Utah Division of Radiation Control

Summary of work completed, data results, interpretations and recommendations
For the July 2007 Sampling Event
At the Denison Mines, USA, White Mesa Uranium Mill
Near Blanding, Utah

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Submitted
May 2008

EXECUTIVE SUMMARY

Increasing and elevated trace metal concentrations in monitoring wells at a uranium processing facility near Blanding, UT, may indicate leakage from tailings cells is occurring. To investigate this potential problem, a groundwater study was done to characterize groundwater flow, chemical composition, noble gas composition, and age.

The White Mesa Uranium Mill, operated by Denison Mines Co., USA (DUSA), is located near the western edge of the Blanding Basin. The stratigraphy underlying surficial aeolian deposits is composed of alternating sandstones and shales of varying thicknesses. The principle formation in which groundwater is found is the Burro Canyon Formation of Early Cretaceous age (100 Ma). This formation is composed of sandstone interbedded with shale, and is generally considered to be of low to moderate permeability.

Temperature and salinity profiles taken in each of the wells indicate that stratification of the water column is present. This is supported by dissolved noble gas compositions determined by collecting passive diffusion samples at two depths in most wells. Dissolved noble gases had distinct compositions at two depths in all wells sampled at different depths. Low-flow sampling was employed to attempt to isolate flow paths within the water column, and samples were collected for tritium, sulfur and oxygen isotopes of sulfate, hydrogen and oxygen isotopes of water, nitrate and sulfate, and trace metal concentrations in groundwater. Based on temperature and salinity profiles and dissolved gas compositions, stratification of the water column is evident. However, stratification is not delineated in low-flow sampling results of trace metal concentrations or isotopic fingerprinting.

Measurable levels of tritium were found in several wells in the northeast portion of the site. Because these wells also indicated stable isotope fingerprints similar to those of surface water sites, it is likely that they are being influenced by hydrologic loading from the wildlife ponds in the northeast corner of the Mill. Isotopic similarities between wildlife ponds and tailings cells suggest some interaction among surface water sites. Tritium concentrations of less than 0.5 TU in a number of monitoring wells suggest water infiltrated the land surface more than 50 years ago, while small but measurable amounts of chlorofluorocarbons indicates recharge to the saturated zone is occurring. Trace metal concentrations observed in monitoring wells are similar to concentrations measured recently in routine groundwater sampling at the Mill.

The data show that groundwater at the Mill is largely older than 50 years, based on apparent recharge dates from chlorofluorocarbons and tritium concentrations. Wells exhibiting groundwater that has recharged within the last 50 years appears to be a result of recharge from wildlife ponds near the site. Stable isotope fingerprints do not suggest contamination of groundwater by tailings cell leakage, evidence that is corroborated by trace metal concentrations similar to historically-observed concentrations. While analysis of trace metal concentrations, age-dating methods, and stable isotope fingerprinting do not indicate significant leakage from the tailing cells, active vertical and horizontal groundwater flow is clearly evident. The fact that active groundwater flow occurs at the site confirms the need for on-going monitoring in order to evaluate the future performance of the tailing cells..

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I. INTRODUCTION

The White Mesa Uranium Mill, operated by Denison Mines Co., USA, is located 6 miles south of the town of Blanding in southeastern Utah. It sits on White Mesa near the western edge of the Blanding Basin within the Canyonlands section of the Colorado Plateau physiographic province. Elevations range from approximately 3,000 feet at the bottom of deep canyons in the southwest portion of the region to more than 11,000 feet in the Henry, Abajo, and La Sal Mountains. The average elevation at the Mill is 5,600 feet above mean sea level (Titan, 1994).

The stratigraphy of White Mesa is composed of the following units, in descending order: aeolian silts and fine-grained aeolian sands of variable thickness (several feet to 25 or more feet); the Dakota Sandstone and the Burro Canyon Formation (total thickness ranging from 100 to 140 feet); the Morrison Formation; the Summerville Formation; the Entrada Sandstone; and the Navajo Sandstone. The Morrison Formation is composed of the Brushy Basin Member (shale), the Westwater Canyon Member (sandstone), the Recapture Member (shale), and the Salt Wash Member (sandstone). The Summerville Formation is primarily sandstone with interbedded shale layers. Approximately 1,000 to 1,100 feet of material with low average vertical permeability separates the Entrada and Navajo Sandstones from the Brushy Basin Member (HGC, 2003).

Titan Environmental's 1994 report on the hydrogeology of the Mill, and supported by Hydro Geo Chem, Inc.'s, 2005 site hydrogeology study, identified the primary formations in which groundwater is found beneath the Mill site as the Dakota Sandstone and the Burro Canyon Formation (sandstone interbedded with shale). HGC (2003)

reports the geometrically averaged permeability of the Dakota Sandstone based on field tests as 3.89 x 10^{-5} cm/sec. Titan (1994) reported the geometrically average hydraulic conductivity of the Burro Canyon Formation as 1.1 x 10^{-5} cm/sec. The Brushy Basin Member of the Morrison Formation has generally been considered as impermeable (Intera, 2007), leading to the conclusion that groundwater within the Mill site is perched (Titan, 1994; HGC, 2003; HGC, 2005; Intera, 2007; and others). Water level data collected in June 2007 indicate that groundwater flow is generally from the northeast to the southwest of the site (Intera, 2007).

The White Mesa Uranium Mill became operational in 1980. To date, 4 million tons of conventionally-mined and alternate feed uranium ores have been processed, recovering more than 25 million pounds of U_3O_8 and 34 million pounds of Vanadium. The Mill was in standby status from November 1999 to April 2002 during which alternate feed materials were received and stockpiled. After processing these alternate feed materials, from April 2002 to May 2003, the Mill returned to standby status, where alternate feed materials were again received and stockpiled. The Mill resumed processing of alternate feed materials in March 2005. Processing of conventionally-mined ores is expected to resume in 2008.

In order to evaluate sources of solute concentrations at the Denison Mines Co., USA, White Mesa Uranium Mill, low-flow groundwater sampling was implemented in 15 monitoring wells. Furthermore, surface water samples were collected from three tailings cells and two wildlife ponds. Passive diffusion samplers were also deployed and collected in order to characterize the dissolved gas composition of groundwater at different depths within the wells. Samples were collected and analyzed for the

following: tritium, nitrate, sulfate, deuterium and oxygen-18 of water, sulfur-34 and oxygen-18 of sulfate, trace metals (uranium, manganese, and selenium), and chlorofluorocarbons.

Depth profiles of temperature and salinity measurements were taken in the wells to determine the extent of stratification of different formation waters. Differences in temperature and salinity throughout the water column can indicate flow-paths of differing travel times, as well as potential differences in recharge location. Furthermore, these profiles provided insight regarding the water quality conditions existing in the wells before purging and sampling was conducted.

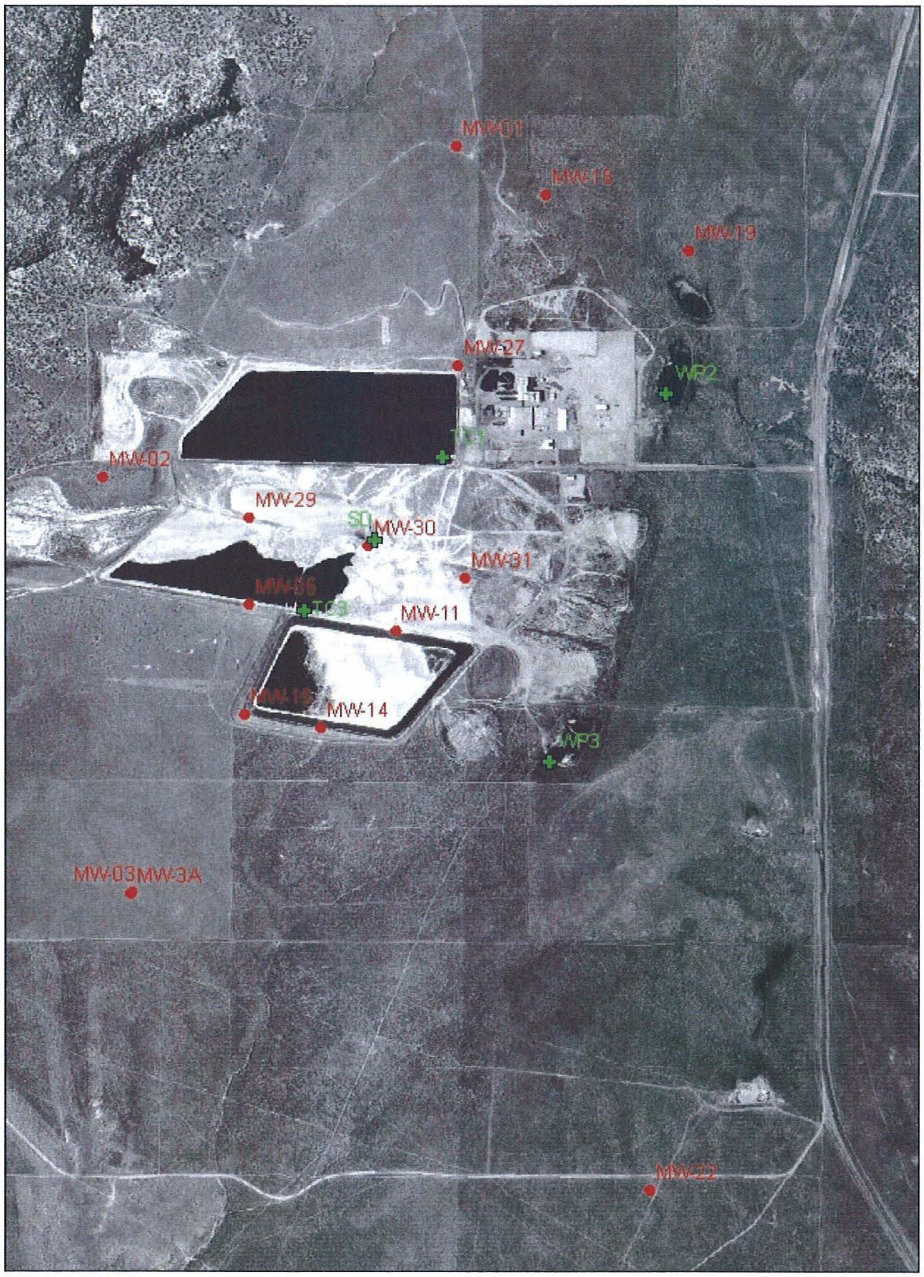
Our approach for evaluating solute sources is as follows. Indicators of groundwater age have been correlated to solute concentrations of the trace metals uranium, manganese, and selenium. Young groundwater found down-gradient of the Mill, that is associated with high levels of solute concentrations, would suggest a solute source at or near the mill. High solute concentrations in waters both up- and down-gradient of the Mill would indicate an aquifer source (i.e. background) for solute concentrations. Old groundwater found up- or down-gradient of the Mill, associated with high solute concentrations, would also indicate an aquifer source for solute concentrations.

Chlorfluorocarbons (CFCs) are anthropogenic gases that have been released to the atmosphere since the early 1940's. CFC's in the vadose zone are likely to be similar to the current atmospheric CFC concentrations, and dissolve in groundwater to provide an apparent age of when water recharged the saturated zone. Tritium, the radioactive isotope of hydrogen containing one proton and two neutrons, was released

to the global hydrosphere during above-ground nuclear weapons testing in the 1950's and 1960's. As part of the water molecule, tritium provides an estimate of the time at which water infiltrated ground surface. The presence of tritium in a water sample, or the presence of tritiogenic helium-3, indicates that water recharged the saturated zone within the last 50 years. These methods are used to determine apparent recharge dates for groundwater within the Mill site.

Analytical results for sulfur-34 and oxygen-18 isotopes of sulfate, and deuterium and oxygen-18 isotopes of water provide a possible fingerprint of water originating from the Mill tailings cells. Down-gradient waters with a similar isotopic fingerprint as the tailings cells, in addition to a significantly different isotopic fingerprint up-gradient of the tailings cells, may imply the tailings cells as contamination point-sources.

Aerial View of White Mesa Mill



Legend

- Surface Sites
- Monitoring Wells

0 0.25 0.5 1 Kilometers

N

Figure 1: Aerial View of White Mesa Mill displaying sample points

II. METHODS

A. Deployment and Collection of Diffusion Samplers

Passive diffusion samplers designed to collect dissolved gases were deployed at two different depths in Monitoring Wells (MW) 1, 2, 3A, 5, 11, 14, 15, 18, 19, 22, 27, 29, 30, and 31. One diffusion sampler was deployed in MW-3 in the center of the saturated portion of the screened interval. Upon arrival at each well, a water level measurement was made, and appropriate depths for sampler placement were determined. Samplers were deployed approximately 1m above the bottom of the screened interval and 1m below the top of the screened interval. In wells that did not have a fully saturated screened interval (MW-2, 3, 3A, 5, 14, 15, 27, 29, 30, 31), the top diffusion sampler was placed approximately 1m below the top of the water level.

A cluster of 6 stainless steel 3/8" nuts were attached to the bottom of the diffusion sampler line in order to counter any buoyant effect from the volume of air inside the samplers at depth. Samplers were attached to nylon line, which was used to avoid twisting of the line while being lowered into the well. Samplers were attached using nylon zip-ties at either end of the sampler. The samplers were attached in such a way to allow stretching in the sampler line, thereby preventing potential separation of the gas-permeable membrane from the copper tubing. Sampler line was secured to the outer well casing, which was then locked and wrapped in security tamper-evident tape.

Diffusion samplers were allowed to equilibrate inside the wells for at least 48 hours. This was to ensure that the dissolved gases in groundwater were at equilibrium with the gaseous volume inside the diffusion samplers. Samplers were removed from the wells prior to taking temperature-salinity profiles and prior to low-flow sampling.

Approximately two-minutes elapsed between commencing removal of the samplers from the well and the time by which all four sample volumes (two sample volumes for one sampler, and one sampler at two different depths for each well) were sealed. This was to minimize any re-equilibration between the sample volume and atmosphere from taking place, preserving the dissolved gas signature of the well water. This time-frame was monitored and all samplers were removed within the two-minute window. The diffusion samplers were sealed using a crimping tool that seals the copper tubes such that they are impermeable to gas leakage, creating a representative sample of the dissolved gases in the groundwater.

Each sample volume was labeled according to the order in which it was sealed, and electrical tape was wrapped around the exposed ends to protect the sealed ends. Samplers were then sealed in zip-lock plastic bags and stored for transport to the laboratory.

B. Temperature-Salinity Profiles

Profiles of temperature and salinity with depth were measured using a Hydrolab MiniSonde 4A and Surveyor 4A handheld unit. Dedicated bladder pumps installed previously by DUSA were left in the well to prevent disturbance of any temperature or salinity gradient that may have been present within the water column. Pump head-caps were secured to the side of the well casing to allow for insertion of the Hydrolab probe into the well.

Measurements of temperature (^{o}C) and specific conductance ($\mu S\ cm^{-1}$) were made at one-foot intervals throughout the saturated interval in the well. Total dissolved gases (mm Hg) and dissolved oxygen ($mg\ L^{-1}$) were made at the depths at which the

passive diffusion samplers were deployed. The probe was allowed to equilibrate until the total dissolved gas measurement did not fluctuate by more than 0.1% over a period of 5 minutes (generally 0.1% equaled approximately 1 mmHG). This equilibration process lasted from 15 minutes to more than one hour at some wells. Profiles were taken until the Hydrolab probe reached the bottom of the well, or until it could not be lowered below the DUSA dedicated bladder pumps.

Upon completion of temperature and salinity profile measurements, the dedicated bladder pump was removed from the well by DUSA employees and stored in plastic bags for the duration of sampling.

C. Low-Flow Sampling

A Grundfos Redi-Flo 2 submersible pump was used for low-flow groundwater sampling in the aforementioned wells. The pump was controlled using the Grundfos Variable Frequency Drive (VFD) control unit, powered by a generator. Generally, the pump was lowered to approximately 1.5 m below the top of the screened interval, or 1.5 m below the top of the water level in wells that did not have fully saturated screened intervals. In several wells (MW-14, MW-18, MW-19, and MW-22), the pump was then lowered to a second sampling depth approximately 1.5 m above the bottom of the screened interval. A pressure transducer was lowered to a depth determined at each well individually in order to monitor the head present above the pump, allowing for drawdown to be monitored while pumping. This was done to ensure low-flow conditions were maintained during the well sampling process.

The discharge tube from the pump was connected to a flow-through cell on the Hydrolab probe. This was used to monitor temperature (^{o}C), dissolved oxygen (mg L^{-1}),

total dissolved gases (mm Hg), and specific conductance (μS cm^{-1}). Discharge from the flow-through cell was monitored periodically using a 1000 mL beaker and a stopwatch.

After turning on the pump, the frequency on the VFD unit was increased slowly until water began flowing from the discharge tubing. Head was monitored constantly while increasing the frequency, and upon filling the flow-through cell on the Hydrolab probe, water quality parameters were then monitored. Parameters were considered stable when their change was less than 5% over a period of 5 minutes. Furthermore, a minimum purge volume of 2 pump tubing volumes (1 pump tubing volume is approximately 3 gallons for the length of tubing installed onto the pump) was removed before sampling occurred. With the exception of MW-18 the field parameters were stable prior to sampling. After 1 hour of purging the field parameters in MW-18 were not stable. Nevertheless, samples were collected in accord with the sampling plan that called for a maximum purge time of 1 hour.

