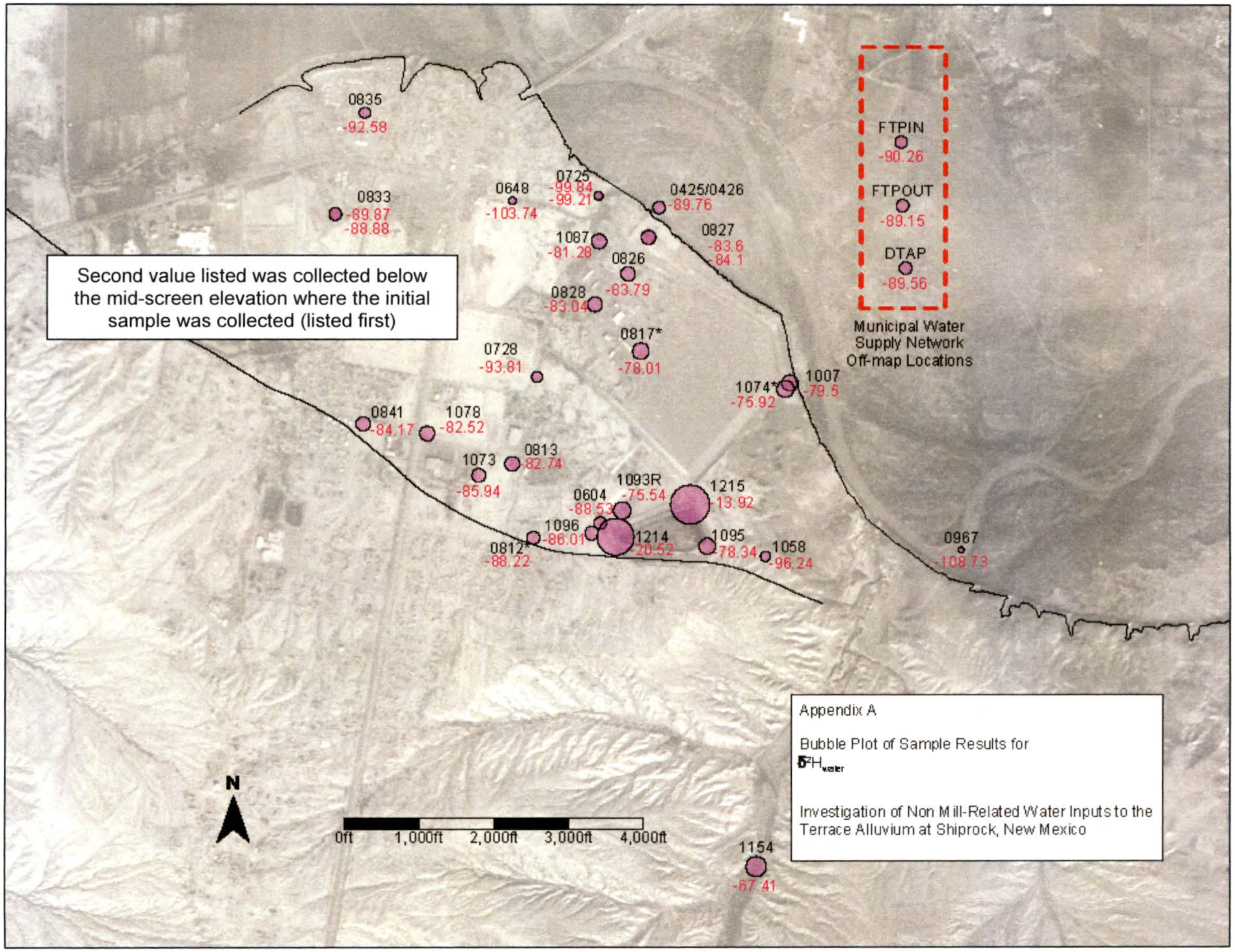


Figure A-7. Bubble Plot of 2015 Sample Results for Tritium (TU)



