An investigation of groundwater age at the Shiprock, NM UMTRCA site

Bryan Lawlis

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An Investigation of Groundwater Age at the Shiprock, NM UMTRCA Site

By

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Master of Water Resources

Water Resources Program
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Abstract

The Shiprock Disposal Site is located in Shiprock, NM and was the site of the former Navajo Mill, a uranium and vanadium ore processing facility. The site occupies approximately 230 acres on a terrace overlooking the San Juan River and its adjacent flood plain. Uranium and Vanadium were extracted from ores mined from various locations from 1954 through 1968. The contaminants of this leaching process percolated into the groundwater on the terrace and the floodplain. The remediation of the Navajo mill site was recommended by the EPA in 1974. The Department of Energy (DOE) completed the Shiprock Uranium Mill Tailings Remedial Action (UMTRA) in 1986, which consisted of consolidating all tailings and other materials from two tailings piles and waste from raffinate ponds that were combined and placed in one on-site disposal cell.

Many Devils Wash (MDW) is one of two prominent arroyos near the former mill site that has a continuous groundwater seeps. Surface water and groundwater in MDW contains the same constituents as the groundwater located under the processing site. Tailings from the mill were not discarded near MDW.

The groundwater constituents at MDW are hypothesized to have two potential sources. Due to similar chemical constituents between MDW and the mill, one of these sources could be the former mill site. The other source suggests that the constituents are naturally occurring from minerals present in the weathered Mancos Shale.

This study examined whether groundwater from beneath the mill site is migrating to or away from MDW. This study depended on various sources including multiple age dating techniques, the directional flow of groundwater, and the relationship of stable isotopes O and H.

Since the mill site operated from 1954 to 1968 elevated levels of age-dating tracers were used in investigating the age of groundwater that recharged from the milling process. The goal of this research was to identify the location of the water recharged during the milling process as well as age of the groundwater in MDW.

The results of this research demonstrate that groundwater from several wells to the west of the mill contain age dating tracers that suggest the majority of groundwater was derived from the mill operation era. The complementary results are not evident elsewhere, thus the constituents in MDW may not be related to past milling operations.
Acknowledgements

Dr. Bruce M. Thomson
Dr. Zachery Sharp
Andrew Robertson
DOE Personnel
People of the Navajo Nation
USGS
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**Introduction**

The Shiprock Disposal Site is located on the Navajo Indian Reservation in northwest New Mexico in the town of Shiprock which is located 30 miles west of Farmington (Figure 1). The site is just south of the San Juan River on a terrace 50-60 ft above the river. The disposal cell and associated infrastructure is constructed on the site of the former Navajo mill that processed approximately 1.5 million tons of ore from 1954 to 1968 (Albrethsen and McGinley, 1982).

Water from the San Juan River was pumped to the site and mixed with the ore to extract Uranium (U) and Vanadium (V). Raffinate (leaching solution from which U and V had been extracted), tailings and waste water was disposed in unlined evaporation ponds (figure 2) (Merritt, 1971). Contamination of the groundwater at the mill site consists of elevated concentrations of sulfate, nitrate, Manganese, Selenium, Strontium, Ammonia, and uranium. Elevated concentrations of these and other constituents are present in the groundwater seeping from MDW. This lead to the assumption that MDW contamination was derived from the mill site and the acceptance of responsibility for the wash by DOE (DOE 2000).

Age-dating tracers were used to interpret the apparent age of the shallow groundwater aquifer under the mill site and in groundwater seeping into MDW. Concentrations of chlorofluorocarbons (CFCs) and tritium (³H) were used in this study to interpret groundwater age. The age of groundwater is viewed as apparent age due to the fact that it is based on an interpretation of measured concentrations of age-dating tracers in the groundwater aquifer (Plummer and Friedman, 1999). Multiple age-dating techniques were applied to supply a more assured apparent age. Stable isotopes were also reviewed from previous studies to identify any correlation between water from the mill site and MDW water.
The main focus of this study was to determine the apparent age of the groundwater seeping into MDW to improve our understanding of the groundwater hydrology at the Shiprock mill tailings site and weather leachates from the stabilized tailings may be contributing contaminants to MDW.

**Site Background**
The Navajo mill in Shiprock, New Mexico was an ore-processing mill for uranium and vanadium from 1954 through 1968. The “Raw Leach” process used sulfuric acid to extract U and V from the ore, ammonium carbonate was then added to the settled slurry and ammonium was used to precipitate U from the “strip solution” (Merritt, 1971). Mill-related contaminants were found to have percolated into the groundwater beneath the site location. Remediation of the site was recommended by the Environmental Protection Agency (EPA) in 1974. The Department of Energy (DOE) completed the Shiprock Uranium Mill Tailings Remedial Action (UMTRA) in 1986, which consisted of consolidating all tailings and other materials from two tailing piles and waste from raffinate ponds that were combined and placed in one on-site disposal cell.

