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Use of Chemical and Isotopic Identifiers to Characterize Ground Water Contamination Near Two Uranium Mill Sites, Central NM

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Use of Chemical and Isotopic Identifiers to Characterize Ground Water Contamination Near Two Uranium Mill Sites, Central NM

by

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THESIS

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ABSTRACT

Chemical and isotopic signatures were used to discriminate between anthropogenic ground water and naturally occurring constituents. The U-234/U-238 activity ratio (AR) was determined in 34 samples from several aquifers underlying two former uranium mills near Milan, NM. Disposal of uranium ore waste into unlined tailings resulted in ground water contamination in the Lower San Mateo Creek Basin area. Ground water contamination from uranium mills have impacted the local ground water for residents down-gradient from the mills.

Previous studies that used uranium isotopes identified activity ratios of mill-derived uranium were near the secular equilibrium of 1, and those from natural ground waters were greater than 1.3. Background water quality show uranium concentrations close to 10 µg/L and AR values above 1.5. Concentrations of uranium down-gradient from the two milling sites had elevated levels of uranium from 31.7 to 1290 µg/L and AR values near 1.

This research utilized several techniques for identifying the source of ground water contamination near two former uranium mills. Analysis of the major ion chemistry indicated similarities in ground water near both sites and were Na-Ca/SO₄-HCO₃ dominant. Oxygen and hydrogen isotopic analyses found the source of the water to be meteoric. There was little to no correlation between U and Mo in the ground water near both sites; however, samples from both sites had strong correlations between U and Se. Dissolved sulfate in Bluewater monitoring wells ground water were enriched with ³⁴S, while wells near Homestake had ground water that were depleted in ³⁴S. Chemical and isotopic analysis and water quality results indicate that the wells with elevated levels of contaminants were likely from anthropogenic sources and not naturally occurring ground water.

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CHAPTER 1: INTRODUCTION

Thesis Objective

This project investigated the fate of contaminants in ground water impacted by uranium mining and milling processes in the lower San Mateo Creek Basin. Specifically, the ground water was sampled at wells located downgradient from two former uranium milling sites, Anaconda Bluewater and Homestake Mining Company (Figure 1). The goal of this research was to use ground water chemistry and stable isotope distributions, specifically uranium $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR), sulfur ^{34}S , nitrogen ^{15}N , oxygen and hydrogen ^{18}O , ^2H , cation and anion analyses to determine the source of the contamination plume in the groundwater near Milan, NM.

The focus was on the contaminated ground water, the sources of the contaminants, and the fate of the contaminants. Field and laboratory analyses were conducted on ground water sampled from domestic wells by using various analytical methods. By measuring isotopic abundance and chemical composition of ground water samples, this study sought to distinguish between mill-derived and naturally occurring contaminants with no known anthropogenic influence on ground water.

Previous Work

This study used isotopic and chemical principles that have been applied in other studies to develop an understanding of the aqueous geochemistry of ground water in the Lower San Mateo Creek watershed. The studies investigated the use of chemical and isotopic identifiers of contaminants associated with uranium mining activities in the Southwest region of the United States. The studies that are most relevant to this study are detailed below.

NMED (2010) details two separate investigations, Bluewater Mill site in 2008 and San Mateo Creek (SMC) Basin in 2009. The two mill sites are located in the Grants Mineral Belt (GMB) mining district in the northwest corner of New Mexico. This district produced more uranium from 1950 to 1981 than any other district in the world. There are four sub districts within GMB: Ambrosia Lakes, Laguna, Marquez, and Bernabe Montañó. The largest of the four sub districts, Ambrosia Lake, contained 96 mines and four mills. Two of the mills, Anaconda Bluewater and Homestake, are located in the Lower San Mateo Creek Basin.

The San Mateo Creek Basin is located in Cibola and McKinley Counties, NM. The basin comprises an estimated 321 square miles within the Rio San Jose drainage basin and the San Mateo Creek Basin comprises an estimated 321 square miles within the Rio San Jose Drainage Basin. The basin is home to 84 legacy uranium mines and 4 uranium mill sites (Figure 1). The majority of the mines are located up-gradient from the Anaconda Bluewater and Homestake Mills in the upper portion of the basin (Figure 1).

The Anaconda Bluewater mill is located approximately 8 miles from the Village of Milan, NM, near the western boundary of the watershed. It began uranium ore-processing in 1953. The mill used a carbonate-leach until 1955 (DOE 2014). In 1955, the mill switched to a sulfuric acid-leach after uranium ore was found in sandstone on the Laguna Reservation. This process also used other chemicals, kerosene and amines to extract the U from the raffinate solvent. The mill processed up to 6000 tons of uranium ore per day. The waste from the processing was placed into large tailings and holding ponds. Contaminants from the tailings and ponds leached into the underlying alluvial ground water. The mill stopped processing uranium ore in 1982, but continued to recover uranium from the leachate for several more years. In 1989, the mill site was approved for decommissioning by the Nuclear Regulatory Commission in accordance with Title II requirements of the Uranium Mill Tailings Radiation Control Act (UMTRCA). The mills decommissioning phase and reclamation was completed in 1995.

The Homestake Mining Company (HMC) mill is approximately 5.5 miles from the Village of Milan, NM. The mill began processing uranium ore in 1958 under the license of the Atomic Energy Commission. Homestake Mill used an alkaline-leach in its uranium ore processing. Due to high levels of radium-226 and radium-228, uranium, selenium, molybdenum and other contaminants in the surrounding soils and ground water, HMC was placed on EPA's NPLs in 1983. The site was decommissioned and demolished from 1993 to 1995. The site is currently undergoing a remediation program to control the leaching of contaminants into the ground water outside of the site's boundary. The remedial program includes a collection/injection system for both the

alluvial and Chinle aquifers and a reverse osmosis and tailings collection wells for both tailings piles.

The NMED (2010) report used isotopic analysis of ^2H , ^{18}O , ^{34}S , ^{234}U and ^{238}U along with metals and major ions to distinguish background water quality to water impacted from uranium mining and milling operations from the mills and mines within the study area. The use of ^{18}O and ^2H isotopes were useful in determining the origin (age) of the ground water. Ground water samples with similar isotope values but different aquifers show a connection or similar recharge source. This study also used ^{34}S isotopes to identify the most likely source of SO_4 in the ground water, biogenic or chemical. The use of $^{234}\text{U}/^{238}\text{U}$ AR values were useful in identifying the likely source of elevated U concentrations in the study area. This study also developed several trilinear diagrams (piper plot) for each of the study areas, Bluewater and SMC. These diagrams are used to highlight similarities and differences between major ions in ground water samples. NMED (2010) also provides hydrology and hydrogeology of the SMC Basin. This will provide useful data for the HMC and Bluewater sites, and help to establish a connection through hydrogeology for the two milling sites.

Kamp and Morrison (2014) sampled ground water near a former uranium mill near Shiprock, NM. The U mill tailings are said to be responsible for elevated levels of contaminants associated with uranium mining and milling production in the ground water. To determine whether wells and ground water seeps were impacted by drainage from the tailings pile, the study used chemical characteristics and isotopic signatures to differentiate between mill-derived ground water and natural occurring ground water

contaminants. Uranium isotopes ^{234}U and ^{238}U , hydrogen isotope ^3H , and sulfur isotope ^{34}S were used to investigate the source of contaminants in ground water near a former uranium mill and to distinguish between natural occurring and anthropogenic mill-derived constituents in ground water near Shiprock, NM.

Bush and Morrison (2012) investigated ground water from a former uranium milling site at Shiprock, NM, and surrounding arroyos. The study used $^{234}\text{U}/^{238}\text{U}$ alpha activity ratio (AR) to determine the distribution of uranium in ground water. The study found AR values sampled near a tailings disposal cell were close to 1, while samples collected up-gradient and further from the disposal cell had AR values near 2. The use of uranium AR values can help determine whether high uranium concentrations are that of background levels or are derived from the uranium disposal site near Shiprock, NM. This study provides useful techniques in uranium isotope ratios and supports the Kamp and Morrison (2014) investigation.

Harmon Craig (1961) investigated the relationship of ^2H and ^{18}O concentrations in natural meteoric waters to determine the correlation of waters which have not undergone extreme or excessive evaporation. The correlation of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/\text{H}$ were determined to be linear in normal non-excessive evaporation environments. This methodology is an important factor in determining the origin of the groundwater and will be a useful technique for this study.

Zielinski et al. (1997) expands on a previous study, Wirt (1993), in the use of uranium isotopes, $^{234}\text{U}/^{238}\text{U}$, activity ratios (AR) to determine the source of contaminants in the area around a former uranium mill site near Cañon City, Colorado. Uranium and Molybdenum data was used along with the AR values to establish a correlation between high concentrations of natural occurring and anthropogenic mill-derived U and Mo in ground water associated with uranium mining. Zielinski et al. (1997) recognized the correlation of AR values near 1 to high concentrations of uranium and molybdenum. Zielinski et al. (1997) also showed AR values above 1.3 were closely related to natural background concentrations of uranium and molybdenum. This study used general water chemistry, dissolved solids and major ions, to identify the source of contaminants and their relationship with high levels of uranium and molybdenum. Molybdenum and selenium are similar to the oxidation and reduction processes of uranium where their mobility increases in aquifers that favor the formation of soluble U(VI). The activity ratios for uranium isotopes $^{234}\text{U}/^{238}\text{U}$ and uranium data used for Zielinski et al. (1997) are the same methods that are applied to this study.

Lower San Mateo Creek Watershed

There are two former uranium mills in the Lower San Mateo Creek Basin, Anaconda Bluewater and Homestake. Anaconda Bluewater and Homestake mills are approximately 5.5 miles and 8 miles from Milan, NM, respectively. Tailings from the mills resulted in high concentrations of uranium, molybdenum, selenium, nitrate, sulfate and other constituents in nearby shallow aquifers.

The lower basin has three aquifers that provide ground water to its residents, alluvial, Chinle formations, Upper, Middle, and Lower and San Andres-Glorieta (SAG) aquifers. The alluvium system underlies both of the mills and extends from the northeast to the south of the Homestake site. Ground water, in the alluvial aquifer, follows the San Mateo Creek drainage, which flows towards the town of Milan, NM (NMED 2008). The Chinle Formation lies below the alluvium aquifer at Homestake mill and is a barrier to the SAG formation. All three of the Chinle aquifers subcrop with the alluvial aquifer connecting the alluvial with the Chinle aquifers in the vicinity of the Homestake mill site. Underneath the Chinle formation is the SAG aquifer and it flows from west to east away from the Anaconda Bluewater site. The SAG is the primary aquifer in the basin that provides both Grant and Milan with water.

The Homestake milling site is one of four milling sites within the Ambrosia Lake sub district, the largest sub district in the Grants Mineral Belt. Homestake Mining Company milling plant began processing uranium in 1958 (EPA 1991). The mill used an alkaline leach circuit for removing uranium from its ore body. The plant continued to mill uranium until 1990. The plant was decommissioned and demolished from 1993 to 1995 (NMED 2008). Prior to its closing, the mill site was placed on the United States Environmental Protection Agency (USEPA) National Priorities List (NPL) in 1983 because of elevated concentrations of selenium in residential wells south of the mill site. These contaminants were the results of seepage from the mill tailings, both large and small tailings pile. High levels of selenium were first detected in residential wells south of Homestake in 1975 (EPA 1991).

Homestake originally operated under two separate partnerships, Homestake-Sapin Partners and Homestake-New Mexico Partners. The two mills had 1,750 tons per day (tpd) and 750 tpd, respectively. In 1961, Homestake-New Mexico Partner was dissolved and Homestake-Sapin purchased the property (EPA 1991). The two facilities were combined increasing the milling capacities to 3,400 tpd. Homestake-Sapin was changed to United Nuclear-Homestake in 1968, and in 1981 the name was changed again to Homestake Mining Company when they bought United Nuclear shares in the company. Waste from processing uranium was placed onto two tailings piles (Figure 2). The small tailings pile contains approximately 1.8 million tons of waste and the larger 20.2 million tons of waste. The tailings piles cover approximately 270 acres with an estimated weight of 22 million tons (USNRC 2016). Both tailings piles were constructed using an earth-fill containment dike (NRC 1993). Both piles were unlined and leachates from the tailings infiltrated the alluvial surface underlying the site.

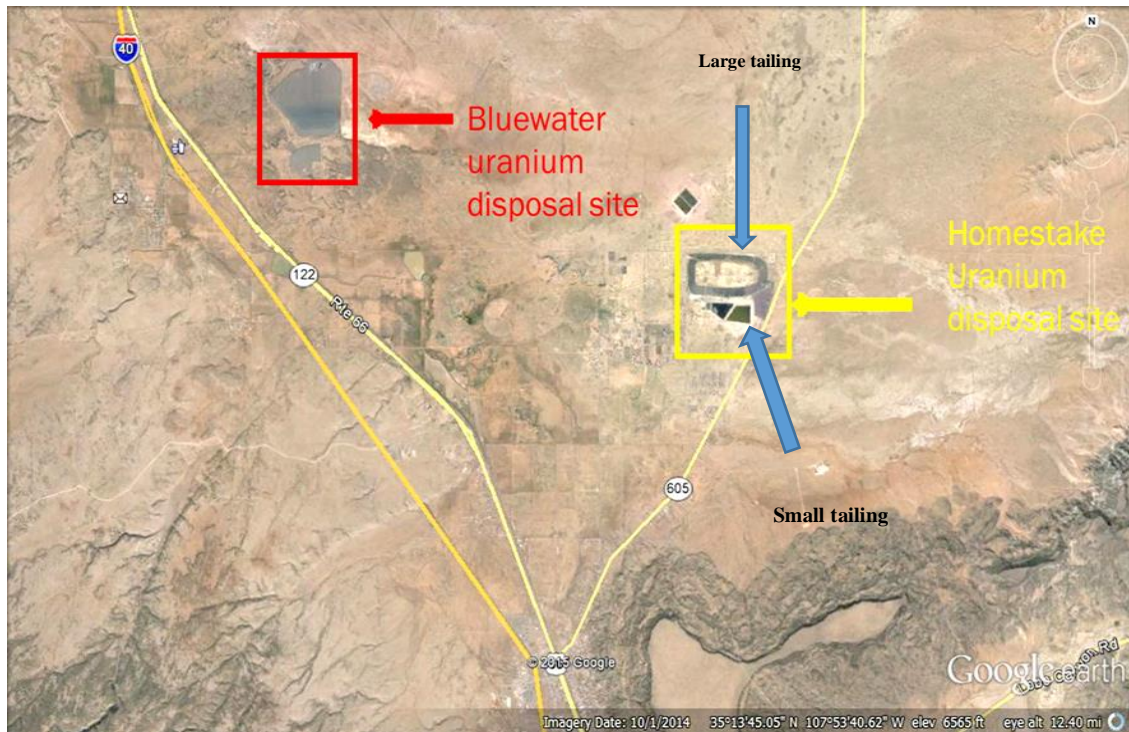


Figure 2 Bluewater and Homestake mill sites. Large and small tailings piles at Homestake Mining Company milling site.

Hydrogeology

Homestake's two unlined tailings piles allowed seepage from them to leach into ground water beneath the site. The Homestake site is underlain by alluvial soils and contains a main aquifer for residents in the area. This alluvial is underlain by thick Chinle formations, upper, middle, and lower, which is made up of shale and siltstones (NRC 1993). The Chinle formation is a barrier for the San Andres formation, the primary source of water for the residents and the Village of Milan. The alluvial and Chinle aquifers were directly affected from the tailings seepage. The leaching of contaminants into ground water from the tailings piles at the Homestake Mining Company site led to high levels of contaminants in residential wells.

Beginning in the 1970s, private wells downgradient from the site, Felice Acres, Broadview Acres, Murray Acres, Valle Verde, and Pleasant Valley Estates subdivisions were sampled for radionuclides, chemical and metals. Ground water sampling for some of the wells showed elevated concentrations of uranium, selenium, and molybdenum which were one to two orders of magnitude greater than ever before (ATSDR, 2009). Because of the high concentrations of these metals in the residential ground water, Homestake Mining Company and USEPA reached an accord and HMC agreed to provide an alternative water source to these subdivisions and be financially responsible for the first 10 years of usage (EPA 1991). Most residents continue to use the alternative water source from the Village of Milan which draws ground water from the SAG aquifer.

The Homestake Mining Company site has conducted a ground water corrective action program to control the seepage of contaminants from the tailing piles since 1978 (NRC 1993). The corrective action includes injecting fresh water into the underlying aquifers to create a hydraulic gradient that forces the ground water to reverse its natural flow (NRC 1993). Pumped wells near the tailings pond create a cone of depression to capture ground water from off site. The contaminated water is treated by RO. The permeate is injected into perimeter wells while the concentrate containing high TDS, U and other contaminants is sent to lined evaporation ponds for disposal.

Chapter 2: Theoretical Background

Background

A comprehensive review of available information was conducted and includes: Historical information on the mining and milling activities in the study area, San Mateo Creek basin; water quality data in the study area which includes isotopic data; and geological investigations in the SMC basin.

Most of the studies in the area were done by governmental agencies: United States Environmental Agency (EPA), New Mexico Environmental Department (NMED), United States Department of Energy (DOE), and Nuclear Regulatory Commission (NRC). The NRC is an independent agency of the US government assigned with protecting public safety and health with issues related to nuclear energy.

There is little data on background water quality in the study area prior to the start of uranium mining in the region. This lack of background data makes it difficult to establish natural ground water conditions of water quality parameters. Although there is a lack of data for background conditions, NMED, 2010 and DOE, 2014 have identified natural background conditions for the aquifers near the Bluewater site. Bluewater wells E(M) and L(SG) have been established as background wells for the alluvial and SAG aquifers, respectively. These background levels are also considered to be representative of those near the Homestake site.

The Homestake Mining Company puts out an annual report to show its progress in the remediation of the site. In 2016, Homestake Mining Company put out a report “*2015 Annual Monitoring Report/Performance Review For Homestake’s Grant Project Pursuant to NRC License SUA_1471 and Discharge Plan DP-200*” for the U.S. Nuclear Regulatory Commission and New Mexico Environmental Department. The report had some important well data for onsite wells and up-gradient wells near the mill. This data is readily available online at adams.nrc.gov.

Another investigation from NMED, 2010 investigates the lower San Mateo Creek Basin, which includes the Bluewater and Homestake mills. All of the data for Anaconda Bluewater site was retrieved from the Department of Energy’s Legacy Management website and NMED studies conducted over the past 10 years. Bluewater data did not contain data for all constituents from year to year, and the 19 wells selected had been analyzed for the isotopes used for this study. These isotopes included uranium ^{234}U and ^{238}U , sulfur ^{34}S , oxygen $^{18}\text{O}/^{16}\text{O}$ and hydrogen $^2\text{H}/\text{H}$ for the 19 monitoring well samples. The data did not contain any results for vanadium or nitrogen isotope ^{15}N . This study also sampled wells upgradient and downgradient from the Homestake mill site. Neither of the combined studies had results for ground water prior to mining in the region.

The data retrieved from Homestake’s Annual Monitoring Reports issued for the USNRC and NMED, are limited to 10 water-quality standards (Cl, Mo, NO_3 , Se, TDS, SO_4 , V, U, Ra-226, + Ra-228, and Th-230), which are used for Homestake’s site standards, set by the NMED and NRC. The site standards were reviewed and approved by three regulatory agencies: EPA, NRC, and NMED and have been in effect since 2008 (GRP 2015). These standards are based on the alluvial background values for each one

of the constituents. Table 1 Figure 1 is a list of site standards for both NRC and NMED for the Homestake mill.

Uranium Fate and Transport

Uranium is a natural occurring element found in most rocks, soils, and water at low concentrations of a few parts per million by weight (Thomson and Heggen 1983). Uranium ore deposits usually range between 0.1% to 2.0% uranium and is the result of aqueous transport and precipitation. Oxidation-reduction is summarized in Figure 3.

The heaviest of all natural occurring elements, atomic weight of 238, is uranium. The solubility of uranium in water depends primarily on pH and its oxidation state (Figure 3). The formation of uranium ore bodies is explained by oxidation-reduction. Under non-reducing conditions, natural ground water dissolves small amounts of uranium. Ground water with a high content of carbon dioxide leads to the formation of carbonate complexes as uranium is oxidized from +4 to +6 state (Thomson and Heggen 1983). The carbonate complexes result in uranium deposition as the ground water transport of dissolved uranium to a more reducing environment. The reduction of uranium from +6 to +4 results in the precipitation of uraninite, monomeric U(IV), and coffinite (Maher, et al., 2012). Other U(IV)-bearing minerals, such as schoepite, carnotite ($K_2(UO_2)_2(VO_4)_2$), truyamunite ($Ca(UO_2)_2(VO_4)_2$), and uranophane ($Ca(UO_2)_2(SiO_3OH)_2$) are also found in surface (Burns 2005). This process of transport, chemical reduction and precipitation is similar for molybdenum, selenium, and

vanadium, resulting in higher concentrations of these chemicals being associated with uranium deposits (Thomson and Heggen 1983).

