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Curtis McHaley

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Curtis Paul McHaley

Candidate

Nuclear Engineering

Department

This thesis is approved, and it is acceptable in quality and form for publication:

Approved by the Thesis Committee:

Cassiano Ricardo Endres de Oliveira, Chairperson

Kenya Moore De Almeida Dias Da Cunha

Jose Manuel Cerrato Corrales

USE OF CHEMICAL AND ISOTOPIC SIGNATURES TO DISTINGUISH BETWEEN URANIUM MILL-RELATED AND NATURALLY OCCURRING GROUNDWATER CONSTITUENTS AT THE BLUEWATER DISPOSAL SITE

by

CURTIS PAUL MCHALEY

B.S. GEOLOGY, UNIVERSITY OF NEW MEXICO, 1985

M.S. CIVIL ENGINEERING,
UNIVERSITY OF NEW MEXICO, 1991

M.S. NUCLEAR ENGINEERING,
UNIVERSITY OF NEW MEXICO, 2015

THESIS

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Use of Chemical and Isotopic Signatures to Distinguish Between Uranium Mill-Related and Naturally Occurring Groundwater Constituents at the Bluewater Disposal Site

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Curtis Paul McHaley

B.S. Geology, University of New Mexico, 1985

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M.S. Nuclear Engineering, University of New Mexico, 2015

ABSTRACT

Uranium mining and milling in the Grants Mining District (GMD) in northwestern New Mexico resulted in environmental impacts on the area's soil, stream sediments, surface water and groundwater. The Bluewater mill, a predominant mill within the GMD, disposed of tailings in unlined tailings piles causing widespread groundwater contamination.

This study utilized Uranium-234/Uranium-238 ($^{234}U/^{238}U$) isotopic ratios in conjunction with chemical and other isotopic data from the Bluewater uranium mill area to discriminate between uranium-mill derived groundwater contamination and groundwater with no known anthropogenic influence and to better understand the interaction of groundwater movement among the alluvial aquifer and adjacent San Andres aquifer.

Analysis of data suggest that groundwater from the two aquifers have similar water quality characteristics yet are distinctly unique and have similar background uranium concentrations of about 14 µg/L.

Isotopic analysis provided an effective tool for assessing the mixing of groundwater and extent of contamination from uranium milling operations.

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1 INTRODUCTION

Thesis Objective

The extent of contamination from mining and milling activities in the Grants Mining District (GMD) in the northwest region of New Mexico has been difficult to quantify. This is due to the lack of available background groundwater quality data collected prior to mining and milling operations as well as sparse and intermittent historical water quality data from GMD investigations that are limited by the number of water quality parameters analyzed.

The goal of this thesis is to use chemical, stable isotopes and uranium isotopic signatures from recent available data collected by the United States Department of Energy (DOE) as part of the Long-Term Surveillance Plan for the DOE Bluewater Disposal Site located in the GMD and data from the 2010 New Mexico Environment Department (NMED) study to discriminate between uranium-mill derived groundwater contamination and groundwater with no known anthropogenic influence. Uranium-234/Uranium-238 ($^{234}U/^{238}U$) isotopic ratios in conjunction with chemical data from the Bluewater uranium mill area will be used to determine the extent of uranium contamination, and to better understand the interaction of groundwater movement among the alluvial aquifer and adjacent geologic units. The Bluewater mill and nearby area within the GMD constitute the study area of this research.

This work will serve as the foundation and reference for performing additional laboratory and field studies towards characterizing contaminant transport and the effectiveness of current remediation efforts.

Previous Work

The principles used in this study have been applied to a variety of investigations regarding the groundwater flow and contaminant transport of uranium mill effluent in the southwest and in the vicinity of the Bluewater disposal site. The studies with the greatest significance to this investigation are as follows:

DOE (2014) prepared a very thorough assessment of the groundwater systems impacted by the Bluewater disposal site which included the development of a groundwater conceptual model that describes the aquifers associated with the Bluewater site. This report provides a very useful discussion on the Bluewater site's history, geology, hydrology, hydrogeology, and regional groundwater flow system and is the most comprehensive investigation to date. This report served as a primary reference for this investigation.

Although no detailed quantitative assessment of background concentrations of uranium at the Bluewater site have ever been conducted, the DOE report provides an estimate of 10 µg/L (parts per billion) for both aquifers based on the results of previous studies in the area.

NMED (2010) conducted separate site investigations of the Bluewater mill and San Mateo Creek middle and upper basins between 2008 and 2009 in order to characterize the impacts of legacy uranium mining and milling activities on the San Mateo Creek regional groundwater system. This investigation provides a good understanding of the hydrogeology and geochemistry of the of the San Mateo Creek basin as well as identifies and characterizes legacy uranium environmental impacts. This investigation provides a useful comparison to the data, recommendations and conclusions provided by DOE (2014).

Otton (2011) provides a very comprehensive annotated bibliography of reports that describe the hydrology and geochemistry of groundwater and surface water including information on the soils and sediments in the GMD and adjacent areas. The reports referenced and discussed by Otton provide a large volume of information relevant to understanding the impact of uranium mining and milling on the environment in the area after mining started in the early 1950's. This report references techniques using isotopic ratios of uranium to differentiate between natural background or baseline conditions and contamination due to mining and milling and identifies studies that describe how the use of uranium, other isotopes and trace elements may help in this discrimination.

Zieslinski et al. (1997) used uranium isotope ratios, combined with uranium and molybdenum data, to determine the processes that include mixing and chemical precipitation that affect uranium concentrations as well as the extent of groundwater contamination from effluent at the Canon City uranium mill site in Colorado. The study shows that uranium isotope and trace element data can be used to determine the distribution of uranium contamination in groundwater and can help identify contamination by mine or mill wastes from elevated levels that may be in the natural background. Zieslinski et al. (1997) showed that the activity ratios in groundwater contaminated with uranium had ratios close to 1 whereas water unaffected by mining and milling operations had ratios greater than 1.3 and are indicative of little to no uranium contamination. The methodology used in this study to distinguish between the isotopic differences of uranium from uranium mill effluent from that of local groundwater was used for this investigation.

Kamp and Morrison (2014) identified chemical and isotopic signatures from groundwater in desert arroyos near Shiprock, New Mexico that could be used to discriminate between mill derived groundwater contamination and groundwater with no known anthropogenic influence. The methodology used in this study by comparing activity ratios to uranium concentrations was also used for this investigation to distinguish between the isotopic differences of uranium from uranium mill effluent from that of local groundwater.

Background of Mining and Milling Operations at the Bluewater Disposal Site

The GMD is located in McKinley and Cibola Counties in northwestern New Mexico about 80 miles west of Albuquerque from United States Interstate Highway I-40.

The largest sub-district of the GMD is Ambrosia Lake which included 96 producing mines and 4 mills including the Bluewater mill. The Bluewater disposal site located at the former Bluewater mill is shown in Figure 1.

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Figure 1. General Location of the Bluewater Disposal Site (DOE, 2014)

Uranium deposits were known to occur in the GMD beginning in the 1920's however mining of uranium ore did not occur in the area until 1950. In 1953, the

Anaconda Copper Company built the Bluewater mill which began processing ore the same year. The Bluewater mill initially used a carbonate leach process to extract uranium from ore derived from nearby mines in the Todilto Limestone which by 1966 accounted for approximately 4.2 percent of the uranium produced in the Grants districts. By 1955, the carbonate leach process was replaced by an acid leach process when higher-grade sandstone ores in the Morrison Formation were discovered. Greater than 94 percent of the uranium produced from the GMD came from sandstones within the Morrison formation (Kittel et al., 1966). In 1977, the Atlantic Richfield Company (ARCO) purchased the Anaconda Copper Company and by 1978 uranium ore processing at the Bluewater mill peaked at 6,000 tons per day. The mill stopped processing ore in early 1982 but continued recovering uranium from leachate fluids for several years thereafter.

The Jackpile mine provided a major source of ore from the Morrison Formation to the Bluewater mill with the primary uranium bearing minerals being coffinite and uraninite. The most common secondary minerals were tyuyamunite, metatyuyamunite, and carnotite. These minerals and other minerals shown in Table 1 below have been identified as occurring at the Jackpile mine and nearby Paguant mine which also supplied ore to the Bluewater mill.

Table 1. Common Minerals found in the Jackpile Mine (Kittel et al., 1966)

Mineral (*mineral type*)	**Chemical Formula**
Autunite (*phosphate-arsenate*)	$Ca(UO_2)_2(PO_4)_2 \cdot 10\text{-}12H_2O$
Becquerelite (*oxide*)	$7UO_3 \cdot 11H_2O$
Carnotite (*vanadate*)	$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$
Coffinite (*silicate*)	$U(SiO_4)_{1\text{-}x}(OH)_{4x}$
Hydrogen-autunite (*phosphate-arsenate*)	$HUO_2PO_4 \cdot 4H_2O$
Metatorbernite (*phosphate-arsenate*)	$Cu(UO_2)_2(PO_4)_2H_2O$
Metatyuyamunite (*vanadate*)	$Ca(UO_2)_2(VO_4)_2 \cdot 5\text{-}7H_2O$
Phosphuranylite (*phosphate-arsenate*)	$Ca(UO_2)_4(PO_4)_2(OH)_4 \cdot 7H_2O$
Schoepite (*oxide*)	$4UO_3 \cdot 9H_2O$
Sklodowskite (*silicate*)	$Mg(UO_2)_2(SiO_3)_2(OH)_2 \cdot 6H_2O$
Soddyite (*silicate*)	$(UO_2)_5(SiO_4)_2(OH)_2 \cdot 5H_2O$
Tyuyamunite (*vanadate*)	$Ca(UO_2)_2(VO_4)_2 \cdot 5\text{-}10H_2O$
Uraninite (*oxide*)	UO_2
Uranophane (*silicate*)	$Ca(UO_2)_2(SiO_3)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$

Noncommercial quantities of selenium, molybdenum, and vanadium were also present in association with the uranium with jordisite, MoS_2 as a common accessory mineral (Kittel et al., 1966).