**Climate**
Shiprock is located in an arid area with an annual precipitation of 7.00 in/yr (Stone and others, 1983). The majority of the precipitation occurs during the monsoon season which generally occurs from July to October. The annual pan of evaporation rate is 70 in. (Robson and Banta, 1995). The annual snowfall is approximately 3.9 in and generally occurs from November to March.
Local Geology
Late Cretaceous Mancos Shale, up to 220 ft, underlies the entire Shiprock site and this formation slopes slightly eastward from the site (DOE, 2000). Terrace material, loess, and alluvial unconsolidated Quaternary deposits overlay the Mancos Shale. This alluvial formation is 10 ft to 40 ft thick and resides on top of weathered Mancos Shale.

The Mancos Shale is composed of dark grey shale with a sporadic siltstone, dolomite and bentonite beds and is approximately 1,000 ft thick (DOE 2011). This formation was deposited in the late Cretaceous as an open marine mud stone. This portion is characterized by a loss of organic carbon and increase in iron oxide minerals (DOE 2005). Up to a 40 ft layer of weathered Mancos Shale resides on top of the Mancos Shale; the fractures within the weathered formation contain gypsum, which was formed by oxidation of disseminated pyrite, creating sulfuric acid that reacts with calcite to form gypsum (White and Greenman 2008). Interaction between the groundwater and the weathered Mancos Shale may contribute to release of contaminants from naturally occurring soil minerals (Hollaway and others, 2005).

Groundwater
The alluvial groundwater was suggested to have result from anthropogenic sources, primarily mill tailings water, with potential influence from irrigation and leaking municipal piping systems (DOE 2000). Groundwater from the milling operation may have been introduced through unlined tailings pond, ore piles and raffinate ponds, all of these sources could have contributed to the alluvial aquifer contamination. The groundwater contours (figure 3) illustrate a northwestern flow away from the mill site with a slight flow towards MDW located on the edge of the Disposal Cell. These groundwater contours consist of 33 wells around the mill site. This
data was collected in March 1999 and was provided by the DOE (DOE, 2000). The aquifer contains a saturated thickness of 14 ft near Highway 491 and decreases eastward to 2 ft in well 731 just southeast of the disposal cell (Figure 4). Moving eastward from well 731 to MDW the saturated thickness decreases and groundwater is not apparent on top of the Mancos Shale. The wells sampled in this study were screened just above or slightly in the Mancos Shale with the exception of well 824 which was screened 174 ft into the Mancos Shale.

**Pre-milling site conditions**

The only two structures shown in a 1935 aerial photograph (Figure 5) of Shiprock are two houses that were located just south of the San Juan River. The aerial photo also depicts a barren environment with little vegetation consistent with the site location in an arid environment. The only evidence of irrigated agriculture is a small lot of land just south of the river.

In the 1940s Shiprock began to grow due to the production of helium, natural gas and oil. A helium processing plant was constructed by the U.S. Bureau of Mines in 1944. A community of 54 houses and streets were constructed just south of the helium plant (Foster 1945). Water was pumped from the San Juan River to supply the helium plant and the new housing community. Wastewater from the helium plant and housing area were piped to a sewage lagoon off the terrace west of U.S. Highway 491 Bridge. The production of helium ended in 1945 due to the end of World War II. In 1952 the Korean War increased demand for helium, thus the helium plant was placed into operation once more.
In the 1950s uranium, oil and gas exploration progressed in the Shiprock area. This resulted in the growth of Shiprock. In 1954 a uranium mill was constructed by Kerr-McGee Oil Industries, and the mill was operational by the end of 1954 (Albrethsen and McGinley 1982). Figure 2 is a photo the Navajo Mill in its production years. The Navajo Mill operated through 1968 and processed approximately 1.5 million tons of U and vanadium ore.

In 1974, the Environmental Protection Agency (EPA) suggested that the tailing piles be stabilized and the mill site decontaminated. The decontamination process began in 1975 and continued through 1980. In 1986 DOE initiated surface cleanup of the site to meet EPA criteria under provisions established by the Uranium Mill Tailings Radiation Control Act (UMTRCA). The surface remediation activities included the construction of a disposal cell which consolidated waste from two tailing piles and other contaminated materials into a single tailings pile.

Tailings and other solid wastes from the mill were placed in a disposal cell on site that is approximately 76 acres (Figure 6). This cell was designed to encapsulate the contaminants for at least 200 yrs. This disposal cell was constructed with a clay cap, a sand layer, and a thick outer layer of cobble (DOE 2000).

The disposal cell is located adjacent to the former mill site and has an elevation of 5000 ft. The alluvial formation under the disposal cell consists of 10 to 35 ft of sand and gravel. The Mancos Shale underlies the alluvial.
Leaching Process
The leaching process at the mill utilized a strong sulfuric acid to extract U and vanadium from finely ground ore. Ammonium carbonate was added to the settled slurry (referred to as lixiviant) during the milling process to raise the pH, and ammonium (NH$_4^+$) was used to precipitate U from the “strip solution” (Merritt, 1971). Contaminants of concern (COCs) released from the milling process consist of ammonia, selenium, strontium, NO$_3^-$, U, and sulfate. These COCs percolated into the alluvial groundwater in the terrace and the floodplain. The highest concentrations of COCs are found in groundwater from the mill site, disposal cell, and MDW (DOE, 2000).