The milling process of uranium is essentially the reversal of the oxidation-reduction and precipitation of uranium in natural environments. After the ore has been recovered by mining, the ore is sent to a mill where it is crushed and processed. The process involves oxidizing the crushed ore to dissolve precipitated uranium and using a solvent to extract the uranium metal. The metal is then processed and dried to uranium yellowcake U_3O_8 . Yellowcake is then shipped to enrichment plants where it is enriched to a higher concentration of ^{235}U .

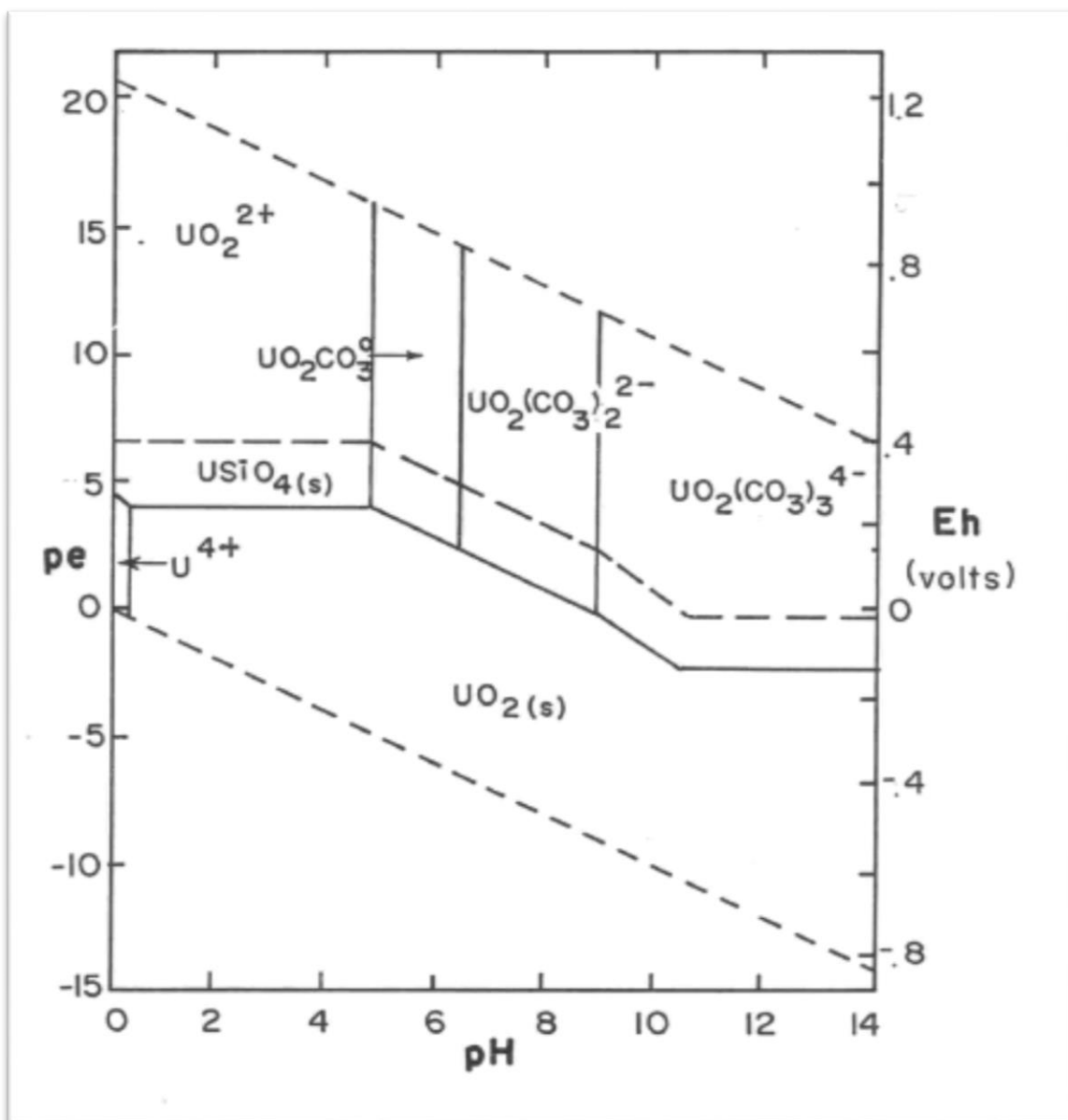


Figure 3 pe-pH diagram summarizing the oxidation-reduction and acid-base chemistry of uranium in solution. Total U concentration is 10⁻⁶ M while the concentration of H₄SiO₄ and dissolved CO₂ is 10⁻³ M. Diagram prepared by Thomson.

Uranium

Three isotopes of U occur in nature, ^{238}U , ^{235}U , and ^{234}U with half-lives of 4.5 Byrs, 704 Myrs and 245 Kyr, respectively. The natural abundance of ^{238}U , ^{235}U , and ^{234}U is 99.3%, 0.72% and 0.0055%, respectively. Metallic U is approximately 1.7 times denser than lead, 18.95 to 11.4 (g/cm³).

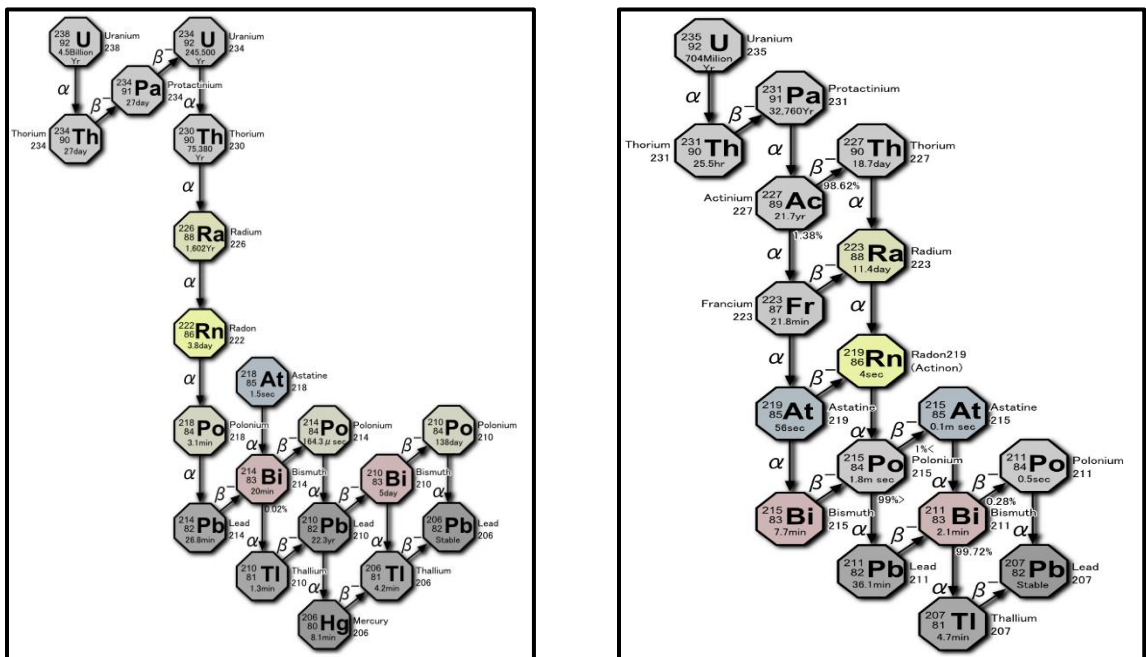


Figure 4 Radioactive decay chain for ^{238}U and ^{235}U .

Uranium-238 emits an α alpha particle during its decay and eventually decays to ^{206}Pb (Figure 4). In a closed system, U will reach a secular equilibrium between ^{234}U and ^{238}U . Secular equilibrium is when the rate of ^{234}U decay is equal to its parent ^{238}U decay (Zeilinski, 1997). It takes approximately 1.0×10^6 years for the ^{238}U series to reach

secular equilibrium. A way to measure secular equilibrium is to calculate the activity ratio (AR) of $^{234}\text{U}/^{238}\text{U}$. The values from these measurements will determine whether or not secular equilibrium has been reached between the two isotopes. Ores that have not been aggressively leached will retain their natural occurring activity ratios, but ores that have been processed for their uranium will keep activity ratios near its secular equilibrium value of 1.

Most uranium milling plants in the GMB, used an acid leach circuit (Figure 5) to extract uranium from the ore. For milling plants that used an alkaline leach circuit (Homestake), sodium carbonate was used in the leaching solution. Homestake Mining Company milling plant near Milan, NM, used an alkaline leach to extract uranium from the ore. The milling process at Homestake included a carbonate leach in a combination of Pachuca and autoclave tanks. This was followed by a countercurrent filtration system that separated the uranium solution from the leached solids. The leached solids were made up of sands, slimes and liquid wastes. The uranium solution was treated with a caustic soda to precipitate the initial product (Merritt 1971). After roasting and quenching (leaching) with water, another filtration was used to reduce the vanadium content in the product. If needed, the sodium content of the final product is reduced by re-dissolving the initial product in a lower concentration of sulfuric acid and re-precipitated with ammonia. The sodium and ammonium sulfate is filtered out and the final uranium product, yellowcake, is dried and packaged.

When uranium ore is received at the mill, it is ground to a finely crushed sample making it easier for the oxidizing solution to remove the uranium. Raffinate, a solution of targeted ore products and a strong alkali or acid left over from milling process, AR

values should remain near its secular equilibrium value of 1 because the milling process dissolves ^{234}U and ^{238}U equally (Zeilinski 1997). This holds true for the leachate, too, because of the efficiency of the processes to remove the targeted uranium and not further fractionate ^{234}U and ^{238}U isotopes.

In an undisturbed ore body, U in ground water has AR values >1 (Osmond and Cowart 1976). Studies have shown that typical AR values of $^{234}\text{U}/^{238}\text{U}$ are in the range of 1-3, but have been shown to go as high as 10 (Cherdyntsev 1971). This phenomenon happens due to the mild leaching effect and prolong interaction of groundwater with uranium minerals. Within the ore minerals the isotopes have different leachability because while ^{238}U was in the mineral since its formation, ^{234}U is a decay product and the high energy alpha particles damage the surrounding crystal lattice which slightly increases its leachability. For this reason, AR values for $^{234}\text{U}/^{238}\text{U}$ are much greater than 1 for solutions originating from undisturbed U minerals (Kamp and Morrison 2014).

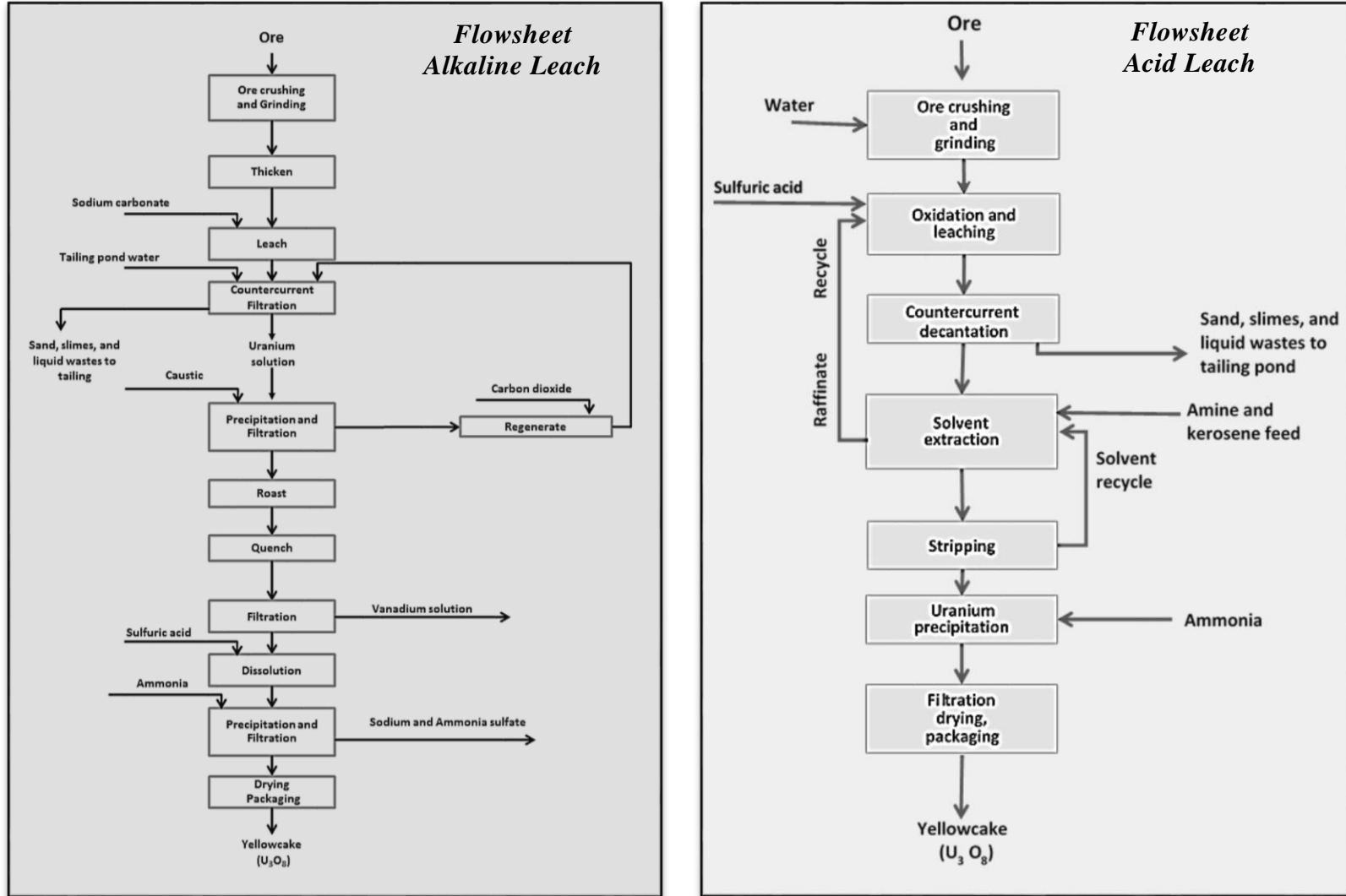


Figure 5 Process flow diagrams for alkaline and acid leach circuits for uranium milling (USDOE 1980), (Thomson and Heggen 1983).

Deuterium-Oxygen isotopic ratios

Isotope fractionation in water occurs when water goes from a liquid to gas or from solid to a liquid. The heavier isotopes of hydrogen (^2H) and oxygen (^{18}O) become enriched over H and ^{16}O , the lighter isotopes in H_2O . During the evaporation of water, the lighter isotopes, H and ^{16}O , evaporate at a greater rate than the heavier isotopes ^2H and ^{18}O , leaving the heavier isotopes behind in the seawater. Precipitation is enriched with the lighter isotopes and are reported in parts per thousands (permil) (‰). The results are calculated using equation 1 below and displayed as delta (δ).

$$\delta = \left[\left(\frac{R}{R^*} \right) - 1 \right] 1000 \quad (1)$$

Where R is either isotopic ratio of $^2\text{H}/\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ and R^* is the Vienna standard mean ocean water (VSMOW) ratio (Craig 1961). In 1961, Craig used precipitation values from approximately 400 samples of water from various sources, rivers, lakes and precipitation and found a linear relationship between the two isotopes known as the Global Meteoric Water Line (GMWL) (equation 2). The slope of this line varies depending on the source. The GMWL is not a good fit when excessive or dominant evaporation is a factor (Craig 1961). In temperate or humid climates, the composition of groundwater is similar to that of the precipitation, but semi-arid or arid climates evaporative losses of recharged water shift the isotopic composition to higher delta values (Hoefs 2004).

$$\delta D = 8 \delta O + 10 \quad (2)$$

Where D represents hydrogen isotope ^2H .

Nitrogen isotopes

Nitrogen has two stable isotopes, ^{14}N (99.64%) and ^{15}N (0.36%). Isotopic analysis for nitrogen is done by establishing the ratio of ^{15}N to ^{14}N in nitrate of samples of interest compared to the standard ratio of atmospheric nitrogen. These comparisons show a positive (enriched) or negative (depleted) value in the samples of interest and are reported as permil (‰) and calculated using equation 1. Values for terrestrial $\delta^{15}\text{N}$ vary for specific sources but fall in the range of -20‰ and 30‰ (USGS 2004).

Numerous studies have used nitrogen isotopes values to determine the source of the nitrogen. The source of most nitrate pollution in surface or ground water comes from fertilizers, manure or animal waste and sewage (septic systems). The $\delta^{15}\text{N}$ values can help distinguish them from each other. Fertilizers have $\delta^{15}\text{N}$ values that range from -4 to +4‰. These values reflect its source of nitrogen which commonly comes from atmospheric nitrogen. Animal waste will have higher $\delta^{15}\text{N}$ values > 5‰. Other sources of nitrogen come from sediment and metamorphic rocks and can have $\delta^{15}\text{N}$ values ranging from 0 to 10‰ (Hoefs 2004). Use of nitrogen isotopes as an indicator of the source of nitrate is suggested. U is recovered from acid leach solutions by solvent extraction using an amine compound (Merritt 1971). Some of this amine is carried over to the tailings pile and is subsequently oxidized to nitrate, thereby producing a large nitrate plume. However, amine use is much smaller in alkaline leach processes and nitrate impacts on ground water are much less at the Homestake site.

Sulfur isotopes

Sulfur is a chemical element with an atomic mass of 32. Sulfur occurs naturally in rocks, soils, and minerals and has 25 known isotopes, but only four isotopes are stable

^{32}S , ^{33}S , ^{34}S , and ^{36}S at an abundance of 95.02%, 0.75%, 4.21% and 0.02%, respectively. Sulfur, in ground water, is released by contact of water with the sulfur bearing materials. It is most commonly found in three ions, sulfate SO_4^{2-} , bisulfide HS^{-1} , and hydrogen sulfide H_2S . According to Clark and Fritz, 1997 (as cited in Kamp and Morrison 2014) ground water systems which involve chemical and biological processes result in the fractionation of ^{34}S and ^{32}S . Reduction of SO_4 to sulfide results in fractionation (depletion) of 20 to 40‰ of ^{34}S , and oxidation of sulfide to SO_4 result in a fractionation of approximately 5‰. Both of these processes favor the transfer of the lighter ^{32}S atom into a product phase of a lower energy, which is required for bond cleavage (Kamp and Morrison 2014).

Sulfur isotopes ^{32}S and ^{34}S can be a useful tool to distinguish between naturally occurring and anthropogenic sources of sulfur. The standard used for measuring sulfur isotopes fractionation is the Canon Diablo troilite. Variations in isotopic ratios of ^{34}S can be useful to determine the source of the sulfur. For instance, sea spray has been measured to contain a ratio of $\delta^{34}\text{S}\text{‰}$ at approximately +20. Volcanic sulfur has been measured in the range of -5 to +5 for $\delta^{34}\text{S}\text{‰}$. The use of $\delta^{34}\text{S}\text{‰}$ will be a useful tool in determining the sulfate origin and determine if S is naturally occurring or from an anthropogenic source.

Sulfuric acid was the primary acid used in the acid-leaching process (Bluewater) of uranium extraction but not alkaline-leaching process (Homestake). Homestake used an alkaline leaching process to extract uranium from the crushed ore and when needed used a sulfuric acid to reduce the sodium content in the final product. The use of sulfuric acid as a leaching product increases the concentration of SO_4 due to oxidizing conditions

associated with uranium milling. In oxidizing environments, SO_4 is the stable species, while in reducing environments elemental S or sulfide species are stable.

The NM ground water standard for SO_4^{2-} is 600 mg/L while the federal SDWA has a secondary (i.e. recommended but not enforceable) standard of 250 mg/L. Sulfur has multiple oxidation states from S (-II) to S (VI). Sulfides will be present as H_2S or HS^- depending on solution pH, where hydrogen sulfide (H_2S) dominates below pH 7 (rotten egg smell) (Oregon, 2016).