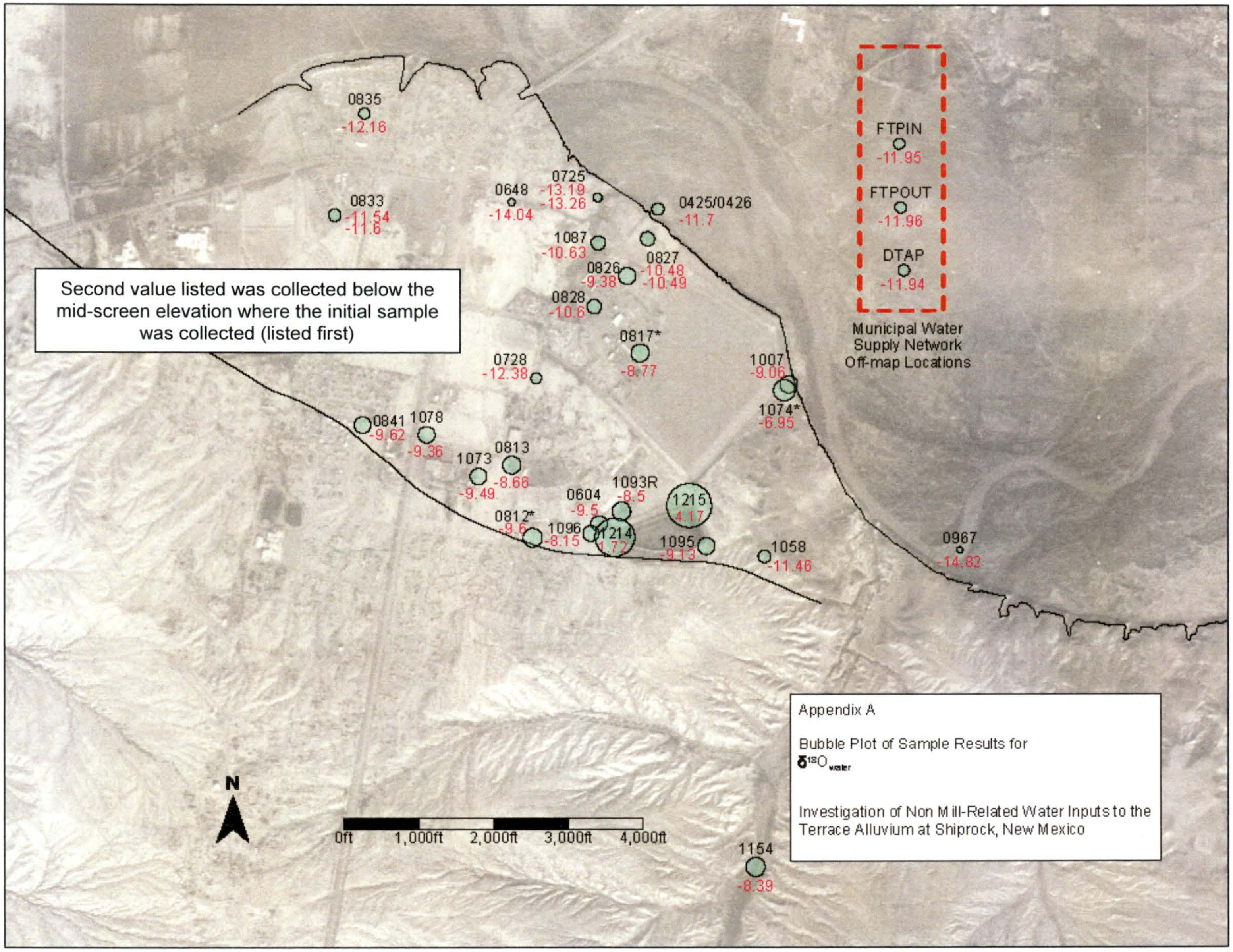
Second value listed was collected below the mid-screen elevation where the initial sample was collected (listed first)

Appendix A

Bubble Plot of Sample Results for δ^2H_{water}

Investigation of Non Mill-Related Water Inputs to the Terrace Alluvium at Shiprock, New Mexico

Figure A-8. Bubble Plot of 2015 Sample Results for δ^2H_{water}



Second value listed was collected below the mid-screen elevation where the initial sample was collected (listed first)