Many Devils Wash
Groundwater seeps out of the ground along the southeast wall of the arroyo (Figure 7). The visible white efflorescence (salt deposits) in MDW naturally occurs in the Mancos Shale and contains a mixture of calcium, sodium, and magnesium sulfate evaporate mineral species (Evangelou and others, 1984). This efflorescence is an indicator of groundwater discharge into MDW. The arroyo walls consist 20-30 ft of steeply incised channels within the loess deposits. Weathered Mancos shale is present under the loess with as much as 3 ft of gravelly alluvium residing on top of the weathered Mancos Shale. The origin of the groundwater in MDW is unknown; it contains dissolved constituents that have changed the color of the water from light yellow to a deep red. The groundwater discharge is estimated to be 0.3 gpm and flows to the San Juan River (DOE, 2010). The constituents of concern (COCs) in MDW are nitrate, manganese, selenium, sulfate, and U. The same COCs are found in contaminated groundwater under the mill site, thus leading DOE to the conclusion that MDW was contaminated by the mill site (DOE 2000).
Figure 1: Locations of Shiprock, NM and the Disposal Site in Shiprock, NM
Figure 2: 1965 view Southwest of Navajo Mill Area (altered from DOE, 2000)
Figure 3: Groundwater contours of the mill site and MDW (DOE, 2000)
Figure 4: Saturated thickness in the alluvial portion of the terrace aquifer (DOE, 2000)
Figure 5: 1935 Aerial View of Shiprock, NM (altered from DOE 2000)
Figure 6: 1987 Aerial photo of completed disposal cell, view Northwest (altered from DOE, 2000)
Figure 7: Groundwater seeps in Many Devils Wash looking North
**Methods**

Tritium and Chlorofluorocarbons that have been released into the atmosphere, dissolve in rain and subsequently recharge groundwater can be used to determine the apparent age of groundwater and are referred to as age-dating tracers. The use of these tracers produce an apparent age of groundwater that may be determined by a tracer that has been introduced into the groundwater system since the water was in contact with the atmosphere. Younger groundwater has different anthropogenic constituents as a result of industrial gases introduced in the 20th century (Plummer and Friedman, 1999).

Two age-dating tracers were used to assess the special extent of mill water at the mill site and in MDW. These age-dating tracers may reveal the apparent age of the groundwater or constrain conceptual models.

The wells sampled were sampled in November and December of 2012 and are located around the former mill site and in MDW (figure 8). These wells were selected based on location and the ability to produce a substantial amount of groundwater needed to collect the required sample volume.

**Tritium**

The tritium samples were collected with two 500 ml high-density polyethylene bottles and sealed with polycone caps. The tritium samples were collected by purging groundwater via dedicated low flow bladder or peristaltic pump. Water was purged from the well until field parameters dissolved Oxygen, pH, temperature and conductivity were stable and then a sample was collected (USGS Field Manual). The samples were collected from 9 wells around the mill.
site and one sample within MDW. Samples were analyzed at Lamont Doherty Earth Observatory and the tritium is reported as tritium units (TU).

Tritium ($^3$H) is a radioactive isotope of hydrogen with a half-life of 12.32 years. During the late 1950s to the mid-1960s, atmospheric testing of nuclear weapons raised the atmospheric concentrations of $^3$H hundreds of times above the normal background concentration (Plummer and others, 1993). The Nuclear Test Ban Treaty was signed in the 1960s and most nuclear weapons testing ceased. Since then $^3$H levels have decreased and are almost back to natural levels. These bomb $^3$H concentrations still continue precipitate out but have a much lower concentration than that of the mid-1960s. Tritium concentrations alone can generally only be used qualitatively without Tritiogenic Helium ($^3$He) concentrations to determine the amount of $^3$H that has decayed from initial recharge, but are useful in determining whether the source of groundwater is modern or pre-modern (Clark and Fritz, 1997). $^3$H is not affected by microbial degradation and can be useful in identifying groundwater mixing. Because of various meteorological processes and atmospheric moisture sources the construction of local $^3$H in precipitation model is necessary (figure 9). This precipitation model was constructed from an excel program designed by the USGS called tracer LPM. In this study, the historic $^3$H in precipitation records were taken from Albuquerque, NM (USGS Tracer LPM).

**Tritiogenic Helium samples**

Water samples for Helium analysis was collected from many of the same wells that $^3$H samples were collected. The helium samples were collected using a special copper tube engineered from the USGS Reston Chlorofluorocarbon Laboratory which allows water from the well to be sealed to prevent $^3$He loss. The samples were collected from the well using dedicated and
peristaltic pumps. The copper tubes were flushed with sample water and then sealed after determining that all air bubbles were absent from the copper tube.