When the field water quality parameters were considered stable, and when the minimum purge volume of two tubing volumes had been pumped, sampling began. Samples were generally taken in the following order: tritium (1 L sample), nitrate (125 mL sample), sulfate (125 mL sample), $\delta D/\delta^{18}O$ (15 mL sample), $\delta^{34}S/\delta^{18}O$ (1 L sample), trace metals (1x250 mL sample; 2x125 mL samples), CFC's (5x125 mL samples). Bottles containing samples for tritium, $\delta D/\delta^{18}O$, and $\delta^{34}S/\delta^{18}O$, were rinsed three times to eliminate contamination from atmospheric or other sources. Nitrate, sulfate, and trace metal sample bottles were not rinsed because bottles were pre-acidified by the analyzing laboratory.

Trace metals collected as 1x250 mL sample were unfiltered, while one 125 mL

sample was filtered and the second was left unfiltered. 125 mL trace metal samples were collected using a field collection hood made of a sterile garbage bag clipped to a PVC frame. Pump discharge tubing was run through the top of the garbage bag, and samples were collected within the bag to decrease the possibility for contamination of the samples by the atmosphere. Dust particles or other atmospheric input to the sample could contaminate the sample and create interference in analyzing for trace amounts of metals. Filtered samples were obtained using a Waterra FHT-45 micron inline disposable filter, attached directly to the end of the discharge tubing, and disposed of after each use.

Upon finishing trace metal sample collection, discharge tubing was disconnected from the pump reel connection and a length of 3/8" diameter copper tube was attached to the pump reel. This was used to collect CFC samples in order to eliminate as much plastic from the pump line as possible, and also to allow for the discharge tubing to be inserted directly into the sample bottles. CFC sampling procedures were followed as specified by the United States Geological Survey Reston CFC Laboratory (USGS, 2007). A 3 gallon glass desiccator was used as the sample collection vessel, and was filled with purge water after the minimum purge volume had been removed from the well. Bottles were submerged and the copper discharge tube was inserted into the bottles, which were then positively purged for approximately 10 bottle volumes (1250 mL). Bottles were filled underwater in order to eliminate any contact with the atmosphere, and caps were also submerged and placed securely on bottle mouths underwater. After checking for bubbles within the sample bottle, the cap was wrapped tightly with electrical tape to protect the cap from any dislodgement during transport.

After collecting all of the samples, the pump was disengaged. In the four wells that sampling was to occur at multiple depths, the water was allowed to discharge from the pump tubing into the well, and then the pump was lowered to the next depth. Purging was then only completed for 2 tubing volumes before sampling began again, which was completed in the same fashion as for the previous depth.

D. Sampling of Surface Water Sites

To sample the wildlife ponds, a 5-foot long, 4-inch diameter section of perforated PVC pipe (well-screen pipe) was lowered onto the sloping bank of each pond and completely submerged. The Grundfos pump was then lowered into the tubing, and connected to the control unit and Hydrolab flow-through cell. Pumping and sampling was then conducted as previously described. Purging was conducted for two pump tubing volumes before sampling commenced.

For sampling the tailings cells, a Global Water Instrumentation, Inc., super submersible pump (part number GP9216B) was used to collect water samples. Because these pumps are inexpensive, replaceable, and easily disposed of, it was used in place of the Grundfos submersible. For tailings cells 1 and 3, the pump tubing was draped over and secured to the railing of platforms on top of the pond. The pump was lowered to several feet below the water surface, and was then purged for approximately two tubing volumes. Purge water was collected and returned back to the tailings cells. For sampling the Tailings Cell 2 slimes drain, the pump was simply lowered down the vertical drain access pipe and lowered several feet below the observed water surface. Purge water was collected and disposed of in what was previously Tailings Cell 2. During sampling of the tailings cells, heavy rubber gloves were worn because of the

acidity of the solution.

E. Decontamination Procedures

Decontamination procedures of the pump and pump tubing were conducted in order to eliminate the possibility of well-to-well cross contamination. Upon removal of the pump from the well, it was lowered into a 5 foot long, 4 inch diameter vertical PVC column that was capped and sealed on the bottom end. De-ionized (DI) water was then poured into the column, and the pump was turned on. Approximately 5 gallons of DI water was then purged through the system to eliminate residual well water in the pump tubing. This water was collected and containerized in the same fashion as well purge water.

After purging the pump and pump tubing with DI water, the pump was disconnected from the pump tubing and connected to a tank of compressed Nitrogen gas. N_2 gas was allowed to flow through the pump tubing for approximately 60 seconds in order to flush residual DI water from the pump tubing. In order to more effectively purge DI water from the pump tubing, the pump reel was placed on its side while purging with N_2 gas. This purged DI water was also containerized in the same fashion as the well purge water.

F. Equipment Blank Samples

Equipment blank samples were collected at the conclusion of the sampling event. These samples were collected for the following constituents: nitrate (125 mL sample), sulfate (125 mL sample), and trace metals (1x125 mL sample, 1x250 mL sample). Blanks were collected after sampling the final well and immediately after purging the pump and pump tubing with 5 gallons DI water. Equipment blank samples were

collected using DI water directly from the pump discharge tubing.

III. FIELD RESULTS

A. Temperature and Salinity Profiles

Temperature and salinity profiles with depth are presented below for the 15 wells sampled. Salinity is presented as specific conductance in units of $\mu S\ cm^{-1}$, which is nominally about 1.5 times the level of total dissolved solids in $mg\ L^{-1}$. Vertical stratification of specific conductance and temperature are apparent in all of the wells, with a general increasing trend in specific conductance with depth in the saturated interval and a general decreasing trend in temperature with depth in the saturated interval. Dashed lines represent the top of the well screens, while dotted lines represent the bottom of the well screens. Figures marked with an asterisk (*) are profiles taken entirely within the screen and saturated interval; therefore neither the top or bottom of the well screen is indicated. These wells are MW-2 and MW-5 (Figures 3 and 6, respectively). Figures marked with a dagger (†) are sites at which the static water level was below the top of the well screen and do not include a dashed line. These wells are MW-3, MW-3A, MW-14, MW-15, MW-27, MW-29, MW-30, and MW-31 (Figures 4, 5, 8, 9, 13, 14, 15, and 16, respectively).