Geology and Hydrogeology of the Lower San Mateo Creek Watershed

The Lower San Mateo Creek watershed is located on the southern end of the San Mateo Creek Alluvial system (Figure 8). The alluvial system extends from the northeast of HMC to the lower portion of the aquifer (NMED 2010). The alluvium, below the Homestake site, overlays the Chinle Formation, a formation formed in the Upper Jurassic (Figure 7). The Chinle is made up of mostly shale and has three layers, the upper, middle and lower. The Chinle is a barrier for the underlying San-Andres Formation. This formation is part of the primary water source for the communities of Bluewater and Milan, NM.

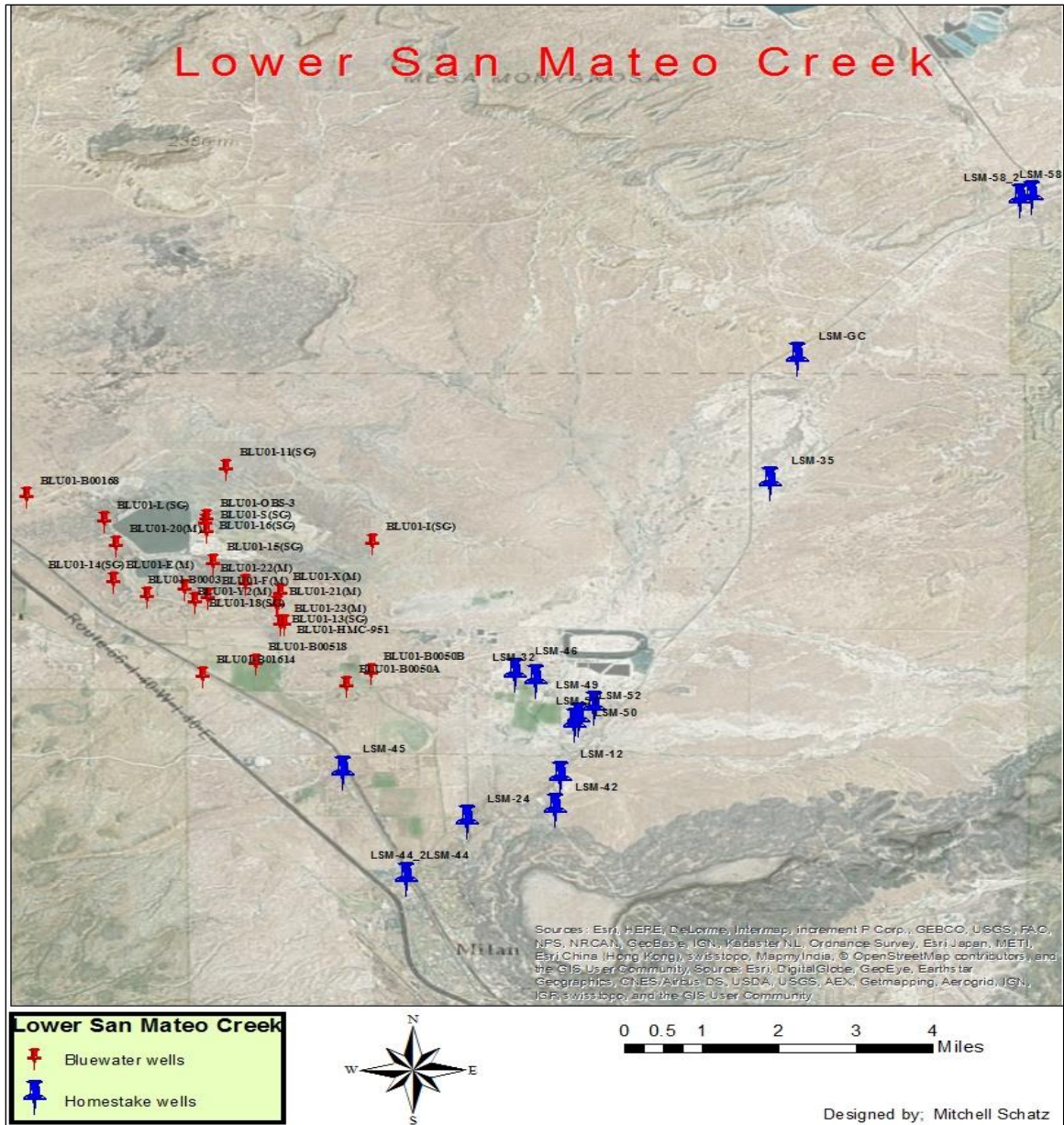


Figure 6 Lower San Mateo Creek Basin. Bluewater and Homestake mills and location of wells used for this study. Red are Bluewater sites collected by DOE and Red are Homestake sites collected by UNM.

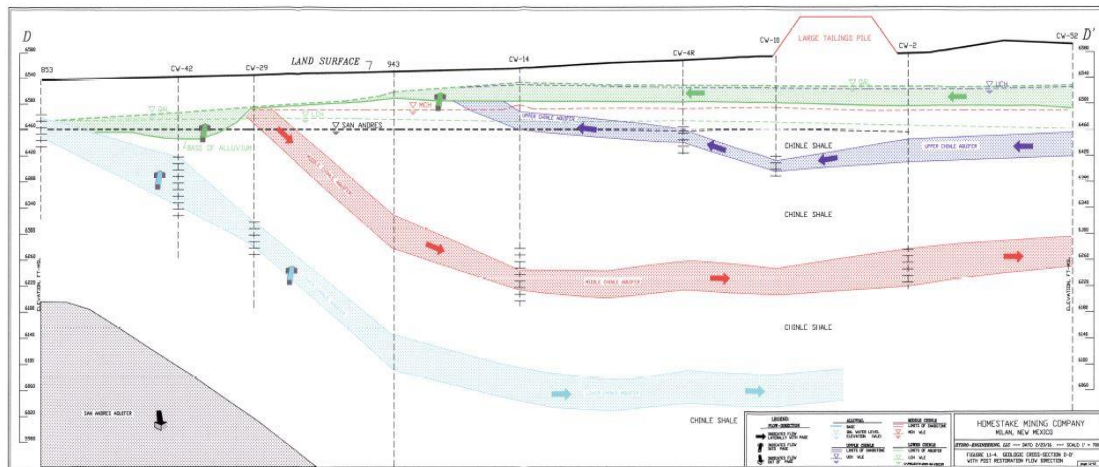


Figure 7 Stratigraphy of the lower San Mateo Creek Basin (NRC 2016).

The surface geology of the area is dominated by alluvium (Figure 8). The alluvium, 40 to 120 feet thick, is north of the HMC site following the path of San Mateo Creek and to the south of Milan, NM. It also extends to the west, passed the Bluewater mill site and a large section to the east. A large area east of the site is covered by a basalt formation. This section is part of the Zuni-Bandera volcanic field. Another surface in the Homestake area is clastic rock formation. Clastic is composed of pre-existing rocks and minerals. There are several major faults along the Zuni Uplift and several minor faults. These faults tend to be reversed and trend towards the northeast of the site (NRC 1993).

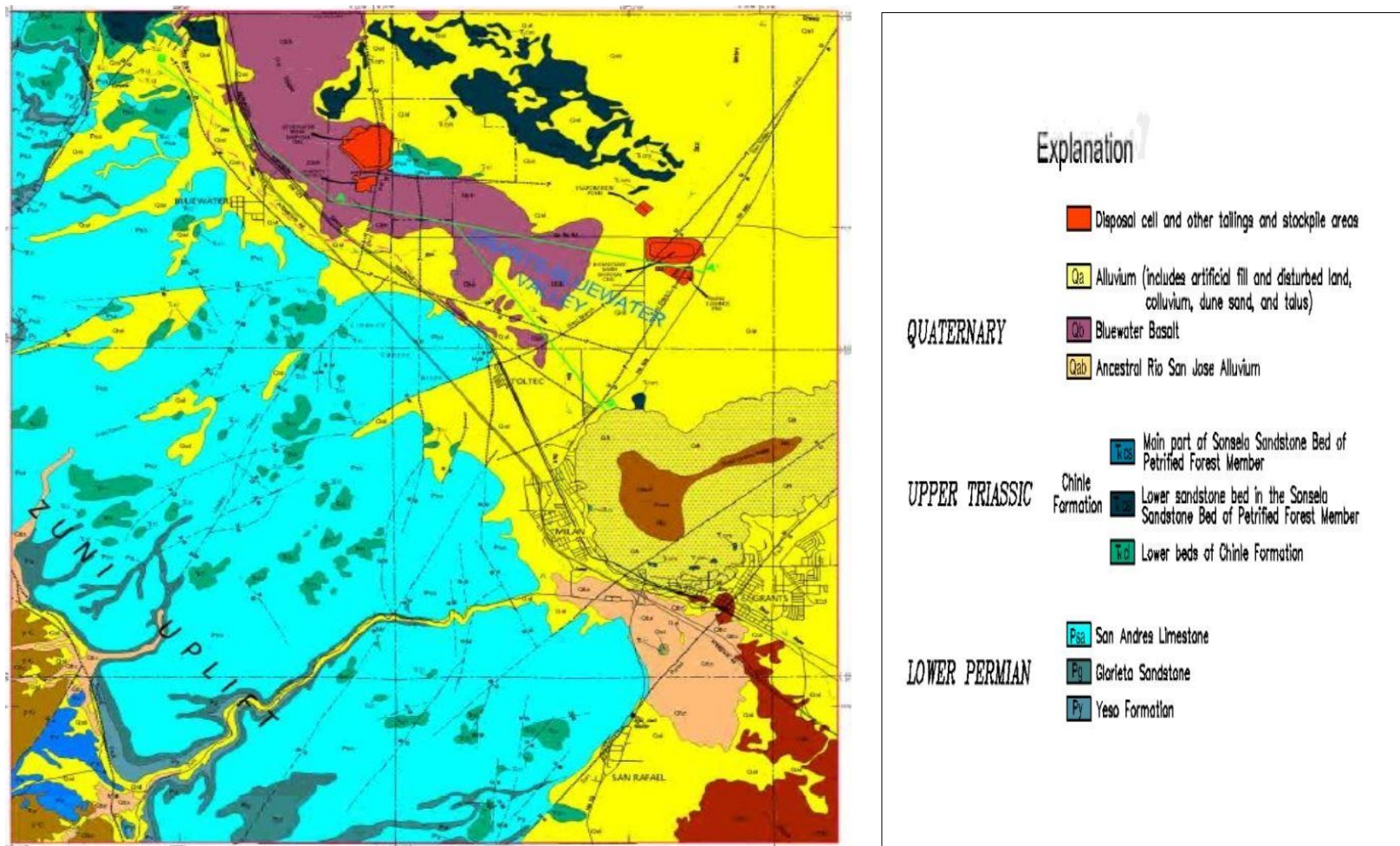


Figure 8 Surface geology of the Lower San Mateo Creek Basin (DOE 2014).

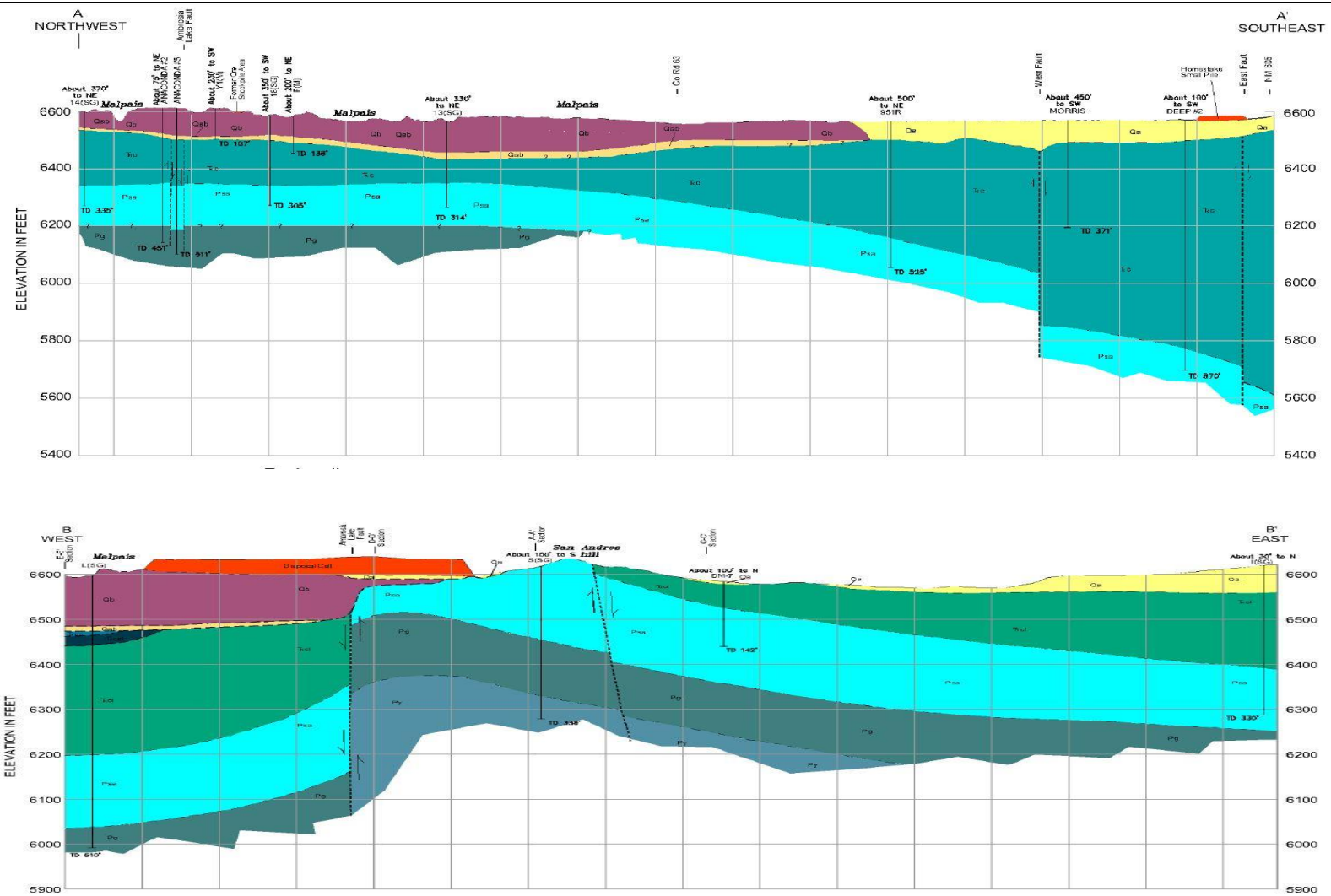


Figure 9 Cross-sections AA' and BB' from Figure 8. Red area represents tailings pile. Homestake is the top figure and Bluewater the bottom (DOE 2014)

The Homestake mill site is located on an alluvial system which trends to the southwest towards the Village of Milan, NM (NRC 1993). The local climate is arid to semi-arid and precipitation is approximately 10 inches per year. The area is dominated by an unconsolidated alluvium and varies in thickness from 60 to 120 feet thick. The alluvial water tables vary in depth from 40 to 60 feet deep (NRC 1993). Alluvial ground water flows from the northeast towards the southwest near the Homestake site and towards the Village of Milan, NM (Figure 10). The Chinle formations underlies the alluvial fill near the Homestake site (Figure 7).

The Chinle Formation is of Jurassic age and underlies the alluvium in the Grants and Milan area. The total thickness of the three Chinle Formations, Upper, Middle, and Lower varies from 60 to 225 feet (Cooper 1967) (Figure 9). The Middle Chinle is the most productive aquifer of the three. The middle portion of the aquifer is made up of grey sandstone, siltstone, and mudstone. Recharge for the Chinle is from precipitation, leakage from the alluvial, or at its outcrops in the mountain. Recharge can also be from the underlying San Andres-Glorieta aquifer when its head is greater than that of the Chinle. The groundwater flow near Homestake is complicated because of the east and west faults under the site. Cross-sections B to B' (Figure 7) show the west and east fault beneath Homestake, and cross-section D to D' represents a sub-surface from south to north through the Homestake site (NRC 2016).

The most productive aquifer in the Grants and Milan region is the San Andres-Glorieta aquifer. The San Andres formation is underlain by the Glorieta formation which are both of Permian age. The two form a single hydrologic system in the area with the

San Andres yielding more water than the Glorieta due to more fractures and solution channels which can serve as conduits for the water (Cooper 1967). The Glorieta and San Andres are naturally recharged at their outcrops on the flanks of the Zuni Mountains. Recharge comes from runoff and infiltration of snowmelt in the spring and precipitation during the summer time monsoon season. Ground water flow for both the alluvial and SAG are shown in Figure 10. Flow direction for SAG, below Bluewater site, travels towards the southeast and near the Homestake site. The alluvial ground water flows towards the southwest (NMED 2010).

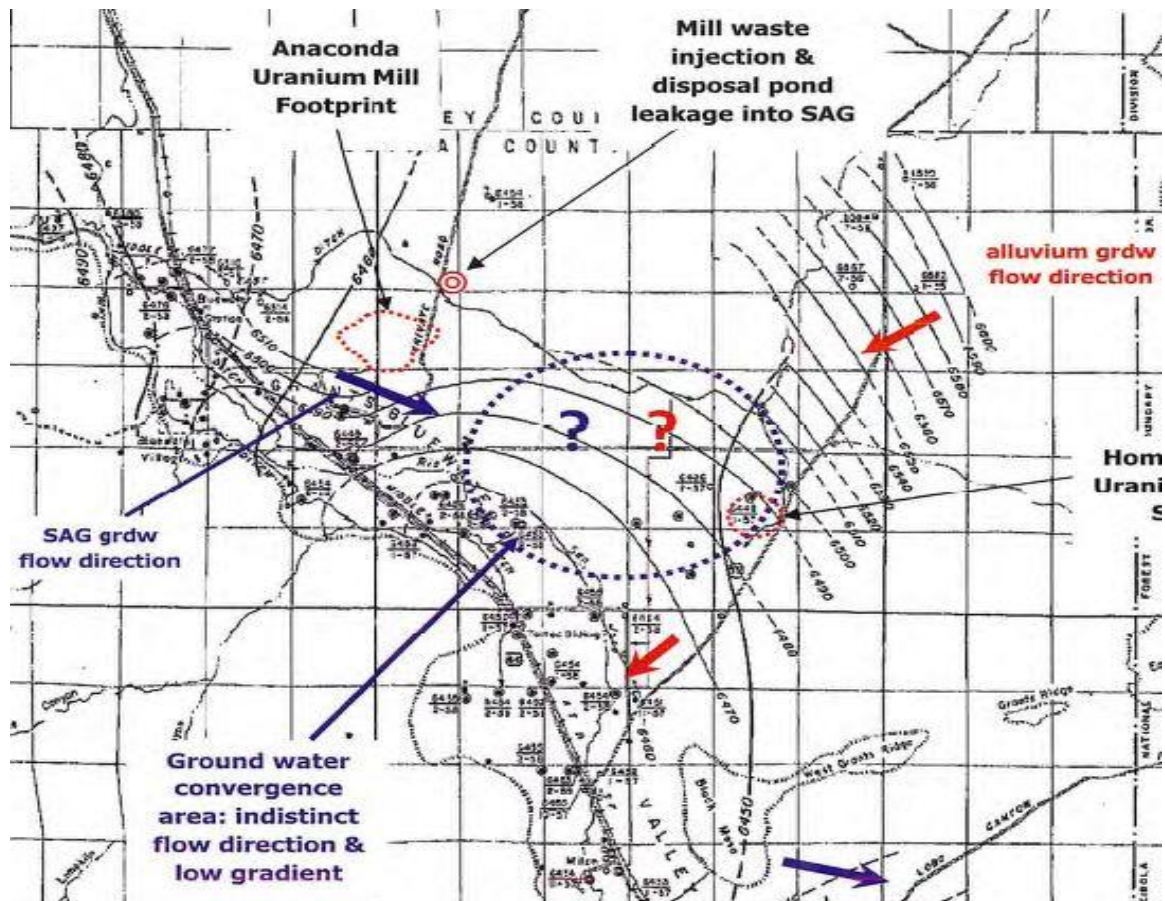


Figure 10 Ground water flow in the Lower San Mateo Creek (NMED 2010). Alluvial groundwater flow indicated by red arrows. Blue arrows indicate SAG ground water contouring with flow traveling in a SE direction.