$^3$He/$^3$H is a more accurate groundwater tracer. As part of a water molecule $^3$H is transformed by radioactive decay to helium-3. By measuring both the $^3$H and $^3$He content from a groundwater sample, an apparent age can be determined because the rate that $^3$H decays to helium-3 is known (Lucas and Unterwager, 2000).

**Chlorofluorocarbon (CFCs)**
The CFCs were collected with 125ml (4oz) clear boston round bottles and the bottles were sealed with an aluminum lined cap. Samples were collected using a dedicated low flow bladder or peristaltic pumps. Replicate CFC samples were collected from 2 wells with a Waterra Hydrolift pump and nylon tubing to ensure sample integrity due to tubing construction. Limited water, depths to water and access restricted the technique to be used in all wells. The sampling process consist of placing a bottle in a 2 liter beaker, fill the sampling bottle from the bottom of the bottle, overflowing the sampling bottle with at least 2 liters of purged groundwater, and sealing the bottle with an aluminum lined cap while the bottle is still submerged in the 2 liter beaker (USGS Reston Chlorofluorocarbon Laboratory). This allows the collection of groundwater samples without interaction between groundwater and the atmosphere.

Chlorofluorocarbons (CFCs) CFC-11, CFC-12 and CFC-113 were introduced into the atmosphere from anthropogenic sources from 1950s to the 1980s. CFCs can be found in groundwater that has been recharged in the last 60 years. The age of groundwater concentrations can be determined by comparing groundwater to the known historical atmospheric concentrations of CFCs and some basic assumptions. Anaerobic Microbial degradation will reduce the
concentration of CFC-11 in the aquifer making CFC-11 appear as if they were recharged at an earlier date when CFCs had a much lower atmospheric concentration. Some assumptions and factors can affect the concentration of CFCs including: temperature of the water table during recharge, thickness of the unsaturated zone, entrapment of excess air, uncertainty of recharge elevation, microbial degradation, and mixing of younger and older water in the aquifer (Plummer and Busenburg, 1999).

**Dissolved Gases**

Water samples for dissolved gas analyses N\textsubscript{2} and Ar were collected using a dedicated low flow bladder or peristaltic pumps. Replicate dissolved gas samples were collected from 2 wells with a Waterra Hydrolift pump and nylon tubing to ensure sample integrity due to tubing construction. A 125ml (4oz) clear boston round bottle was submerged into a 2 liter plastic beaker with water flowing through the bottle when submerged into the beaker. The bottle was sealed with a rubber stopper and a syringe needle in place while the bottle was still submerged. The syringe needle was then removed from the stopper to ensure that air bubbles were not present in the bottle. The samples were then placed in a cooler to confirm that the rubber stopper will not burst due to temperature increase (USGS Reston Chlorofluorocarbon Laboratory). The concentrations of dissolved gasses were determined by gas chromatography at USGS Dissolved Gas Laboratory in Reston, Virginia.

Ar and N\textsubscript{2} are collected the estimate recharge temperature and excess air of the groundwater aquifer. This is a useful method to help determine the concentrations of CFCs in the aquifer at the time of recharge (Plummer and others, 1993).
Hydrogen-2 ($\delta^2$H) and Oxygen-18 ($\delta^{18}$O) Isotopes in Groundwater

Isotopic data was compiled from previous studies (DOE, 2012, Garvin, 2012). Data from 28 wells was identified for this study. Data was identified for thirteen wells near MDW and for fifteen wells around the mill site. Data for the San Juan River and the Morrison aquifer (a deep aquifer) were also evaluated in this study (DOE 2012). These two sources were compiled to compare their isotopic data to the aquifers isotopic data.
Figure 8: Location of Sampling points
Figure 9: Tritium in precipitation in Albuquerque, NM. The parallel lines indicate the path of decay of tritium in groundwater if recharged during any particular year.
Results

Tritium
Tritium ($^3$H) samples were collected from the monitoring wells at the mill site and MDW on November, 14 and December, 11 & 12, 2012 and the concentrations are reported in Tritium Units (TU). The $^3$H sample concentrations range from 1.66 TU to 34.03 TU. The concentrations of tritium are plotted in figure 10.

Nine samples were collected from wells around the mill site and one sample was collected from well 1048 in MDW. The locations of the wells sampled for $^3$H are illustrated on figure 11 as well as the $^3$H concentration contours. The $^3$H activity was lowest in the MDW well with a value of 1.66 TU. Wells 815 and 813 have $^3$H values of 33.21 and 34.03 respectively, indicating that the water was recharged during the 1960’s (Clark and Fritz, 1997). Based on the activity of the mill during this time, groundwater at these locations was likely recharged from surface water used for the milling process. Well 827 has a $^3$H level of 19.98 TU which could also be a representative of mill recharged water. This value is the third highest among samples collected. The other $^3$H activities of the mill site samples ranged from 3.43 to 12.98 TU.