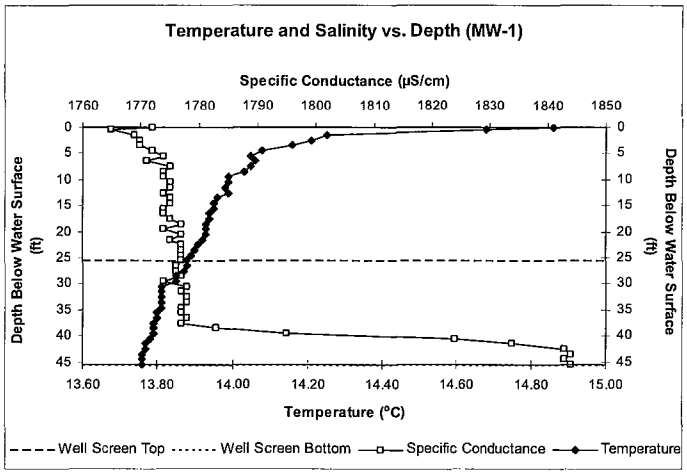


Figure 2: MW-1

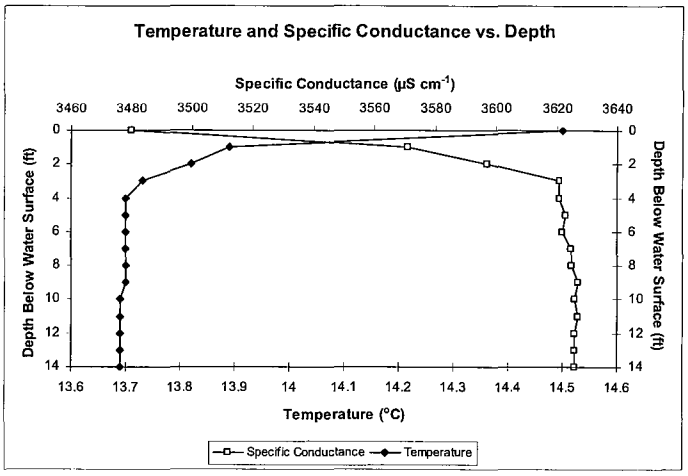


Figure 3: MW-2 *

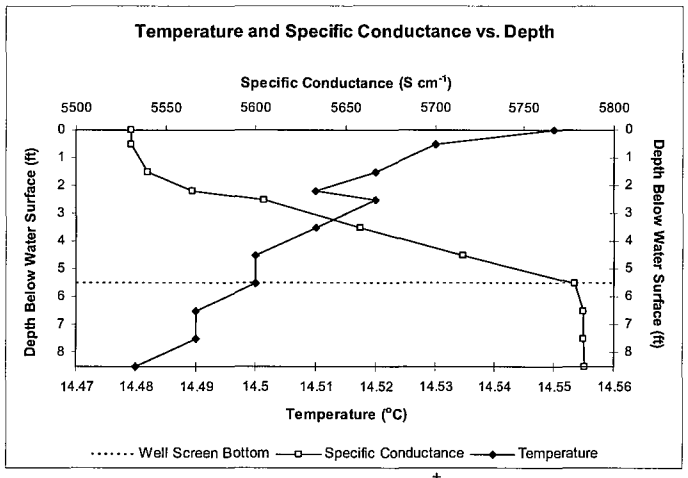


Figure 4: MW-3 †

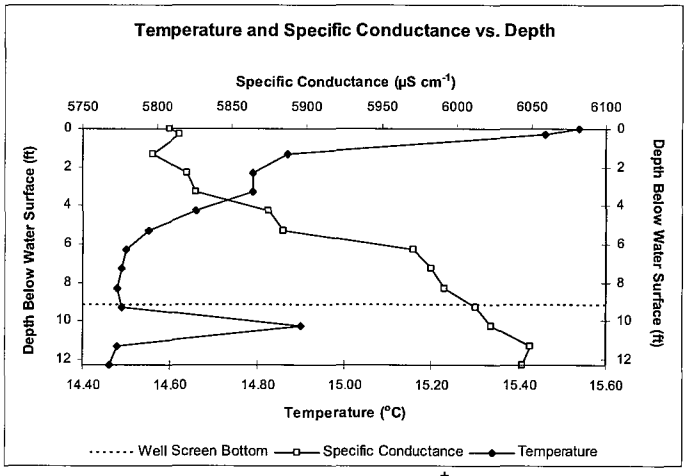


Figure 5: MW-3A †

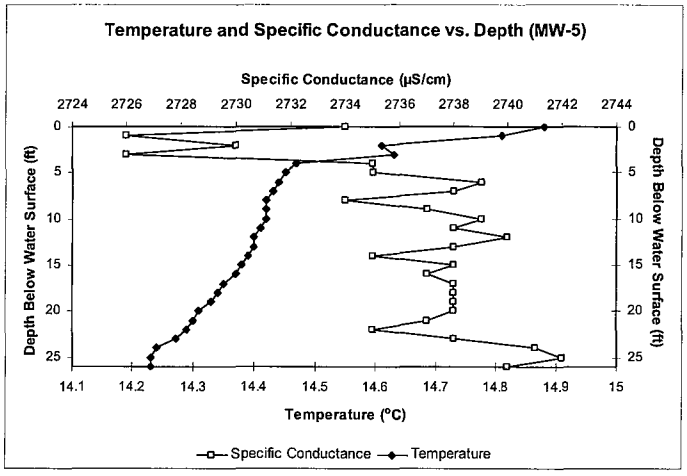


Figure 6: MW-5 *

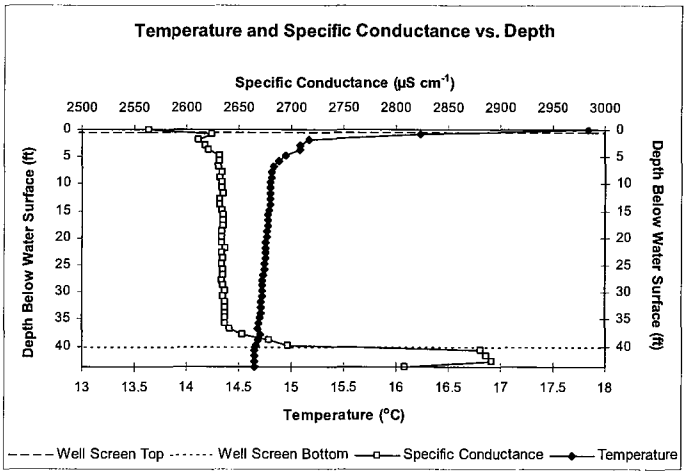


Figure 7: MW-11

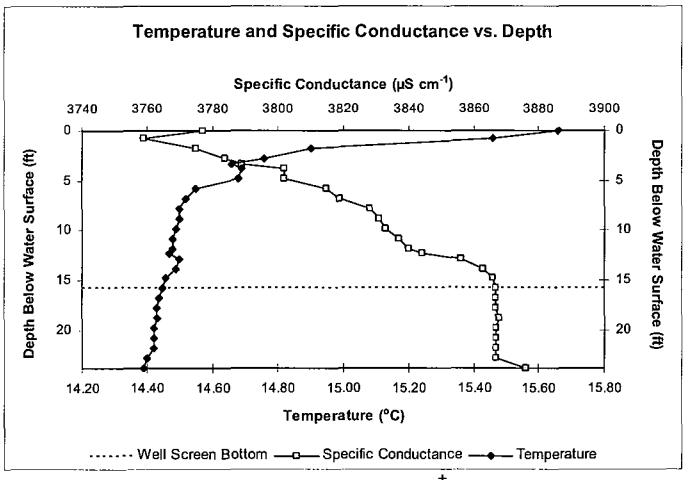


Figure 8: MW-14 †

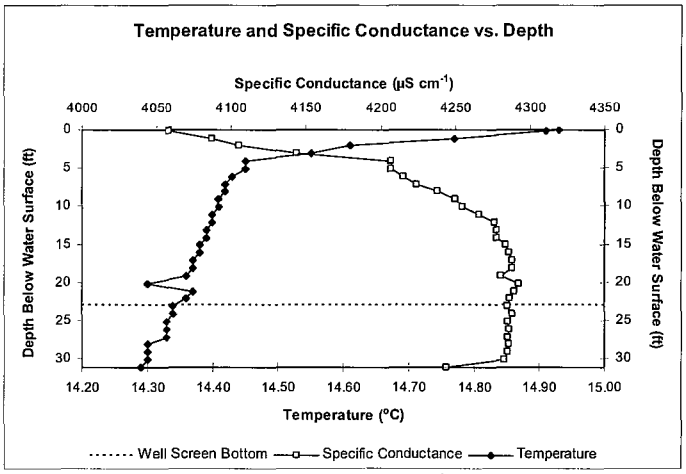


Figure 9: MW-15 †

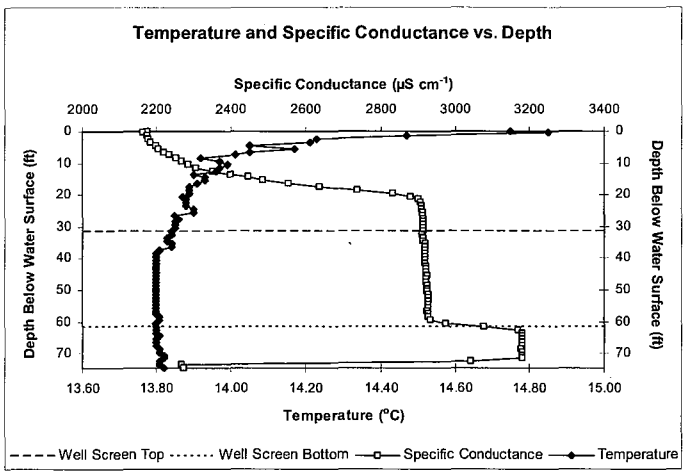


Figure 10: MW-18

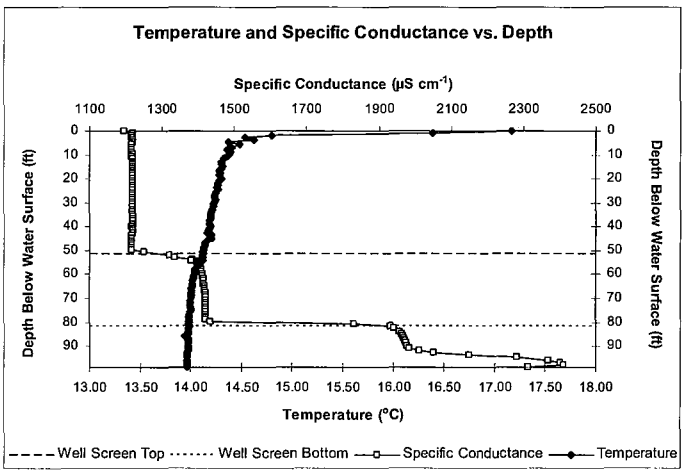


Figure 11: MW-19

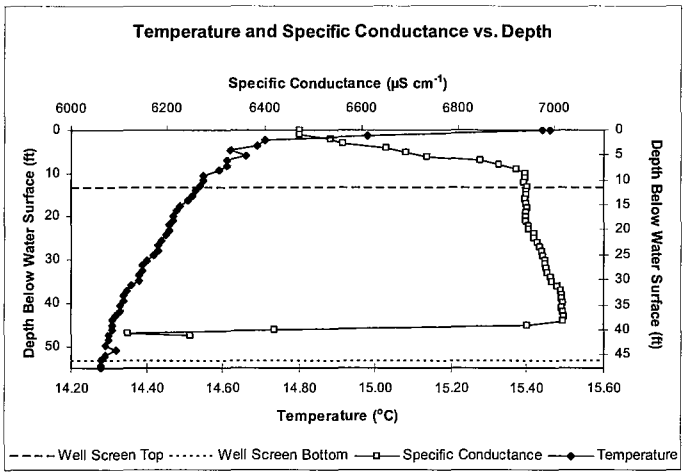


Figure 12: MW-22

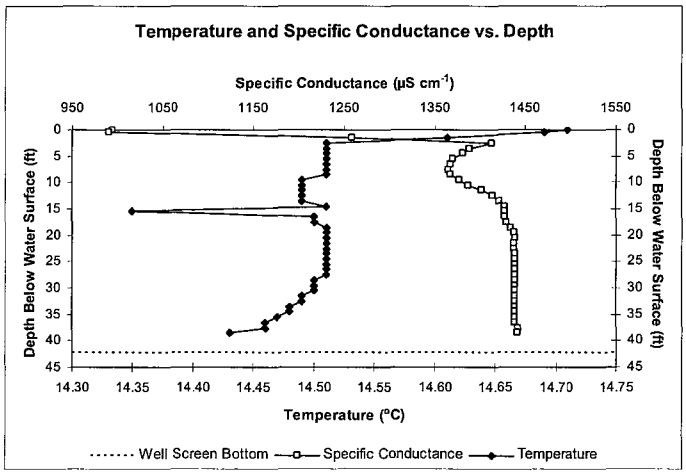


Figure 13: MW-27 †

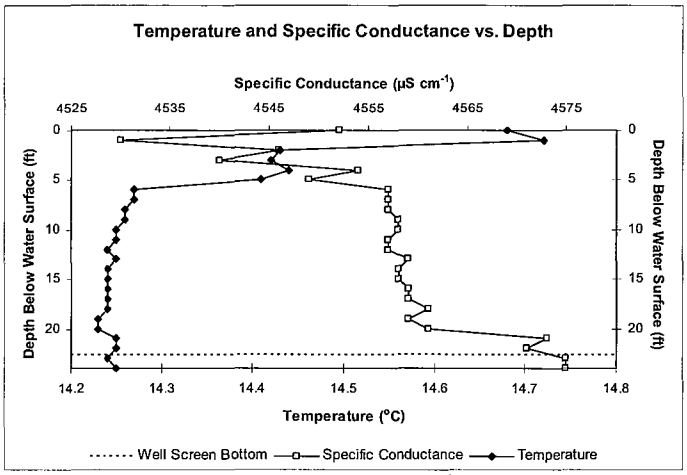


Figure 14: MW-29 †

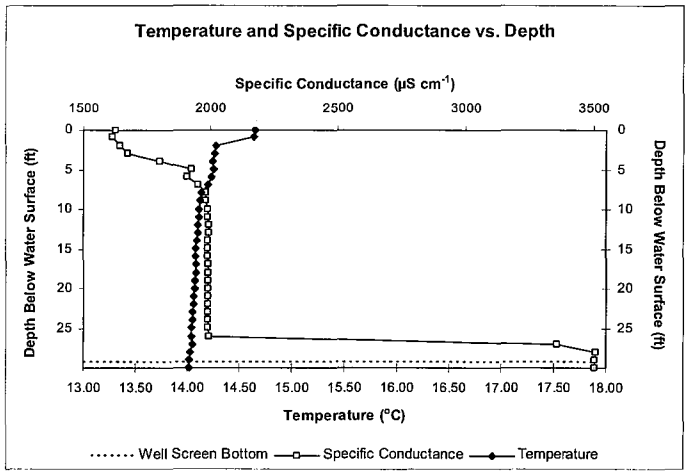


Figure 15: MW-30 †

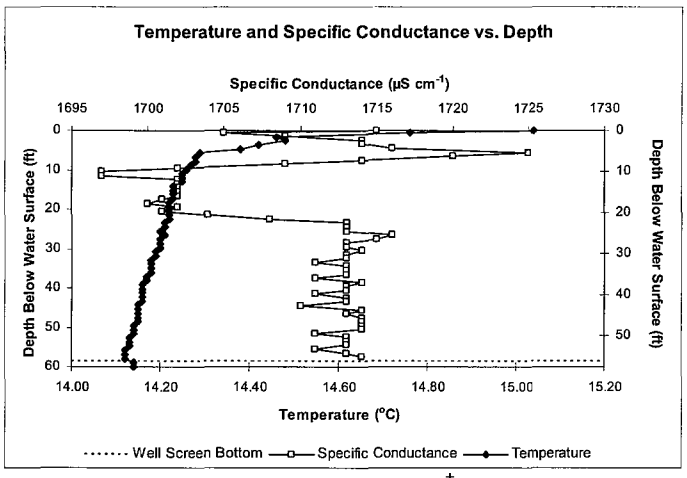


Figure 16: MW-31 †

Note: * Indicates the profile was taken entirely within the screened and saturated interval; neither well screen bottom or top are displayed in the figure.

† Indicates the static water level was below the top of the well screen, therefore well screen bottom is not displayed in the figure.

B. Low-Flow Sampling: Well-Pumping Field Notes and Observations

Low-flow sampling techniques were implemented for collecting groundwater samples from the Mill. Theoretically, this technique allows for sampling a specific depth in the water column, ostensibly isolating the groundwater flow path at that depth. From this specific sample depth, stratification within the water column, if present, with respect to groundwater ages and solute concentrations can be determined. Solute concentrations can then be correlated to groundwater ages, information that can ultimately be used in identifying potential sources of solute concentrations.

While very dependent on the hydrogeology of individual sites, flow rates used in low-flow sampling are often on the order of 0.1-0.5 L min^{-1} (100-500 ml min^{-1}), but can be as high as 1 L min^{-1} (1000 mL min^{-1}). This is the rate at which the pump is extracting water from the formation at the depth at which the pump is placed, assuming the formation is able to produce water at that rate. If the formation is unable to produce water at the rate demanded by the pump, drawdown occurs in the water column. Thus, the term "Low-flow" sampling is often referred to as "Minimal Drawdown" sampling. Minimal drawdown is considered less than 0.1 m (10 cm) during purging (Puls and Barcelona, 1995).

Pumping was conducted at the Mill so as to produce minimal drawdown within each well (i.e., <0.1 m) during purging. Water levels in the wells were monitored during pumping using a pressure transducer that converted the pressure head of the water column into a reading in feet of hydrostatic head above the instrument. The transducer was generally placed approximately 15-20 feet below the measured surface of the water, or immediately above the pump unit when the pump was within 15 to 20 feet of

the surface of the water.

In some instances where wells were extremely low-yielding, drawdown was occurring even when the pump was being operated at or near 0.1 L/min (100 mL/min). This was the case for wells MW-1, MW-3, and MW-3A. For this type of situation, the pump was lowered to the bottom of the well, at which time the wells were pumped to a water level near the bottom of the screened interval. MW-1 was pumped to only 1 meter below the top of the screened interval because purging had been taking place for almost 60 minutes. MW-1 was allowed to recover for approximately 12 hours (overnight). Well MW-3A was pumped to approximately 1 m above the bottom of the well screen. MW-3 was pumped to approximately 0.25 m above the bottom of the well screen. Wells MW-3 and MW-3A were allowed to recover for a period of 3 days due to both exhibiting extremely low-yielding properties during previous pumping events. Water levels were monitored periodically during this recovery period in MW-3 and MW-3A. MW-1 was sampled using the Grundfos pump, while MW-3 and MW-3A were sampled with DUSA's dedicated bladder pumps. A full suite of samples was taken from MW-1 during well pump-down, and also after recovery. Samples taken after recovery are hereafter denoted as MW-1B.

The passive sampler initially placed at the lower depth in MW-22 is suspected to have been resting on sediment at the bottom of the well. A second passive diffusion sampler was installed following removal of the first set, and is denoted as "MW-22(b) deep" in tables where noble gas data are presented.

IV. ANALYTICAL RESULTS

A. Chlorofluorocarbon Age Dating

Chlorofluorocarbons in the atmosphere can be used to provide an estimate of groundwater recharge date due to their changing concentration over time and their solubility in water. Samples were collected from all 15 wells, including 4 wells sampled at two depths, 2 wildlife ponds, tailings cells 1 and 3, and cell 2 slimes drain. Analyses were conducted on most sites, analyzing a minimum of three bottles per site, with analysis of the fourth and fifth sample bottles if necessary. This was needed when outliers were found during the analysis of the first three bottles at a site (MW-2, MW-18 Deep, and MW-27). Tailings cells 1 and 3, and the cell 2 slimes drain, have not been analyzed because of potential damage that extremely high levels of organics could inflict on the analytical equipment. Both sampling depths in MW-22, and MW-30 have not yet been analyzed because of strong signal interference with the CFC-12 signal, potentially attributable to dissolved CO_2 or N_2O gases. This interference could potentially damage the laboratory instruments; therefore, these samples were not analyzed. CFC concentrations are presented in Table 1.

Table 1: Mean CFC concentrations in White Mesa water samples

SAMPLE ID	Mean CFC-11 (pmoles/kg)	Mean CFC-12 (pmoles/kg)	Mean CFC-113 (pmoles/kg)
MW-1	2.594	1.896	0.092
MW-1B	2.750	1.683	0.093
MW-2	2.157	1.272	0.154
MW-3	1.285	0.826	0.130
MW-3A	2.759	1.885	0.223
MW-5	0.693	0.284	0.000
MW-11	0.179	0.090	0.000
MW-14 shallow	0.305	0.118	0.000
MW-14 deep	0.262	0.129	0.000
MW-15	0.686	0.678	0.014
MW-18 shallow	0.510	0.000	0.000
MW-18 deep	1.428	0.140	0.026
MW-19 shallow	1.503	0.974	0.028
MW-19 deep	1.622	1.110	0.087
MW-22 shallow	n/a	n/a	n/a
MW-22 deep	n/a	n/a	n/a
MW-27	0.809	3.709	0.016
MW-29	0.511	0.244	0.000
MW-30	n/a	n/a	n/a
MW-31	0.846	0.982	0.000
WP2	0.000	0.849	0.010
WP3	1.675	0.961	0.056
Tailings Cell 1	n/a	n/a	n/a
Tailings Cell 2	n/a	n/a	n/a
Tailings Cell 2 Slimes Drain	n/a	n/a	n/a

note: n/a indicates samples were not analyzed because of potential damage to analytical equipment from sample composition.

Results are reported in units of pico-moles per kilogram, or 10^{-12} moles of CFC per kilogram of water sample. Samples MW-1, MW-1B, MW -2, and MW -3A show a moderate amount of CFC-11, with MW -3, MW -18 deep, and both depths for MW -19 show slightly lower amounts of CFC-11. The remaining samples have very little dissolved CFC-11. CFC-12 concentrations range from below detection to 3.7 pmoles kg^{-1}. Only small amounts of CFC-113, if any, were detected in the samples. CFC concentration in the atmosphere since introduction of CFC's in the 1940's and 1950's have been monitored, and a historical record of CFC concentrations over the last 60 years allow groundwater ages to be estimated. These concentrations are plotted in

Figure 17. Measured CFC concentrations in a groundwater sample are compared with corresponding atmospheric concentrations, and a groundwater recharge date is obtained. These ages should be considered as apparent ages as a given sample may contain a range of ages, and there are numerous processes such as degradation that can affect CFC concentrations. The ranges are represented by the different calculated recharge date for each CFC and are presented in Table 2. Samples collected near the water table are always higher in concentration than deeper samplers. Because higher concentrations are associated with younger water, this indicates that some recharge is occurring at the site (i.e. placing younger water on top of older water.)

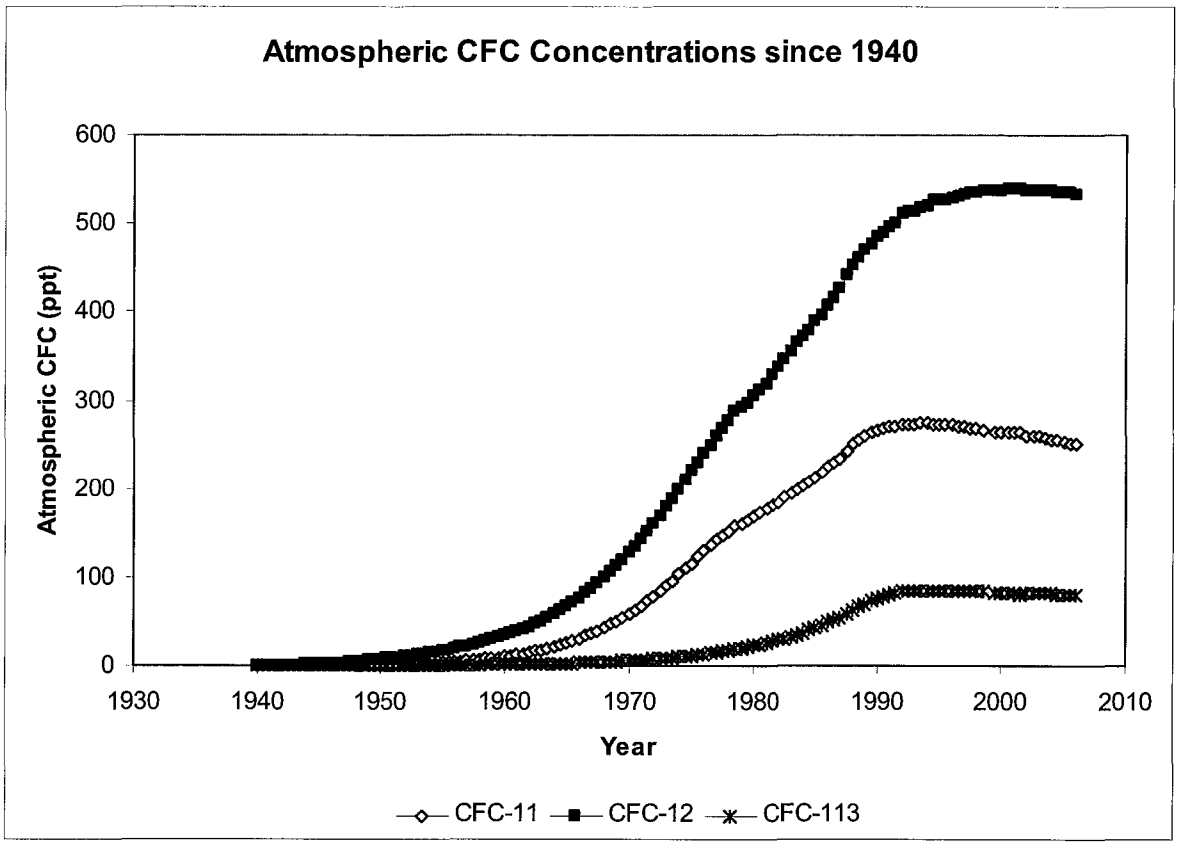


Figure 17: CFC's in the atmosphere since 1940

Table 2: Calculated CFC recharge date ranges

Site	CFC-11 Recharge Year	CFC-12 Recharge Year	CFC-113 Recharge Year
MW-1	1984	2001.5	1980
MW-1B	1985	1991	1980
MW-2	1979.5	1983	1984
MW-3	1971	1972.5	1980
MW-3A	1981.5	1989.5	1985.5
MW-5	1969.5	1966.5	1943
MW-11	1961.5	1958	1943
MW-14 Shallow	1962	1957	1943
MW-14 Deep	1961.5	1958	1943
MW-15	1967	1971	1963.5
MW-18 Shallow	1967.5	--	1943
MW-18 Deep	1974.5	1961.5	1971
MW-19 Shallow	1975	1978.5	1971.5
MW-19 Deep	1975.5	1981.5	1979.5
MW-22 Shallow	n/a	n/a	n/a
MW-22 Deep	n/a	n/a	n/a
MW-27	1967.5	2001.5	1963.5
MW-29	1967	1965	1943
MW-30	n/a	n/a	n/a
MW-31	1970.5	1978.5	1943
WP2	--	1973.5	1962
WP3	1973.5	1975	1974.5

note: n/a indicates samples were not analyzed because of potential damage to analytical equipment from sample composition

Table 2 cells in which no data values are reported (--) represent situations in which either no CFC's were detected, giving a recharge date of pre-modern (before 1950's), or CFC contamination occurred (i.e. values greater than equilibrium with the modern atmospheric concentration). No recharge date is presented for wildlife pond 2 (CFC-11 and 113) or MW-18 shallow (CFC-12 and 113) because analytical errors occurred for two of the three CFC compounds. Samples from wildlife pond 2 and MW-18 shallow can be considered to have age ranges of ±5 years from the presented recharge year.

Recharge elevations and temperatures are presented in Table 3. The recharge temperature for most samples was obtained from noble gas analyses presented in Section IV B. Samples for which noble-gas recharge temperatures were unavailable

were assumed to recharge at 15°C. All samples were assumed to have recharged at 1830 m elevation, or 6000 ft. This is based on the assumption that recharge occurs at an elevation that is intermediate between the elevation of the study site (1700 m) and the adjacent topographic highlands (i.e. the Abajo Mountains north of Blanding at about 3000 m.) The uncertainty in apparent age due to uncertainty in the recharge elevation is about 1 year/1000 m for water that recharged in 1975. The uncertainty in the CFC recharge year that results from uncertainty in recharge temperature is approximately 1 year/°C (Solomon and Cook, 2000).