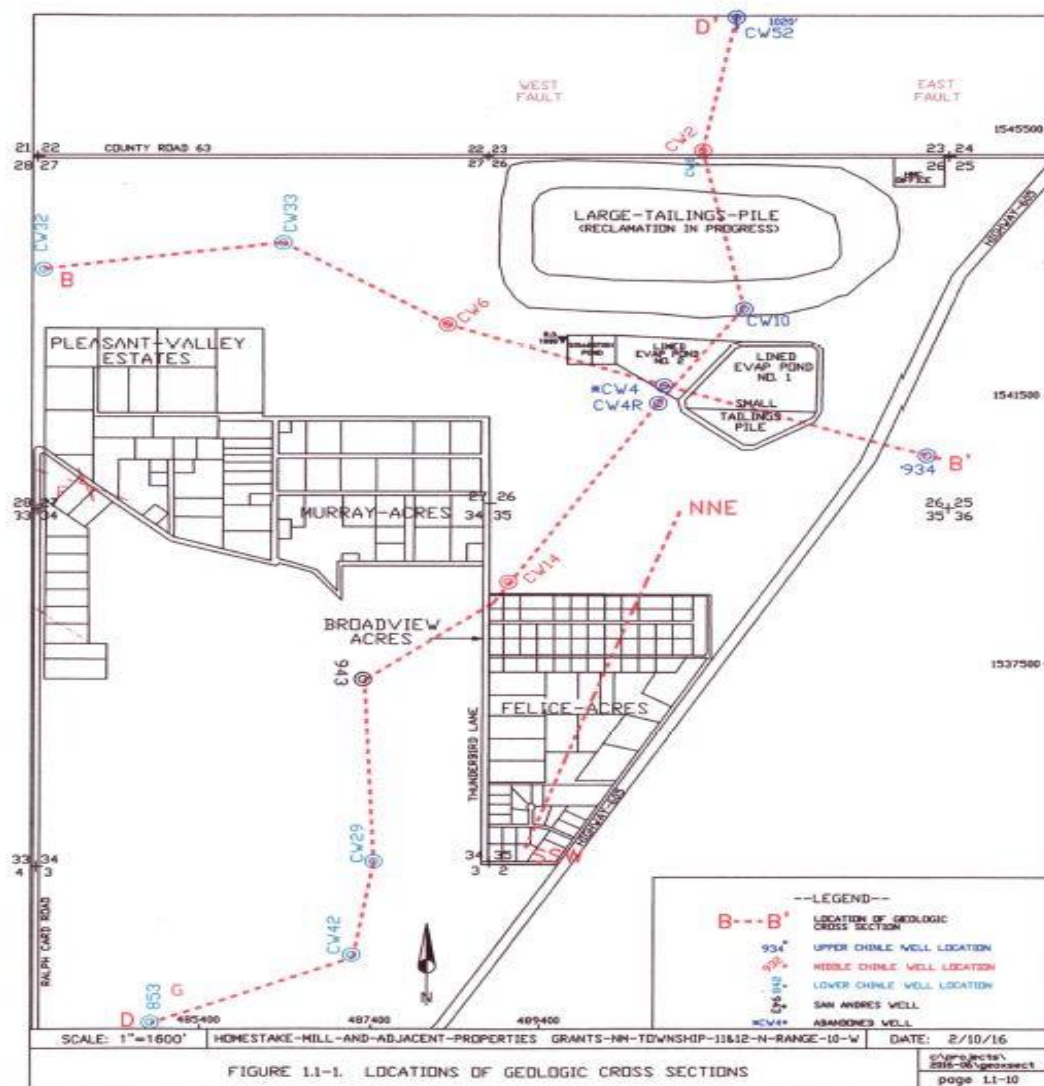


Figure 11 Locations of geologic cross sections near Homestake site (NRC 2016).

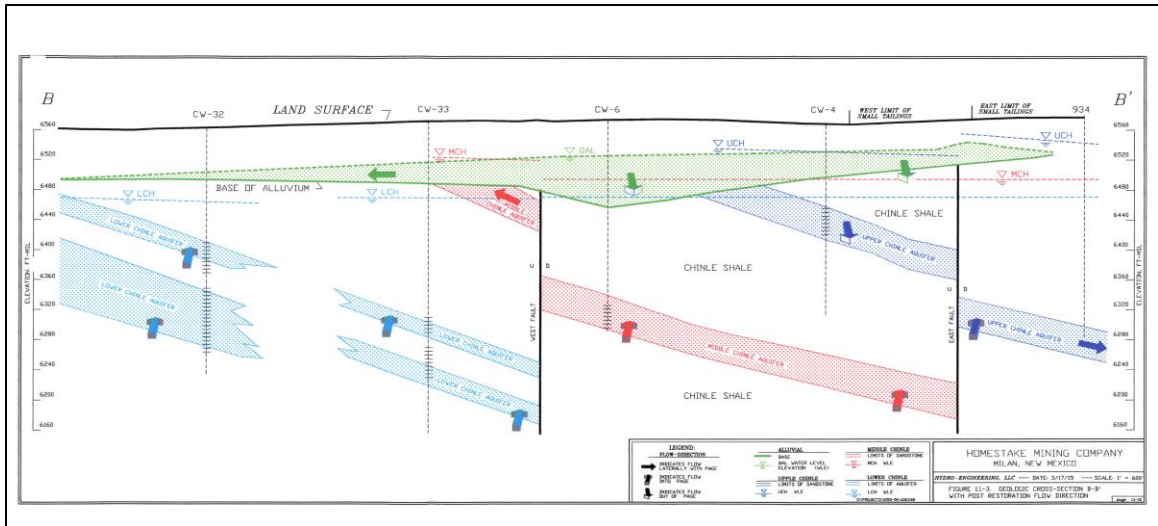


Figure 12 Cross section of Homestake from BB'. Green area represents alluvium, and the blue, red and light-blue represent the upper, middle and lower aquifers, respectively from left to right. Arrows represent ground water flow direction for each aquifer (NRC 2016).

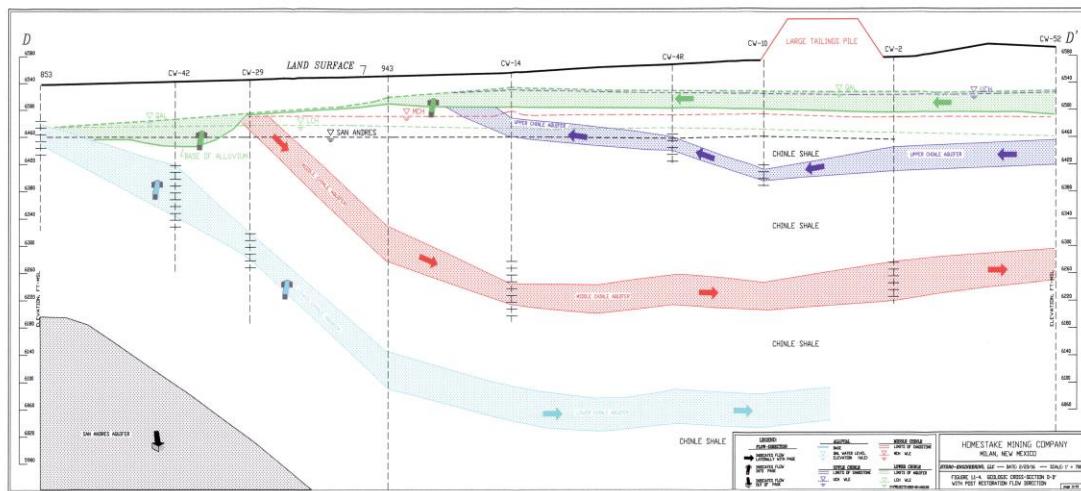


Figure 13 Cross section near Homestake mill from DD' (NRC 2016).

Chapter 3: Methods

Sampling

The NMED sampled 26 wells in the lower San Mateo Creek Basin in the fall of 2014. This study collected ground water from 15 of the 26 wells sampled by NMED (2014) in the fall of 2015 and nine in the spring of 2016. There were 13 residential wells and two public water supply wells which provide water to the Village of Milan. In the spring of 2016, seven of the 15 wells were re-sampled and two other wells not sampled in 2015, LSM-53 and The-Bar, were also sampled. All samples were analyzed for major ions and trace metals. Samples collected in the fall were also analyzed for stable isotopes $^2\text{H}/\text{H}$, $^{18}\text{O}/^{16}\text{O}$, ^{34}S , and $^{234}\text{U}/^{238}\text{U}$, while samples in the spring were analyzed for stable nitrogen isotopes $^{15}\text{N}/^{14}\text{N}$. Samples were only collected from residents with working wells on their property.

All samples were filtered in the field through 0.45 μm in-line filters. Prior to sampling, wells were purged for a minimum of 10 mins. Field parameters, DO, pH, temperature, and conductivity were measured during the purging process until a constant measurement was established. Four ground water samples were collected from each well and stored in Nalgene bottles, (125, 250, and 1000 mL) and a 60 mL glass amber bottle with cone cap. Only the 125 mL sample were preserved to a pH < 2.0 with a concentrated nitric acid. The 1000 mL samples for sulfur isotopes were preserved with approximately 1.0 g of zinc acetate. All samples were kept on ice in the field and refrigerated at the lab until samples were analyzed.

Field parameters, DO, pH, conductivity, and temperature were measured with water quality meters. Total alkalinity was measured at the end of each day in laboratory by titration with sulfuric acid. Anions were analyzed and measured by ion chromatography (IC). Cations were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) (PerkinElmer Optima 5300). Trace metals, beryllium, chromium, lead, molybdenum, selenium, uranium, and vanadium were measured by inductively coupled plasma mass spectroscopy (ICP-MS) (Agilent 7500). All lab analyses were performed at New Mexico Institute of Mining and Technology (NMT) Geochemist/Chemistry Lab.

Isotopic analyses for ^2H , ^{18}O , and $^{234}\text{U}/^{238}\text{U}$ were analyzed at NMT Geology laboratory. Hydrogen isotopic data can be compared to a different standard, but the most common is Vienna-Standard Mean Ocean Water (VSMOW). The delta value for VSMOW is zero. Hydrogen gas (H_2) is used when determining the D/H ratio and the technique is done by equilibration of small sample sizes with gaseous hydrogen gas. Oxygen isotopes were determined by mass-spectrometric measurements. 1000 mL of filtered sample preserved with zinc-acetate were collected for measurement of S isotopes. The samples were transferred to glass beakers in the laboratory and acidified with a sulfate-free HCl acid to a value of $3 < \text{pH} < 4$. The water was heated to approximately 50 °C and then 0.25M BaCl_2 solution was added to samples and let stand for approximately 24 hours to precipitate BaSO_4 . Samples were collected with a pre-weighed 0.45 μm membrane and stored in plastic vials until analyzed. Sulfur isotopic composition was measured by Continuous Flow-Elemental Analysis Isotope-Ratio-Mass Spectrometry (CF-EA-IRMS) in the isotopic lab at the University of New Mexico. Uranium isotopes

were analyzed at NMT Geology lab using an Agilent 7900 ICP-MS mass-spectrometry and reported as delta ^{234}U and ^{238}U . Ground water samples for nitrogen isotope analyses were collected in April 2016. Approximately 100 mL of ground water samples were filtered through a 0.1 μm syringe filter and preserved to $\text{pH} < 2$ with a nitrate-free HCl acid. Samples were packaged and shipped to the IsoLab at the University of Washington in Seattle, WA.

Other Sources of Data

Homestake

Historical water quality data for both mill sites is sporadic and limited to very few reports. All of the data for the Anaconda Bluewater site was retrieved from the Department of Energy's Legacy Management website and NMED studies conducted over the past 10 years. The Bluewater data did not contain a yearly or bi-yearly analysis of ground water constituents and isotopes for the 19 wells and lacked background water-quality conditions prior to the 2000s

Homestake water quality data is limited to EPA, NMED, and NRC annual monitoring reports. Most of the data retrieved from Homestake's Annual Monitoring Reports, issued for the USNRC and NMED, are limited to 10 water-quality standards (Cl, Mo, NO_3 , Se, TDS, SO_4 , V, U, Ra226, + Ra228, and Th230), which are used for Homestake's site standards set by the NMED and NRC. The site standards were reviewed and approved by the EPA, NRC, and NMED and have been in effect since 2008

(GRP 2015). These standards are based on the alluvial background values for each one of the constituents. Table 1 is a list of site standards for both NRC and NMED.

Table 1. Ground water standards for the Homestake mill site (NRC, 2016).

Constituents	Units	NRC Site Standards	NMED Site Standards
Chloride	(mg/L)	250	250
Molybdenum	(mg/L)	0.10	1.0
Nitrate	(mg/L)	12	12
Ra226 + Ra228	(pCi/L)	5	30
Selenium	(mg/L)	0.32	0.32
Sulfate	(mg/L)	1500	1500
Th-230	(pCi/L)	0.3	-----
TDS	(mg/L)	2734	2734
Uranium	(mg/L)	0.16	0.16
Vanadium	(mg/L)	0.02	-----

Background wells for the San Mateo alluvial aquifer are located upgradient of the Homestake site and north of the large tailings pile (LTP). Ground water flow in the alluvial aquifer near the Homestake site flows from northeast to the southwest.

Background water quality has been measured and monitored since 1976 (NRC 2016).

Homestake uses 10 wells to monitor background water-quality, (Figure 14), DD, DD2, P, P1, P2, P3, P4, Q, R, and ND. The wells just north of the LTP are referred to as near up-

gradient wells. There are an additional five wells further away from the site that are referred to as far up-gradient wells, 914, 920, 921, 922, and 950 (Figure 14). Water-quality constituents measured for near and far up-gradient wells are Cl, Mo, NO₃, SO₄, Se, TDS, and U. Point of compliance (POC) wells, D1 and S4 are located west and south of LTP and well X is south of the Small tailings pile (Figure 14). These wells are used for monitoring water-quality site standards for alluvial aquifer.

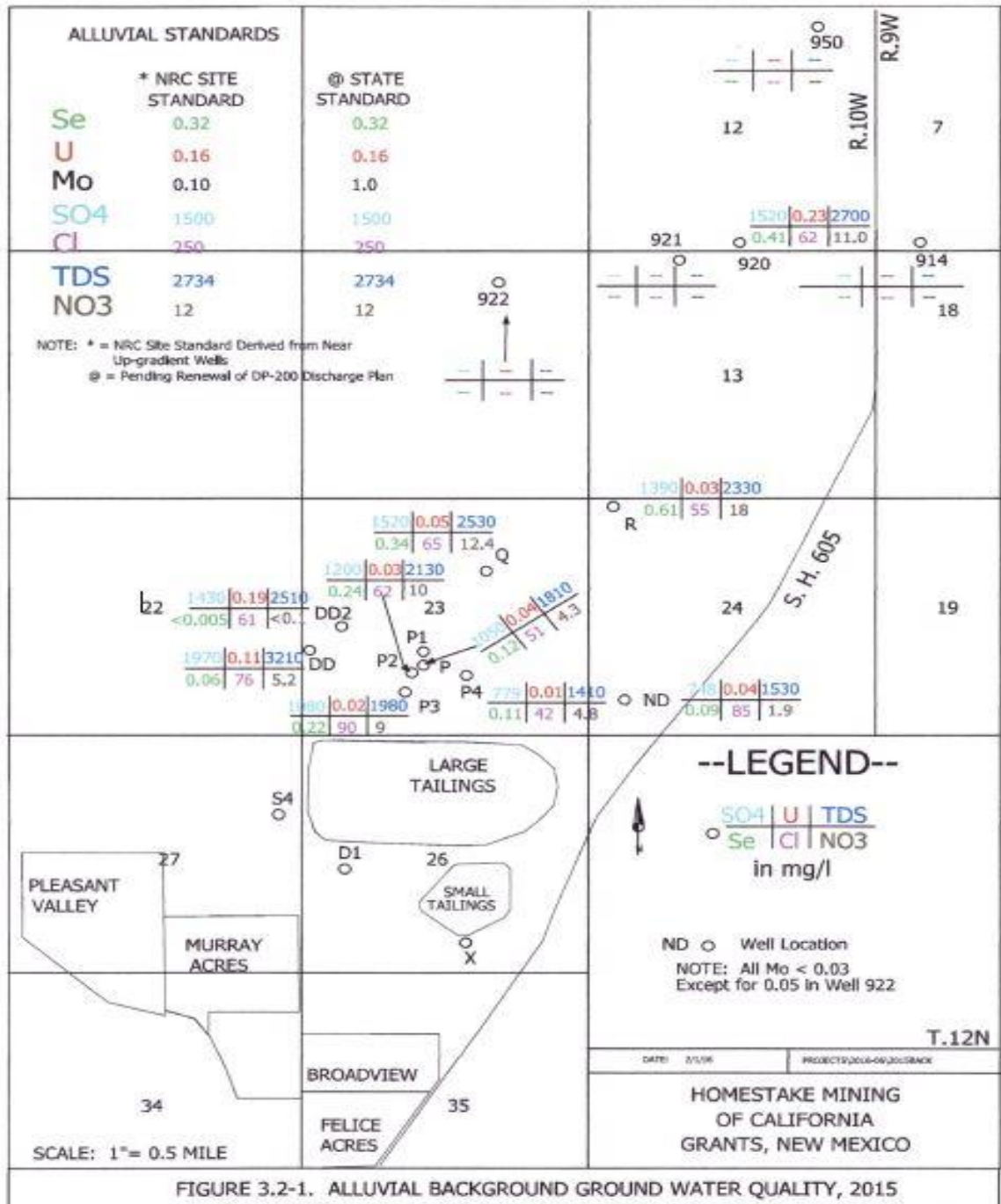


Figure 14 Location of up-gradient monitoring wells at the Homestake site and background water quality data (NRC 2016).

The NRC and NMED have established water-quality standards for the Chinle aquifer at the Homestake site for eight parameters (Cl, Mo, NO₃, Se, SO₄, TDS, U, and V). These site standards are based on background concentrations sampled from near up-gradient wells within the Chinle aquifer. There are four Chinle aquifer zones, Chinle mixing, upper Chinle non-mixing, middle non-mixing, and lower non-mixing Figure 8. Each zone has a site standard set by EPA, NRC, and NMED (Table 2).

The mixing zone is the area where the alluvial water has entered the Chinle aquifer and changes the type of water in the mixing zone (NRC 2016). This zone is similar to alluvial aquifer water which has higher concentrations of calcium. The Chinle formation has the ability to change the water chemistry as it moves further into the non-mixing Chinle zones (NRC 2016).

Table 2. Ground water standards for the Homestake site (NRC, 2016).

Constituent (mg/L)	Aquifer Zone			
	Chinle Mixing	Chinle upper non-mixing	Chinle middle non- mixing	Chinle lower non-mixing
Chloride	250	412	250	634
Molybdenum	0.10	0.10	0.10	0.10
Nitrate	15	*	*	*
Selenium	0.14	0.06	0.07	0.32
Sulfate	1750	914	857	2000
TDS	3140	2030	1560	4140
Uranium	0.18	0.09	0.07	0.03
Vanadium	0.01	0.01	*	*

* Water quality standard for background were not necessary for these zones.

The Chinle aquifers had a total of 24 wells used to establish background levels and to determine site standards for each aquifer. The mixing zone has 10 wells, CW9, CW50, CW52, CW15, CW24, CW35, CW36, CW37, CW39, AND CW43. Upper, middle, and lower zone wells are; 931, 934, and CW18; ACW, CW1, CW2, CW28, and WCW; CW26, CW29, CW31, CW32, CW33, and CW41, respectively (Figure 10).

Anaconda Bluewater Mill Site

Water quality information for the Bluewater site was obtained from NMED and DOE. New Mexico Environmental Department performed a site investigation for the

Bluewater site in 2008 and San Mateo Creek Basin in 2009 (NMED 2010). Data for Bluewater was retrieved from DOE Legacy Management website. There were 19 wells sampled from two different aquifers used for this study from the DOE LM site (Figure 15). Sampling from the spring of 2014 is used for this study because of the number of water quality parameters, including ^2H , ^{18}O , ^{34}S , and $^{234}\text{U}/^{238}\text{U}$ isotopes.

Five of the 19 wells, F(M), Y2(M), OBS-3, S(SG), and 16(SG), used in this study are for Bluewater's point of compliance (POC). M represents alluvial formation and SG represents the San Andres-Glorieta. Point of compliance wells are used for monitoring ground water quality for specific levels of contaminants, known as alternative concentration levels (ACL). These wells are monitored by DOE for molybdenum, selenium, and uranium (McHaley 2015) for both aquifers in the Bluewater area. There are two wells, E(M) and L(SG), that have been designated to represent background wells. Figure 16 shows the location of wells for both Bluewater and Homestake site in the lower San Mateo Creek Basin. EPA and NMED have collected data from other sites near Homestake, but only the wells sampled by UNM in the fall 2015 and spring 2016 were mapped on Figure 16.