The uranium mining and milling in the GMD that was performed from the early 1950's to early 1980's resulted in environmental impacts on the area's soil, stream sediments, surface water and groundwater. The Bluewater mill disposed tailings in unlined tailings piles causing widespread groundwater contamination and by the end of 1981 it was estimated that there were 23.6 million tons of mill tailings near the Bluewater mill occupying an area of 341 acres (Albrethsen et al., 1982) with the majority of tailings deposited in the main tailings impoundment.

Reclamation at the mill site was completed in 1995 following the encapsulation of the main tailings impoundment in an engineered clay and rock covered disposal cell.

The main tailings disposal cell covers an area of 354 acres with an estimated 22.9 million tons of tailings with the remaining tailings covered at the carbonate tailings disposal cell. General features of the Bluewater disposal site are shown in Figure 5 that includes DOE well locations.

It is estimated that 5.7 billion gallons of fluid have seeped through the tailings impoundment prior to 1995. Furthermore, it is estimated that groundwater contaminants from tailings liquor for molybdenum, selenium, and uranium have seeped from the impoundment at concentrations of 1.33, 4.0, and 19.5 mg/L respectively resulting in the release of 63,300 pounds of molybdenum, 190,500 pounds of selenium, and 928,300 pounds of uranium to the area underlying the impoundment (DOE, 2014). The area underlying the main disposal cell (and to a lesser extent the carbonate tailings disposal cell) is considered by DOE to be a mineralized zone that extends more than 100 feet below the base elevation of the cells and laterally along fault zones. This mineralized zone is the source of uranium through solid phase dissolution for the alluvial and San Andres aquifers at the Bluewater site.

The Bluewater mill is a site presently managed by the DOE Legacy Management (LM) Program and is administered under the provisions of the Nuclear Regulatory Commission (NRC) general license and has been investigated by NMED as part of their study of the San Mateo Creek basin (NMED, 2010). Important compliance requirements for the long-term surveillance and maintenance of the Bluewater site by DOE is monitoring groundwater with respect to alternate concentration limits as approved by the NRC and verifying that the disposal cell functions as designed to ensure the protection of human health and the environment. In 2003, the United States Environmental Protection Agency set the maximum contaminant level of uranium in community water supplies at 30 µg/L to reduce the risk of cancer and kidney disease.

2 THEORETICAL BACKGROUND

Uranium Fate and Transport

The presence and behavior of uranium in the aquatic environment is dependent on a complex interaction of physical and chemical conditions. The amount of dissolved uranium present in water is a function of many variables that include the environment's oxidation/reduction potential (redox), pH, concentrations of complexing agents, the availability of sorption sites, and the hydrological interaction of the uranium source materials with the surrounding environment.

Uranium occurs in 4+, 5+, and 6+ oxidation states and are typically identified as U(IV), U(V), and U(VI). Uranous U(IV) and uranyl U(VI) are the most common forms in nature. Under reducing conditions, uranium is in its tetravalent (IV) state and include U^{4+}, UOH^{3+}, and $U(OH)_4^0$. The stable aqueous species of uranium in its hexavalent (VI) oxidation state in natural waters include UO_2^{2+}, UO_2H^+, $(UO_2)_3(OH)_5^+$, and $(UO_2)_3(OH)_7^-$. Uranium can also complex with alkaline earth metals and carbonate (Dong and Brooks, 2006).

Uranium U(VI) minerals are typically oxidized products from the weathering of primary (U^{4+}) ore minerals such as uraninite and coffinite. Uranium U(IV) minerals also form by the evaporative concentration of dissolved U(VI) in arid conditions. Schoepite is a fairly soluble mineral and is therefore rare whereas carnotite and tyuyamunite have low solubilities and are the more common oxidized ore minerals of uranium (Langmuir, 1997).

Uranium is about 10,000 times more soluble in its oxidized hexavalent (VI) state than that of uranium at a tetravalent (IV) state (Ingebritsen, 1998). As such, groundwater environments with oxidizing conditions and elevated uranium concentrations in the geologic materials have a greater potential for high uranium concentrations in groundwater. The presence of elevated uranium in groundwater is a strong indicator of oxidizing conditions.

Uranium Isotopes and Activity Ratios

Uranium occurs in nature in the form of three different isotopes, ^{238}U, ^{235}U, and ^{234}U with ^{238}U having a half-life ($T_{1/2}$) of 4.47×10^{9} years, ^{234}U ($T_{1/2} = 2.45 \times 10^{5}$ years) and ^{235}U ($T_{1/2} = 7.04 \times 10^{8}$ years). Natural uranium contains 99.2745% ^{238}U, 0.0055% ^{234}U and 0.72% ^{235}U by mass. The percent of the isotopic mass of a particular uranium isotope (x) can be calculated using the equation below where the mass of the ^{x}U isotope is divided by the total uranium mass. The total uranium mass is the sum of the combined mass of the uranium isotopes.

$$\frac{{}^{x}\text{U Mass}}{{}^{238}\text{U Mass} + {}^{235}\text{U Mass} + {}^{234}\text{U Mass}} = \%\ {}^{x}\text{U Mass}$$

Figure 2 is a simplified schematic that illustrates the decay series of ^{238}U.

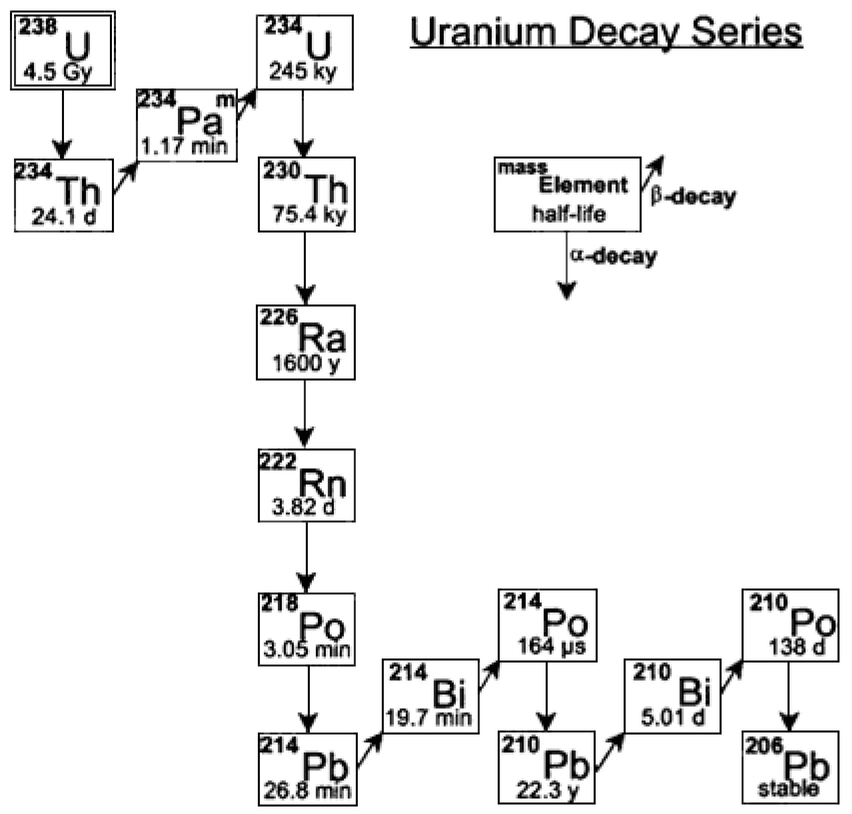


Figure 2. Decay Scheme for Natural Occurring ^{238}U Chain (National Research Council, 1999)

In a closed system after approximately a million years ^{234}U and ^{238}U in the host rock are in radiological (secular) equilibrium. When uranium isotopes are measured in terms of their alpha emission rates, the alpha activity ratio of ^{234}U to ^{238}U is close to 1.0 where the rate of decay of ^{234}U is equal to the rate of decay in the parent ^{238}U. However the ^{234}U/^{238}U ratio has been found to vary considerably due to natural causes in many water, soil, sediment, and uranium ores of different geographical origin. ^{234}U/^{238}U activity ratios are generally between 1 and 3, though they have been measured from 0.5 to greater than 10 (Osmond and Cowart, 1992). In general, weathering under ordinary environmental conditions will result in groundwater ^{234}U/^{238}U activity ratios to be in equilibrium.

High grade uranium ores are in secular equilibrium with an activity ratio of 1. The ore is processed by finely chopping and crushing the ore samples and bringing the uranium into solution with strong oxidizing agents into leachate. Further chemical processing is performed to remove most uranium from solution by solvent exchange, sorption or precipitation. Throughout the process the uranium mill liquid retains the uranium isotope composition of the original processed ore sample. Aggressive leaching of uranium ore is required to generate $^{234}U/^{238}U$ alpha activity ratios of 1.0 ± 0.1 in solution that are lower than ratios that are expected to occur in response to the prolonged mild leaching of uranium in most natural water (Zielinski et al., 1996). The strong dissolution of uranium minerals leads to high groundwater uranium concentrations and low $^{234}U/^{238}U$ activity ratios. Low weathering rates may result in low groundwater U concentrations and high $^{234}U/^{238}U$ activity ratios.

$^{234}U/^{238}U$ activity ratios higher than 1.3 in groundwater are the result of the ^{234}U atom displacement from the crystal lattice and are indicative of little or no contamination from milling operations (Zielinski et al., 1996). The recoil atom ^{234}U is likely to be oxidized to the hexavalent stage and can be leached into the water phase more easily than its parent nuclide ^{238}U. When ^{238}U decays by alpha decay to ^{234}Th, the Th nucleus may be recoiled out of the mineral into the groundwater. The ^{234}Th decays via ^{234}Pa to ^{234}U, resulting in an excess of ^{234}U in the groundwater.

The spatial and temporal distribution of $^{234}U/^{238}U$ activity ratios provide a technique for determining mixing trends, and identifying uranium flow patterns. Osmond and Cowart (1992) developed plots of $^{234}U/^{238}U$ activity ratios versus the reciprocal of uranium concentration and interpreted straight-line arrays as evidence of mixing or dilution of different groundwater.