Most sites exhibited CFC recharge date ranges of 1960's and 1970's, with several sites in the early and mid 1980's. Only MW-1 (B sample) and MW-3A had CFC's representative of the late 1980's or early 1990's. In both cases, wells were pumped dry (according to Section IV) because of low-yielding characteristics, and well MW-3A was subsequently sampled using DUSA dedicated bladder pumps. Potential CFC contamination could have occurred in these wells, as well as MW-3, because of exposure to atmosphere after pumping the boreholes dry. Furthermore, MW-3 and MW-3A could have been contaminated because of the plastic tubing in the DUSA dedicated bladder pumps. Plastics are often a source of contamination in CFC analysis, and while the Grundfos pump and tubing had been tested for CFC contamination prior to the sampling event, no such tests had been conducted on the DUSA bladder pumps.

Table 3: Approximate Recharge Elevation and Temperature of Sampled Sites

Site	Recharge Elevation (m)	Recharge Temperature (°C)
MW-1	1830	15.00
MW-1B	1830	15.00
MW-2	1830	13.96
MW-3	1830	7.95
MW-3A	1830	11.04
MW-5	1830	15.00
MW-11	1830	15.00
MW-14 Shallow	1830	6.93
MW-14 Deep	1830	7.60
MW-15	1830	7.79
MW-18 Shallow	1830	15.00
MW-18 Deep	1830	15.00
MW-19 Shallow	1830	15.00
MW-19 Deep	1830	15.00
MW-22 Shallow	n/a	n/a
MW-22 Deep	n/a	n/a
MW-27	1830	6.50
MW-29	1830	13.10
MW-30	n/a	n/a
MW-31	1830	15.00
WP2	1830	10.25
WP3	1830	10.25

B. Tritium/Helium-3 and Noble Gas Analysis

Water samples from all 15 wells, including 4 wells sampled at two depths, 2 wildlife ponds, and tailings cell 3 and cell 2 slimes drain, were analyzed for tritium (^3H), the only radioactive isotope of hydrogen, and a suite of dissolved noble gases. Tailings cell 1 was not analyzed for tritium due to complications that arose during the helium-3 in-growth period (the acid water corroded the metal holding flask). Using the ratio of tritium and ^3He, the daughter product of decayed tritium, in water, an approximate age of the water sample can be calculated. This age is representative of the time at which the water parcel was last in equilibrium with the atmosphere in the last 40 to 50 years, as the tritium incorporated into water molecules has been steadily changing since a wide-scale atmospheric injection of tritium during above-ground thermonuclear weapons

testing in the 1950s and 1960s. As such, tritium concentrations in water samples give a good idea of when groundwater recharged to the saturated zone. Tritium concentrations for each site are presented in Table 4.

Table 4: Tritium concentrations in White Mesa water samples

Site	Tritium		Tritium - repeat	
	(TU)	(error ±)	(TU)	(error ±)
MW-1	0.02	0.34	<0.3	
MW-1B	0.03	0.11	n/a	
MW-2	0.24	0.73	n/a	
MW-3	<0.3		n/a	
MW-3A	<0.3		n/a	
MW-5	<0.3		n/a	
MW-11	<0.3		0.16	0.05
MW-14 Shallow	0.36	1.05	0.04	0.05
MW-14 Deep	<0.3		n/a	
MW-15	<0.3		<0.3	
MW-18 Shallow	<0.3		<0.3	
MW-18 Deep	0.05	0.40	<0.3	
MW-19 Shallow	3.11	0.31	n/a	
MW-19 Deep	3.96	0.37	n/a	
MW-22 Shallow	<0.3		n/a	
MW-22 Deep	0.87	0.31	<0.3	
MW-27	8.67	0.92	n/a	
MW-29	<0.3		0.07	0.16
MW-30	<0.3		n/a	
MW-31	<0.3		n/a	
TC1	n/a†		n/a	
TC2 Slimes Drain	0.93	0.68	1.04	0.13
TC3	6.01	1.37	7.24	0.55
WP2	5.98	0.39	n/a	
WP3	5.94	0.40	n/a	

Note: n/a indicates no analysis conducted, † indicates corrosion of metal holding flask preventd analysis.

Error reported is 1σ. Concentration units are reported as tritium units (TU), which represents a single molecule of $^{3}H^{1}HO$ in 10^{18} molecules of $^{1}H_2O$, or 6.686×10^{7} tritium atoms kg^{-1} (Solomon and Cook, 2000). Analyses were repeated on samples that were not completely degassed during sample preparation. These analyses provided better resolution in the final concentration and are presented in the "Tritium – Repeat" column.

Most sites exhibited very low to no tritium levels, with a few exceptions. Wildlife ponds 2 and 3 had about 6 TU in both, in concert with the nature of a surface water site receiving modern water from the atmosphere. MW-19 had tritium levels of 3.1 and nearly 4.0 TU for the shallow and deep sampling points, respectively. MW-27 also

exhibited elevated tritium levels (8.67 TU). Small amounts of tritium were observed in the deep sampling point at MW-22 (0.87 TU).

MW-19 (shallow and deep) and MW-27 are close to the northern wildlife ponds and are likely to be influenced by recharge from the ponds. Recharge occurring due to the wildlife ponds would contain some amount of tritium due to pond water interacting with the atmosphere. This means groundwater flow near the wildlife ponds is being influenced by artificial recharge and the tritium seen in MW-19 and MW-27 is evidence of water derived from the wildlife ponds. Tritium in MW-22 deep indicates a small amount of recharge taking place near the well. The southern margin of artificial recharge is likely to be between MW-27 and MW-31 while the northern margin appears to be between MW-18 and MW-19.

That MW-27 has the highest tritium levels of all sites, including surface water sites, does not necessarily mean that it is the youngest water. Atmospheric tritium concentrations have varied over time, therefore tritium concentrations alone do not provide an absolute age-date for a given sample. Heilwell et. al (2006) plotted Tritium concentrations in the atmosphere for the western United States, shown in Figure 18. The fact that significant and measurable quantities of tritium are present in MW-27, MW-19, and the wildlife ponds, indicates recharge to the aquifer from the wildlife ponds is occurring. Tritium in MW-22 deep suggests that an extremely localized area of recharge is occurring near that well.

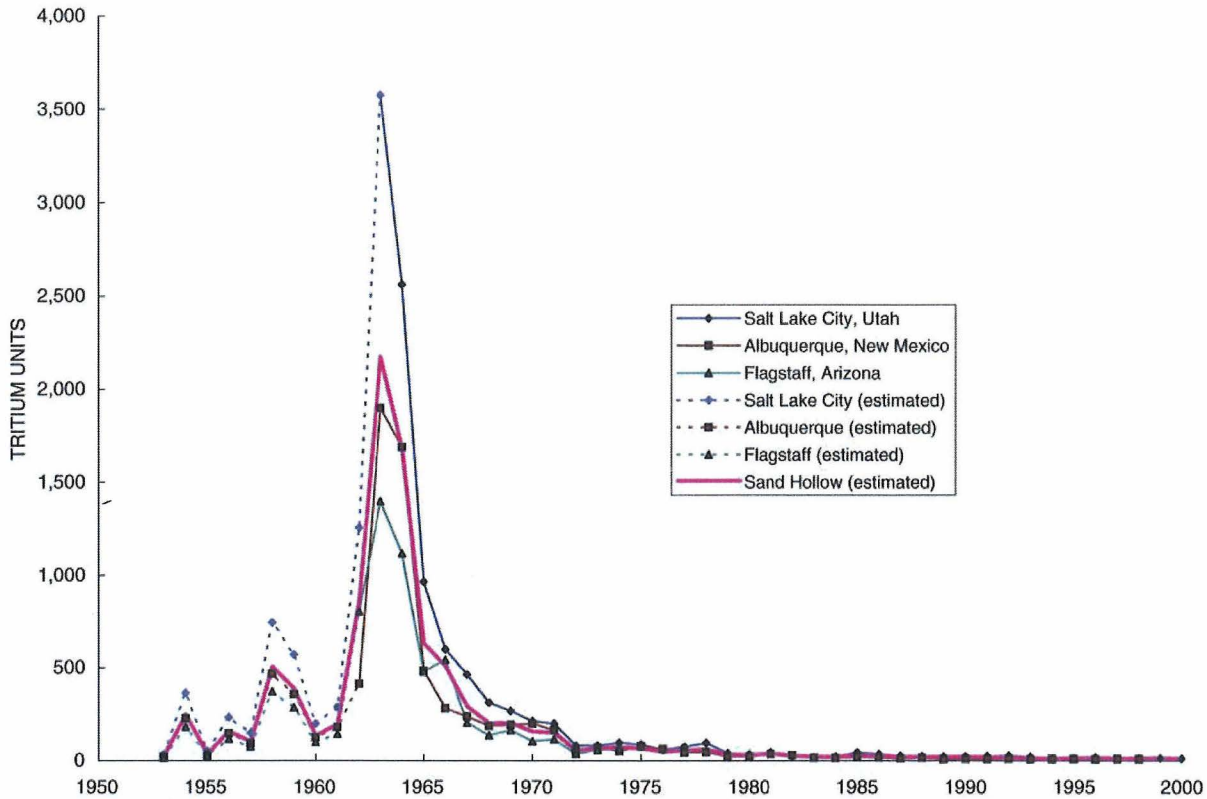


Figure 18: Atmospheric tritium concentrations in the southwest United States (Heilwell et. al, 2006)

Ten of the wells have small but measurable amounts of CFCs (excluding samples where contamination during sampling may have occurred), but contain essentially no tritium. This is likely the result of differences between where the CFC and tritium "clocks" start. Tritium is part of the water molecule and the travel time associated with this tracer starts at the land surface. In contrast, CFCs are gases that can dissolve into water and the clock associated with this tracer is set near the water table. In the unsaturated zone, CFCs from the atmosphere may be transported as a gas phase by way of either diffusion or advection. Since transport in the gas phase is typically much more rapid than transport in the aqueous phase, CFCs can be transported to the water table in much less time than tritium. In other words, the observation of small amounts of CFCs with no tritium is interpreted to mean that aqueous phase transport through the

unsaturated zone requires more than 50 years, whereas gas phase transport of CFCs requires much less time. Nevertheless, the mere presence of CFCs below the water table does suggest that recharge is occurring (if there were no downward water movement across the water table CFCs from the unsaturated zone would not be transported to depth.)

Passive diffusion samplers were used to measure dissolved gas composition of groundwater. These analyses provide insight to the temperature at which a parcel of groundwater recharged to the saturated zone, and also information about the origin of water using the ratios of helium-3 to helium-4, and helium-4 to neon-20, along with the theoretical solubility of noble gases in water. Of the two sample volumes sealed on-site (two sample volumes for each sampler at each depth), the first volume was initially analyzed to get the best possible result for dissolved gas concentrations. The first volume sealed had less time to equilibrate with the atmosphere after being removed from the well and will therefore be more representative of the *in situ* dissolved gases. Concentrations of dissolved gases are presented in Table 5.

An unusually high amount of helium-4 was present in the cell 2 slimes drain sample (sample TC2 SD). While some amount of helium-4 would be present due to uranium-thorium decay since construction of the cells, it is highly unlikely that the majority of helium-4 seen in the sample (9×10^{-6} ccSTP/g) is due to recent uranium-thorium decay because of the extremely long half-life of the major isotopes of uranium. Instead, it is likely that the milling process has accelerated the release of helium that accumulated within the sediment over geologic time.

Table 6 presents concentrations of measured total helium-4 and R/R_a, along with

calculated concentrations of terrigenic helium-4. R is the measured $^3He/^4He$ ratio in a sample and R_a is the $^3He/^4He$ ratio of a global air standard (1.384×10^{-6}.) Thus, R/R_a represents the ^3He content of the sample and is the customary manner used to report helium isotope measurements. To obtain the absolute concentration of ^3He, the R/R_a value can be multiplied by R_a (1.384×10^{-6}) and the measured concentration of ^4He. Total helium-4 ($^4He_{tot}$) is the total measured amount of helium-4 in the sample and is representative of the amount of helium-4 dissolved in water. Terrigenic helium-4 ($^4He_{terr}$) is calculated by subtracting the amount of helium-4 expected to be present in water due to interaction with the atmosphere at the time of recharge from the measured total helium-4 in water, assuming all other sources of helium-4 are negligible. The helium-4 derived from atmospheric solubility is determined by combining estimates of recharge temperature and elevation with laboratory measurements of the solubility. The amount of atmospheric helium in excess of solubility (known as excess air) was determined using neon measurements. Terrigenic helium-4 is helium-4 that is derived from Uranium-Thorium series decay in the aquifer material and subsequently escapes from the rock structure into the water via diffusion.

Table 5: *In situ* Dissolved Gas Concentrations

Site		N_2	^{40}Ar	^{84}Kr	^{20}Ne	^{4}He	^{129}Xe
		(ccSTP/g)	(ccSTP/g)	(ccSTP/g)	(ccSTP/g)	(ccSTP/g)	(ccSTP/g)
MW-1	Shallow	1.69E-02	5.05E-04	6.37E-08	2.25E-07	6.12E-08	3.89E-09
MW-1	Deep	1.96E-02	5.66E-04	7.17E-08	2.53E-07	7.08E-08	4.57E-09
MW-2	Shallow	9.56E-03	2.64E-04	3.40E-08	1.28E-07	3.26E-08	2.25E-09
MW-2	Deep	1.19E-02	3.19E-04	4.20E-08	1.52E-07	4.15E-08	2.78E-09
MW-3		1.25E-02	3.35E-04	4.24E-08	1.56E-07	3.98E-08	3.10E-09
MW-3A	Shallow	1.26E-02	3.48E-04	4.45E-08	1.66E-07	4.31E-08	2.71E-09
MW-3A	Deep	1.38E-02	3.31E-04	3.88E-08	1.88E-07	4.96E-08	2.65E-09
MW-5	Shallow	1.68E-02	4.12E-04	5.27E-08	1.72E-07	4.80E-08	3.67E-09
MW-5	Deep	1.75E-02	3.99E-04	5.14E-08	1.81E-07	5.20E-08	3.43E-09
MW-11	Shallow	1.79E-02	4.67E-04	5.96E-08	2.27E-07	8.69E-08	3.63E-09
MW-11	Deep	2.05E-02	4.86E-04	6.05E-08	2.66E-07	1.05E-07	3.84E-09
MW-14	Shallow	1.41E-02	3.90E-04	4.93E-08	1.78E-07	4.34E-08	3.12E-09
MW-14	Deep	1.66E-02	4.40E-04	5.38E-08	2.18E-07	5.48E-08	3.36E-09
MW-15	Shallow	1.52E-02	4.06E-04	4.88E-08	1.92E-07	4.87E-08	2.86E-09
MW-15	Deep	1.63E-02	3.79E-04	4.40E-08	2.21E-07	6.58E-08	2.74E-09
MW-18	Shallow	1.81E-02	4.85E-04	5.92E-08	2.34E-07	6.96E-08	3.64E-09
MW-18	Deep	1.81E-02	5.32E-04	6.67E-08	2.28E-07	7.18E-08	3.95E-09
MW-19	Shallow	2.63E-02	7.16E-04	8.60E-08	3.56E-07	9.62E-08	4.70E-09
MW-19	Deep	2.72E-02	7.08E-04	8.42E-08	3.63E-07	9.44E-08	4.80E-09
MW-22	Shallow	1.20E-02	3.24E-04	4.01E-08	1.71E-07	4.89E-08	2.47E-09
MW-22b	Deep	1.19E-02	3.24E-04	4.02E-08	1.66E-07	4.91E-08	2.52E-09
MW-22	Deep	1.22E-02	3.26E-04	4.14E-08	1.84E-07	5.68E-08	2.41E-09
MW-27	Shallow	1.04E-02	3.58E-04	5.32E-08	1.30E-07	3.33E-08	3.39E-09
MW-27	Deep	1.10E-02	3.69E-04	5.38E-08	1.37E-07	3.42E-08	3.36E-09
MW-29	Shallow	1.75E-02	3.49E-04	4.20E-08	2.52E-07	6.34E-08	2.76E-09
MW-29	Deep	2.01E-02	3.93E-04	4.52E-08	3.02E-07	8.37E-08	2.84E-09
MW-30	Shallow	1.24E-02	3.62E-04	4.69E-08	1.55E-07	3.96E-08	2.94E-09
MW-30	Deep	1.35E-02	3.85E-04	4.94E-08	1.64E-07	4.11E-08	3.35E-09
MW-31	Shallow	1.48E-02	4.19E-04	5.60E-08	1.95E-07	6.16E-08	3.52E-09
MW-31	Deep	1.62E-02	4.48E-04	5.84E-08	2.12E-07	6.53E-08	3.85E-09
TC1		1.66E-02	4.19E-04	9.49E-08	6.70E-08	2.73E-08	8.31E-09
TC2 SD		1.31E-02	7.32E-04	1.57E-07	7.85E-08	9.00E-06	2.80E-09
TC3		4.72E-03	2.84E-04	5.13E-08	5.86E-08	1.85E-08	6.35E-09
WP2		1.45E-02	7.39E-04	1.50E-07	1.49E-07	3.46E-08	3.53E-08
WP3		7.50E-03	3.76E-04	7.05E-08	7.74E-08	1.70E-08	3.18E-08