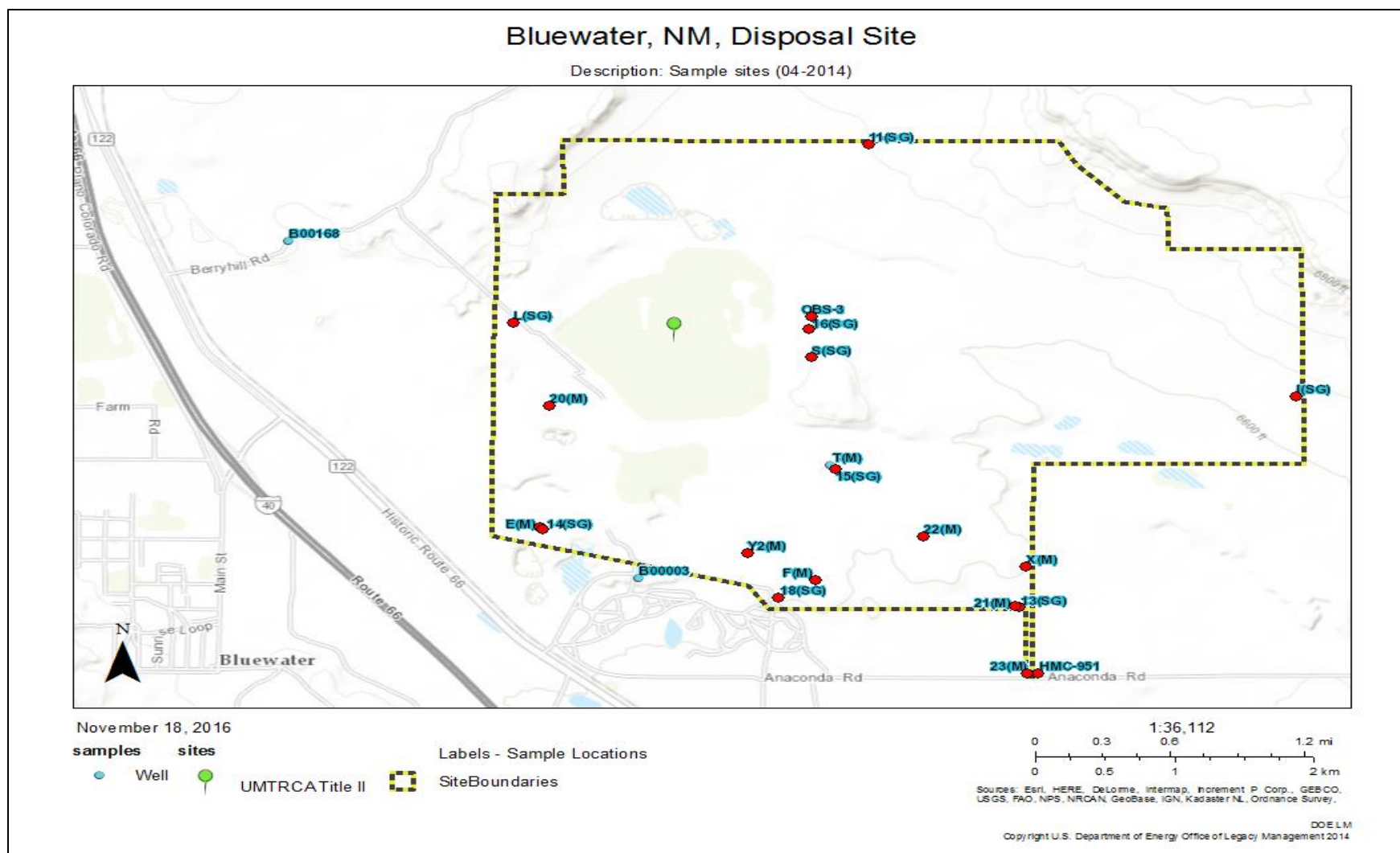


Figure 15 Monitoring well locations at the Bluewater mill site (DOE LM 2016).

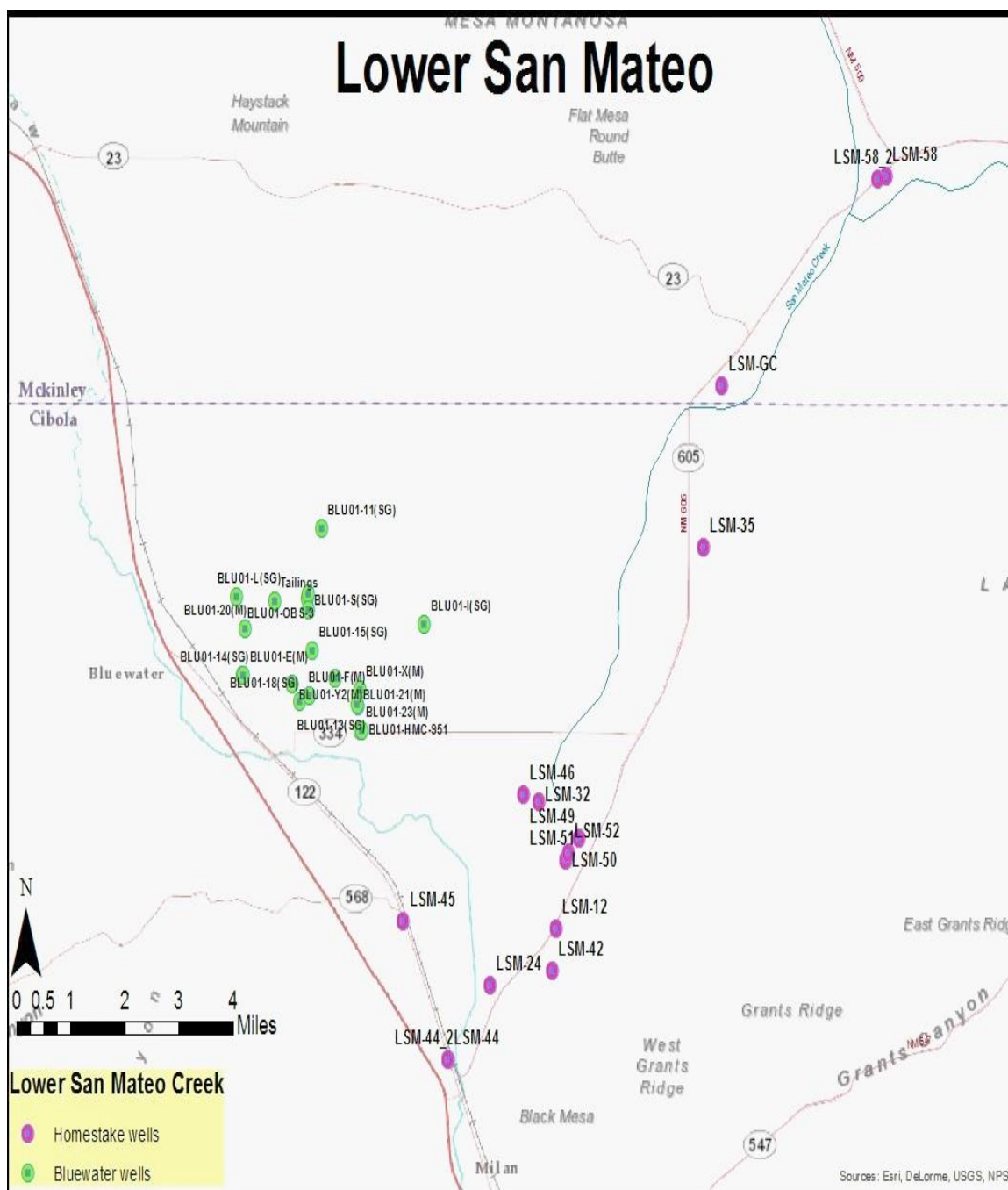


Figure 16 Location of monitoring wells at the Bluewater mill site (green) and private wells sampled for this project at the Homestake mill site (magenta).

Data Analysis

The following water quality parameters were chosen for analysis based on previous studies: U, Se, Cl, NO₃, SO₄, HCO₃, Ca, Na, K, and Mg. Each data set consists of 34 well location samples from the two study areas, Bluewater and Homestake, in Figure 9. The major ion chemistry was summarized through use of a trilinear diagram. This was calculated and plotted using USGS GW Chart version 1.29.0.0 (USGS 2015). The data is separated by cations and ions and plotted on two separate ternary plots. The two ternary plots are then projected onto a diamond. The diamond represents a graph of anions and cations on one graph.

Relationships between various chemical and isotopic constituents were explored by plotting selected parameters against one another. Statistical correlations were determined by linear regression analysis. Of particular interest were relationships between constituents known to be present at high concentrations in U mill leachates. Pearson's *r* correlation was used in this study for statistical analysis. This analysis is used to indicate if there is a positive or negative relationship between two variables. These values are always between -1 and 1, and the closer they are to -1 or 1 the stronger the relationship of the two variables. There are several values that are important and should be considered in these types of analyses. Values from +0.5 to 1 and -0.5 to -1 indicate a moderate to strong positive or negative relationship between the variables. Numbers that do not fit into these two categories indicate a very weak relationship between the two variables.

Chapter 4: Results

Sixteen samples were collected from privately-owned wells in September 2015, and nine in April 2016. The results are presented in sections throughout this chapter. The concentrations of all water quality data are available in a separate table in the Appendix. Data for Bluewater was retrieved from DOE's LM website because of the quantity of parameters analyzed, results are from April 2014. Results for general chemistry and isotopes for Lower San Mateo (LSM) wells are from September 2015. The nitrogen isotope analyses are from April 2016 well sampling.

Major Ion Chemistry

Concentrations of SO_4 near the Homestake site ranged from 107 to 1930 mg/L. Wells LSM-GC, LSM-52, and LSM-58 (#2) had the highest values of sulfate, 1150, 1930, and 2040 mg/L, respectively. Wells LSM-GC and LSM-52 (#2) are north of the site near the SR 509 and SR 605. Well LSM-52 is just south of Homestake. Two wells near Bluewater had SO_4 concentrations above 1000mg/L, 15(SG) and S(SG) with values of 1910 and 1290 mg/L, respectively. Wells F(M) and X(M) had the lowest concentrations of SO_4 , 109 and 104 mg/L, respectively. Background SO_4 concentrations for the near up-gradient wells (site standards) for Homestake (Figure) ranged from 748 to 1970 mg/L, while only one of the far up-gradient wells were sampled in 2015, well 920, had a concentration of 1520 mg/L. Concentrations of NO_3 were highest for wells LSM-58 (#2), 16.2 mg/L and 22(M), 36.0 mg/L. A sample collected by HMC from the

Homestake near up-gradient well R had highest concentration of 18.0 mg/L, exceeding site standard values of 12.0 mg/L. The HMC site standards for selenium is 0.32 mg/L in the lower Chinle non-mixing zone. The highest concentration of Se downgradient from the HMC was well LSM-52, 0.182 mg/L. The highest concentration for both sites, except LSM-52, was 0.0210 mg/L, well below HMC site standards of 0.32 mg/L. Major ions, Ca, Mg, Na, K, HCO_3 , Cl, SO_4^{2-} , and NO_3^- (Appendix) varied throughout the study area. Bluewater aquifers, alluvial and SAG, showed similar results of cations and anions equivalents. Cations were dominated by Ca and Na and anions by HCO_3 and SO_4 . This was also true for wells in the alluvial and Chinle aquifers near the Homestake site. Both of the alluvial aquifers had lower concentrations of ions than the underlying Chinle and SAG aquifers. Figure 17 shows major ions distribution in ground water near both sites.

Bluewater ground water results (Figure 17) show a closer relationship (tighter grouping) between the two aquifers than the ground water in wells near Homestake. While the wells near Homestake were sampled in four different aquifers, alluvial, Chinle, SAG, and unknown, there was not as close of a relationship between the wells or aquifers. These results may indicate that mixing between the aquifers near Bluewater is more evident than those near the Homestake site.

Uranium and Other Chemical Constituents

Mill tailings leachates have high concentrations of other chemicals associated with uranium. Selenium, molybdenum, and vanadium have been measured at high concentrations in tailing samples (NRC 2016). The concentrations of these metals are presented in Figures 18 and 19. Vanadium concentrations were not available for Bluewater's 19 sites used in this study. Homestake did have measurable concentrations of vanadium and are presented in Figure 19. Figure 18 shows the results for 18 out of 19 wells for the Bluewater site. Well 16(SG) was not plotted because of the extremely high level of uranium concentration when compared to the second highest concentration of uranium, 15(SG), and is an outlier when compared to the other 18 wells. There were 11 wells that had concentrations of uranium higher than EPA's maximum contamination level (MCL), 30 µg/L, for public drinking water systems. Concentrations of Se were well below the MCL of 50 µg/L in all of the 19 wells at Bluewater. There are no MCLs or secondary standards for V and Mo in public drinking water systems (EPA 2016). The majority of the wells at Bluewater had concentrations of Mo < 5 µg/L with the highest at 7.94 µg/L, well 15(SG). The highest concentrations of selenium were wells 18(SG), 21(M) and S(SG), 17.1, 12.1 and 12.2 µg/L, respectively.

Figure 19 is a bar graph of the concentrations of U, Se, Mo, and V for wells near the Homestake site. Four of the sites, LSM-49, LSM-50, LSM-51, and LSM-52, had concentrations of uranium 70.8, 141, 86.7, and 146 µg/L, respectively. The two up-gradient wells had high concentrations of uranium, LSM-58, and LSM-58 #2 at 22.9 and 27.9 µg/L, respectively. Well LSM-52 had the highest value of Se, 182 µg/L. Molybdenum and vanadium concentrations were highest for well LSM-12, 14.1 and 7.94, respectively.

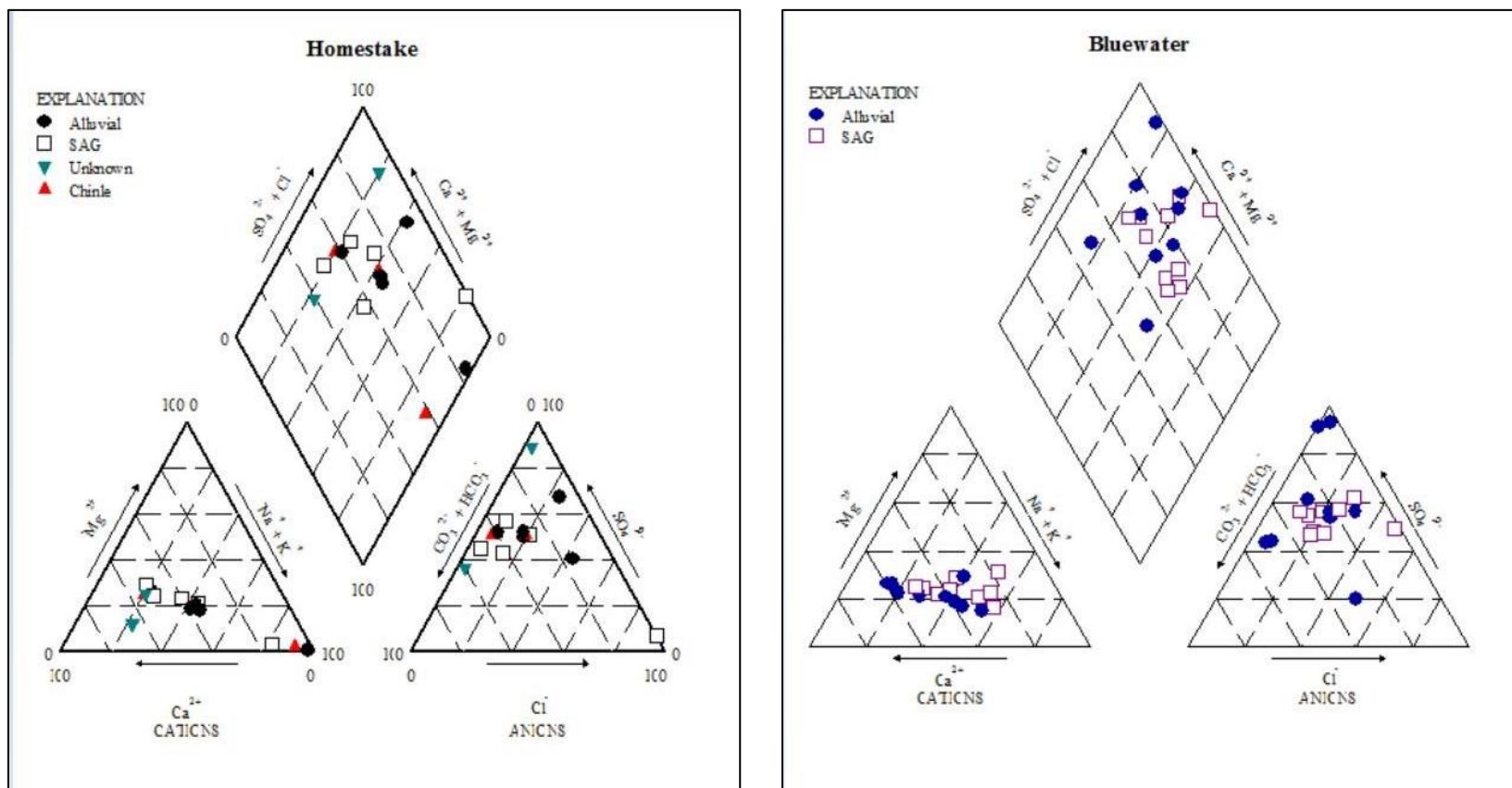


Figure 17 Trilinear diagrams summarizing the major ion chemistry for the Homestake wells (left) and Bluewater wells (right).

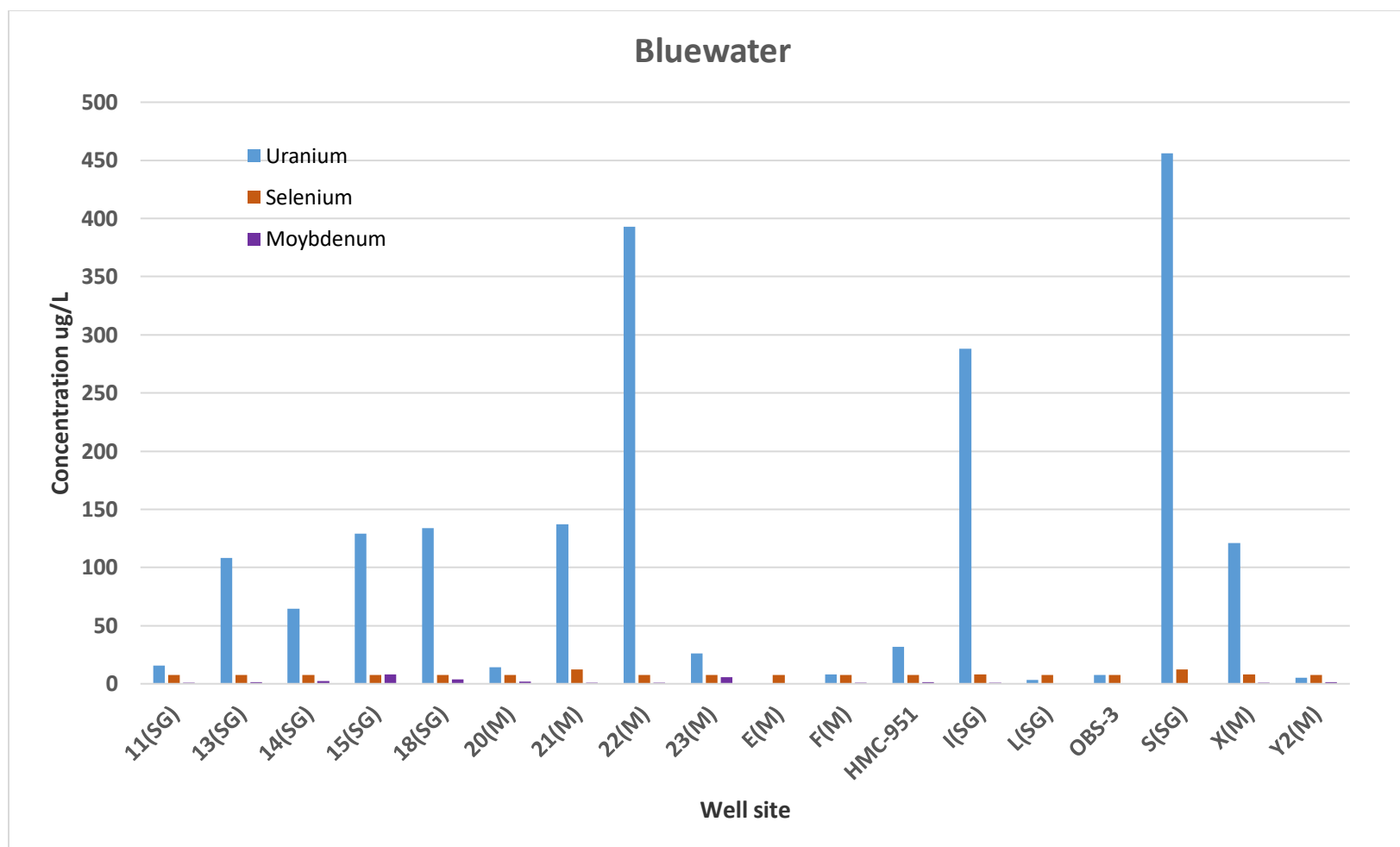


Figure 18 Concentrations of U, Se, and Mo at the Bluewater site (DOE LM 2016).