The $^3$He samples were discarded due to excessive CO$_2$ in the sample. The excessive CO$_2$ is believed to have stripped the helium from the samples, thus the lab was unable to obtain a viable measurement of $^3$He (written communications Peggy Widman USGS CFC Laboratory).

CFCs
Samples were analyzed from seven wells from around the mill site and one sample was collected from well 1048 in MDW on November, 14 and December, 11 & 12, 2012 (figure 13). Samples were collected in replicate and were analyzed for low-level CFC-11, CFC-12 and CFC-
113 at the U.S. Geological Survey CFC Laboratory, in Reston, VA. Average concentrations of CFCs from the replicate are shown in Figure 12. Wells 815 and 728 had the lowest values of CFCs. Groundwater from Well 815 has an average concentration for two replicate samples of CFC-11 and CFC-113 of 9.1 pptv and 5.6 pptv, respectively. CFC-12 was not reported in well 815 due to peak interference at the lab. Groundwater from Well 728 has an average concentration of CFC-11, CFC-12, and CFC-113 of 17.5 pptv, 110.3 pptv, and 6.2 pptv, respectively. Well 841, this is the furthest well west of the mill site that was sampled, is located in a neighborhood and has the highest average values of CFC-12 and CFC-113. Groundwater from well 841 has an average concentration of CFC-11, CFC-12, and CFC-113 of 100.3 pptv, 328.6 pptv, and 634.2 pptv, respectively. Well 813 has an average concentration of CFC-11, CFC-12, and CFC-113 of 38.5 pptv, 577.8 pptv, and 11.3 pptv, respectively. Samples collected from well 817 have an average concentration of CFC-11, CFC-12, and CFC-113 of 22.8 pptv, 148.0 pptv, and 9.4 pptv, respectively. The sixth sample was collected from well 824 which had CFCs CFC-11, CFC-12, and CFC-113 with average concentrations of 139.9 pptv, 325.4 pptv, and 41.1 pptv, respectively. Well 833 is located the furthest northwest on the site has an average concentration of CFC-11, CFC-12, and CFC-113 of 113.3 pptv, 292.4 pptv, and 24.9 pptv, respectively. The well 1048 is located in MDW with CFC-11, CFC-12, and CFC-113 average concentrations of 138.2 pptv, 328.6 pptv, and 43.3 pptv, respectively. CFC contours based on apparent age is illustrated in figure 13.

Recharge temperatures are need to determined accurate CFC concentrations in the water samples and this is accomplished by sampling for dissolved N\textsubscript{2} gas and Ar concentrations (Stute and Schlosser, 1999). Recharge temperatures can be estimated by analyzing concentrations of N\textsubscript{2} and Ar. N\textsubscript{2} and Ar concentration were lower than should be expected. It is believed that
these excessively low concentrations are due to excess CO₂ in the water samples (written communications Peggy Widman USGS CFC Laboratory). In order to calculate the solubility in the absence of the gasses, the elevation of Shiprock was used as the estimated recharge elevation and the average annual temperature of Shiprock was used as recharge temperature. Groundwater ages calculated from CFC concentrations decrease with an increase in recharge temperature. Uncertainties of CFC ages result from uncertainties in recharge temperature are less than 1 year of error prior to 1975 and can be ignored (Busenburg and Plummer, 1992). Uncertainty of recharge temperature can result in 2 to 3 years of error from water recharged from 1980 to 1989. Recharge that occurs after 1989 is extremely sensitive to uncertainties in recharge temperature and local variations in atmospheric CFC concentrations resulting from the decrease in atmospheric emissions of CFCs (Elkins et al., 1993).

CFC-11 is highly biodegradable (Cook et al., 1995) which appears to be the cause of low CFC-11 concentrations in the samples analyzed when compared to CFC-12 and CFC-113 (figure 14). CFC-11 concentrations were not used in this study due to consistently lower concentrations of CFC-11 when compared to the apparent age of CFC-12 and CFC-113.