Water Fractionation

When water changes from a gas to a liquid or from a solid to a liquid, isotopic fractionation occurs. Fractionation is the result of heavier isotopes (^{18}O and ^{2}H) being more abundant in the condensed (water) phase. The stable isotope composition of a water sample is measured as the ratio of the heavy isotope to the light isotope [$^{18}O/^{16}O$ and $^{2}H/^{1}H$ (D/H)] where the ratios are expressed in delta units (δ) as per parts per thousand.

$\delta\,^{18}O$ and $\delta\,^{2}H$ (δ D) are defined by the following equations:

$$\delta\,^{18}O = [(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{VSMOW}/(^{18}O/^{16}O)_{VSMOW}] \times 10^{3}\ ‰$$

$$\delta D = [(D/H)_{sample} - (D/H)_{VSMOW}/(D/H)_{VSMOW}] \times 10^{3}\ ‰$$

where VSNOW is the Vienna Standard Mean Ocean Water standard against which isotopic compositions of both hydrogen and oxygen are reported.

Craig (1961) determined that precipitation values of $\delta\,^{18}O$ and δ D values have the following linear relationship:

$$\delta D = 8 \delta ^{18}O + 10$$

This equation is known as the "Global Meteoric Water Line" (GMWL) and is based on precipitation data from various locations around the world, and has a very high correlation coefficient of $r^2 > 0.95$ due to the close association of the oxygen and hydrogen stable isotopes in water molecules. Consequently, the isotopic ratios and fractionations of the two elements are usually evaluated together. The slope of this equation is 8 due to the difference in the fractionation behavior of ^{18}O and D. From a similar study conducted at near Shiprock, New Mexico, $\delta ^{18}O$ values varied widely from -15 to -5‰ and δ D values ranged from about -100 to -60‰ (DOE, 2012).

Since evaporation ponds were used to store tailings fluids from the milling operation, enriched concentrations of ^{18}O and D will identify groundwater that has mixed with water from the evaporation ponds. It is important to note that $\delta ^{18}O$ versus δ D signatures can provide information about the origin of water, however taken by themselves, are insufficient to differentiate individual water sources and must therefore be used in conjunction with uranium isotopic signatures.

Water with an isotopic composition that lies on the GMWL is considered to have originated from condensation of water vapor (precipitation) and to be unaffected by other isotopic processes. Water with enriched concentrations of ^{18}O and D is observed in strongly evaporated surface water and plot off the GMWL. Water that has evaporated or has mixed with evaporated water typically plots below the meteoric water line along lines that intersect the meteoric water line at the location of the original un-evaporated composition of the water (Kendall et al., 1995).

Geology of the Bluewater Mill Area

The most recent geologic map of the Bluewater site is from the New Mexico Bureau of Geology and Mineral Resources (Rawling, 2013). The majority of the area's surface is comprised of basalt lava which originated from a small shield volcano known as the "El Tintero" (the inkwell) about 68,000 years ago located about 4 miles north of the Bluewater main tailings disposal cell. The thickness of the basalt in the Bluewater site area varies between 70 to 130 feet with an average thickness of 100 feet. The exposed rough surface is referred to as the "El Malpais" (the badlands). The basalt covers alluvium comprised of sands and gravels that originated from the Rio San Jose and have an average thickness of approximately 25 feet at the site and is partially saturated and is the uppermost aquifer at the site. Anthropogenic deposits in the Bluewater mill area include artificial fill and reclaimed mine tailings. Windblown sediments of sand, silt and clay of Quaternary origin also cover the site.

The reminder of the area's surface is comprised of a small outcrop of the Permian San Andres Limestone and shale, siltstone and sandstone members of the Triassic Chinle Formation (Rawling, 2013). At the Bluewater mill, the San Andres Limestone contains more sandstone than limestone. Underlying the San Andres Limestone is the Permian Glorieta Sandstone. The combined thickness of these two Permian formations at the Bluewater mill is approximately 250 feet which dip to the northeast.

Structural geology at the site is complex due to a number of faults. The Ambrosia Lake Fault follows a north-south direction across the main tailings disposal cell and appears to act as a partial barrier to eastward flowing groundwater and another fault (unnamed) that tracks east-west crosses the Ambrosia Lake Fault beneath the southern end of the main tailings disposal cell. The arrangement of faults at the Bluewater site has resulted in four fault blocks. The northeast fault block has experienced the greatest upward displacement while the northwest block has the greatest downward displacement with a total vertical change of more than 400 feet. The southeast and southwest fault blocks have a displacement of approximately 50 feet and the vertical displacement difference between the northeast and southeast fault blocks is approximately 370 feet (DOE, 2014). There are also many small east-west faults that cross the site. These faults impact groundwater flow in the San Andres aquifer by blocking flow where vertical offsets occur and by providing a preferential flow path to groundwater through vertical seepage.

Surface geology and faults in the Bluewater mill area are shown in the following figure.

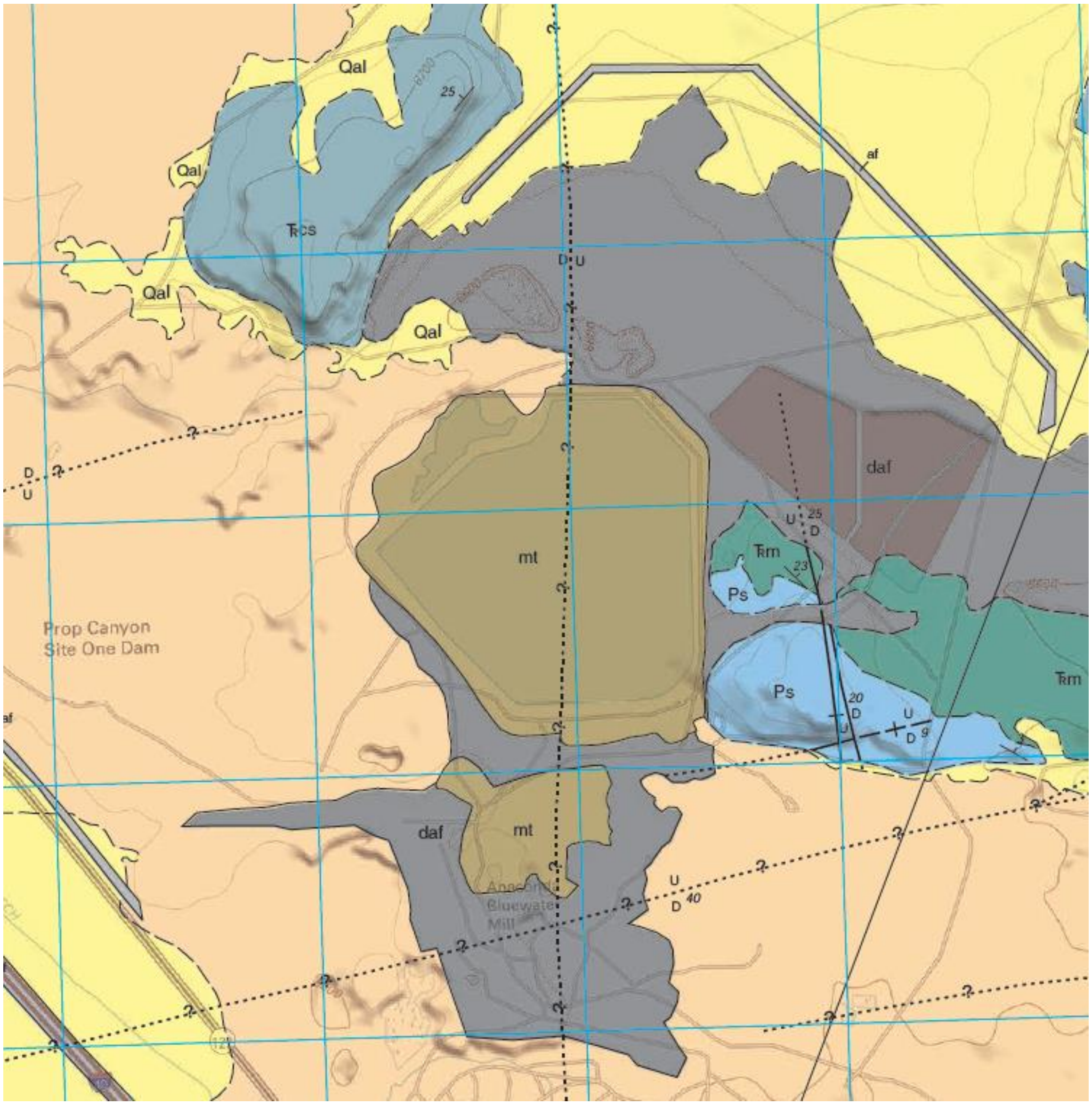
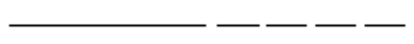


Figure 3. Geologic Map of the Bluewater Mill Area (Rawling, 2013)

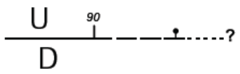
Unit Descriptions

af	Artificial fill for roads and cattle tanks
daf	Artificial fill and/or disturbed land
mt	Mounds of reclaimed mine tailings
Qal	Alluvial deposits, undivided
Qbt	**Basalt flows from El Tintero**—Data from drill holes indicate at least 5 separate flows aggregating 122 feet (37 m) in thickness are present in the southwestern part of the quadrangle.
TRcs	**Sonsela Sandstone Bed of Petrified Forest Member**—White, pale yellowish-brown, yellow, and brown conglomeratic sandstone interbedded with white, blue, purple and brown claystone. 290 feet (88 m) thick.
TRm	**Moenkopi Formation**—Pale reddish-brown and grayish-red arkosic and micaceous sandstone interbedded with lenticular pebble conglomerate and layers of mudstone galls. Cross-bedded near top, horizontally-bedded near base. About 26 feet (8 m) thick.
Ps	**San Andres Limestone**—Grayish-yellow and brown to red dense limestone interbedded with yellow fine-to medium-grained, cross-bedded to structureless sandstone in upper part, 80 feet (24 m) thick. Yellow sandstone similar to that above in middle part, 15 feet (4.5 m) thick. Dense, gray limestone with streaks and zones of coarse-grained calcite in lower part, 20 feet (6 m) thick. Upper surface is karst. Total thickness 115 feet (35 m).

Map Symbols



Geologic contact, solid where exposed, dashed where approximately located.