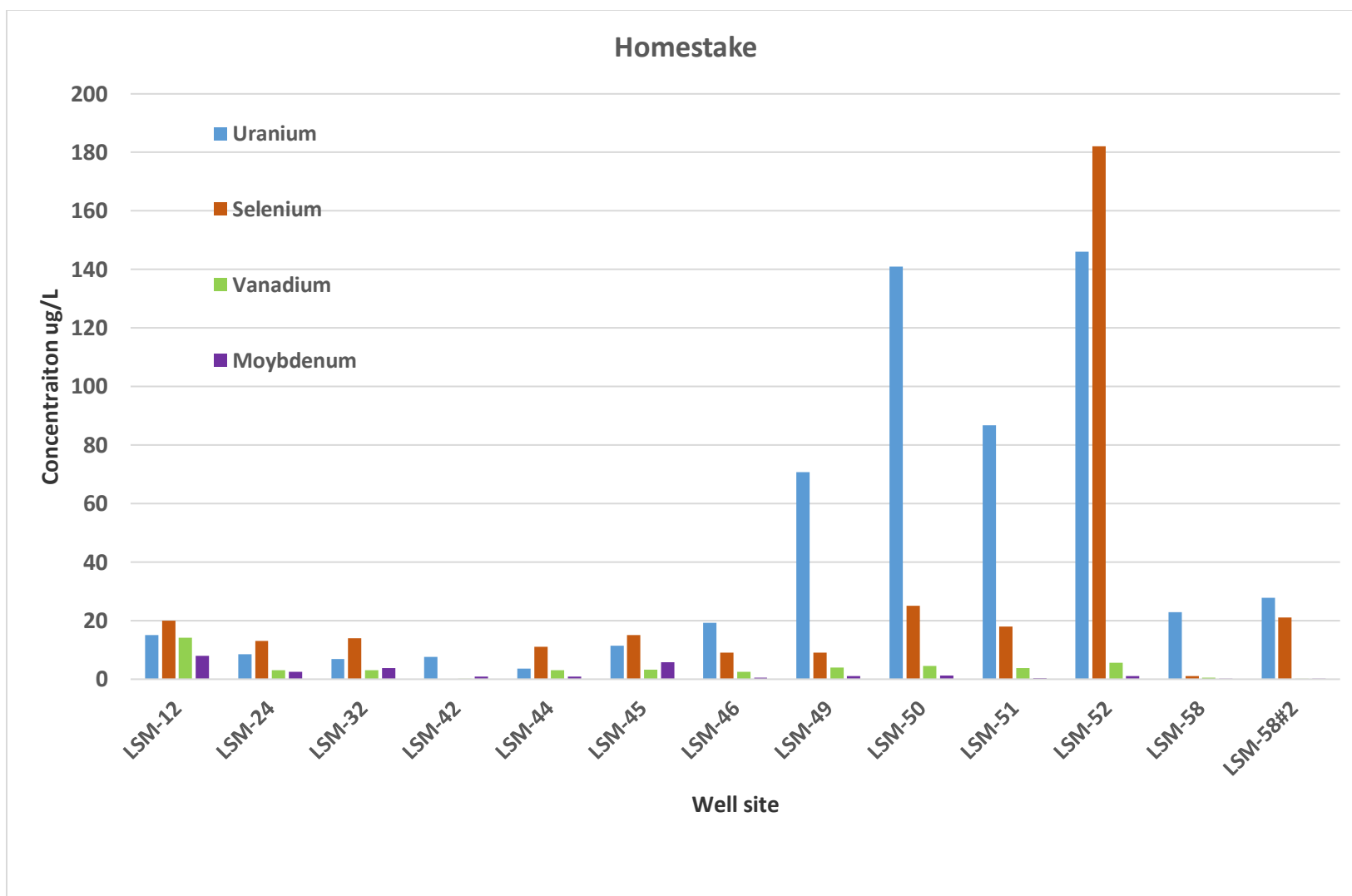


Figure 19 Concentrations for U, Se, V, and Mo near the Homestake site.

Isotopes

Nitrogen-15 isotopic analyses

The Pearson's Correlation Coefficient (r) test concluded the association between nitrate and nitrogen ^{15}N isotope concentrations for samples near Homestake mill were statistically significant and have a positive relationship (Figure 20). Nitrogen ^{15}N isotopes in ground water were sampled in April 2016. There were nine wells sampled for nitrogen isotopes, LSM-24, LSM-49, LSM-50, LSM-51, LSM-52, LSM-53(well), LSM-53(Milan), LSM-58, LSM-58(#2), and The-BAR (Figure 20). Nitrogen isotope $\delta^{15}\text{N}$ had values ranging from 6.71 to 19.2‰, with the highest values from The-BAR and LSM-58(#2) at 19.2‰ and 18.5‰. Wells LSM-49 to LSM-52 had an average value of 10.5‰. Nitrogen isotopes have been used in environmental studies to show the main source of nitrate in the hydrosphere (Hoefs 2004). There is wide range of values used to show the source of NO_3 : Atmosphere $\sim 0\text{‰}$, Ocean waters ~ -4 to 13‰ , Anthropogenic fertilizers ~ -4 to 4‰ values reflect atmospheric source of nitrogen, sediments ~ 0 to 10‰ , and animal waste $> 5\text{‰}$. Figure 10 shows the positive relationship between nitrate concentrations and $\delta^{15}\text{N}$ values. The nitrogen isotope values $> 5\text{‰}$ are most representative of sediments and animal waste (Hoefs 2004).

The higher values of $\delta^{15}\text{N}$ could indicate a correlation between mill derived NO_3 and higher ^{15}N isotope values. Homestake used an alkaline leach in their extraction process, which did not include the use amine or ammonia (Figure 5). This resulted in low concentrations of NH_3 in the tailings, averaging 16 mg/L in the alkaline leach tailings compared to 400 mg/L in acid leach tailings (Thomson and Heggen, 1981).

Consequently, NO_3^- concentrations in ground water near the Homestake tailings pile are also low compared to those near the Bluewater pile. The high ^{15}N values from the two up-gradient wells, LSM-58 #2 and The-Bar, may indicate that an acid leach uranium extraction process that used amines in the extraction process could add to the NO_3 concentration in the ground water and eventually over time increasing ^{15}N isotope values, too. The relationship between N concentrations and $^{15}\text{N}\%$ is positive and had a Pearson's r value of 0.900, meaning there is a strong correlation between the two.

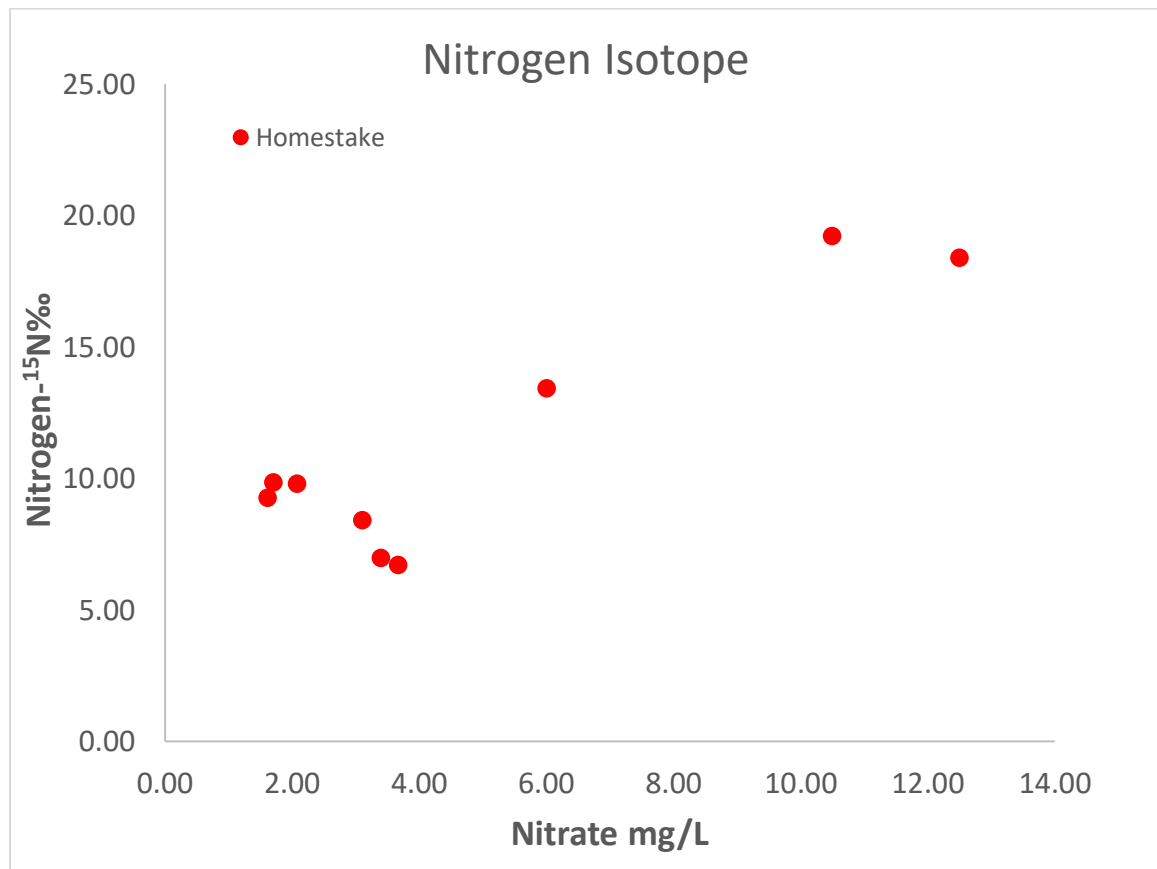


Figure 20 Relationship of Nitrate to Nitrogen- $\delta^{15}\text{N}$ isotopes near Homestake site

Sulfur-34 isotopic analyses

For this study we see a wider range of $\delta^{34}\text{S}$ values – 13.1 to +14.47‰ for samples near Homestake than Bluewater +0.3 to +15.41‰. Statistical analyses for both sites using Pearson's Correlation Coefficient test determined the relationship between SO_4 and ^{34}S isotopes were not statistically significant and had very weak negative relationship. Sulfate in ground water samples for both Bluewater and Homestake had $\delta^{34}\text{S}$ values ranging from -13.1 to 15.4‰. Bluewater data from November 2014 had no values less than 0.0‰. There were four sites in the Homestake area that had depleted values less than -8‰. The wells with depleted values < -8.7 were near SR 509 and SR 605, up-gradient from the Homestake site. Studies have shown a wide range of sulfur isotope ratios have measured $\delta^{34}\text{S}$ values greater than 120‰ (Hoefs 2004). Metamorphic and sedimentary rocks have isotopic values from -20 to +20‰ and -50 to +50‰, respectively. Kamp and Morrison (20014) reported a range of $\delta^{34}\text{S}$ values characteristic of uranium milling operations. They used the values from three different uranium mill sites, Ambrosia Lake sub district, NM (5.8‰ and -1.9 to 6.0‰), Tuba City, AZ (-1.43‰), and Blanding, CO (-1.04, -0.93, and -0.89‰). Kamp and Morrison suggest that sulfur isotopes from uranium milling is between -5 to +5‰. For this study we see a wider range of $\delta^{34}\text{S}$ values – 13.1 to +14.47 which are more in the metamorphic and sedimentary rock ranges.

Sulfuric acid was used at the Bluewater mill. Although Homestake mill was the only mill to use an alkaline leach in its milling process, a small amount of sulfuric acid was needed during the dissolution part of the milling process (Figure 5). Site standards for sulfate concentrations at Homestake mill are set at 1500 mg/L and near up-gradient

samples had a range of 748 to 1970 mg/L. Well E(M) is the designated background well for Bluewater alluvial aquifer and had a sulfate concentration of 795 mg/L. The relationship between sulfate and sulfur $\delta^{34}\text{S}$ is weak and had a Pearson's r value of -0.197, meaning there is weak negative relationship between the two.

Deuterium (H-2) and Oxygen-18

The isotopes show a closer relationship to the Albuquerque Meteoric Water Line, which is more relevant because the climate and weather patterns of Albuquerque and the Grants Mineral Belt area are similar. Isotopic values for deuterium (D) and ^{18}O are shown in Figure 21. The average values for hydrogen and oxygen isotopes near Homestake were -77.2 and -10.3‰, respectively. Bluewater well samples had average values higher for hydrogen and oxygen isotopes at -75.3 and -9.50‰, respectively. Figure 21 shows a linear relationship between the two isotopes and samples plot below the Global Meteoric Water Line (GMWL) developed by Craig (1961).

Uranium-234 and U-238

The results for $^{234}\text{U}/^{238}\text{U}$ isotope analyses showed U AR values near 1 had a negative relationship to elevated U concentrations $> 0.30 \mu\text{g/L}$ for both Bluewater and Homestake samples. Uranium analyses for ^{234}U and ^{238}U were collected from the DOE LM website for April 2014 and samples for the wells near Homestake were analyzed for ^{234}U and ^{238}U for September 2015 sampling. There were a total of 34 sites used for this study, but because some of the sites U isotope values were below the detection limit, they were not used when plotting them against other chemicals used for this study, Mo, Se, U, and V. Wells E(M), LSM-GC, and LSM-35 had AR values of zero because of their low uranium concentrations, and for this they were not plotted in Figure 22. Samples from

the Bluewater monitoring wells showed a high percentage of wells (13) with AR values between 1.00 and 1.26. Homestake ground water samples had three wells with AR values < 1.18 and one with AR value of 1.36. Activity ratio values near 1 suggest that the dissolved U originated from a milling process as natural leaching of undisturbed U minerals have higher ARs (Kamp & Morrison 2014). AR values were also plotted against Mo (Figure 23) and V, but did not show much correlation between U AR values and their concentrations, low Pearson's r values.

Water Quality vs. Distance from Large Tailings

Uranium concentrations used with other chemical and isotopes signatures are a way of determining if leaching from tailings have impacted local ground water near these former milling sites. This study also measured the distance from the large tailings and compared that to the uranium concentrations near each site (Figure 24). Distance from the Bluewater site is much closer than the wells near Homestake. The distance for Bluewater range from 0.8 – 3.7 miles, while wells near Homestake range from 1.5 – 13.5 miles. There appears to be no relationship between distance and U concentrations for Bluewater, Pearson's r value, -0.24. Wells near Homestake show a tight grouping of wells, LSM-49, LSM-50, LSM-51, and LSM-52, that are within 2.14 miles and have concentrations of U > 30.0 µg/L. There was weak negative correlation for wells near Homestake, Pearson's value -0.385, but a tight grouping for the sites that exceeded uranium concentrations > MCLs. Both sites had negative correlations between distance and U concentrations, but wells near Homestake showed a tighter grouping for higher concentrations of U.

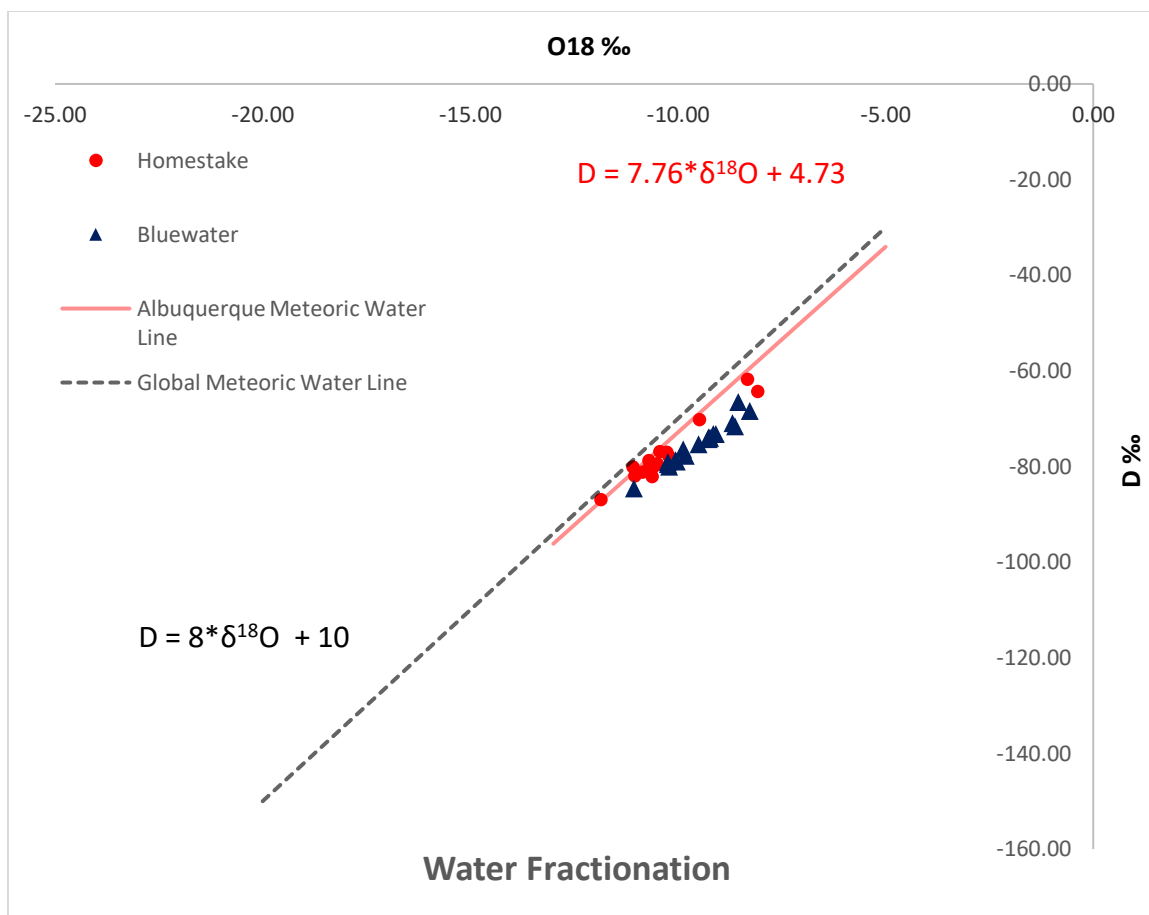


Figure 21 Hydrogen and Oxygen Isotopes for Bluewater Mill and Homestake Mill Ground Water Samples. The GMWL is representative of a global average and AMWL represents the isotope ratios of the Albuquerque, NM, region.