Table 6: Summary of Helium Concentrations

Site	$^{3}He_{tot}$	$^{4}He_{terr}$	$^{4}He_{tot}$	R/Ra
	(ccSTP/g)	(ccSTP/g)	(ccSTP/g)	
MW-1shallow	7.65E-14	4.85E-09	6.12E-08	0.903
MW-1deep	8.55E-14	<1.0E-10	7.08E-08	0.872
MW-2shallow	4.46E-14	2.87E-09	3.26E-08	0.987
MW-2deep	5.42E-14	2.87E-09	4.15E-08	0.944
MW-3	5.46E-14	2.25E-10	3.98E-08	0.992
MW-3Ashallow	5.95E-14	4.03E-10	4.31E-08	0.999
MW-3Adeep	6.77E-14	<1.0E-10	4.96E-08	0.986
MW-5shallow	5.34E-14	5.64E-09	4.80E-08	0.805
MW-5deep	5.44E-14	6.91E-09	5.20E-08	0.757
MW-11shallow	7.14E-14	2.99E-08	8.69E-08	0.594
MW-11deep	8.49E-14	3.76E-08	1.05E-07	0.584
MW-14shallow	5.87E-14	<1.0E-10	4.34E-08	0.979
MW-14deep	7.18E-14	<1.0E-10	5.48E-08	0.946
MW-15shallow	6.32E-14	<1.0E-10	4.87E-08	0.938
MW-15deep	7.60E-14	7.05E-09	6.58E-08	0.835
MW-18shallow	7.91E-14	1.07E-08	6.96E-08	0.821
MW-18deep	8.19E-14	1.64E-08	7.18E-08	0.824
MW-19shallow	1.31E-13	7.44E-09	9.62E-08	0.989
MW-19deep	1.24E-13	4.07E-09	9.44E-08	0.952
MW-22shallow	6.82E-14	4.01E-09	4.89E-08	1.007
MW-22(b)deep	6.81E-14	5.95E-09	5.68E-08	0.965
MW-22deep	7.58E-14	5.25E-09	4.91E-08	1.003
MW-27shallow	4.74E-14	1.32E-09	3.33E-08	1.029
MW-27deep	4.76E-14	1.32E-09	3.42E-08	1.006
MW-29shallow	8.58E-14	<1.0E-10	6.34E-08	0.978
MW-29deep	1.14E-13	<1.0E-10	8.37E-08	0.991
MW-30shallow	5.55E-14	5.26E-10	4.11E-08	1.013
MW-30deep	5.37E-14	3.37E-10	3.96E-08	0.944
MW-31shallow	6.58E-14	1.30E-08	6.16E-08	0.773
MW-31deep	7.59E-14	1.24E-08	6.53E-08	0.840
TC1	3.35E-14	1.26E-08	2.73E-08	0.887
TC2 Slimes Drain	1.96E-14	8.96E-06	9.00E-06	0.002
TC3	2.17E-14	6.42E-09	1.85E-08	0.853
WP2	4.72E-14	<1.0E-10	3.46E-08	0.987
WP3	2.26E-14	2.99E-09	1.7E-08	0.963

In general, higher concentrations of helium-4 indicate older water relative to waters with lower concentrations of helium-4. High terrigenic helium-4 values are expected in waters that have been in contact with aquifer material for longer periods of time as these waters will have had more time to accumulate helium-4 derived from sediment and rocks thru the in-growth of progeny from the Uranium and Thorium decay series. R/R_a values greater than one may be an indication of tritiogenic helium-3 in the

water. Because helium-3 is the daughter product of tritium decay, water that contained tritium at one point in time will exhibit relatively higher concentrations of helium-3 than water that did not contain tritium. R/R_a of less than one may be indicative of an accumulation of terrigenic helium-4 in the water being sampled.

Measurable amounts of tritium in MW-19 shallow and deep, MW-22 deep, and MW-27 suggest the presence of younger water mixing with older groundwater (see Table 4, above). Additionally, the proximity of MW-19 and MW-27 to the northern wildlife ponds supports the possibility of young water mixing with older groundwater in those wells. Tritium would be expected in water that is recharging from ponds that were constructed within the last 15 years, and this tritium is now observable in MW-19 and MW-27.

MW-30 shallow exhibited an R/R_a value greater than one, suggesting a small amount of tritiogenic ^3He near the top of the water column (see Tables 4 and 6). MW-19 deep had a tritium concentration of nearly 4 TU, but exhibited an R/R_{aA} value less than one (compare Tables 4 and 6). This is likely the result of a small amount of tritiogenic ^3He with a larger amount of terrigenic ^4He. Excluding MW-19 shallow, which also had an R/R_a less than one, other samples that contained tritium exhibited R/R_a values greater than one. This is expected from the decay of tritium to helium-3, increasing the ratio of helium-3 to helium-4 to a value greater than that of the atmosphere. Thus, some samples near the wildlife ponds have helium isotope values that are consistent with transport of young water being recharged at the ponds [e.g., MW-27 (shallow and deep) and MW-30 (shallow)]. With the exception of MW-22, the remainder of samples exhibited R/R_a values less than one, indicating helium-3 was

proportionally lower, or helium-4 was proportionally higher to that of the atmosphere.

Evaluating the contribution of various sources for helium-3 and helium-4 inputs can be accomplished by plotting the following:

$$\frac{{}^{3}He_{tot} - {}^{3}He_{EA}}{{}^{4}He_{tot} - {}^{4}He_{EA}} vs. \frac{{}^{4}He_{sol}}{{}^{4}He_{tot} - {}^{4}He_{EA}}$$

where $^{3}He_{tot}$ is the measured total helium-3 in the sample, $^{3}He_{EA}$ is the excess air component of helium-3 in the sample, $^{4}He_{tot}$ is the measured total helium-4 in the sample, $^{4}He_{sol}$ is the equilibrium solubility of helium-4 in the sample, and $^{4}He_{EA}$ is the excess air component of helium-4 in the sample (Solomon, 2000). Excess air results when the water table rises and traps small amounts of the soil atmosphere as bubbles that are now below the water table. Due to the increased fluid pressure that now exists on these bubbles, they partially or completely dissolve thereby imparting extra gas above thermodynamic equilibrium. The solubility component of helium is determined by using estimates of the temperature and elevation at which the water sample recharged combined with laboratory measurements of solubility. If there was no helium-4 input from excess air or from alpha-decay in the subsurface (i.e. decay from uranium-238, thorium-230, radium-226, radon-222, etc.), the left-hand side of the equation would simply be the helium-3/helium-4 ratio observed in the atmosphere, or 1.384×10^{-6}. The right-hand side of the equation, or the fraction of atmospheric helium-4, in this case would be 1.

Table 7: Excess air-corrected helium isotope ratios

Site	$^3He_{tot}$	$^3He_{EA}$	$^4He_{EA}$	$^4He_{sol}$	$^4He_{tot}$	$(^3He_{tot}-^3He_{EA})/(^4He_{tot}-^4He_{EA})$	$^4Hesol/(^4He_{tot}-^4He_{EA})$
	(ccSTP/g)	(ccSTP/g)	(ccSTP/g)	(ccSTP/g)	(ccSTP/g)		
MW-1shallow	8.55E-14	3.90E-14	2.82E-08	3.94E-08	7.08E-08	1.09E-06	9.24E-01
MW-1deep	7.65E-14	2.66E-14	1.92E-08	3.94E-08	6.12E-08	1.19E-06	9.38E-01
MW-2shallow	5.42E-14	1.93E-15	1.39E-09	3.73E-08	4.15E-08	1.30E-06	9.29E-01
MW-2deep	4.46E-14	0.00E+00	0.00E+00	3.60E-08	3.26E-08	**1.37E-06**	1.00E+00
MW-3	5.46E-14	2.87E-15	2.07E-09	3.76E-08	3.98E-08	**1.37E-06**	9.98E-01
MW-3Ashallow	6.77E-14	2.01E-14	1.45E-08	3.67E-08	4.96E-08	1.36E-06	1.00E+00
MW-3Adeep	5.96E-14	7.64E-15	5.52E-09	3.75E-08	4.31E-08	**1.38E-06**	9.97E-01
MW-5shallow	5.45E-14	9.63E-15	6.96E-09	3.87E-08	5.20E-08	9.95E-07	8.60E-01
MW-5deep	5.35E-14	4.66E-15	3.37E-09	3.91E-08	4.80E-08	1.09E-06	8.76E-01
MW-11shallow	8.50E-14	4.48E-14	3.24E-08	3.93E-08	1.05E-07	5.52E-07	5.41E-01
MW-11deep	7.14E-14	2.80E-14	2.03E-08	3.92E-08	8.69E-08	6.51E-07	5.89E-01
MW-14shallow	7.18E-14	2.96E-14	2.14E-08	3.77E-08	5.48E-08	1.26E-06	1.00E+00
MW-14deep	5.88E-14	1.16E-14	8.41E-09	3.78E-08	4.34E-08	1.35E-06	1.00E+00
MW-15shallow	7.61E-14	3.23E-14	2.33E-08	3.73E-08	6.58E-08	1.03E-06	8.78E-01
MW-15deep	6.32E-14	1.72E-14	1.24E-08	3.80E-08	4.87E-08	1.27E-06	1.00E+00
MW-18shallow	8.19E-14	2.80E-14	2.03E-08	3.94E-08	7.18E-08	1.05E-06	7.64E-01
MW-18deep	7.91E-14	3.08E-14	2.22E-08	3.93E-08	6.96E-08	1.02E-06	8.29E-01
MW-19shallow	1.24E-13	8.74E-14	6.32E-08	3.92E-08	9.44E-08	1.18E-06	1.00E+00
MW-19deep	1.32E-13	8.56E-14	6.19E-08	3.89E-08	9.62E-08	1.34E-06	1.00E+00
MW-22shallow	7.58E-14	1.79E-14	1.29E-08	3.68E-08	5.68E-08	1.32E-06	8.39E-01
MW-22deep	6.82E-14	9.33E-15	6.74E-09	3.69E-08	4.91E-08	**1.39E-06**	8.72E-01
MW-22deep(b)	6.82E-14	1.40E-14	1.01E-08	3.64E-08	4.89E-08	**1.40E-06**	9.36E-01
MW-27shallow	4.76E-14	0.00E+00	0.00E+00	3.80E-08	3.42E-08	**1.39E-06**	1.00E+00
MW-27deep	4.74E-14	0.00E+00	0.00E+00	3.77E-08	3.33E-08	**1.42E-06**	1.00E+00
MW-29shallow	1.15E-13	6.97E-14	5.04E-08	3.68E-08	8.37E-08	1.35E-06	1.00E+00
MW-29deep	8.58E-14	4.76E-14	3.44E-08	3.67E-08	6.34E-08	1.32E-06	1.00E+00
MW-30shallow	5.38E-14	3.26E-15	2.36E-09	3.85E-08	4.11E-08	1.30E-06	9.91E-01
MW-30deep	5.55E-14	1.09E-15	7.88E-10	3.79E-08	3.96E-08	**1.40E-06**	9.77E-01
MW-31shallow	7.59E-14	2.13E-14	1.54E-08	3.93E-08	6.53E-08	1.09E-06	7.88E-01
MW-31deep	6.58E-14	1.55E-14	1.12E-08	3.89E-08	6.16E-08	1.00E-06	7.72E-01
Tailings Cell 1	3.35E-14	0.00E+00	0.00E+00	4.11E-08	2.73E-08	1.23E-06	1.00E+00
Tailings Cell 2 Slimes Drain	1.97E-14	0.00E+00	0.00E+00	4.11E-08	9.00E-06	2.19E-09	4.57E-03
Tailings Cell 3	2.18E-14	0.00E+00	0.00E+00	4.11E-08	1.85E-08	1.18E-06	1.00E+00
Wildlife Pond 2	4.73E-14	0.00E+00	0.00E+00	4.33E-08	3.46E-08	**1.37E-06**	1.00E+00
Wildlife Pond 3	2.26E-14	0.00E+00	0.00E+00	4.33E-08	1.70E-08	1.33E-06	1.00E+00
				Atmospheric Helium		1.37E-06	1

Note: Bold-faced type indicates samples with excess air-corrected helium-3/helium-4 ratios greater than that of atmospheric. Excess air corrections are not needed for the surface water sites (see previous discussion regarding the formation of excess air.)

The amount of helium-3 in the sample due to excess air input ($^3He_{EA}$) was calculated using the ratio in the sample of helium-3 to neon-20 multiplied by the difference of the measured neon-20 in the sample and the theoretical solubility of neon-

20. The calculation was conducted as follows:

$$R_{{}^{3}He/{}^{20}Ne} * \left({}^{20}Ne_{meas} - {}^{20}Ne_{sol}\right) = {}^{3}He_{EA}$$

where R(^{3}He/^{20}Ne) is determined as the ratio of helium-3 to neon-20 in the atmosphere, $^{20}Ne_{meas}$ is the measured amount of ^{20}Ne in the sample, and $^{20}Ne_{sol}$ is the expected solubility of neon in the water. Neon is useful in this calculation because the ratio of neon-20 to helium-3 in the atmosphere is constant. Furthermore, the expected solubility of neon is only a weak function of the temperature and salinity of the water.

Helium-4 dissolved in the sample due to excess air input was calculated in much the same way as helium-3 due to excess air, but with the ratio of helium-4 to neon-20 in the atmosphere only. It was conducted as follows:

$$R_{{}^{4}He/{}^{20}Ne} * \left({}^{20}Ne_{meas} - {}^{20}Ne_{sol}\right) = {}^{4}He_{EA}$$

where R(^{4}He/^{20}Ne) is the ratio of helium-4 to neon-20 in the atmosphere, $^{20}Ne_{meas}$ is the measured amount of ^{20}Ne in the sample, and $^{20}Ne_{sol}$ is the expected solubility of neon in the water.

The expected solubility of helium-4 in the sample, $^{4}He_{sol}$, is calculated based on the salinity and temperature of the well water at the time of the sample. Lastly, the total amount of helium-4 in the sample, $^{4}He_{tot}$, is the total amount of helium-4 in the sample measured in the laboratory.

The helium-3/helium-4 ratio of He produced in Earth's crust is lower than the ratio in the atmosphere (Solomon, 2000.) Therefore, as a parcel of water moves through the aquifer and acquires helium generated within the aquifer, both the helium-3/helium-4 ratio and the fraction of helium-4 derived from atmospheric equilibration will decline. Figure 19 plots the above helium isotope relationships for monitoring wells at the Mill.

Samples from MW-11 plot at one end of the graph as they contain the largest amounts of terrigenic helium and thus contain the largest components of old water. Figure 20 plots the above helium isotope relationships for surface water sites (tailings cells and wildlife ponds) at the Mill.

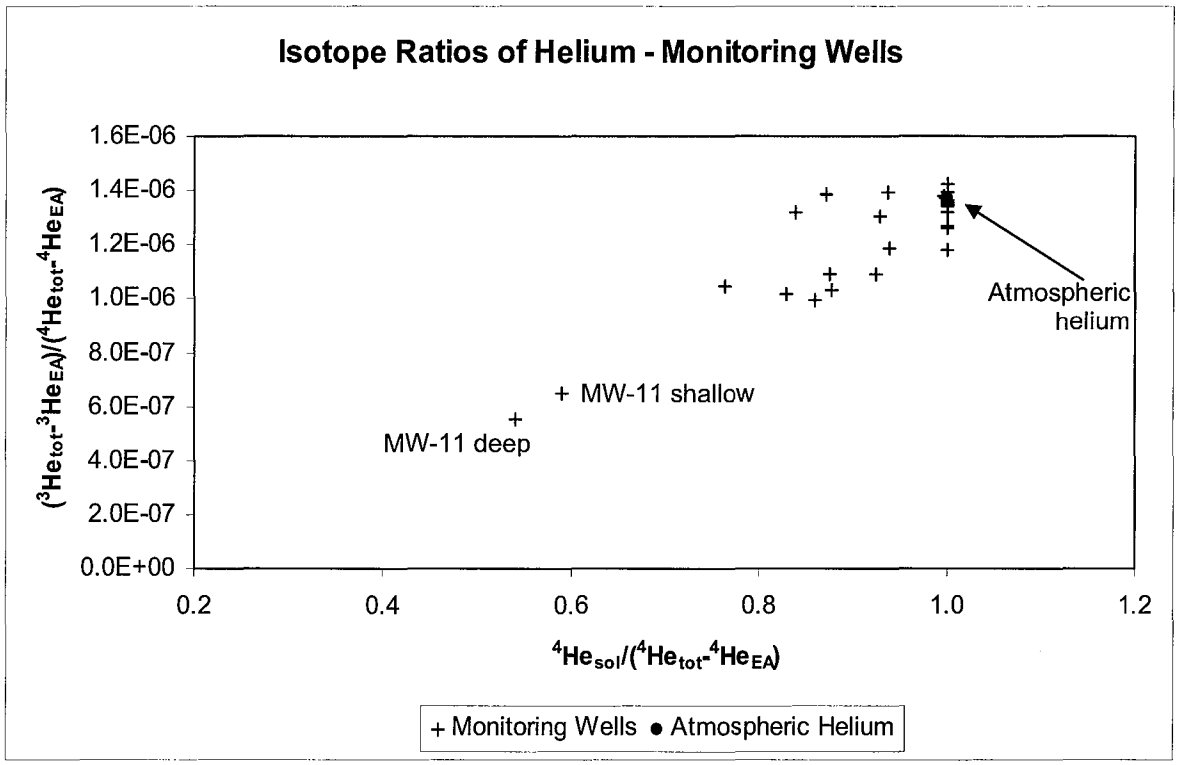


Figure 19: Helium isotope ratios, corrected for input due to excess air; monitoring wells only