Hydrogen-2 (δ²H) and Oxygen-18 (δ¹⁸O) Isotopes in Groundwater
Approximately 28 stable isotope measurements of groundwater were obtained around the mill site and MDW as well as the San Juan River and the Morrison aquifer. Isotopes of hydrogen and oxygen can be used to identify different sources of water in a catchment area. The isotope values in figure 17 are reported in units of “per mil” (₀/₀₀). The groundwater in MDW has δ²H values between -65 ₀/₀₀ to -82 ₀/₀₀ per mill and δ¹⁸O values ranging from -8.20 ₀/₀₀ to -8.80 ₀/₀₀ (figure 17). The groundwater surrounding the mill site has δ²H values between -78 ₀/₀₀ to -96
with the exception of well 731 which has a $\delta^2$H value of -65.0/oo. The $\delta^{18}$O values range from -6.95.0/oo to -11.60.0/oo. Well 731 has an isotopic measurement similar to MDW which could indicate a hydrologic connection between MDW and well 731. The groundwater contours in 1999 provided by DOE (figure 3) depict groundwater flow moving eastward from 731 to MDW. The wells surrounding the mill site are marginally more depleted than MDW $\delta^2$H with the exception of well 731 which is slightly more enriched with $\delta^2$H than MDW. Well 1058 which located directly southeast of well 731 is significantly depleted in both $\delta^2$H and $\delta^{18}$O relative to other around the mill site and MDW. The isotopic data in 1058 contains values similar to the San Juan River. The San Juan River sample that was collected in September 2010 has a $\delta^2$H and $\delta^{18}$O values of -95.0/oo and -12.6.0/oo, respectively. The Morrison has a $\delta^2$H and $\delta^{18}$O values of -103.0/oo and -14.1.0/oo, respectively. Table 1 provides all of the isotopic values for in this study.
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Figure 10: Tritium concentrations from the Shiprock uranium mill site and MDW
Figure 11: Concentrations of Tritium in TU units
Figure 12: This illustrates the average value of each CFC sample analyzed from the wells.
Figure 13: Contour map based on average age of CFCs concentrations
Figure 14: Concentrations of CFC-11, CFC-12, and CFC-113 samples compared to historic CFC concentrations
Discussion
This study hypothesized that recharge water from the mill site is not currently migrating toward from MDW. The analyses of $^3$H in groundwater samples from wells 813 and 815 and the analyses of CFCs in in groundwater wells 728 and 815 illustrates that the flow path of mill water could potentially be migrating east away from the disposal cell. Since the mill age groundwater appears to be migrating westward this may suggests that the COCs in MDW could be naturally occurring or derived from another source.

Dating groundwater with age-dating tracers provides new information in developing the conceptual flow model and constraining potential sources and ages of the alluvial groundwater underlying the Disposal site. Information on dissolved $N_2$, Ar, and $^3$He would have provided a better understanding of the processes that may be affecting the concentrations of CFCs and $^3$H, on which the estimated ages are based. $^3$H concentrations could provide a more accurate source of apparent age than CFCs since no other interpretation is needed to accurately analyze the concentrations of the $^3$H samples.

Changes in CFCs concentrations can be attributed to seasonal recharge with subsequent gas confinement, solubility equilibrium in response to temperature change, and gas exchange between trapped air bubbles and unsaturated-zone air in the recharge area (Plummer 1999). This may explain the discrepancy in CFCs tracer age when compared to $^3$H tracer age in MDW, since the groundwater depth in well 1048 is only 6.48 ft.

Due to excessive $CO_2$ in the groundwater dissolved gases, and $^3$He concentrations were far below expected the values. This prevented use of these constituents as tracers at this site.
CFCs values were not compromised during lab analysis, because CFCs gases stripe out at a slower rate when compared to other dissolved gasses and $^3$He (Peggy Widman, USGS Reston Chlorofluorocarbon Laboratory).

In all of the sampled wells the mean ages of CFC-11 were lower than atmospheric loading predicted concentrations (figure 11) which is possibly caused by biodegradation, CFC-11 is more vulnerable to this process. CFC ages sampled from the wells were based on mean concentrations of CFC-113 and CFC-12 (figure 11) with the exception of CFC-12 in wells 813, 841 and 815, due to the apparent contamination of CFC-12 in wells 813 and 841 and peak interference of CFC-12 in well 815 while being analyzed at the lab.

**Mixing Models**

Water recharged from the mill and other potential sources of groundwater could potentially mix at certain points in the aquifer. The mean age of the mixed groundwater could affect the interpretation of groundwater dating methods (Bohlke, 2002). Three different mixing models can be used to describe the mixing of water within the aquifer. These three methods consist of piston flow, exponential mixing, and binary mixing. Piston flow is nearly uniform in age and the water would flow from the point of recharge to the point of discharge without mixing. The piston flow model assumes no mixing with a tracer flows from the recharge area to the sampled location. Piston flow indicates that tracers can be measured from shallow monitoring wells in an unconfined aquifer with a small recharge area (Jurgens and others, 2012). If piston flow is present then the water in the well is considered nearly uniform in age. Homogeneous, unconfined aquifer receiving uniform recharge validates exponential mixing. Vertical stratification of groundwater age occurs with this model, which increases from zero at the
water table to older ages at the bottom depth of the aquifer. This model can be appropriate for fully penetrating wells and is applicable when mixing results within the well instead of the aquifer (Appelo and Postma, 1996). Binary mixing model occurs when young water and old (pre-tracer) water are present in fractured rock environments. These three models are illustrated in figure 15. The dilution of tracers occurs when old water is mixed with young water making determination of an appropriate mixing model important in interpreting the results. Because of potential biodegradation or contamination of tracers it is important to compare multiple tracers simultaneously to determine age, flow and mixing regime. In this study exponential and binary mixing are not considered as important as piston flow due to the uncertainty of groundwater age in these mixing regimes.