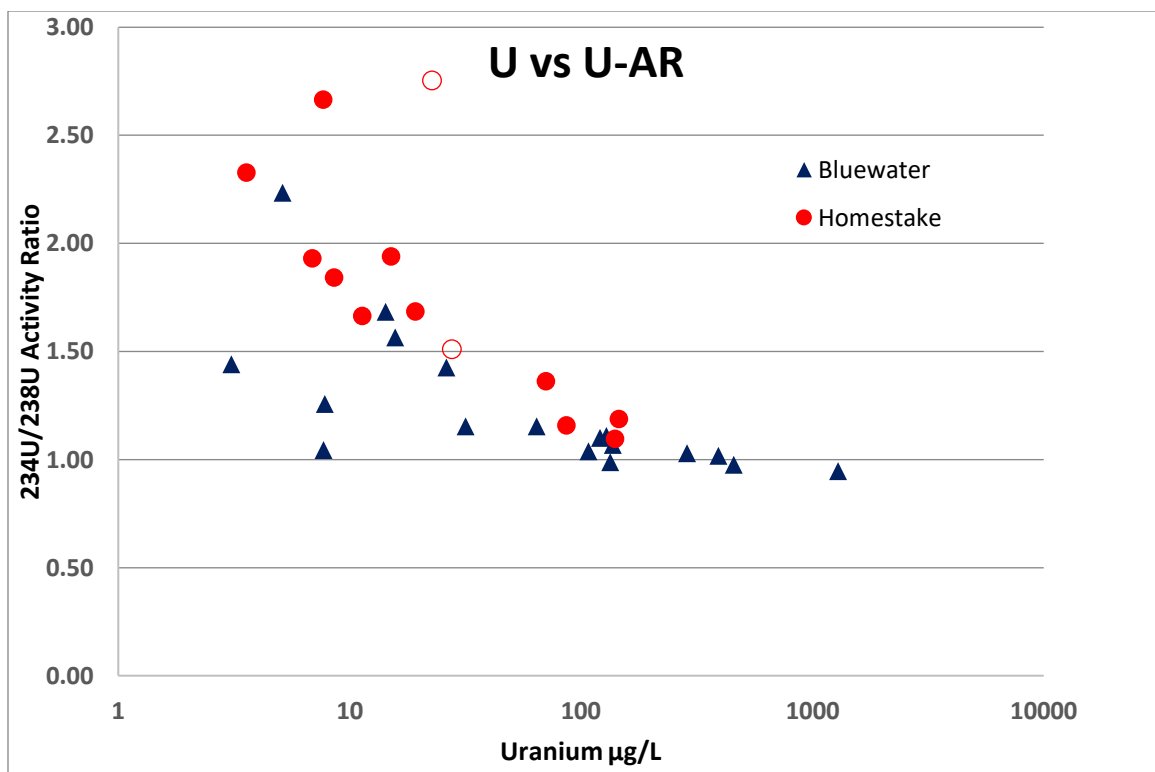


Figure 22 Uranium and activity ratio results for Bluewater and Homestake.

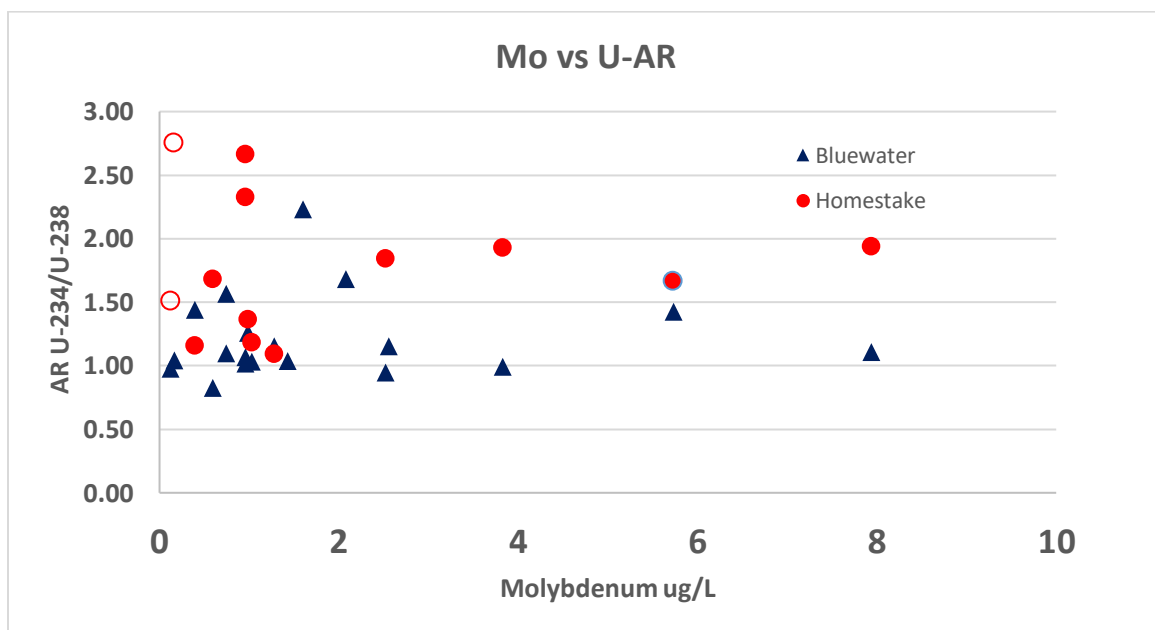


Figure 23 Molybdenum and U activity ratios. Open circles represent up-gradient wells near Homestake.

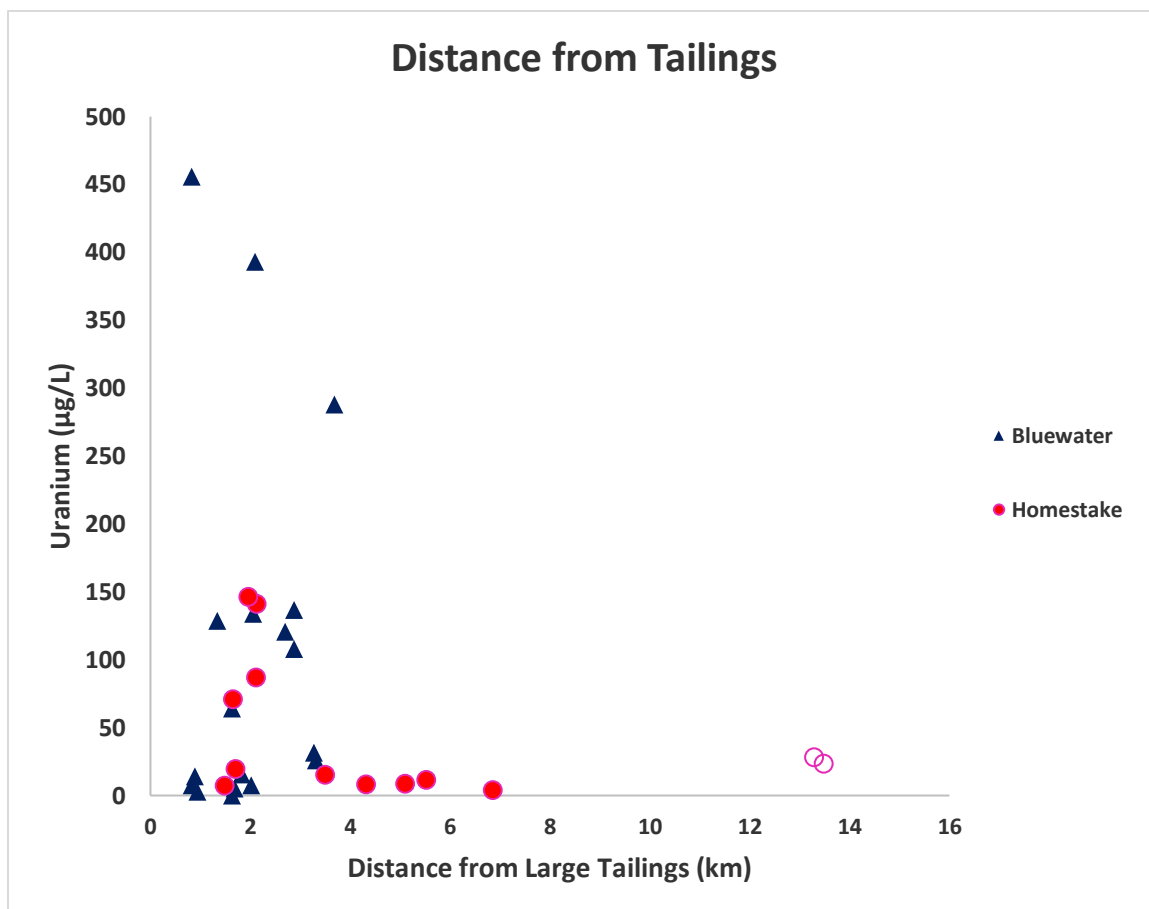


Figure 24 Uranium vs distance from large tailings pile. Uranium vs distance from large tailings pile. Bluewater (blue triangles), Homestake (red circles), and Homestake up-gradient from site (red open circles).

Chapter 5: Discussion

The Lower San Mateo Creek Basin is home to two former uranium mills, Anaconda Bluewater and Homestake Mining Company. Local ground water near these sites were contaminated with high levels of U, Se, Mo, and other chemicals associated with mining and milling processes of uranium from its ore. The aquifers near the two sites consist of the alluvial and SAG near Bluewater, and alluvial and Chinle near Homestake. The alluvial aquifer is recharged directly by precipitation and infiltration from local surface water during and after local storm events. In the Homestake area the aquifer was also recharged by dewatering of mines, in the upper portion of the basin, into the Arroyo del Puerto and SMC, and would infiltrate the alluvial several miles downstream from its origin. Recharge to the Chinle aquifer is by downward seepage of the alluvial aquifer into portions of the upper section of the formation. Also, recharge may occur along the base of the Zuni Mountains (DOE 2014). The SAG aquifer is recharged near the outcrops in the Zuni Mountains by either precipitation and seasonal runoff events.

Ground water formations in the Lower San Mateo Creek Basin consist of Quaternary-age alluvium, Chinle, and SAG aquifers. There are two faults that run through Homestake site, an east and west fault. These faults interrupt the natural flow of ground water beneath the site. Alluvial ground water flows from the north to the southeast in the Homestake area and from the west to southeast from the Bluewater site. The Chinle formation is divided into three aquifers: the upper, middle and lower. The upper aquifer flows from the north to south underneath the Homestake site, but the middle aquifer flows in the opposite direction, south to North. The San Andres-Glorieta aquifer is not in direct hydraulic connection in the Homestake area because of the Chinle formation. The

Chinle formation works as a barrier to the SAG aquifer because of its low permeability. This is not true in the Bluewater site area, where the flow direction is similar to the alluvial flow, west to southeast. Most of the area is dominated by the Quaternary alluvium and underlying SAG aquifers, because of the absence of the Chinle formation in most parts of the Bluewater location, the alluvial and SAG are considered to be in direct hydraulic connection (DOE 2014).

This investigation used several techniques that have been applied to other studies related to the uranium mining and milling industries. These techniques include isotopic identifiers, ground water movement between underlying aquifers, and anthropogenic influences on local ground water. There were 34 wells used in this study from the Bluewater and Homestake site areas. Bluewater data consisted of 19 wells and was retrieved from DOE's LM program. These wells are located within the site's boundary. Homestake's 15 wells data were collected from previous studies by NMED (2010), DOE (2014) and samples collected by the University of New Mexico (UNM) in the fall of 2015 and spring of 2016. These sites were previously sampled by NMED in 2014 and were selected by the availability of each well owner's cooperation for sampling.

Figure 17 is a trilinear (piper) diagram of both sets of water samples near the Bluewater and Homestake mill sites. The diagram summarizes the similarities and differences between the major ions for samples near both sites. The figure shows a much closer relationship between the Bluewater samples than the LSM samples near Homestake. In part, this may be due to the fact that all of the water samples are from monitoring wells located close to the tailings pile and constructed with short screens to provide water from a discrete formation. In contrast, all of the wells sampled for this

study were water supply wells with long screens that draw a blend of ground water from many depths. The Bluewater alluvial aquifer is a Na-Ca/SO₄-HCO₃ type water, while the SAG is a Ca-Na/SO₄-Cl-HCO₃ type water. The pH values for both aquifers were slightly more alkaline than acidic. Alluvial ground water samples had a pH value of 7.5, while the SAG ground water was 7.1. Background pH values for these two aquifers are 7.45 E(M) and 6.87 L(SG), respectively. Also, McHaley (2015) reported that the dissolved oxygen (DO) values were higher in the alluvial samples than the SAG samples. Dissolved oxygen values indicate that ground water in the alluvial is more recently recharged than the SAG ground water.

Ground water samples in the Homestake area (Figure 14) were also a Ca-Na/SO₄-HCO₃ type water. The samples for the Homestake area are not as tightly grouped as those on the Bluewater diagram. This would be expected because of the lack of hydraulic connection between the alluvial and SAG aquifers. Also, the samples from the Chinle are from the lower section and not the upper section of the aquifer. This makes it more difficult to determine if mixing between aquifers is occurring. The three samples, plotted in the bottom right part of the cation triangle, are grouped separately from the other sites, which indicate they have different chemistry composition than the other samples. Two of these site, LSM-35 and LSM-GC, are up-gradient from Homestake.

Analysis for uranium, selenium, molybdenum, and vanadium show different results for the two sites. Uranium for the Bluewater site, Figure 18, was present at relatively high concentrations, while Se and Mo concentrations were smaller. Well 16(SG) had the highest value of uranium at 1290 µg/L and also had the highest value for Se, 17.1 µg/L well below the MCL value for drinking water of 50 µg/L. This well was not plotted

on Figure 18 because of the extremely high value of U compared to the other wells represented on the bar chart. Wells near Homestake had a variety of U and Se concentrations. Four of the wells near the Homestake site, LSM-49 thru LSM-52 had U concentrations that exceeded the drinking water standard of 30 µg/L. These wells are directly south and downgradient from the large tailings piles (Figure 16). The highest concentration of U was measured in well LSM-52, 146 µg/L. This well also had the highest concentration of Se, 182 µg/L. There was a positive correlation between U and Se with Pearson's r values of 0.871 and 0.674 for Bluewater and Homestake, respectively. Uranium comparison with other chemicals, TDS, SO₄, and Cl had Pearson's r values of 0.642, 0.542, and 0.577, respectively, for Bluewater. These values are significant and show a strong relationship between the two species. These results were not the same for samples near Homestake. Those samples had Pearson's r value less than 0.5, meaning a weak correlation between the species. The low concentrations of molybdenum were lower than expected for ground water near the uranium mill site. Because of the low values, there was no relationship between the two metals.

Figure 24 is a plot of uranium concentration versus distance from the large tailings on both sites. The distances were measured using Google Earth and the wells' latitude and longitude location. Figure 24 shows that wells closer to the Homestake tailings pile also had the highest concentrations of U. These wells are directly south of the tailings pile (Figure 6). There were two other sites within a two-mile radius of the tailings pile, LSM-32 and LSM-46. Both of these sites are southwest of the tailings and have U concentrations less than 20 µg/L (Figure 24). There appears to be a negative correlation between U concentrations and distance for LSM wells, except for wells within a 2.5-mile

radius. This does not seem to be true for the Bluewater wells. The average distance is roughly 1.9 miles, while the average distance for Homestake is approximately 5.0 miles. The two wells farthest away from Homestake are LSM-58 and LSM-58#2, and these wells have U concentrations of 22.9 and 27.9 $\mu\text{g/L}$, respectively. These wells are approximately 13.4 miles away from the site. These higher U concentrations may be attributed to their locations to the upper basin and ground water impacted from the two upper Ambrosia Lake mills (DOE 2014).

To better understand the chemistry of ground water, some isotopes were measured to identify the source of the contaminants, isotopic signatures, especially ^{234}U and ^{238}U activity ratios (AR). Isotopes ^2H (D), ^{18}O , ^{34}S , and ^{15}N were also measured in ground water near Homestake. Figure 21 shows the relationship between D and ^{18}O for both sampling sites. The samples near Homestake displayed a wider range of isotopic fraction than the Bluewater group. These results may be because of the greater distance between the samples near Homestake than Bluewater; Bluewater sites are known to have a hydraulic connection (alluvial and SAG), while the LSM samples are not hydraulically connected and the samples from up-gradient are influenced by unknown recharge. While there is a slight difference between the two sample sites, they both plot close to the GMWL (Craig, 1961). The samples near Homestake are slightly more enriched than Bluewater samples, but both sample sites are closer to the Albuquerque Water Line (AWL).

Sulfur isotope results did not show a strong correlation to other species of concern. Kamp and Morrison (2014) used Sulfur isotopes $^{34}\text{S}/^{32}\text{S}$ to discriminate between anthropogenic sources and naturally occurring sources of sulfur. They used data from

former uranium mills to find a range that represented mill ^{34}S . The range was -5 to +5‰. Sample from this investigation ranged from -13.1 to 14.5‰ for Homestake, and 0.30 to 15.4‰ for Bluewater samples. While Homestake samples were more depleted than Bluewater samples, there was not a separation from samples with high uranium values and ^{34}S values from those with low uranium concentrations and ^{34}S values outside of the -5 to +5‰ range.

Nitrogen ^{15}N data were not measured for samples from the Bluewater monitoring wells so there is no comparison between the two sites. Nitrogen isotope values for site wells near Homestake only included 9 samples. Figure 20 shows the results for ^{15}N isotopes and NO_3 . The correlation between the two species is significant, Pearson's r value of 0.900. Because of a limited amount of research using ^{15}N isotopes for identifying the source of high NO_3 near uranium mining and milling operations, there was no comparison values for this study. What is interesting is that the two samples with the highest ^{15}N values, 19.2 and 18.4, The-Bar and LSM-58#2, respectively, are both up-gradient from Homestake. The mills in the Ambrosia Lake area used an amine in the ore processing and may have introduced additional nitrogen to the ground water through discharge and tailings leaching. The use of ^{15}N , as an identifier for anthropogenic sources of high levels of NO_3 , may be a useful tool for future investigation.

Uranium isotopes ^{234}U and ^{238}U have been used in several investigations, Kamp and Morrison (2014), DOE (2014), NMED (2010), and Zielinski (1997), to discriminate between mill derived and naturally occurring contaminants associated with uranium milling. This study compared U isotopic data from Bluewater Mill and ground water samples near the Homestake mill. Uranium activity ratios (AR) $^{234}\text{U}/^{238}\text{U}$, on average, were lower

near the Bluewater site than the Homestake site, 1.21 and 1.78, respectively. There were 11 out of 18 Bluewater samples that had U concentrations higher than 30.0 µg/L, Figure 22. These same samples also had an average $^{234}\text{U}/^{238}\text{U}$ AR value of 1.05. There were four sites near Homestake with U concentrations greater than 30 µg/L and an average $^{234}\text{U}/^{238}\text{U}$ AR value of 1.20. Uranium background for the alluvial and SAG aquifer are approximately 10.0 µg/L (DOE 2014). These same values are estimated to be the same background concentrations for downgradient wells near the Homestake site. Investigations have identified higher concentrations of uranium up-gradient from Homestake, but believe they may be from ground water impacted by the upper San Mateo Creek uranium mining and mill operations, DOE (2014), NMED (2010).

Figure 22 represents a comparison of U concentrations and $^{234}\text{U}/^{238}\text{U}$ AR values. The plot shows a negative correlation between the U and U AR. This relationship between U and U AR values suggest that the samples with high uranium concentrations and low AR values < 1.3 are representative of U mill raffinate (Zielinski, 1997). Samples with AR values between 1.3 -1.5, and U values above background levels of 10 µg/L are most likely a mixture of mill derived and natural waters. Low uranium concentrations and higher AR values are most likely representative of naturally occurring ground water, NMED (2010). A comparison of AR values with Mo displayed a similar relationship, but because of the low values of Mo, there is a tighter grouping among the data points for the Bluewater samples.

Chapter 6: Conclusion

The purpose of this study was to use ground water chemistry and isotopic signatures to identify the source of contaminants in ground water in the Lower San Mateo Creek watershed near Milan, NM. Ground water samples collected in this study were analyzed for chemical and isotopic characteristics. The collection of ground water samples near the Homestake mill and Bluewater mill data results provided some valuable insight to ground water quality and the impact from two former uranium mills.

Isotopic results for uranium near Bluewater and Homestake mill sites show a strong correlation between elevated U concentrations and AR values near its secular equilibrium value of 1, indicating that the source of the contamination is mill-derived and is not naturally occurring. Nitrogen isotopes ^{15}N up-gradient from the Homestake site were almost twice the values of those down-gradient from Homestake. These values would indicate that the two sites up-gradient from Homestake may be the result of leaching from tailings piles in the upper San Mateo Creek Basin.

A major weakness in this study was the lack of on-site data, chemical and isotopic analysis for contaminants of concern. Uranium isotopes and dissolved solids data would have been very useful for comparison. Also, the lack of properly constructed wells in the Homestake area hindered this investigation. Those types of wells in this area would help with providing a better understanding of the hydrogeology of the area.

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Appendix

Table 3. Pearson's r values for wells near Homestake mill (Analyse-it).