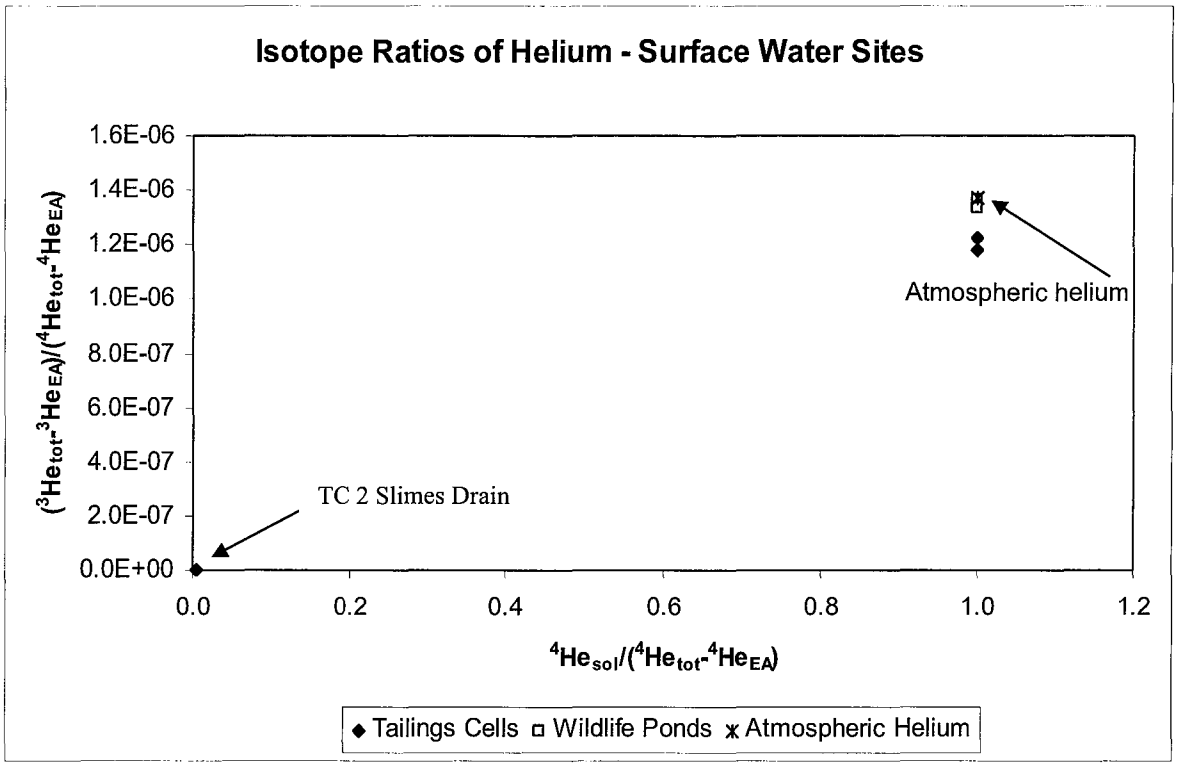


Figure 20: Helium isotope ratios, corrected for input due to excess air; surface water sites only

C. Anions

Nitrate and Nitrite levels as nitrogen, and sulfate levels in water samples were analyzed by the Utah State Department of Health, Division of Laboratory Services. The Utah groundwater quality standard (GWQS) of 10 mg L^{-1} was exceeded by wells MW-30 and MW-31 (UAC R317-6-2).

Sulfate concentrations can be compared with the National Secondary Drinking Water Regulation, as set by the United States Environmental Protection Agency (USEPA, 2003), at 250 mg L^{-1} sulfate in a community water system. This concentration was exceeded by all monitoring wells except MW-27. This value was also greatly exceeded by the tailings cells and Cell 2 slimes drain. No GWQS or site-specific groundwater protection limit (GWPL) is currently in effect for sulfate concentrations.

Table 8 presents the concentrations of inorganic constituents in monitoring wells and surface water sites.

Table 8: Concentrations of Anions

Site	NO2+NO3, N	Sulfate
	(mg/L)	(mg/L)
MW-01	0.35	644
MW-01B	0.25	708
MW-02	<0.1	1,780
MW-03	0.19	2,960
MW-03A	1.07	3,070
MW-05	<0.1	980
MW-11	<0.1	947
MW-14 Shallow	<0.1	2,120
MW-14 Deep	<0.1	2,050
MW-15	0.13	2,200
MW-18 Shallow	0.36	1,690
MW-18 Deep	<0.1	1,810
MW-19 Shallow	2.62	556
MW-19 Deep	2.69	581
MW-22 Shallow	3.36	5,060
MW-22 Deep	3.24	5,100
MW-27	5.46	52.1
MW-29	0.79	2,830
MW-30	**15.5**	859
MW-31	**24.6**	598
TC1	113	2,500,000
TC2 Slimes Drain	5.19	666,000
TC3	19.6	107,000
WP2	<0.1	39.9
WP3	<0.1	33.1
Equipment Blank	<0.1	<20.0

Note: Bold-faced type indicates samples that exceeded the state GWQS

D. Trace Metals

Concentrations of manganese, selenium, and uranium in groundwater samples and surface water samples were analyzed by the Utah State Department of Health, Division of Laboratory Services. Uranium concentrations exceeded the Utah State GWQS of 30 µg L^{-1} in 8 of the monitoring wells, and in all three tailings cells (UAC R317-6-2). MW-3, both depths sampled at MW-14, MW-15, both depths sampled at MW-18, and both depths sampled at MW-22 had uranium concentrations greater than

30 μg L^{-1}.

Concentrations of manganese exceeded the ad-hoc groundwater quality standard of 800 μg L^{-1} as put forth in the Groundwater Discharge Permit for International Uranium (USA) Corporation, now Denison Mines, Co., in 7 monitoring well samples (Utah Water Quality Board). Wells MW-3, MW-3A, both depths sampled at MW-14, both depths sampled at MW-18, both depths sampled at MW-22, and MW-29 had concentrations greater than 800 μg L^{-1}. The equipment blank likely exhibits a presence of manganese because it was taken after decontamination of the pump following sampling MW-22, the well with highest manganese concentrations. Residual manganese in the pump tubing following MW-22 sampling thus may have been present in the equipment blank sample.

Only MW-3A, MW-15, and MW-31 had concentrations of selenium that exceeded the State GWQS of 50 μg L^{-1} set forth by the Utah Division of Water Quality (UAC R317-6-2). Tailings cell 3 was reported to have a selenium concentration of 1550 μg L^{-1}, while the sample from cell 2 Slimes Drain was reported only as having a concentration of selenium less than 400 μg L^{-1}. Trace metal concentrations are presented in Table 9.

Table 9: Trace Metal Concentrations

Site	**Selenium** (µg/L)	**Manganese** (µg/L)	^{238}**U** (µg/L)
MW-01	<2.0	78.8	<1.0
MW-01B	<2.0	115	<1.0
MW-02	8.7	<10.0	10.5
MW-03	10.2	**2,460**	**35.9**
MW-03A	**74.2**	**1,360**	19.9
MW-05	2.42	190	<1.0
MW-11	<2.0	64.7	<1.0
MW-14 Shallow	<2.0	**2,080**	**59.4**
MW-14 Deep	<2.0	**2,020**	**59.4**
MW-15	**96.4**	<10.0	**42.9**
MW-18 Shallow	2.5	84	**41.2**
MW-18 Deep	2.3	202	**33.3**
MW-19 Shallow	10.4	<10	6.94
MW-19 Deep	10.4	<10.0	7.68
MW-22 Shallow	15.2	**32,900**	**38.8**
MW-22 Deep	15.3	**35,500**	**39.7**
MW-27	10.1	<10.0	29.5
MW-29	3.35	**5,100**	10.2
MW-30	32.6	<10.0	6.31
MW-31	**58.7**	<10.0	7.01
TC1	**16,200**	**869,000**	**581,000**
TC2 Slimes Drain	<400.0	**139,000**	**23,700**
TC3	**1,550**	**248,000**	**68,100**
WP2	<2.0	17	9.92
WP3	<2.0	16.2	<1.0
Equipment Blank	<2.0	31.5	<1.0

Note: bold-faced type indicates samples that exceeded the state Groundwater Quality Standard (GWQS) or, in the case of manganese, the ad-hoc GWQS

E. D and ^{18}O Isotope Ratios in Water

Deuterium and oxygen-18 can be used as environmental tracers of groundwater because they are part of the water molecule and have a conservative nature. Enrichment of deuterium and oxygen-18 (i.e. isotopically heavier) may indicate significant evaporation is occurring at the recharge point, while depletion of deuterium and oxygen-18 (i.e. isotopically lighter) may indicate groundwater recharge is occurring at higher elevations and lower temperatures. Enriched values are less negative and represent a relatively heavier isotopic composition, while depleted values are more negative and represent a relatively lighter isotopic composition. Groundwater and

surface water samples were analyzed for deuterium and oxygen-18 isotope ratios, the results of which are presented in Table 10 below.

Table 10: δD and $\delta^{18}O$ Isotope ratios in water

Site	Depth	δD (‰)	δD σ (±‰)	$\delta^{18}O$ (‰)	$\delta^{18}O$ σ (±‰)
MW-01		-113	1.6	-14.8	0.13
MW-01B		-113	0.3	-14.3	0.02
MW-02		-113	0.5	-14.2	0.01
MW-03		-106	1.0	-13.2	0.16
MW-03A		-107	1.4	-13.3	0.19
MW-05		-112	2.3	-14.1	0.03
MW-11		-115	0.3	-15.6	0.04
MW-14	shallow	-110	0.0	-13.8	0.05
MW-14	deep	-112	0.5	-13.9	0.03
MW-15		-111	0.5	-14.0	0.09
MW-22	shallow	-110	1.7	-13.5	0.23
MW-22	deep	-107	0.2	-13.2	0.05
MW-27		-83	0.5	-9.8	0.07
MW-29		-107	2.0	-13.3	0.00
MW-30		-95	0.3	-11.7	0.09
MW-31		-95	1.1	-11.9	0.22
MW-18	shallow	-103	1.7	-13.7	0.05
MW-18	deep	-107	2.1	-13.9	0.18
MW-19	shallow	-81	1.5	-9.6	0.05
MW-19	deep	-81	2.0	-9.5	0.04
WP2		-45	1.9	-1.3	0.15
WP3		-60	0.3	-5.3	0.14
TC1		--	--	--	--
TC2 Slimes Drain		--	--	--	--
TC3		-12	7.9	4.9	0.92

Note: isotope ratios are calculated as $\partial^{18}O_{sample} = \left(\frac{\left(^{18}O/^{16}O\right)_{sample}}{\left(^{18}O/^{16}O\right)_{reference}} - 1 \right) * 1000‰$ VSMOW, where VSMOW is the name of the reference.

Isotope ratios for deuterium relative to the standard VSMOW for monitoring wells ranged from -115‰ to -81‰. The highest values of -81‰ and -83‰ were found in wells MW-19 at both depths and MW-27, respectively. Wildlife ponds 2 and 3 showed deuterium isotope ratios of -45‰ and -60‰, respectively. Tailings cell 3 had a deuterium isotope ratio of -12‰.

Isotope ratios for oxygen-18 relative to the standard VSMOW for monitoring wells

ranged from -15.6‰ to -9.5‰. The highest values of -9.6‰, -9.5‰, and -9.8‰ were found in MW-19 shallow, MW-19 deep, and MW-27, respectively. Wildlife ponds 2 and 3 had oxygen-18 isotope ratios of -1.3‰ and -5.3‰, respectively. Tailings cell 3 had an oxygen-18 isotope ratio of 4.9‰.

Tailings cell 1 and cell 2 slimes drain were not analyzed by the contract laboratory because of damage that could have been incurred upon the laboratory equipment due to the low-pH of the wastewater collected.

Figure 21 plots the deuterium and oxygen-18 isotope ratios for each sample site. Figure 22 plots the regressed isotope ratio data along with the Global Meteoric Water Line after Craig (1961) and the Utah Meteoric Water Line after Kendal and Coplen (2001).

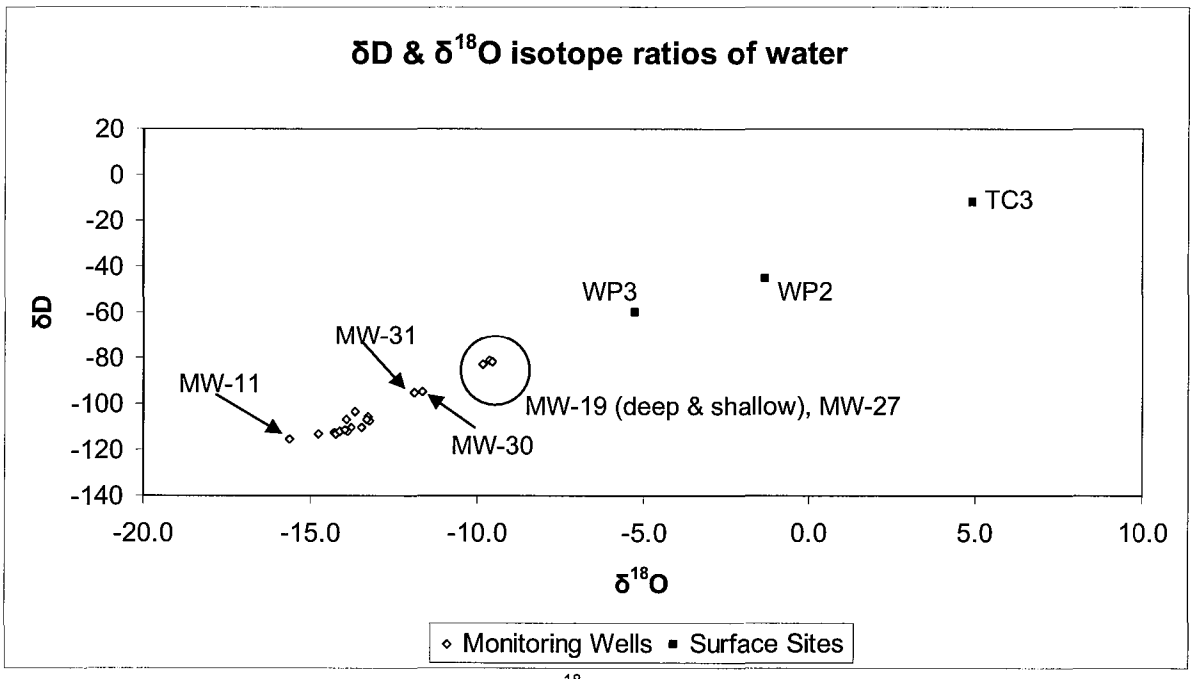


Figure 21: δD and $\delta^{18}O$ isotope ratios of water

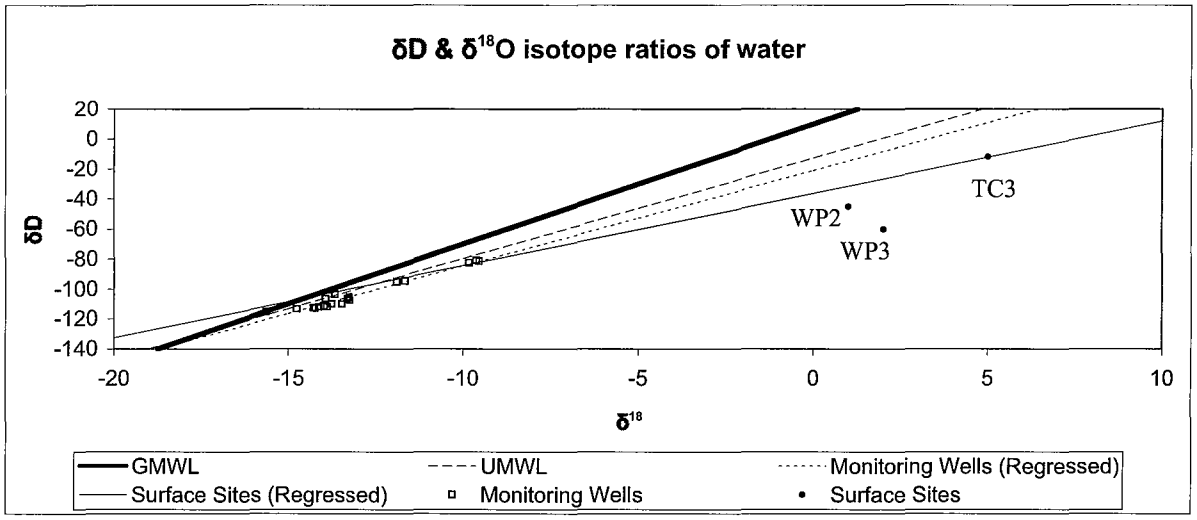


Figure 22: and $\delta^{18}O$ isotope ratios of water, regressed δ-Deuterium vs. $\delta^{18}O$ data with Global Meteoric Water Line and Utah Meteoric Water Line

The monitoring wells plot along a line of similar slope to the Utah (local) meteoric water line, but offset slightly. The surface water sites plot along a line with a slope one might expect to see in evaporated waters. Wells MW-19 (shallow and deep), MW-27, MW-30, and MW-31 have enriched (more positive) values for $\delta^{18}O$ and plot along the evaporation line suggesting that these wells have been influenced by evaporated surface water from the wildlife ponds. Nevertheless, the δD values for evaporated versus meteoric water for these wells is small suggesting the presence of non-evaporated background water (i.e. a mixture of pond and background water.) Well MW-11 does not show an evaporated signal suggesting that neither pond water or leakage from tailing cells is present at this well today.

Monitoring wells MW-3, MW-3A, MW-14 (shallow and deep), MW-15, MW-18 (shallow and deep), and MW-22 (shallow and deep) have more depleted $\delta^{18}O$. These wells have elevated uranium concentrations, but as they do not bear an evaporated

stable isotope signal it does not appear that the elevated uranium values are the result of leakage from tailing cells (or wildlife ponds.)