Fault, solid where certain, dashed where approximately located, dotted where buried, queried where location or termination is uncertain. U and D indicate sense of throw. Number indicates vertical separation in feet.

Strike and dip of bedding

Figure 4. Unit Descriptions and Map Symbols of Geologic Map (Rawling, 2013)

Hydrology of the Bluewater Mill Area

Surface water flow in streams in the GMD generally occurs only during large precipitation events due to the semiarid to arid climate of west-central New Mexico. The mean annual precipitation for the Bluewater area is about 10 inches. The Rio San Jose which lies west of the Bluewater site is heavily used for agriculture and diversions from the Rio San Jose downstream of Grants allow the Rio San Jose to remain dry most of the time. Consequently the Rio San Jose is considered to be an ephemeral stream within the study area (DOE, 2014).

Recharge to the alluvial aquifer occurs by several mechanisms: from direct precipitation on the alluvium; direct precipitation on the overlying Bluewater Basalt that quickly seeps to the underlying alluvium; seepage losses from waterways; and from upward leakage from the San Andres aquifer where its hydraulic head is greater than that in the overlying alluvium and the Chinle Formation is absent. Similarly discharge from the alluvial aquifer can occur by leakage into the underlying San Andres aquifer (when the Chinle Formation is absent or migration through faults) when the hydraulic head of the alluvial aquifer is greater than that of the San Andres aquifer.

Recharge to the San Andres aquifer occurs by direct precipitation on or surface water flow across sandstone and limestone outcrops in the Zuni Mountains southwest of the Grants-Bluewater Valley or from leakage from the alluvial aquifer as previously described. Water moves down-gradient along solution channels and fractures in the San

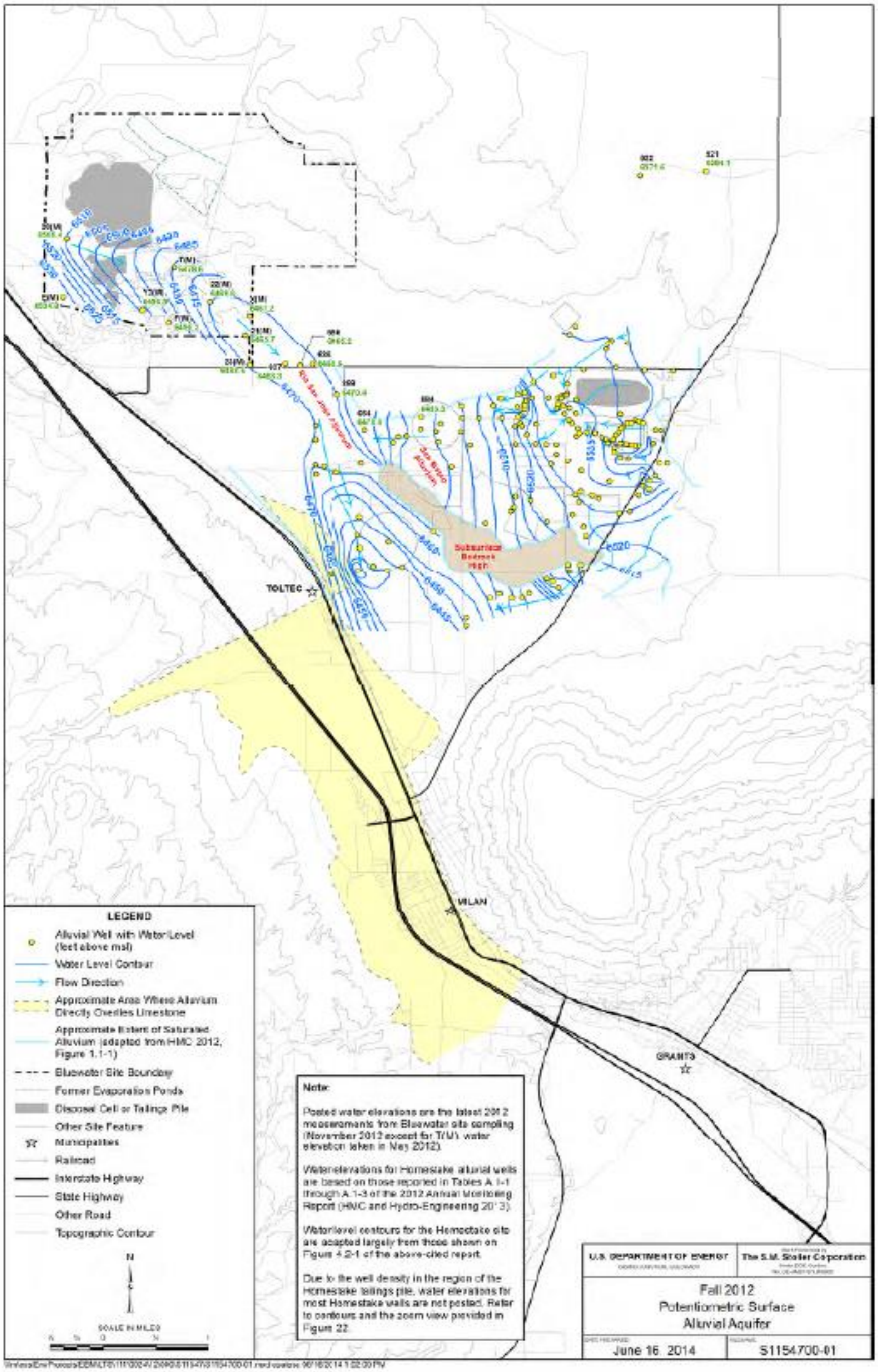
Andres Limestone and to a lesser extent through interconnected pore spaces and fractures in the Glorieta Sandstone (Baldwin and Rankin, 1995).

Hydrogeology of the Bluewater Mill Area

The alluvial aquifer in the Bluewater area consists predominantly of ancestral Rio San Jose Quaternary alluvium comprised of sands, gravels, silts, and clays and is considered to be an aquitard. Where the underlying Chinle Formation is present, the alluvial aquifer is not in direct connection with the San Andres aquifer. The estimated hydraulic conductivity for alluvium in the vicinity of the Bluewater site ranges between 75 to 150 ft/day (DOE, 2014). Groundwater flow in the alluvial aquifer primarily follows the same route as surface water flow in the Rio San Jose in a southward direction.

The San Andres aquifer is the most productive aquifer in the study area and is the primary water source in the area for municipal, commercial, irrigation, domestic, and livestock uses. Because of the gradual contact and good hydraulic connection between the San Andres Limestone and Glorieta Sandstone, the two units are typically considered as one aquifer. In most parts of the Bluewater area, groundwater flow in the San Andres aquifer occurs under confined conditions. The estimated hydraulic conductivities for the San Andres aquifer in the Grants-Bluewater Valley area are highly variable ranging from 0.25 to 1,800 ft/day and well yields are as much as 2,830 gallons per minute (Baldwin and Rankin, 1995). Additionally, estimates of effective porosity of the San Andres aquifer range between 0.02 to 0.25. These hydraulic properties of the aquifer vary, both increasing and decreasing with depth in the aquifer. Given this, contaminant concentrations measured at a particular well depth downgradient of the contaminant source (tailings) should generally represent a mixture of different concentrations that are fed into the well at different rates. Groundwater in the San Andres aquifer west of Interstate 40 flows to the northeast due to the geologic structure, topography of the unit, including the many faults which are located in the area.

Figure 5 presents the potentiometric surface and flow direction of alluvial aquifer groundwater based on 2012 DOE data and Figure 6 presents groundwater flow directions in the San Andres aquifer.



Note:

Posted water elevations are the latest 2012 measurements from Bluewater site sampling (November 2012 except for T(M) water elevation taken in May 2012).

Water elevations for Homestake alluvial wells are based on those reported in Tables A.1-1 through A.1-3 of the 2012 Annual Monitoring Report (HMC and Hydro-Engineering 2013).

Water level contours for the Homestake site are adapted largely from those shown on Figure 4.2-1 of the above-cited report.

Due to the well density in the region of the Homestake tailings pile, water elevations for most Homestake wells are not posted. Refer to contours and the zoom view provided in Figure 22.

Figure 5. Potentiometric Surface of the Alluvial Aquifer in 2012 (DOE, 2014)