Appendix A

Bubble Plot of Sample Results for $\delta^{18}O_{water}$

Investigation of Non Mill-Related Water Inputs to the Terrace Alluvium at Shiprock, New Mexico

Figure A-9. Bubble Plot of 2015 Sample Results for $\delta^{18}O_{water}$

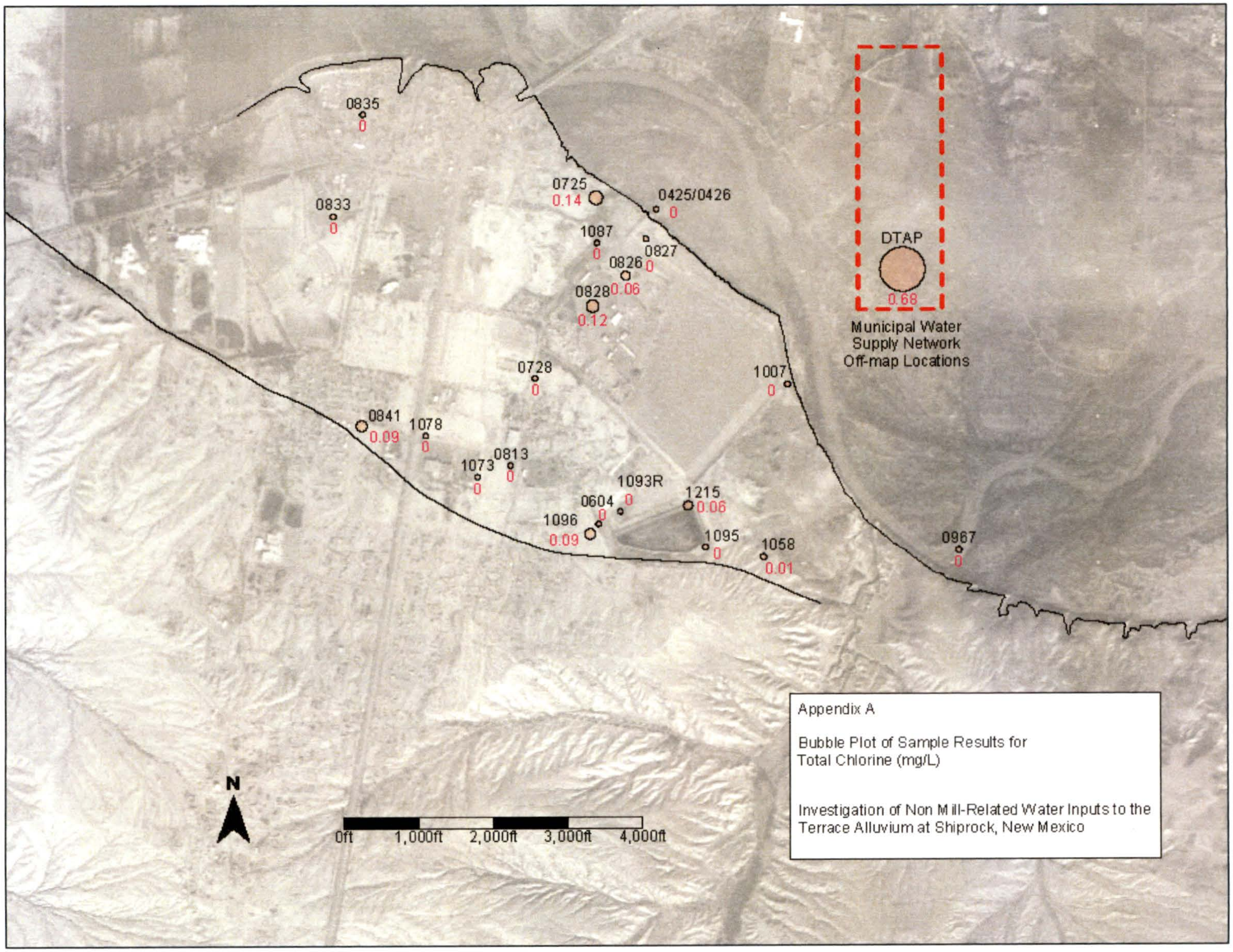


Figure A-10. Bubble Plot of 2015 Sample Results for Total Chlorine (mg/L)