F. ^{34}S and ^{18}O Isotope Ratios in Sulfate

Sampled wells and surface water sites were analyzed for isotope ratios of $^{34}S/^{32}S$ and $^{18}O/^{16}O$ as sulfur-34 and oxygen-18 in the dissolved sulfate molecule. These isotope ratios can be used in fingerprinting waters of a common source, i.e. if leakage from tailings cells were occurring, wells impacted by leakage might have similar isotopic fingerprints of ^{34}S and ^{18}O as the tailings cells wastewater. Conversely, if no leakage from tailings cells were occurring, wells might have significantly different isotopic fingerprints of ^{34}S and ^{18}O as compared to the tailings cells. This is because of fractionation processes occurring in the ore refining process, and the use of sulfuric acid from an outside source in ore refinement. Furthermore, evaporation from the surface water sites would preferentially fractionate for oxygen-18 over oxygen-16, meaning the residual solution would become enriched in oxygen-18. This means that if isotopic ratios are different between wells and surface water sites, it is expected that surface water sites would have enriched (e.g. isotopically heavier) isotopic ratios of oxygen-18 relative to well waters. Table 11 shows analytical results for ^{34}S and ^{18}O isotope ratios as they pertain to the sulfate ions in solution.

Table 11: ^{34}S and ^{18}O isotope ratios of sulfate

Site	$\delta^{18}O$ - SO_4 (‰)	$\delta^{34}S$ - SO_4 (‰)
MW-1	-2.36	9.17
MW-1B	-2.22	9.88
MW-2	-8.59	12.13
MW-3	-7.03	13.69
MW-3A	-6.69	12.66
MW-5	-3.93	9.55
MW-11	-5.08	9.34
MW-14	-2.69	9.63
MW-14	-1.81	9.86
MW-15	-4.61	9.07
MW-18	-4.03	5.05
MW-18	-3.63	5.23
MW-19	-4.08	7.40
MW-19	-4.88	7.27
MW-22	-9.99	-2.44
MW-22	-10.27	-3.07
MW-27	2.02	-0.20
MW-29	-5.58	9.73
MW-30	-3.31	11.04
MW-31	-2.18	6.39
TC1	3.97	-0.89
TC2 Slimes Drain	4.58	-0.93
TC3	4.34	-1.04
WP2	4.52	0.90
WP3	3.15	0.19

Note: isotope ratios are calculated as $\partial^{34}S_{sample} = \left(\frac{\left(^{34}S/^{34}S\right)_{sample}}{\left(^{34}S/^{34}S\right)_{reference}} - 1 \right) * 1000‰$. The reference standard is Canyon Diablo Troilite having a $^{34}S/^{32}S$ ratio of 0.04500451.

Isotope ratios for ^{18}O of sulfate ranged from -10.3‰ to -1.8‰ in monitoring wells. Wildlife ponds 2 and 3 had positive ^{18}O isotope ratios of 4.5‰ and 3.1‰, respectively. Ratios in tailings cell 1, Cell 2 slimes drain, and tailings cell 3 were also positive at 3.9‰, 4.5‰, and 4.3‰, respectively. ^{34}S isotope ratios ranged from -3.0‰ to 13.6‰ in monitoring wells. Wildlife ponds 2 and 3 had ^{34}S isotope ratios of 0.9‰ and 0.19‰, respectively. ^{34}S isotope ratios in tailings cell 1, Cell 2 slimes drain, and tailings cell 3 were -0.89‰, -0.92‰, and -1.04‰, respectively.

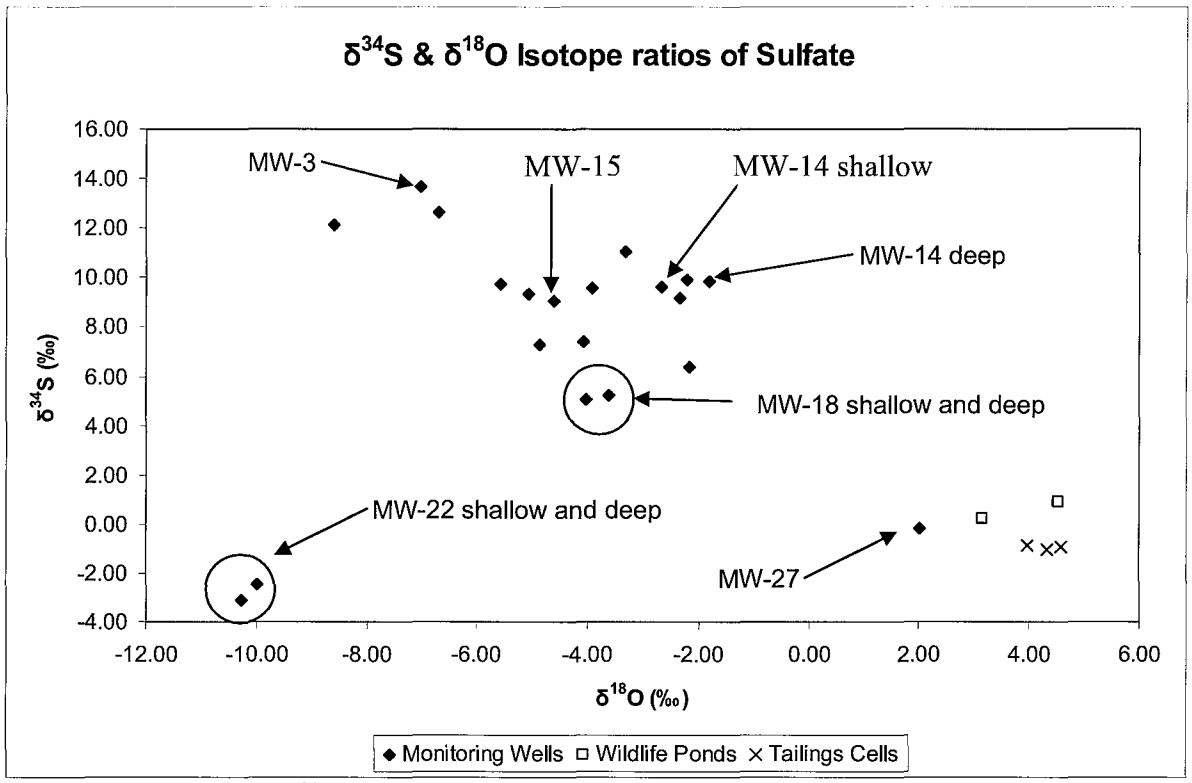


Figure 23: ^{34}S and ^{18}O isotope ratios as sulfur-34 and oxygen-18 in sulfate

Figure 23 shows the results of analyses done at the University of Waterloo Environmental Isotope Laboratory for ^{34}S and ^{18}O isotope ratios in sulfate. Several distinct relationships are apparent. The surface water sites (wildlife ponds and tailings cells) are heavily enriched in ^{18}O, and yet depleted in ^{34}S relative to monitoring wells. This is likely due to evaporative fractionation of lighter water molecules, causing enrichment of heavier water molecules in the ponds, and subsequent enrichment of oxygen-18. MW-27 is also similar in isotopic composition to the surface water sites. This suggests groundwater there has been influenced by the wildlife ponds found directly upgradient.

Most monitoring well sites exhibit a slight depletion of oxygen-18 with significant enrichment of sulfur-34. Both sampling depths for MW-22 exhibited ^{34}S isotope ratios similar to surface water sites, but ^{18}O-SO_4 is distinct from the surface water sites. This

may be explained by a recharge of surface water that isn't evaporated. Wells MW-3, MW-14 shallow and deep, MW-15, and MW-18 all exhibited elevated concentrations of uranium, but are isotopically distinct from the surface water sites.

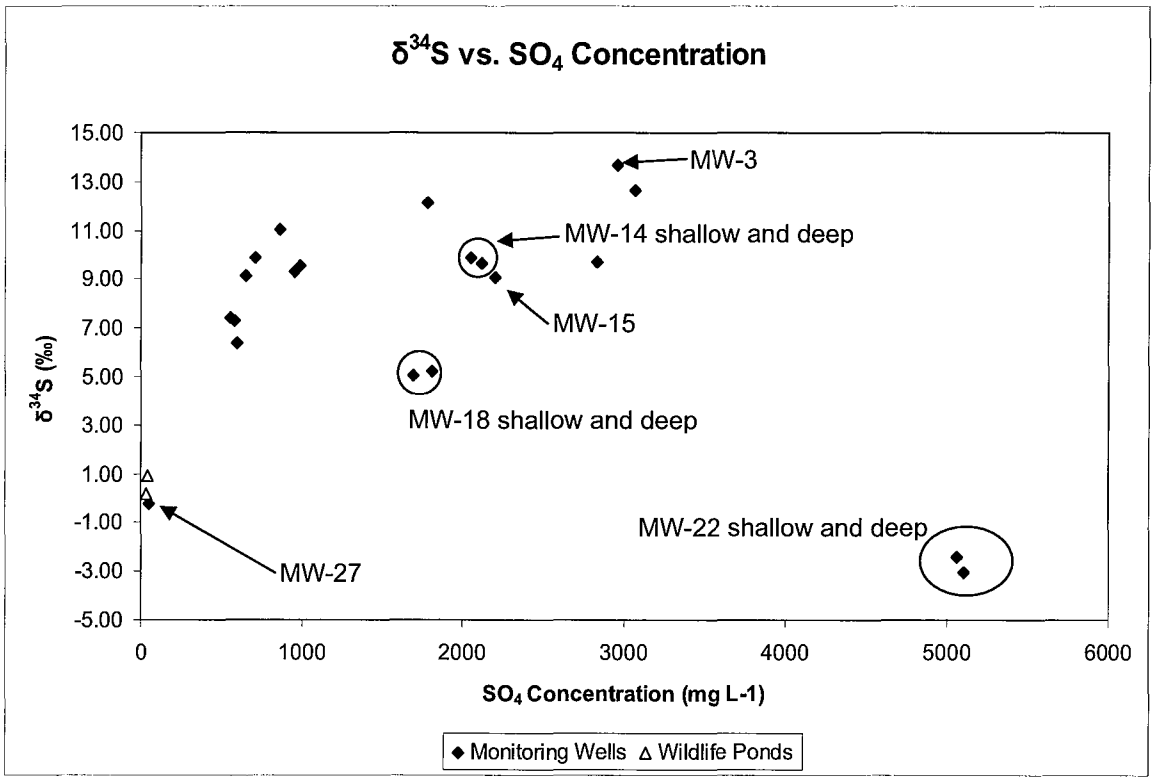


Figure 24: ^{34}S isotope ratios of Sulfate vs. dissolved SO_4 Concentration

Figure 24 presents sulfate concentration versus the ^{34}S isotopic ratios for each site. Because of extremely high sulfate levels in the tailings cells and Cell 2 slimes drain, those points are not included in Figure 24. Figure 25 below presents the log of sulfate concentration versus the ^{34}S isotopic ratios on the sulfate ions for each site.

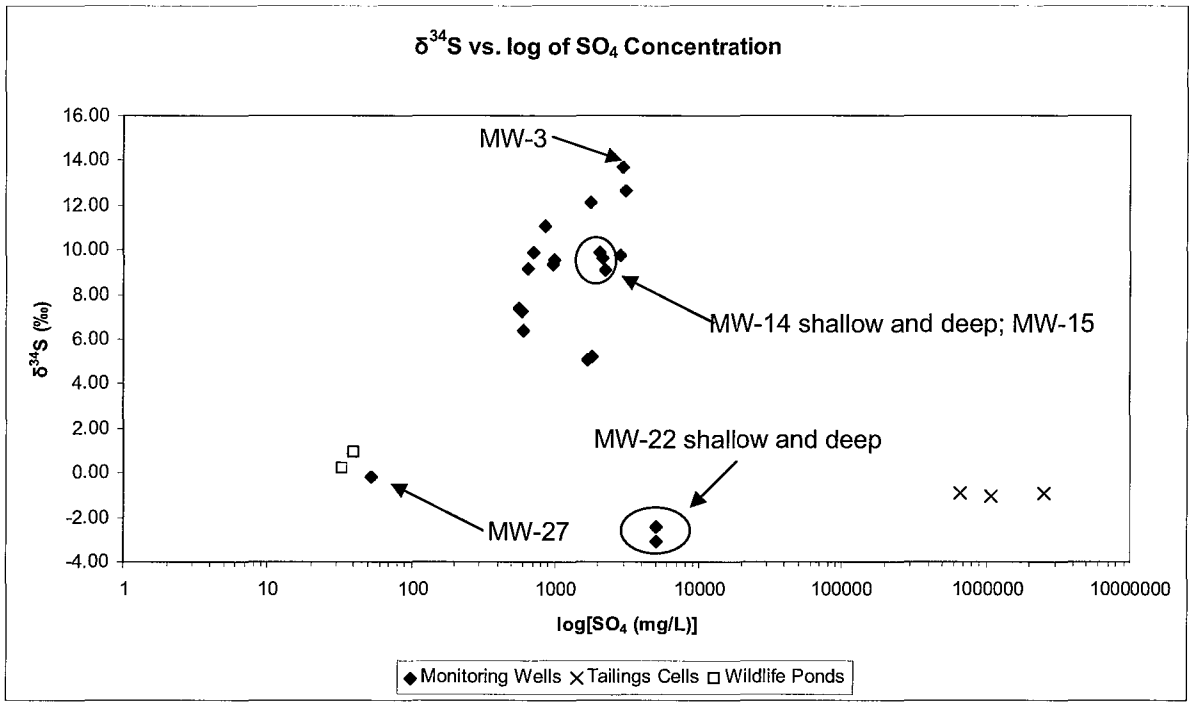


Figure 25: ^{34}S isotope ratios of Sulfate vs. log dissolved SO_4 concentration

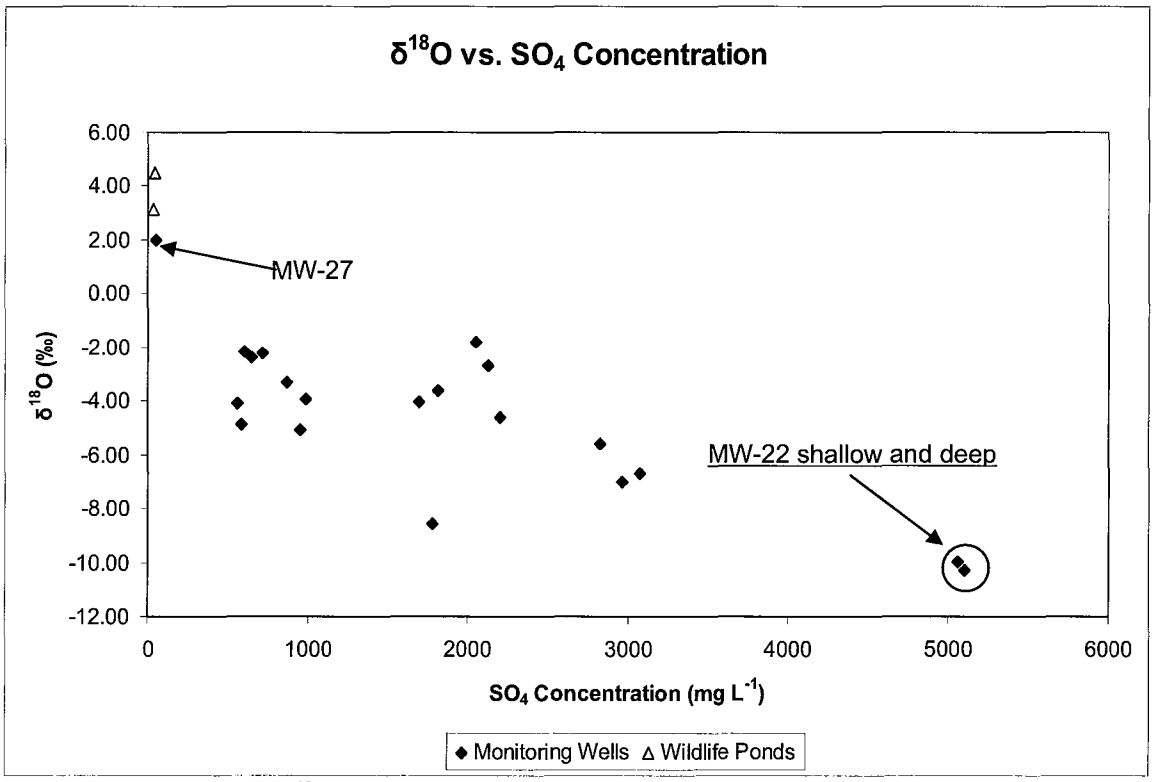


Figure 26: ^{18}O isotope ratios of Sulfate vs. dissolved SO_4 concentration

Figure 26 relates the oxygen-18 isotope ratios to the dissolved sulfate

concentration for each of the sample sites. A very general inverse correlation between increasing sulfate concentrations and oxygen-18 depletion is seen. MW-27 exhibits an isotopic fingerprint very similar to that of the wildlife ponds, as well as similar sulfate concentrations. MW-22 is anomalous in that it exhibits a significantly more depleted $\delta^{34}S$ value but has elevated sulfate. However, because of its location it is unlikely MW-22 is being influenced by similar aspects of the groundwater system as the other monitoring wells.