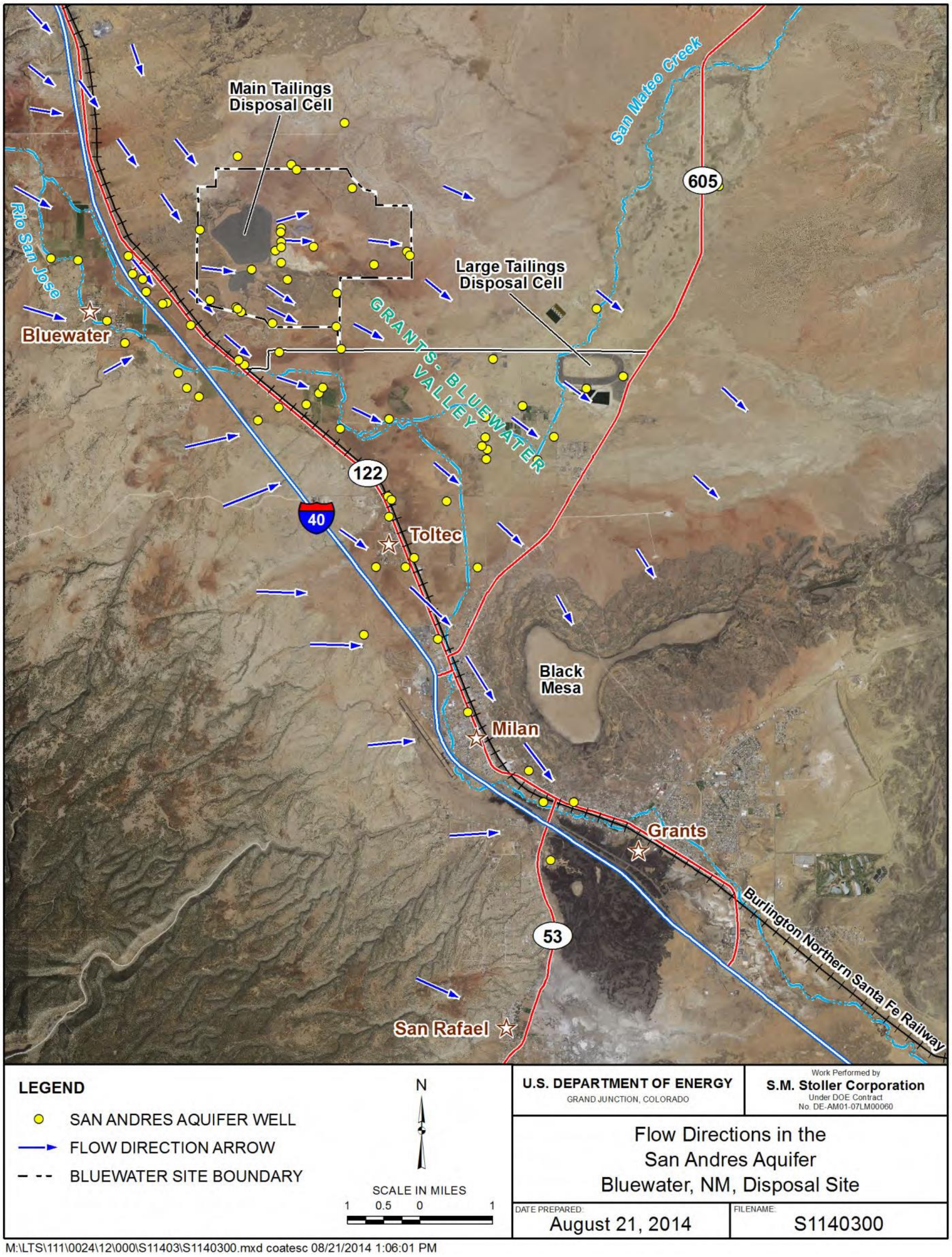


Figure 6. Ambient Flow Directions in the San Andres Aquifer (DOE, 2014)

3 METHODOLOGY

Sources of Existing Data

A background literature review was performed to include: historical information about the mining operations; previous studies conducted both in and outside of the study area with similar scope; hydrological and geological investigations; and information that includes water quality and isotopic data from the study area.

Historical water quality data at the Bluewater site from previous investigations is sparse. Generally much of the existing data at the Bluewater site was collected intermittently from various sources and did not include a comprehensive suite of analytes. Additionally the validity of the data and protocols used during field sampling from previous studies is uncertain.

Very few studies were conducted on the natural environment in the GMD prior to the beginning of uranium and milling operations in the early 1950s and no baseline sampling was conducted to determine the natural background conditions of groundwater quality parameters. With the exception of the DOE's recent report (November, 2014) titled "Site Status Report: Groundwater Flow and contaminant Transport in the Vicinity of the Bluewater, New Mexico, Disposal Site," no detailed quantitative assessment of background concentrations of uranium has ever been conducted.

The DOE LM and NMED data were the key sources of water quality information used for this study. Data from DOE and NMED was readily available, has undergone the proper validation process by both organizations, and reflects recent (within the last seven years) conditions.

For the Bluewater site, DOE performs groundwater monitoring twice a year from 20 wells which include nine ARCO wells that DOE inherited in 1997, 10 wells installed by DOE in 2011 and 2012, and an off-site private well (HMC-951) that DOE began to sample in 2013. The data used in this study was obtained from DOE's groundwater sampling program and is available to the public from the DOE LM website (www.lm.doe.gov). Additionally, NMED (May 2010) performed a site investigation of the Bluewater mill area in 2008. Data from this investigation that included water samples from 8 wells in proximity to the Bluewater site were used in this analysis. Five of the eight wells are identical wells sampled by DOE but are referenced differently by NMED. The following table is a list of DOE and NMED wells with relevant information.

Table 2. Bluewater Site Monitoring Wells

DOE LM Alluvial Aquifer Groundwater Monitoring Wells

Monitoring Well Number	Date Installed	Purpose	Screened Depth (feet below ground surface)
E(M)	1978	Background Well	68.6 – 89.8
F(M)	1978	Point of Compliance	94.2 – 114.9
T(M)	1980	Point of Compliance	128 - 133
Y2(M)	1986	Point of Compliance	98 - 123
X(M)	1980	Point of Exposure	123 - 132
20(M)	2012	Up-gradient Well	110 - 125
21(M)	2011	Point of Exposure	139.6 – 149.6
22(M)	2011	Downgradient Well	136.8 – 146.8
23(M)	2012	Downgradient Well	89 - 109

DOE LM/NMED San Andres Aquifer Groundwater Monitoring Wells

Monitoring Well Number	Date Installed	Purpose	Screened Depth (feet below ground surface)
L(SG)[1]/BW-25	1981	Background Well	413.28 - 610
OBS-3/BW-27	1981	Point of Compliance	152.4 - 350
S(SG)[1]/BW-26	1981	Point of Compliance	159 - 280
I(SG)/BW-28	1979	Point of Exposure	236.1 - 330
11(SG)	2012	Cross-gradient Well	265 - 295
13(SG)	2012	Point of Exposure	270 - 300
14(SG)	2012	Cross-gradient Well	285 - 315
15(SG)	2012	Downgradient Well	341 - 371
16(SG)	2012	Point of Compliance	195 - 125
18(SG)	2012	Downgradient Well	260 - 290
HMC-951[1] (BW-34 by NMED)	1957	Off-Site Private Downgradient Well	242 - 272

NMED San Andres Aquifer Groundwater Monitoring Wells

Monitoring Well Number	Date Installed	Purpose	Screened Depth (feet below ground surface)
BW-05[2]	Unknown	Up-gradient Well	147-518
BW-14	Unknown	Background Well	340-380
BW-24[2]	Unknown	Up-gradient Well	137-587

[1] Well screen was not installed; the borehole was left open below the bottom of the casing

[2] Depth to water at completion to well depth

The E(M) well has been designated by DOE as representing background conditions in the alluvial aquifer. The total depth of well E(M) is 100 feet, with alluvium encountered below the Bluewater Basalt between 73 feet and 82 feet. The slotted well screen starts in the basalt at about 69 feet and extends into the Chinle Formation to a depth of about 90 feet. The E(M) well is the shallowest well among the Bluewater site monitoring wells and has considerable lower concentrations of uranium and other chemical constituents than all the Bluewater site monitoring wells.

The point of compliance (POC) for a groundwater well refers to where DOE monitors groundwater quality with regards to a specified cleanup level known as the alternative concentration limit (ACL). The ACL for molybdenum, selenium, and uranium for the POC wells completed in the alluvial and San Andres aquifers at the Bluewater site are shown in Table 3.

Progress toward meeting an ACL is measured at the point of compliance using groundwater monitoring wells. The locations of these monitoring wells may change during different stages of a groundwater cleanup action. For instances where groundwater is not a current or potential future drinking water source, or total restoration is not practical for near-term goals, the expectation is that human health and the environment *must* be protected at the point of exposure. Where groundwater beneath a facility cannot be remediated to drinking water standards in the near-term such as at the Bluewater disposal site, the point of exposure (POE) is placed at the facility boundary.

Table 3. Alternative Concentration Limits for Point of Compliance Wells

POC Well	Analyte	ACL (µg/L)
Alluvial	Molybdenum	100
	Selenium	50
	Uranium	440
San Andres	Selenium	50
	Uranium	2150

Well locations for DOE and NMED wells at the Bluewater disposal site are shown in the following figures.