Correlation							
	Pair	Pear- son's r	95% CI		0		p-value
	Ca, Mg	0.812	0.512	to 0.935	0	0.422751274	¹ 0.0002
	Ca, Na	0.843	0.582	to 0.947	0	0.364405275	¹ <0.0001
	Ca, K	0.658	0.220	to 0.875	0	0.655512942	¹ 0.0077
	Ca, HCO ₃	-0.544	-0.826	to -0.043	0.782507704	0	¹ 0.0362
	Ca, Cl	0.844	0.584	to 0.947	0	0.362982753	¹ <0.0001
	Ca, SO ₄	0.669	0.239	to 0.880	0	0.640758092	¹ 0.0063
	Ca, TDS	0.908	0.741	to 0.970	0	0.2285459	¹ <0.0001
	Ca, Uranium ug/L	0.109	-0.427	to 0.588	0.427282599	0.588271105	² 0.6995
	Ca, Selenium ug/L	0.202	-0.346	to 0.647	0.346286572	0.647143137	² 0.4708
	Ca, Molybdenum ug/L	-0.186	-0.638	to 0.360	0.637658166	0.36041997	² 0.5064
	Ca, NO ₃	0.197	-0.350	to 0.644	0.350281958	0.644492643	² 0.4807
	Mg, Na	0.385	-0.158	to 0.750	0.158089022	0.749651777	² 0.1560
	Mg, K	0.740	0.366	to 0.908	0	0.541532445	¹ 0.0016
	Mg, HCO ₃	-0.220	-0.658	to 0.330	0.657815917	0.329825112	² 0.4318
	Mg, Cl	0.381	-0.163	to 0.747	0.16296951	0.747449209	² 0.1611
	Mg, SO ₄	0.897	0.711	to 0.965	0	0.254624246	¹ <0.0001
	Mg, TDS	0.508	-0.006	to 0.810	0.005885414	0.809542543	² 0.0532
	Mg, Uranium ug/L	0.413	-0.126	to 0.763	0.126458072	0.763455478	² 0.1265
	Mg, Selenium ug/L	0.477	-0.046	to 0.795	0.046474863	0.795074395	² 0.0721
	Mg, Molybdenum ug/L	-0.388	-0.751	to 0.155	0.750865978	0.155379474	² 0.1533
	Mg, NO ₃	0.549	0.052	to 0.828	0	0.776867248	¹ 0.0339
	Na, K	0.391	-0.152	to 0.752	0.15189204	0.7524198	² 0.1498
	Na, HCO ₃	-0.580	-0.842	to -0.097	0.745241176	0	¹ 0.0233
	Na, Cl	0.998	0.992	to 0.999	0	0.006917947	¹

							<0.0001
	Na, SO4	0.271	-0.280	to 0.688	0.28012262	0.687801063	² 0.3285
	Na, TDS	0.990	0.971	to 0.997	0	0.026381638	¹ <0.0001
	Na, Uranium ug/L	-0.167	-0.626	to 0.378	0.62562179	0.377718827	² 0.5524
	Na, Selenium ug/L	-0.088	-0.574	to 0.444	0.574337963	0.444330323	² 0.7553
	Na, Molybdenum ug/L	0.053	-0.472	to 0.550	0.472188982	0.550223671	² 0.8516
	Na, NO3	-0.209	-0.651	to 0.340	0.651441646	0.339729415	² 0.4550
	K, HCO3	0.081	-0.450	to 0.570	0.449597836	0.569910054	² 0.7730
	K, Cl	0.402	-0.139	to 0.758	0.138833785	0.758149847	² 0.1374
	K, SO4	0.484	-0.037	to 0.798	0.037117546	0.798496988	² 0.0673
	K, TDS	0.466	-0.061	to 0.790	0.060701746	0.789765918	² 0.0799
	K, Uranium ug/L	0.282	-0.269	to 0.694	0.269446141	0.693838152	² 0.3091
	K, Selenium ug/L	0.060	-0.466	to 0.556	0.466255964	0.555506267	² 0.8306
	K, Molybdenum ug/L	-0.477	-0.795	to 0.046	0.795111298	0.046374752	² 0.0720
	K, NO3	0.088	-0.444	to 0.574	0.444466557	0.57422419	² 0.7557
	HCO3, Cl	-0.594	-0.848	to -0.118	0.730421381	0	¹ 0.0195
	HCO3, SO4	-0.218	-0.657	to 0.331	0.656770426	0.331464634	² 0.4356
	HCO3, TDS	-0.586	-0.845	to -0.106	0.739142648	0	¹ 0.0216
	HCO3, Uranium ug/L	0.466	-0.060	to 0.790	0.060166503	0.789967967	² 0.0796
	HCO3, Selenium ug/L	-0.034	-0.537	to 0.486	0.537175466	0.486457239	² 0.9032
	HCO3, Molybdenum ug/L	-0.156	-0.619	to 0.387	0.618801474	0.387219748	² 0.5788
	HCO3, NO3	-0.187	-0.638	to 0.360	0.63788893	0.360081467	² 0.5055
	Cl, SO4	0.240	-0.310	to 0.670	0.310269592	0.669999403	² 0.3886
	Cl, TDS	0.987	0.961	to 0.996	0	0.03483609	¹ <0.0001
	Cl, Uranium ug/L	-0.185	-0.637	to 0.361	0.63716195	0.361146971	² 0.5082
	Cl, Selenium ug/L	-0.108	-0.588	to 0.428	0.587982761	0.42764287	² 0.7007
	Cl, Molybdenum ug/L	0.050	-0.475	to 0.548	0.474596111	0.548056836	² 0.8602
	Cl, NO3	-0.226	-0.662	to 0.324	0.661508862	0.323985812	² 0.4185

	SO4, TDS	0.391	-0.152	to 0.752	0.152002618	0.752370686	² 0.1499
	SO4, Uranium ug/L	0.452	-0.078	to 0.783	0.078257532	0.783034906	² 0.0906
	SO4, Selenium ug/L	0.605	0.134	to 0.853	0	0.718866308	¹ 0.0169
	SO4, Moybdenum ug/L	-0.326	-0.718	to 0.223	0.71840927	0.223403869	² 0.2354
	SO4, NO3	0.685	0.265	to 0.886	0	0.620629119	¹ 0.0049
	TDS, Uranium ug/L	-0.095	-0.579	to 0.439	0.579010523	0.438694324	² 0.7366
	TDS, Selenium ug/L	-0.006	-0.516	to 0.508	0.516372267	0.508129829	² 0.9842
	TDS, Moybdenum ug/L	-0.006	-0.517	to 0.508	0.516828805	0.50766774	² 0.9825
	TDS, NO3	-0.106	-0.586	to 0.430	0.586379431	0.429640288	² 0.7071
	Uranium ug/L, Selenium ug/L	0.674	0.247	to 0.882	0	0.634630229	¹ 0.0059
	Uranium ug/L, Moybdenum ug/L	-0.312	-0.711	to 0.238	0.710642514	0.238426423	² 0.2577
	Uranium ug/L, NO3	0.242	-0.309	to 0.671	0.308503665	0.671074216	² 0.3849
	Selenium ug/L, Moybdenum ug/L	-0.084	-0.571	to 0.448	0.571329996	0.447916339	² 0.7673
	Selenium ug/L, NO3	0.565	0.074	to 0.835	0	0.761263146	¹ 0.0282
	Moybdenum ug/L, NO3	0.109	-0.427	to 0.588	0.427346894	0.588219665	² 0.6997

H0: $\rho = 0$

The correlation coefficient ρ of the bivariate population is equal to 0.

H1: $\rho \neq 0$

The correlation coefficient ρ of the bivariate population is not equal to 0.

¹ Reject the null hypothesis in favour of the alternative hypothesis at the 5% significance level.

² Do not reject the null hypothesis at the 5% significance level.

Table 4. Anaconda Bluewater Pearson's r results (Analyse-it)

Pair	Pearson's r	95% CI	0		p-value
Ca, Mg	0.786	0.537 to 0.909	0	0.372645991	<0.0001 ¹
Ca, Na	0.539	0.140 to 0.787	0	0.647705864	0.0117 ¹
Ca, K	0.728	0.432 to 0.882	0	0.450472159	0.0002 ¹
Ca, HCO ₃	0.288	-0.164 to 0.640	0.163675517	0.640354732	0.2049 ²
Ca, Cl	0.609	0.241 to 0.824	0	0.58308327	0.0034 ¹
Ca, SO ₄	0.462	0.038 to 0.745	0	0.707173222	0.0350 ¹
Ca, TDS	0.819	0.599 to 0.924	0	0.325148129	<0.0001 ¹
Ca, Uranium ug/L	0.672	0.338 to 0.855	0	0.51724718	0.0009 ¹
Ca, Selenium ug/L	0.672	0.339 to 0.856	0	0.516827682	0.0008 ¹
Ca, NO ₃	-0.189	-0.574 to 0.264	0.57370578	0.264468155	0.4125 ²
Ca, Molybdenum ug/L	-0.185	-0.571 to 0.268	0.571264064	0.267842959	0.4214 ²
Mg, Na	0.828	0.617 to 0.928	0	0.310728846	<0.0001 ¹
Mg, K	0.922	0.814 to 0.968	0	0.154332728	<0.0001 ¹
Mg, HCO ₃	0.228	-0.226 to 0.600	0.226194335	0.600392672	0.3208 ²
Mg, Cl	0.940	0.855 to 0.976	0	0.120878187	<0.0001 ¹
Mg, SO ₄	0.590	0.213 to 0.814	0	0.601796115	0.0049 ¹
Mg, TDS	0.967	0.919 to 0.987	0	0.067799712	<0.0001 ¹
Mg, Uranium ug/L	0.615	0.249 to 0.827	0	0.577864713	0.0030 ¹
Mg, Selenium ug/L	0.627	0.268 to 0.833	0	0.565037302	0.0023 ¹
Mg, NO ₃	-0.246	-0.613 to 0.208	0.612664979	0.207693072	0.2823 ²
Mg, Molybdenum ug/L	-0.273	-0.630 to 0.180	0.63007164	0.180404674	0.2321 ²
Na, K	0.881	0.726 to 0.951	0	0.225547227	<0.0001 ¹
Na, HCO ₃	0.518	0.111 to 0.776	0	0.664943304	0.0162 ¹
Na, Cl	0.862	0.686 to 0.943	0	0.257089455	¹

						<0.0001 ²
Na, SO4	0.429	-0.004	to 0.726	0.00375525	0.725982848	0.0525 ¹
Na, TDS	0.904	0.775	to 0.961	0	0.185647889	<0.0001 ¹
Na, Uranium ug/L	0.449	0.022	to 0.738	0	0.715954695	0.0410 ¹
Na, Selenium ug/L	0.455	0.029	to 0.741	0	0.712346369	0.0384 ²
Na, NO3	-0.134	-0.535	to 0.316	0.534637686	0.316109925	0.5630 ²
Na, Molybdenum ug/L	-0.173	-0.563	to 0.280	0.562540378	0.279734468	0.4538 ²
K, HCO3	0.335	-0.113	to 0.670	0.112793531	0.66995437	0.1374 ¹
K, Cl	0.894	0.752	to 0.956	0	0.204218871	<0.0001 ¹
K, SO4	0.510	0.100	to 0.772	0	0.671592753	0.0183 ¹
K, TDS	0.940	0.855	to 0.976	0	0.121003268	<0.0001 ¹
K, Uranium ug/L	0.505	0.094	to 0.769	0	0.675398344	0.0196 ¹
K, Selenium ug/L	0.479	0.059	to 0.754	0	0.695289437	0.0282 ²
K, NO3	-0.233	-0.604	to 0.221	0.604155164	0.220584839	0.3087 ²
K, Molybdenum ug/L	-0.229	-0.601	to 0.225	0.601217027	0.224969977	0.3181 ²
HCO3, Cl	0.130	-0.320	to 0.532	0.319655553	0.531814953	0.5745 ²
HCO3, SO4	0.126	-0.323	to 0.529	0.323316534	0.528880398	0.5864 ²
HCO3, TDS	0.371	-0.073	to 0.692	0.072747542	0.691622624	0.0982 ²
HCO3, Uranium ug/L	0.271	-0.181	to 0.629	0.181485568	0.629397312	0.2339 ²
HCO3, Selenium ug/L	0.191	-0.262	to 0.575	0.262284689	0.575277649	0.4068 ²
HCO3, NO3	-0.025	-0.452	to 0.411	0.451501325	0.411446675	0.9157 ²
HCO3, Molybdenum ug/L	0.036	-0.402	to 0.460	0.402136458	0.460338683	0.8777 ¹
Cl, SO4	0.539	0.139	to 0.787	0	0.648019327	0.0118 ¹
Cl, TDS	0.916	0.801	to 0.966	0	0.164516599	<0.0001 ¹
Cl, Uranium ug/L	0.575	0.191	to 0.806	0	0.615937284	0.0064 ¹
Cl, Selenium ug/L	0.600	0.227	to 0.819	0	0.592528666	0.0041 ²
Cl, NO3	-0.208	-0.587	to 0.246	0.586821458	0.245982163	

Cl, Moybdenum ug/L	-0.163	-0.555	to 0.289	0.555346577	0.289349904	0.3661 ²
SO4, TDS	0.550	0.155	to 0.793	0	0.638031691	0.4812 ¹
SO4, Uranium ug/L	0.544	0.147	to 0.790	0	0.643358754	0.0098 ¹
SO4, Selenium ug/L	0.582	0.200	to 0.810	0	0.609645537	0.0108 ¹
SO4, NO3	-0.263	-0.624	to 0.190	0.624000229	0.190066653	0.0057 ²
SO4, Moybdenum ug/L	-0.159	-0.553	to 0.293	0.552844795	0.292654377	0.2490 ²
TDS, Uranium ug/L	0.637	0.284	to 0.838	0	0.554706246	0.4908 ¹
TDS, Selenium ug/L	0.651	0.304	to 0.845	0	0.540538458	0.0019 ¹
TDS, NO3	-0.184	-0.570	to 0.269	0.5702375	0.269255698	0.0014 ²
TDS, Moybdenum ug/L	-0.239	-0.608	to 0.215	0.607998484	0.214797947	0.4252 ²
Uranium ug/L, Selenium ug/L	0.871	0.704	to 0.947	0	0.242738313	0.2967 ¹
Uranium ug/L, NO3	0.240	-0.214	to 0.609	0.213872747	0.608609393	<0.0001 ²
Uranium ug/L, Moybdenum ug/L	0.023	-0.413	to 0.450	0.412767343	0.450233869	0.2948 ²
Selenium ug/L, NO3	0.073	-0.370	to 0.489	0.370160824	0.489442109	0.9211 ²
Selenium ug/L, Moybdenum ug/L	-0.078	-0.493	to 0.366	0.493145301	0.365940647	0.7524 ²
NO3, Moybdenum ug/L	-0.182	-0.569	to 0.271	0.568883161	0.271114003	0.7366 ²
						0.4301 ²

H0: $\rho = 0$

The correlation coefficient ρ of the bivariate population is equal to 0.

H1: $\rho \neq 0$

The correlation coefficient ρ of the bivariate population is not equal to 0.

¹ Reject the null hypothesis in favour of the alternative hypothesis at the 5% significance level.

² Do not reject the null hypothesis at the 5% significance level.

Table 5. List of parameters and laboratory analytes for ground water samples near Bluewater and Homestake.

Location	Aquifer	Distance fi	pH	Ca	Mg	Na	K	HCO ₃	Cl	SO ₄	NO ₃	Uranium ug/L	Selenium ug/L	Vanadium ug/L	Moybdenum ug/L	U234/U238 AR	S34/S32
11(SG)	SG	1.83	7.04	176	63.7	357	10.6	468	207	815	0.017	15.7	7.5		0.744	1.56	9.83
13(SG)	SG	2.87	7.01	172	52.5	114	6.33	287	90.2	459	5.2	108	7.5		1.43	1.04	5.86
14(SG)	SG	1.63	7.11	134	55.2	256	5	422	160	500	0.017	64.3	7.5		2.56	1.15	6.62
15(SG)	SG	1.34	7.23	105	38.2	259	6.02	342	182	456	0.017	129	7.5		7.94	1.11	3.23
16(SG)	SG	0.791	6.76	314	158	403	12.9	387	641	1910	4.89	1290	17.1		2.52	0.95	0.30
18(SG)	SG	2.06	6.95	168	50.9	149	7.12	324	100	463	1.87	134	7.5		3.83	0.99	5.99
20(M)	AL	0.896	7.4	143	36.7	90.2	4.17	234	59.6	410	3.93	14.3	7.5		2.08	1.68	3.78
21(M)	AL	2.87	7.29	152	41.1	213	5.71	257	155	521	12.1	137	12.1		0.955	1.07	1.62
22(M)	AL	2.1	7.34	87	24.9	169	4.53	312	31.2	225	36	393	7.5		0.959	1.02	8.93
23(M)	AL	3.31	7.73	124	28.8	49.3	4.41	148	92	274	1.78	26.2	7.5		5.73	1.43	6.60
E(M)	AL	1.63	7.45	203	54.3	55.7	4.17	27.7	30	795	0.017	0.067	7.5		0.591	0.83	15.41
F(M)	AL	2.02	7.73	69.8	18.9	20.8	3.27	163	11.6	109	0.737	7.82	7.5		0.985	1.26	10.16
HMC-951	SG	3.27	7.09	146	44	81.9	4.94	273	60.6	378	4.82	31.7	7.5		1.28	1.15	7.26
I(SG)	SG	3.68	6.75	263	99.8	297	13	370	305	932	1.71	288	8.05		1.03	1.03	3.83
L(SG)	SG	0.946	6.87	141	77.4	354	8.05	591	213	653	0.017	3.08	7.5		0.394	1.44	9.53
OBS-3	SG	0.821	7.55	126	136	428	13.3	35.2	689	920	0.017	7.71	7.5		0.165	1.04	8.61
S(SG)	SG	0.826	6.97	276	158	404	13.2	362	523	1290	2.77	456	12.2		0.123	0.97	1.28
X(M)	AL	2.7	7.57	153	44.3	187	5.23	204	196	104	10.8	121	7.86		0.747	1.10	1.72
Y2(M)	AL	1.68	7.63	55	16.6	57.7	3.09	199	16.4	1860	1.81	5.13	7.5		1.6	2.23	9.85
LSM-GC	SG	7.93	7.5	1040	119	6650	8.95	46	12000	1150	ND	ND	ND	0.25	2.56	ND	14.47
LSM-12	LC	3.51	8.2	18	4.1	298	2.12	344	74.6	259	9.379	15.1	20	14.1	7.94	1.94	-8.20
LSM-24	LC	5.11	7.4	143	39.3	60.7	3.95	328	30.7	308	4.3166	8.6	13	3.1	2.52	1.84	2.10
LSM-32	AL	1.5	7.4	118	36.9	60.5	3.2	273	32.8	279	3.0962	6.9	14	3.1	3.83	1.93	3.51
LSM-35	AL	4.95	8.3	14.1	1.37	752	1.09	346	534	674	ND	ND	ND	0.25	2.08	0.00	0.04
LSM-42	SG	4.33	7.4	120	42.6	170	5.13	440	90	345	ND	7.7	ND	0.25	0.955	2.66	8.03
LSM-44	SG	6.87	7.6	90.7	31.2	39.6	2.69	255	16.9	181	2.7798	3.6	11	3	0.959	2.33	4.31
LSM-45	SG	5.54	7.3	156	44.2	85.8	3.81	308	51	409	3.5708	11.4	15	3.2	5.73	1.66	4.12
LSM-46	SG	1.72	7.2	224	75.1	222	10.2	443	200	636	3.5482	19.3	9	2.5	0.591	1.68	3.83
LSM-49	AL	1.66	7.1	165	49.8	243	5.96	423	162	538	1.70178	70.8	9	3.9	0.985	1.36	6.32
LSM-50	LC	2.14	7	232	69.1	287	6.24	534	205	733	1.94134	141	25	4.5	1.28	1.09	4.76
LSM-51	AL	2.13	7	223	72	305	7.49	566	205	769	1.5481	86.7	18	3.8	0.394	1.16	2.19
LSM-52	AL	1.97	7.1	456	131	561	5.68	286	520	1930	12.3622	146	182	5.6	1.03	1.18	-4.76
LSM-58	MO	13.5	7.5	79.5	8.74	29.9	4.05	224	6.22	107	ND	22.9	1	0.6	0.165	2.75	-8.76
LSM-58#2	UK	13.3	7.3	532	150	234	7.52	221	52.7	2040	16.2042	27.9	21	0.25	0.123	1.51	-13.07

Note: Not detected (ND), Ca, Mg, Na, K, HCO₃, Cl, SO₄, and NO₃ concentrations are in mg/L. U, Se, Mo, and V concentrations are in µg/L. Distance from large tailings are in km.