Hypothetical deviations in the concentrations of CFCs and $^3$H in reaction to piston flow, exponential mixing, and binary mixing are shown (Figure 16). Figure 16 was created in Tracer LPM by plotting the tracers concentrations from the samples to historical atmospheric concentrations. These concentrations will plot within the areas on the graph by curves representing dissimilar concentrations of the modeled tracer, if no other process has affected them (Plummer and others, 2003). Concentrations that plot far outside the bounded areas are probably degraded or contaminated meaning the CFC concentrations are above historical atmospheric concentrations.

The age dating tracers used as part of the mixing model consist of CFCs and $^3$H. Well 813 is considered to be contaminated due to the high level of CFC-12, however CFC-113 and $^3$H in
well 813 appear to be around historic levels, thus the CFC-113 and $^3$H concentrations can still be used to evaluate potential mixing (Plummer and Busenberg, 1999).

The relationship between $^3$H and CFC-12 (figure 16A) indicates that water from well 728 lies between exponential mixing and binary mixing of modern and old (pre tracer) water. Wells 824, and 833 lie between exponential mixing and binary mixing of modern and old (pre tracer) water. The well 1048 which is located in MDW lies below the binary mixing line; this is due to elevated CFC levels in comparison to $^3$H levels in MDW. CFC-12 in well 813 is assumed to have been contaminated which results in the well lying out of range to determine mixing.

Comparison of $^3$H and CFC-113 (figure 16B) depicts that water from wells 813, 815, are primarily piston flow and wells 824 and 833 are located just below the piston flow line. Strong indication of piston flow is specified in wells 813 and 815 due to high $^3$H values that could have only been recharged in the 1960s bomb peak. Water from well 1048 which is located in MDW lies below the binary mixing line; this is due to elevated CFC levels in regards to $^3$H levels in MDW.

Concentrations of CFC-113 and CFC-12 (figure 16C) almost all lay between exponential mixing and piston flow lines. Wells 1048 and 824 are located directly on or near the exponential mixing line. CFC-12 in well 813 is assumed to have been contaminated which results in the well lying out of range to determine mixing. Due to bio degradation of CFC-11 all of the wells lie under the flow and mixing lines (figure 16D).
Mill Site

The $^3$H concentrations that indicate mill recharged water are found in wells 813 and 815 (figure 8). Groundwater in these two wells has the highest concentrations $^3$H on the site. The enriched values suggest water was recharged during milling production even without $^3$He concentration to determine decay rate. However, only CFCs in well 815 concur with the $^3$H data as water recharged during the milling era. Well 827 also indicates possible mill water $^3$H value but this study was unable to collect CFCs from this well due to minimal water production. These three wells contain $^3$H values that correlate with groundwater contours flowing west away from the mill site (figure 4). Well 815 $^3$H value also correlates with the CFC values which indicate piston flow through this portion of the mill site which was most likely recharged from the milling operation (figure 12).

Based on groundwater from wells 731 and 824 they appear to have been recharged during the remediation of the site between 1975 and 1980. Well 824 was drilled in 1998 to a total depth of 201 ft and the screen was set in unweathered Mancos Shale. This well is the only well sampled that was drilled below the weathered Mancos Shale. The mixing model of $^3$H and CFC-113 concentrations sampled from well 824 indicate piston flow through this portion of the aquifer. Due to the location of the screen in the Mancos Shale this could indicate that the mill water potentially percolated through fractures or the well casing and settled in the well. This well may also be recharged from the San Juan River and may not have any relationship with groundwater recharged from the mill site.
The far west well 841 from the mill site appears to be modern water potentially recharged from anthropogenic sources. A Neighborhood is located directly above the locations of the sampled well and is likely the source of the modern water.

Based on the apparent ages of groundwater samples collected around the site wells 728, 813, and 815 are composed primarily of 1960s age water that would correspond to the operation of the mill. Although well 815 is the only well with firm tracer evidence of 1960s water, wells 813 and 728 contain “bomb” spike $^3$H and 1960s CFC concentrations, respectively. The location of the wells strongly suggests that the majority of the groundwater recharged near the mill has migrated directly west of the mill site based on tracer and groundwater contour data.

**MDW**

Water from well 1048 exhibits inconsistent results when comparing CFCs and $^3$H concentrations. The $^3$H concentrations could have only been recharged prior to 1956 with a $^3$H concentration of 1.66 TU, this value can only be derived from an atmospheric $^3$H concentration prior to 1956. This indicates that MDW seep water if derived from the mill site was recharged within the first two years the mill was in production. However, the CFC data from MDW indicates that this water was recharged in the early 1980s.