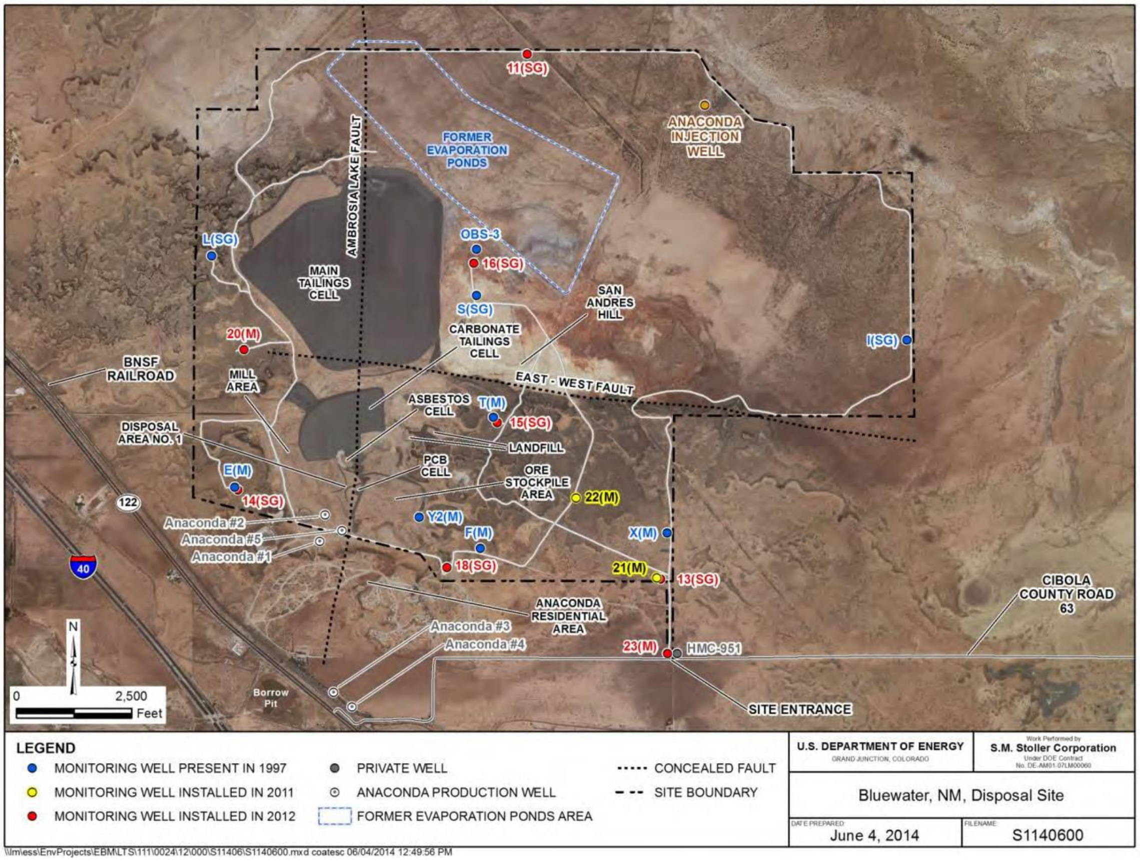


Figure 7. DOE Well Locations at the Bluewater Disposal Site

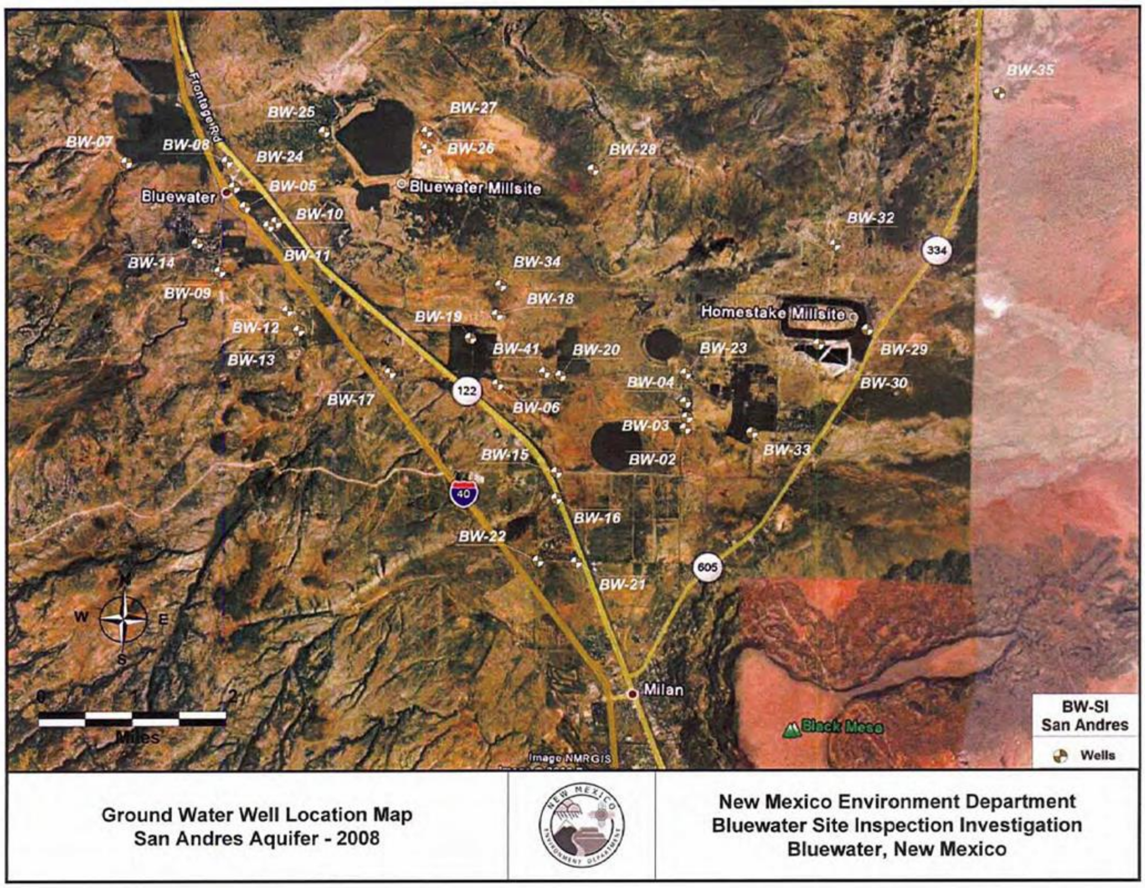


Figure 8. NMED San Andres Aquifer Well Locations at the Bluewater Disposal Site

Table 4 identifies recent sampling events by DOE by well as part of their commitment towards the long-term surveillance and maintenance of the Bluewater site. Included in Table 4 are the wells sampled by NMED as part of their 2008 investigation.

Water quality constituents analyzed in this investigation are based on average values from the sampling events identified in Table 4. For some years, not all wells were analyzed for the same constituents. As such, average water quality values for some wells are based on two sampling events whereas for other wells four years of data was available. For concentrations less than the detection limit, a value equal to one-half of the detection limit was used for this analysis. The actual dates of the water sampling events for each of the wells used in this investigation are shown in Table 4.

Table 4. Sampling Events for Averaging Water Quality Constituent Data by Well

Monitoring Well Number	Sampling Event				
	August 2008	November 2010	July 2011	November 2013	July 2014
E(M)		✓	✓	✓	✓
F(M)		✓	✓	✓	✓
T(M)		✓	✓		
Y2(M)		✓	✓	✓	✓
X(M)				✓	✓
20(M)				✓	✓
21(M)			✓	✓	✓
22(M)			✓	✓	✓
23(M)				✓	✓
L(SG)		✓	✓	✓	✓
OBS-3		✓	✓	✓	✓
S(SG)		✓	✓	✓	✓
I(SG)		✓	✓	✓	✓
11(SG)				✓	✓
13(SG)				✓	✓
14(SG)				✓	✓
15(SG)				✓	✓
16(SG)				✓	✓
18(SG)				✓	✓
HMC-951				✓	✓
BW-05	✓				
BW-14	✓				
BW-24	✓				

Table 5 presents a listing of the average values for the different water quality parameters evaluated in this investigation from the sampling events shown in Table 4.

Table 5. Average Values of Water Quality Parameters for Bluewater Wells

Well No.	^{234}U (pCi/L)	^{238}U (pCi/L)	^{234}U/U^{238} AR	U (µg/L)	Mo (µg/L)	Se (µg/L)	DO[2] (mg/L)	Cond[3] (µS/cm)
11(SG)	6.97	4.43	1.57	13.70	1.31	0.75	1.09	2627
13(SG)	36.15	34.30	1.05	103.25	1.71	6.23	3.01	1500
14(SG)	24.00	21.05	1.14	69.20	2.93	0.75	0.73	1944
15(SG)	55.05	50.40	1.09	151.50	13.92	1.14	0.89	1907
16(SG)	392.00	413.50	0.95	1345.00	2.70	15.90	1.36	3905
18(SG)	43.00	42.95	1.00	130.50	3.88	0.75	0.79	1638
20(M)	6.77	4.40	1.54	14.10	2.31	5.66	7.44	1289
21(M)	45.90	41.60	1.10	137.00	1.20	11.10	4.52	1827
22(M)	118.67	116.33	1.02	370.33	1.74	3.77	2.67	1343
23(M)	9.98	6.98	1.43	23.55	6.60	1.38	3.03	1000
E(M)[1]	-	-	-	0.03	0.43	0.75	0.62	1588
F(M)	3.49	2.61	1.34	7.66	0.76	1.21	3.08	577
HMC-951	12.35	11.00	1.12	31.50	1.31	0.75	4.01	1240
I(SG)	38.96	37.99	1.03	110.20	0.88	2.01	2.30	1784
L(SG)	1.19	0.85	1.40	2.31	4.77	0.75	0.79	2308
OBS-3	14.36	11.38	1.26	34.53	0.47	1.98	0.51	3511
S(SG)	129.33	137.13	0.94	413.67	1.41	10.72	2.56	3975
T(M)	168.50	175.50	0.96	543.50	25.05	3.46	1.26	1709
X(M)	45.95	42.45	1.08	133.00	1.28	7.23	3.47	1870
Y2(M)	2.85	1.68	1.69	5.11	1.83	0.75	5.59	658
BW-05	6.40	3.00	2.13	10.50	1.00	4.00	1.98	1613
BW-14	13.80	3.40	4.06	10.50	1.00	10.00	5.32	1688
BW-24	14.40	3.20	4.50	10.90	1.00	4.10	1.53	2101

[1] Undetermined due to data below detection limits

[2] Dissolved Oxygen

[3] Specific Conductivity

^{234}U/^{238}U Isotopic Ratios and Relationship to Uranium Concentration and other Chemicals

^{234}U/^{238}U isotopic ratios in conjunction with chemical data and conditions that favor uranium mobility to promote the formation of highly soluble oxidized U(VI) species are used and analyzed respectively in this investigation to determine the spatial distribution of uranium contamination and to better understand the interaction of groundwater movement among the aquifers. Chemical data includes soluble constituents of liquid wastes produced during mill operations such as molybdenum and selenium which are diagnostic indicators of uranium mill derived water.

The relationship between water field parameters (conductivity, dissolved oxygen (DO) concentration) and uranium (including molybdenum and selenium) concentration was evaluated to better understand geochemical stratification within and among the aquifers. Additionally, the processes (evaporation, dilution/attenuation, precipitation, and mixing) affecting uranium concentration and isotopic concentration in the alluvial aquifer were evaluated as well as illustrated on plots of $^{234}U/^{238}U$ activity ratio relative to the reciprocal of uranium concentration as shown in Section 4.

The Mann-Whitney nonparametric test statistic was used to determine whether two different water quality parameters (e.g., uranium and molybdenum) had similar statistical properties. To perform this test, data from each water quality parameter was ranked (from 1,2…) in ascending order of magnitude, regardless of which water quality parameter the data belonged to. N is the total number of samples where n_1 represents the number of samples in the first group and n_2 is the number of samples in the second group. R_1 is the sum of the rank of samples for the first group and R_2 is the sum of the rank for the second group (Zar, 1999). Using the following equations the U, U’,μ_U, and $\sigma_U$values were determined:

$$U = n_1 n_2 + n_1 \frac{(n_1 + 1)}{2} - R_1$$

$$U' = n_1 * n_2 - U$$

$$\mu_U = \frac{1}{2}(n_1 n_2)$$

$$\sigma_U = \sqrt{\left(\frac{1}{12} n_1 n_2 (\boldsymbol{N} + \mathbf{1})\right)}$$

$$Z_c = \left(\frac{U' - \mu_U}{\sigma_U}\right)$$

The resultant Z_c was then compared to the one tailed critical $Z_{\alpha(1)}$ or equivalently $t_{\alpha(1),\infty}$; and if $Z_c \geq Z_{\alpha(1),}$ the critical value, the H_o (the null hypothesis) was rejected. The larger the absolute value of Z_c, the smaller the probability that H_o is true. Rejection of the null hypothesis indicated the two sampled water quality parameters correlated demonstrating the result was considered statistically significant and the relationship is caused by something other than mere random chance. The level of significance for the critical values was assigned 0.05 in a one tailed test, meaning that there was a probability of 5 percent error for the two water quality parameters not sharing the same source(s) of contamination.