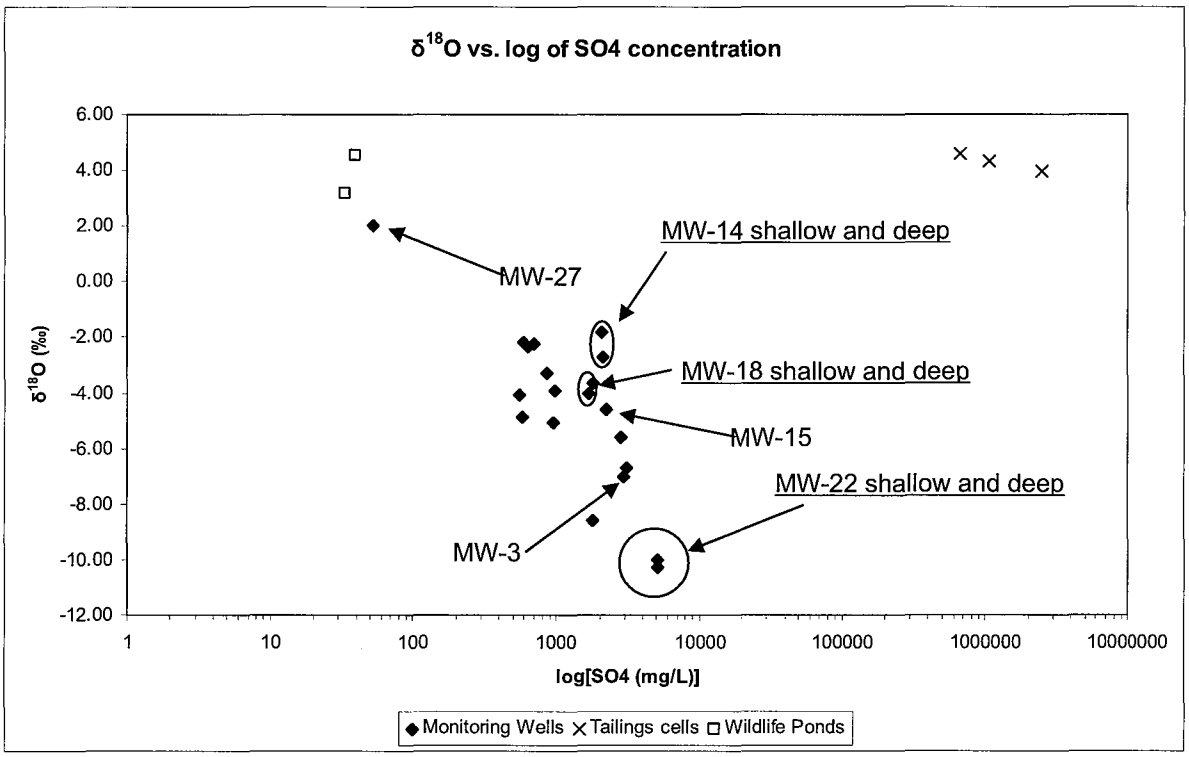


Figure 27: ^{18}O-SO_4 isotope ratios of sulfate vs. log of dissolved sulfate concentration

Figure 27 plots oxygen-18 isotope ratios of sulfate to the log of sulfate concentrations for each of the sample sites in order to include tailings cells. In this case the tailings cell wastewater is seen to exhibit both an enriched ^{18}O signature and extremely high sulfate content.

V. DISCUSSION

Most groundwater samples from the Mill contain significant amounts of terrigenic helium-4, indicative of older waters. Several samples have tritiogenic helium-3, indicative of young water, however these are only found in areas influenced by the wildlife ponds (MW-19, and MW-27). Tritiated water is introduced into the system by recharge from the wildlife ponds and appears in wells around the wildlife ponds. As recharge water from the wildlife ponds propagates through the system, evidence of tritiated water will appear in successive monitoring wells further from the ponds.

Wells MW-19 (both sample depths) and MW-27 exhibited the most enriched (heaviest) $\delta D/\delta^{18}O$ isotopic signatures of all the monitoring well samples. This can likely be attributed to the water table mounding that is occurring because of the nearby wildlife ponds. Water that is isotopically enriched due to evaporation, the wildlife ponds, when mixed with water that is isotopically depleted, groundwater, would produce an isotopic fingerprint that is isotopically heavier than that of groundwater but isotopically lighter than that of surface water. That the isotopic signatures of MW-19 and MW-27 are being influenced by recharge from the wildlife ponds is also supported by the elevated tritium concentrations in both wells. Significant amounts of tritium in MW-19 and MW-27 suggest younger water, and because of only modest amounts of precipitation, recharge is likely to mostly be occurring from the nearby wildlife ponds.

The influence of evaporated isotopic signatures is most prominent in MW-19 and MW-27, but is not evident in wells immediately down-gradient from MW-19 and MW-27, such as MW-30 and MW-31. This suggests the southern margin of artificial recharge due to the wildlife ponds, and the southernmost extent of the water table mound, is

likely between MW-27, and MW-30 and MW-31. Furthermore, mixing of the evaporated isotopic signatures with groundwater in MW-18 is not apparent, suggesting that the northern extent of the water table mound is likely between MW-19 and MW-18.

Because of the consistent similarities seen in $\delta^{34}S$ values, $\delta^{18}O$ values, and sulfate concentrations between MW-27 and the wildlife ponds, it is likely that water in MW-27 has its origin in the wildlife ponds. Furthermore, young water as evidenced by the presence of tritium in MW-27 indicates a tritiated recharge source, whereas tritium-free waters in the majority of the other monitoring wells indicates a recharge source composed of older water. Tritiated waters from the wildlife ponds that are likely recharging the aquifer system would show similar isotopic signatures between the monitoring wells and the wildlife ponds, as is seen in analytical data. This strongly suggests the influence of recharge from the wildlife ponds is propagating through the aquifer and has, to date, reached downgradient at least as far as MW-27.

Potential causes of similarities in sulfur isotope ratios between the wildlife ponds and tailings cells include: eolian transport of aerosols from the tailings cells, surface runoff from the Mill facility, and/or rainout of sulfuric acid released to the atmosphere from the Mill. When compared with isotope fingerprints observed in the tailings cells, fingerprints of monitoring wells exhibit strong differences, with the exception of MW-27. This suggests that elevated concentrations of trace metals seen in wells down-gradient of the facility are not being caused by tailings cell leakage.

The uniqueness of the stable isotope fingerprints of the tailings cells provide a valuable tool in monitoring groundwater wells for evidence of leakage from the tailings cells. Because of the extremely high concentrations of sulfate in the tailings cells, even

small amounts leakage could dramatically alter the isotopic signature of the monitoring wells, evidence that would appear much earlier than elevated trace metal concentrations. For example, consider a mixture of 2 mL of water from a tailing cell having a $\delta^{34}S$ value of -1.0 ‰ and a SO_4 concentration of 1,000,000 mg/L with 998 mL of background water having a $\delta^{34}S$ value of 8.0 ‰ and a SO_4 concentration of 1,800 mg/L. The mixture would have a SO_4 concentration of 3,800 mg/L and $\delta^{34}S$ value of 3.3 ‰. The change in SO_4 concentration from 1,800 to 3,800 mg/L would be difficult to attribute to leakage from tailings cells as the SO_4 concentrations in background water varies from less than 1,000 mg/L to more than 5,000 mg/L. However, a change in $\delta^{34}S$ value from 8.0 ‰ to 3.3 ‰ could identify the tailings as the source of contamination.

However, the stable isotope fingerprints of the tailings cells are very similar to that of the wildlife ponds. This may pose a problem for using stable isotopes of sulfate in the future. As the wildlife ponds continue to recharge the groundwater system, the isotopic fingerprint they bear will also be introduced into the aquifer. It is likely that eventually the entire groundwater system will bear an isotopic fingerprint similar to that of both the tailings cells and wildlife ponds, rendering $\delta^{34}S$ and $\delta^{18}O$ on sulfate irrelevant for detecting tailings cell leakage.

In a letter dated 31 January 2008 from Denison Mines (USA) Corp. to the Executive Secretary of the Utah Radiation Control Board, Mr. David Frydenlund, the Vice President of Regulatory Affairs Counsel, stated that several areas of low ground on the Mill site may have had an effect on the isotopic signature of sulfur-34 from sulfate in MW-27. He states that while the site is graded such that surface water runoff drains toward Tailings Cell 1, two areas up-gradient of MW-27 have historically experienced

water pooling to six inches deep after heavy rains. This water is a combination of direct precipitation and runoff from the northern portion of the mill area. This area of the Mill site has since been re-graded to remedy this issue. Although, it is possible that such water may have infiltrated through the vadose zone and recharged the saturated zone, this is a relatively small area and it seems unlikely that such an ephemeral head source could produce the isotopic signature observed in MW-27. More investigation is needed to better understand the occurrence of young water in the vicinity of MW-27.

Mr. Frydenlund also suggested that historical stock watering ponds up-gradient of MW-22 may have influenced the isotopic signature of sulfur-34 of sulfate and the presence of tritium in that well. Reportedly, these stock watering ponds were used during spring and fall from the early 1980s to 2001, but water was not maintained in the ponds for the entire year. The ponds were not utilized between 2001 and 2005, and were filled once between 2005 and 2006. Because the water used to fill the ponds from the 1980s to 2001 was pumped from the deep Entrada/Navajo aquifer, it is unlikely these waters were tritiated, though some tritium input may have occurred due to precipitation. Additionally, water used to fill the ponds in 2005-2006 originated in Recapture Reservoir (north of Blanding). While this water would possibly have been tritiated and, depending on the regional isotopic signature of sulfur-34 on sulfate, may have had a similar isotope fingerprint as the wildlife ponds and tailings cells, it is unlikely for that water to have recharged before the July 2007 sample event. While it seems unlikely that several years of tritiated water versus nearly 20 years of nontritiated water could produce the young isotopic signature in well MW-22, more investigation is needed and the cause the isotopic signatures is currently unknown.

VII. CONCLUSIONS AND RECOMMENDATIONS

A number of important conclusions can be made about the groundwater system at Denison Mine, Co.'s White Mesa Mill based on the presented information. Temperature and salinity profiles suggest that the water column in the aquifer is stratified with respect to chemical composition, as salinity systematically increased with depth. Furthermore, some wells (e.g. MW-1, MW-3, MW-5, MW-15) exhibited markedly different levels of salinity at different depths, differentiated by a drastic change in salinity across a very small depth. Also, noble gas compositions, particularly with respect to helium-4, suggest the water column is stratified with respect to age. Helium-4 concentrations determined from diffusion samplers were in every case greater at depth than samples taken near the water table (with the exception of well MW-19); suggesting longer subsurface residence time or age. Although not delineated by low-flow sampling at multiple depths, the systematic changes in temperature and salinity with depth, as well as helium-4 concentrations at depth, suggest the water column is stratified. Furthermore, this suggests that the existing monitoring wells sample a range of flow paths and groundwater ages. Passive samples from near the top of the well screens are more likely to detect leakage from the tailing cells than samples collected from the bottom of screens. While conventional low-flow sampling at this site does not appear to be practical or effective, passive sampling for dissolved ions (e.g. using dialysis membranes) might be effective.

Helium ratios corrected for inputs from excess air suggest older water farther away from the wildlife ponds. $^{3}He/^{4}He$ ratios closer to atmospheric values suggest water that is younger than 50 years. Most samples exhibiting this characteristic were

located close to the wildlife ponds, while samples farther away from the ponds had ratios less than atmospheric.

Low-flow sampling methods employed in monitoring wells were unable to distinguish stratification in the water column when a monitoring well was sampled at two depths. No significant differences were seen in concentrations of metals or anions, or in isotopic fingerprints, between samples taken at two depths. Additionally, age dating techniques that required active pumping for sample collection did not indicate marked differences in groundwater age between shallow and deep samples. However, this is likely the result of the inability of active pumping to collect depth-specific samples, rather than the lack of an age gradient.

Small but measurable quantities of chlorofluorocarbons were found in 10 wells (MW-1, MW-2, MW-5, MW-11, MW-14 shallow and deep, MW-15, MW-18 deep, MW-29, and MW-31) that did not contain tritium. CFCs are present in the unsaturated zone as gases at near-modern atmospheric concentrations. That CFCs are present in some samples near the water table indicates that water does propagate downward through the vadose zone and ultimately recharge the aquifer, again suggesting stratification in the aquifer. However, the absence of tritium in those waters suggests it takes infiltration water longer than 50 years to travel through the vadose zone. Because some amount of recharge to the aquifer is taking place, as evidenced by the recharge mound near the wildlife ponds, the system elsewhere can therefore be considered recharge-limited and not permeability-limited. Active groundwater flow clearly occurs vertically and horizontally, and if leakage from tailing cells occurs in the future a contaminated plume is likely to result at the water table.

Tritium measured in monitoring wells near the wildlife ponds suggests young water is recharging to those wells (MW-19 and MW-27). Surface water sites also contained significant amounts of tritium. The wildlife ponds contained atmospheric concentrations of tritium. The presence of tritium in the wildlife ponds and nearby monitoring wells strongly suggests recharge is occurring from the wildlife ponds to the aquifer. Because the wildlife ponds were constructed in the mid-1990's, water recharging from the ponds would bear a tritium concentration indicative of the atmospheric tritium in the last 10 to 15 years. Recharge from the wildlife ponds can potentially shift the flow dynamics of the system significantly, as is evidenced by mounding of the water table around the ponds. Such a shift in flow paths could result in temporal variations in groundwater chemistry.

Nitrate concentrations in two wells (MW-30 and MW-31) exceeded the Utah State Groundwater Quality Standard (GWQS) of 10 mg/L. All wells except for one (MW-27) exceeded the National Secondary Drinking Water Standard for sulfate set by the United States Environmental Protection Agency (250 mg/L). Five wells exceeded the GWQS for uranium (30 µg/L), including: MW-3, MW-14, MW-15, MW-18, and MW-22. Five wells exceeded the *ad-hoc* standard for manganese (800 µg/L), including: MW-3, MW-3A, MW-14, MW-22, and MW-29. Three wells exceeded the GWQS for selenium of 50 µg/L (MW-03, MW-15, and MW-31). The majority of wells that exceeded water quality standards were tritium-free, contained very small amounts of CFCs, and did not bear isotopic signatures similar to those of either the tailings cells or the wildlife ponds. This suggests natural, background values of trace metal contamination in the groundwater system.

Evaporative enrichment of δD and $\delta^{18}O$ is seen in surface water samples. Values in monitoring wells fall along a line similar to the Utah Meteoric Water Line, but offset slightly. Some apparent enrichment of both δD and $\delta^{18}O$ is seen in wells MW-27 and MW-19 shallow and deep. This suggests mixing that is occurring between enriched water recharging from the wildlife ponds and older, depleted groundwater. There are no other indications enriched water in any of the other monitoring wells. Even though several wells down-gradient of the tailings cells exhibited elevated levels of uranium concentrations, the stable isotope data does not indicate any amount of mixing between evaporated, enriched surface water and isotopically lighter groundwater. Therefore, it is unlikely that elevated and increasing uranium concentrations in MW-3, MW-14, MW-15, MW-18, and MW-22 can be attributed to leakage from the tailings cells. However, the stable isotope value of groundwater is insensitive to additions of trace amounts of enriched (surface) water.

$\delta^{34}S$ and $\delta^{18}O$ isotopic signatures on dissolved sulfate provide distinction between surface water sites and monitoring wells. The tailings cells and wildlife ponds exhibit significantly enriched $\delta^{18}O$-SO_4 values relative to monitoring wells, and depleted $\delta^{34}S$-SO_4 values relative to monitoring wells. MW-27 is the only monitoring well to bear an isotopic fingerprint closely related to that of the surface water sites, suggesting recharge from the wildlife ponds has reached MW-27 and further evidence that the wildlife ponds are providing recharge to the aquifer. Sites with high concentrations of metals (MW-3, MW-14 shallow and deep, MW-15, MW-18, and MW-22) bear very different isotopic fingerprints than those of the surface water sites.

In general, the data collected in this study do not provide evidence that tailings

cell leakage is leading to contamination of groundwater in the area around the White Mesa Mill. Evidence of old water in the majority of wells, and significantly different isotopic fingerprints between wells with the highest concentrations of trace metals and surface water sites, supports this conclusion. The only evidence linking surface waters to recharging groundwater is seen in MW-27 and MW-19. Measurable tritium and CFC concentrations indicate relatively young water, with low concentrations of selenium, manganese, and uranium. Furthermore, stable isotope fingerprints of δD and $\delta^{18}O$ suggest mixing between wildlife pond recharge and older groundwater in MW-19 and MW-27. $\delta^{34}S\text{-}SO_4$ and $\delta^{18}O\text{-}SO_4$ fingerprints closely relate MW-27 to wildlife pond water, while the exceptionally low concentration of sulfate in MW-27, the only groundwater site to exhibit sulfate levels below 100 mg/L, suggest no leachate from the tailings cells has reached the well.

CFC concentrations in tritium-free sites suggest a recharge-limited aquifer. This means that if a contaminated fluid was introduced to the system, it would likely be transported by the vertical flow of groundwater and would propagate through the system. This site is, therefore, susceptible to contamination due to tailings cell leakage, and must therefore be carefully monitored for such contamination. Sulfur-34 and oxygen-18 isotopes of sulfate will be useful until the isotopic fingerprint of the surface water sites has propagated through the entire system.

Sulfur isotopes that begin indicating input of water with a similar fingerprint as that of tailings cells may be an early indication that a leak in the tailings cell liner has developed. This signal would appear much earlier than elevated metal concentrations because mixing of isotope ratios, with sulfate concentrations as drastically different as

between tailings cells and wildlife ponds, is observable after only a very small amount of water has infiltrated (approximately 1% tailings cell water to 99% groundwater). Trace metal concentrations as well as inorganic anions should also be monitored on a regular basis.

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