If groundwater from the mill site is contaminating MDW then it is expected that the groundwater would seep out of the western side of MDW and not the eastern side. The elevation of the outcrops from which the groundwater seeps is the same on both sides of MDW. Thus, the groundwater would have to follow a nonconforming flow path through Mancos Shale and underneath the MDW to seep out of the east side of MDW.
Hydrogen-2 ($\delta^2$H) and Oxygen-18 ($\delta^{18}$O) Isotopes in Groundwater

The isotopic groundwater data of the mill site has a larger variation of values than those observed in MDW. Isotopic values around the mill site are depleted when compared to MDW and this could be due to the fact that the primary source of groundwater around the mill site is San Juan River water that was used during the milling operation (DOE, 2000). Following the evaporation line (figure 17) it would appear that the mill site wells are an enriched representation of the San Juan River and potentially the Morrison formation. However, it appears that there could be two or more sources of groundwater around the mill site. Well 731 is isotopically enriched and appears to potentially be from the same source as MDW. It is also important to note that since the site was recharged from unlined evaporation ponds the groundwater was isotopically enriched by evaporation. Following the precipitation of Flagstaff may indicate that MDW may be enriched from precipitation recharge.

Additional Evidence

Two other groundwater seeps in the area were sampled by DOE (DOE, 2011) for the same COCs that exist in MDW. These other seeps were also reported to emerge from Mancos Shale outcrops similar to MDW. These other seeps were Salt Creek Wash Seep (SCWS) and Upper Eagle Nest Arroyo Spring (UENAS) which are located less than 8 miles away from MDW and are located on the other side of the San Juan River (figure 13), thus making them hydraulically disconnected. Nitrate (NO$_3$), Uranium (U) and Specific Conductivity were compared in this study among the three seeps (table 2). Table 2 demonstrates that it is possibly for seeps in the area may have high naturally occurring NO$_3$ and U concentrations.
Holloway and Smith researched that nitrate could be naturally released from the Mancos Shale. Four samples of Mancos Shale from the Grand Valley in Grand Junction, Colorado were sampled and found that 58 to 74 percent of the nitrogen sampled was organic and the rest may have been in ammonium associated with clay minerals and nitrate salts (Holloway and Smith, 2005). This study consisted of a treated Mancos Shale sample containing 0.13 percent nitrogen with water for fourteen days and found that 2.22 mg of inorganic nitrogen was released per kilogram of shale.

Uranium concentrations in Mancos Shale seeps were determined by DOE (DOE, 2011) and were found to be relatively high. The groundwater seeps that are derived from shale beds had a much higher concentration of U when compared to seeps derived from sandstone beds. The samples in these seeps were unrelated to anthropogenic activity and still possessed elevated uranium levels. DOE states (DOE, 2011) U concentrations in groundwater that contacts Mancos Shale often exceeds 100 µg/L. The U is thought to have absorbed to organic matter from sea water and was reduced to a uranous state at the bottom of the Late Cretaceous Sea. As Mancos Shale began to uplift and weather, U was able to transfer to groundwater in its oxidized uranyl state (DOE, 2011).

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Table 2: COCs in MDW, UENAS and SCWS (data derived from DOE, 2011)
UENAS and SCWS are hydraulically disconnected to the mill site and had nitrate and U concentrations similar to MDW. It was concluded that these nitrate and U concentrations are derived from natural occurring sources and the mill site may not be the source of these COCs.
Figure 15: This illustrates the three different mixing regimes (Jergens, B.C. and others)
Figure 16: The Relationship between concentrations of environmental tracers in the alluvial groundwater aquifer at UMTRCA Site in Shiprock, NM. A. $^3$H and CFC-12; B. $^3$H and CFC-113; C. CFC-113 and CFC-12; D. CFC-11 and CFC-12. Model lines Piston Flow Model (PFM), Exponential Mixing (EMM), and Binary Mixing (BMM) of modern and old water.
Figure 17: Hydrogen-2 ($\delta^2$H) and Oxygen-18 ($\delta^{18}$O) Isotopes in the mill site, San Juan River, Morrison formation and MDW at Shiprock, NM
**Conclusion**
This study identified the presence of a substantial amount of groundwater that was recharged during the time corresponding to the milling process. The results depict that the highest values of $^3$H and lowest concentrations of CFCs are located west of the mill site in wells 728, 813 and 815. Other age-dating concentrations do occur on the mill site but none indicate 1960s water other than the three wells previously stated. MDW contains a $^3$H value that can be considered to be milling era water, but the CFCs concentrations depict an age of early 1980s water in MDW making MDW water age ambiguous.

**Recommendations**
The research presented focused on a limited number of samples across the mill site. It would be beneficial to increase the number of wells sampled. Identifying wells in ideal location that will produce a sufficient amount of water to sample for multiple age-dating tracers in one particular event.

Annual isotopic samples of local precipitation and the San Juan River would be useful to accurately identify the source of recharge within the mill site and MDW.

A more focused study of Mancos Shale in the Shiprock area would help to identify naturally occurring COCs compared to milling operation COCs.

Installation of more groundwater monitoring wells on the east side of MDW would be beneficial to further study the hydrologic process of MDW.
References