$^{18}O/^{2}H$ Fractionation to Determine Water Origin

DOE LM and NMED data was evaluated based on its origin (San Andres versus alluvial aquifer) and date of analysis (2008 versus 2014). Table 6 presents δ ^{18}O and δ D values as parts per thousand by well for the San Andres and alluvial aquifers.

Table 6. δ ^{18}O and δ D Values for Bluewater Site Wells

2008 NMED San Andres Aquifer Data

Well Number	δ ^{18}O (‰)	δ D (‰)
BW-05	-9.71	-75
BW-14	-12.4	-93.3
BW-15	-10.05	-76.5
BW-23	-10.15	-78.5
BW-24	-10.2	-78.4
BW-25	-10.68	-84.9
BW-26	-9.01	-72
BW-27	-8.99	-73.6
BW-28	-9.35	-73.3
BW-32	-10.24	-77
BW-34	-9.63	-71.8

2014 DOE San Andres Aquifer Data

Well Number	δ ^{18}O (‰)	δ D (‰)
11(SG)	-10.22	-80.01
13(SG)	-9.26	-74.34
14(SG)	-10.25	-79.51
15(SG)	-10.06	-78.72
16(SG)	-9.08	-73.25
18(SG)	-9.5	-75.38
HMC-951	-9.25	-74.22
I(SG)	-9.81	-77.71
L(SG)	-11.06	-84.61
OBS-3	-9.25	-73.92
S(SG)	-9.15	-73.27

2014 DOE Alluvial Aquifer Data

Well Number	δ ^{18}O (‰)	δ D (‰)
20(M)	-8.69	-70.95
21(M)	-8.62	-71.67
22(M)	-8.27	-68.33
23(M)	-10.25	-79.11
E(M)	-10.02	-78.95
F(M)	-8.55	-66.56
X(M)	-9.27	-74.11
Y2(M)	-9.88	-76.4

The Albuquerque local meteoric water line (MWL) has the following linear relationship: δ D = 7.76 δ ^{18}O + 4.73, and is based on historical data on the stable isotope composition of precipitation in the vicinity of the middle Rio Grande basin (USGS, 2012). Data from Table 6 was plotted and evaluated with respect to its location with the GMWL and Albuquerque local MWL. As discussed previously, a plot of the isotopic composition (δ D versus δ ^{18}O) can reveal differences between meteoric sources of water and evaporative sources of water.

Age Dating Based on Tritium Concentration

Tritium (^{3}H) is a radioactive isotope with a half-life of 12.26 years. Tritium is produced naturally in the upper atmosphere from the interaction of cosmic ray neutrons with nitrogen-14 and combines with atmospheric oxygen in the form of water molecules as part of the hydrologic cycle. Additionally high concentrations of tritium were artificially introduced into the atmosphere from atomic bomb testing during the period from 1954 to 1963 when several thousand pCi/L of tritium were measured in rainfall.

Clark and Fritz (1997) developed guidelines for determining the relative ages of groundwater on the basis of ^{3}H concentrations. In 1997, they concluded that waters containing less than 3 pCi/L are sub-modern (recharged prior to 1952); waters with concentrations between 16 and 48 pCi/L are modern (less than 5 to 10 years old); waters with more than 97 pCi/L were probably recharged in the 1960 or 1970's and concentrations greater than 160 pCi/L represent water recharged during the atomic bomb testing in the 1960’s.

Correcting these values to represent 2014 conditions results in sub-modern waters with a ^{3}H value less than 1 pCi/L; modern waters with ^{3}H values between 6 – 18 pCi/L; waters recharged in the 1960 or 1970’s with ^{3}H values more the 37 pCi/L; and waters recharged during the atomic bomb testing in the 1960’s with ^{3}H values greater than 61 pCi/L.

The following table lists ^{3}H values for alluvial and San Andres aquifer groundwater samples analyzed by DOE in April 2014.

Table 7. April 2014 Tritium Values for Bluewater Wells

Alluvial Aquifer Monitoring Wells - ^{3}H value (pCi/L)

20 (M)	21 (M)	22 (M)	23 (M)	E (M)	F (M)	Y2 (M)
7.95	8.00	10.4	5.48	5.76	11.7	5.39

San Andres Aquifer Monitoring Wells - ^{3}H value (pCi/L)

11 (SG)	13 (SG)	14 (SG)[1]	15 (SG)	16 (SG)	18 (SG)	HMC-951	I (SG)	OBS-3	S (SG)
3.71	8.44	Un-detected	5.51	6.56	7.95	8.59	7.84	10.3	8.67

[1] Detection limit = 2.43 pCi/L

4 RESULTS

The DOE LM and NMED data were evaluated with respect to location, source, and association with other groundwater constituents. The results of these analyses are presented in the following subsections. Statistical analyses using the Mann-Whitney test among different water quality parameters are presented in Table 8 where $P < 0.05$ indicates that the relationship exists. The one tailed critical value ($Z_{\alpha(1)}$) with a 0.05 level of significance is 1.644.

Mann-Whitney calculations are presented in Appendix I.

Water Quality Parameters		Z_c	P Value
Uranium	Molybdenum	4.800	<0.00001
Uranium	Specific Conductance	-5.679	<0.00001
Molybdenum	Specific Conductance	-5.811	<0.00001
Uranium	Dissolved Oxygen	4.998	<0.00001
Molybdenum	Dissolved Oxygen	-0.494	0.3105
$^{234}U/^{238}U$ AR	Uranium	5.200	<0.00001
$^{234}U/^{238}U$ AR	Molybdenum	1.067	0.1429
$^{234}U/^{238}U$ AR	Selenium	0.840	0.2004

AR = Activity Ratio

Table 8. Mann-Whitney Test among Different Water Quality Parameters

For convenience to the Reader, the DOE well location map is shown below.

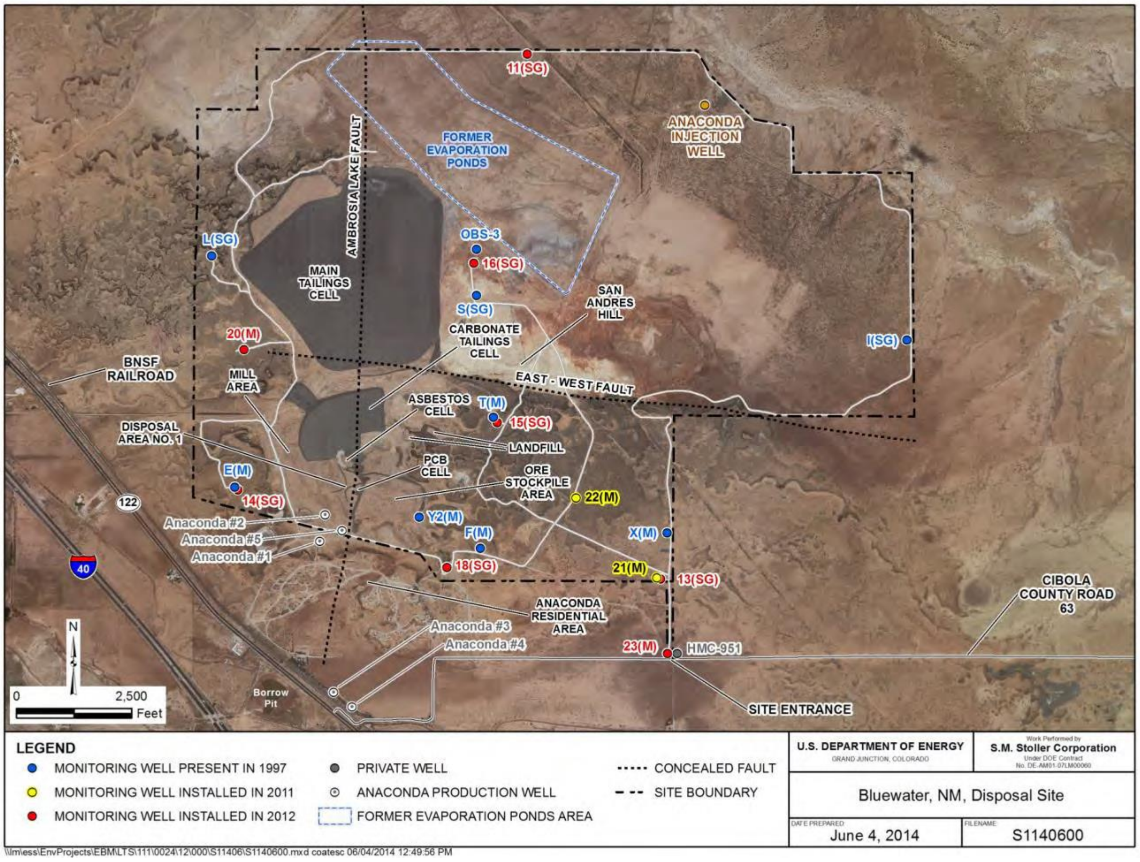


Figure 9. DOE Well Locations at the Bluewater Disposal Site

$^{234}U/^{238}U$ Isotopic Ratios and Uranium Concentration Relationship to other Chemicals

Uranium and Molybdenum Relationship

Uranium and molybdenum concentrations for groundwater samples collected from the study area vary over a large concentration range of <0.1 – 1345 µg/L and <1.0 – 25 µg/L respectively as shown in the log-log plot of uranium and molybdenum in Figure 10. The largest concentration of uranium at 1345 µg/L occurred at well 16(SG), a POC well completed in the San Andres aquifer located directly east and down-gradient of the main tailings cell with a somewhat low molybdenum concentration of 2.7 µg/L when compared to other wells. The well with the highest molybdenum concentration was well T(M) with 25.05 µg/L of molybdenum with also had the second highest concentration of uranium at 543.5 µg/L which exceeds the ACL for a POC alluvial well. Well T(M) is a POC well completed in the alluvial aquifer and is located south of well 16(SG), south of the East-West Fault. The well with the lowest concentrations of uranium and molybdenum was well E(M) with concentrations of these metals at 0.03 µg/L and 0.43 µg/L respectively. As previously noted, well E(M) is designated as a background well by DOE and is completed in the alluvial aquifer. The second lowest uranium concentration was from well L(SG) at 2.31 µg/L which is a DOE designated well completed in the San Andres aquifer. The molybdenum concentration at this well was 4.77 µg/L.

The Mann-Whitney test determined the relationship between molybdenum and uranium concentrations to be statistically significant (other than by random chance) and from Figure 10 it can be seen that there is a positive correlation between molybdenum and uranium concentrations with molybdenum and uranium concentrations being generally greatest with the POC and down-gradient wells. Background and up-gradient wells for the alluvial and San Andres aquifers generally are considerably lower in molybdenum and uranium concentrations than other wells as is expected. Additionally there appears to be no distinct differences in molybdenum and uranium concentrations between the alluvial and San Andres aquifers. Overall, molybdenum concentrations from all samples are considered low by at least an order of magnitude for water collected in the proximity of a uranium mill tailings site.

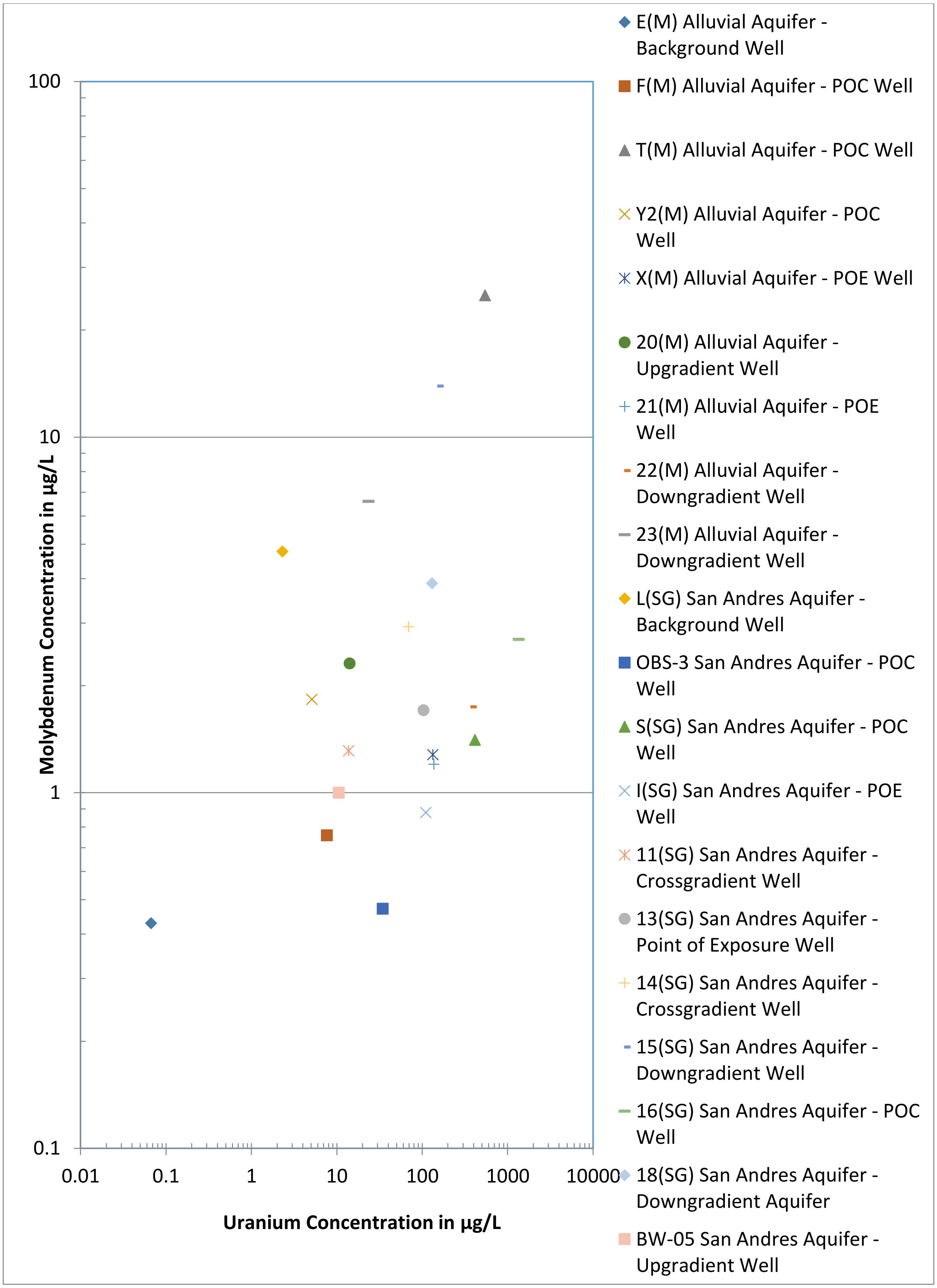


Figure 10. Relationship of Uranium to Molybdenum Concentrations for Alluvial and San Andres Aquifers

Uranium and Molybdenum Relationship to Specific Conductance

Generally lower specific conductance of water from the alluvial aquifer than the San Andres bedrock aquifer is an indication that the alluvial aquifer is fresher than the bedrock aquifer due to greater permeability of the alluvium and relatively more recent recharge. The average specific conductivity from alluvial aquifer wells is 1449 µS/cm versus an average of 2267 µS/cm for samples collected from the San Andres aquifer wells.

The Mann-Whitney test determined the relationship between uranium and molybdenum concentrations to specific conductance to be statistically significant however there are no clear trends in the data. The correlation between uranium concentrations to specific conductance is shown in the log-log plot of uranium and specific conductance in Figure 11. Well 16(SG) had the highest specific conductance at 3905 µS/cm and the highest uranium concentration (1345 µg/L).

There appears to be very little correlation between molybdenum concentrations and specific conductance as shown in the log-log plot of molybdenum and specific conductance in Figure 12.

In general, San Andres wells exhibit greater specific conductance (658 to 3905 µS/cm) than alluvial wells (577 to 1827 µS/cm) irrespective of uranium concentration and molybdenum. There is no correlation between up-gradient wells to background, down-gradient, and cross-gradient wells.

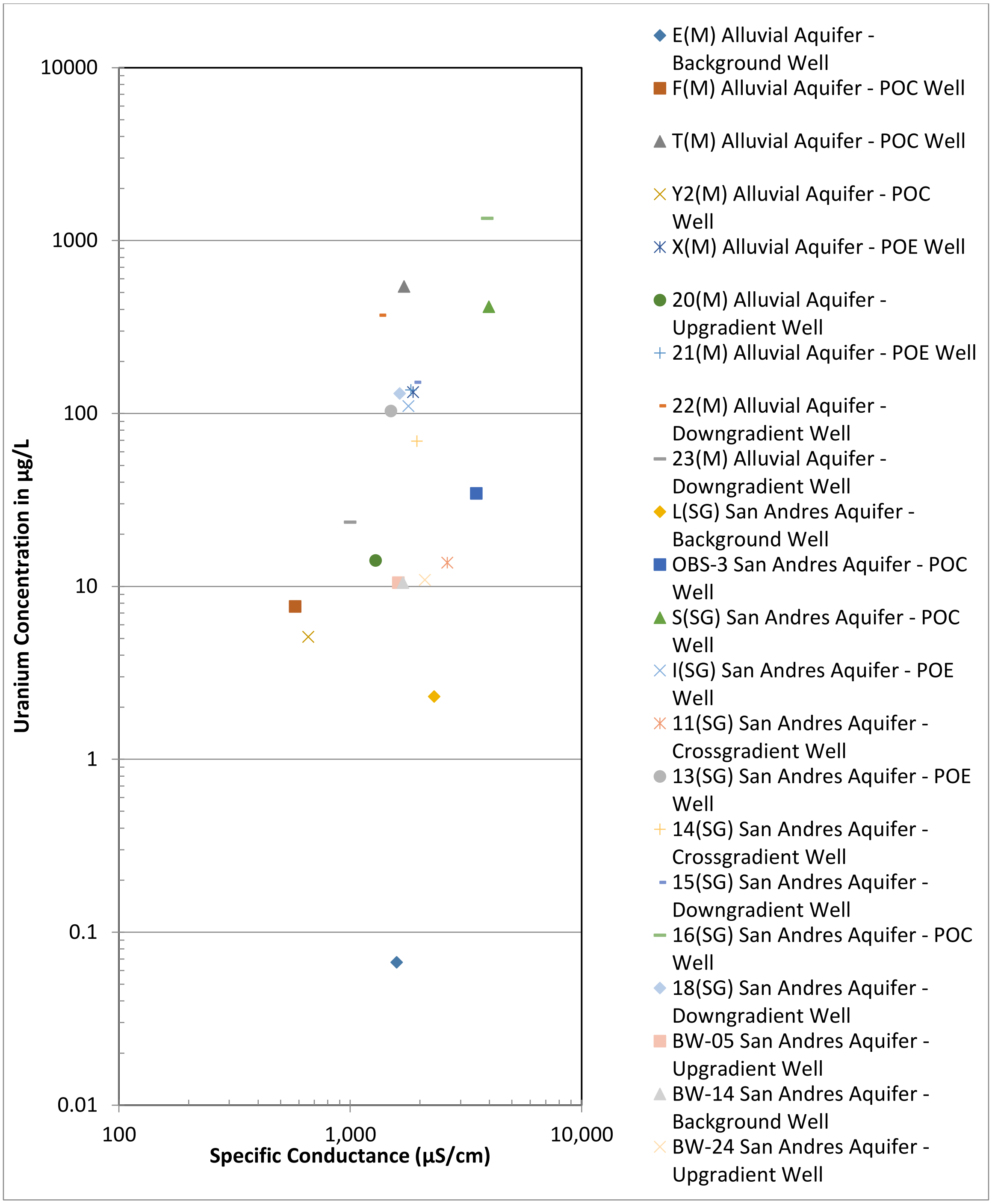


Figure 11. Relationship of Uranium Concentration to Specific Conductance

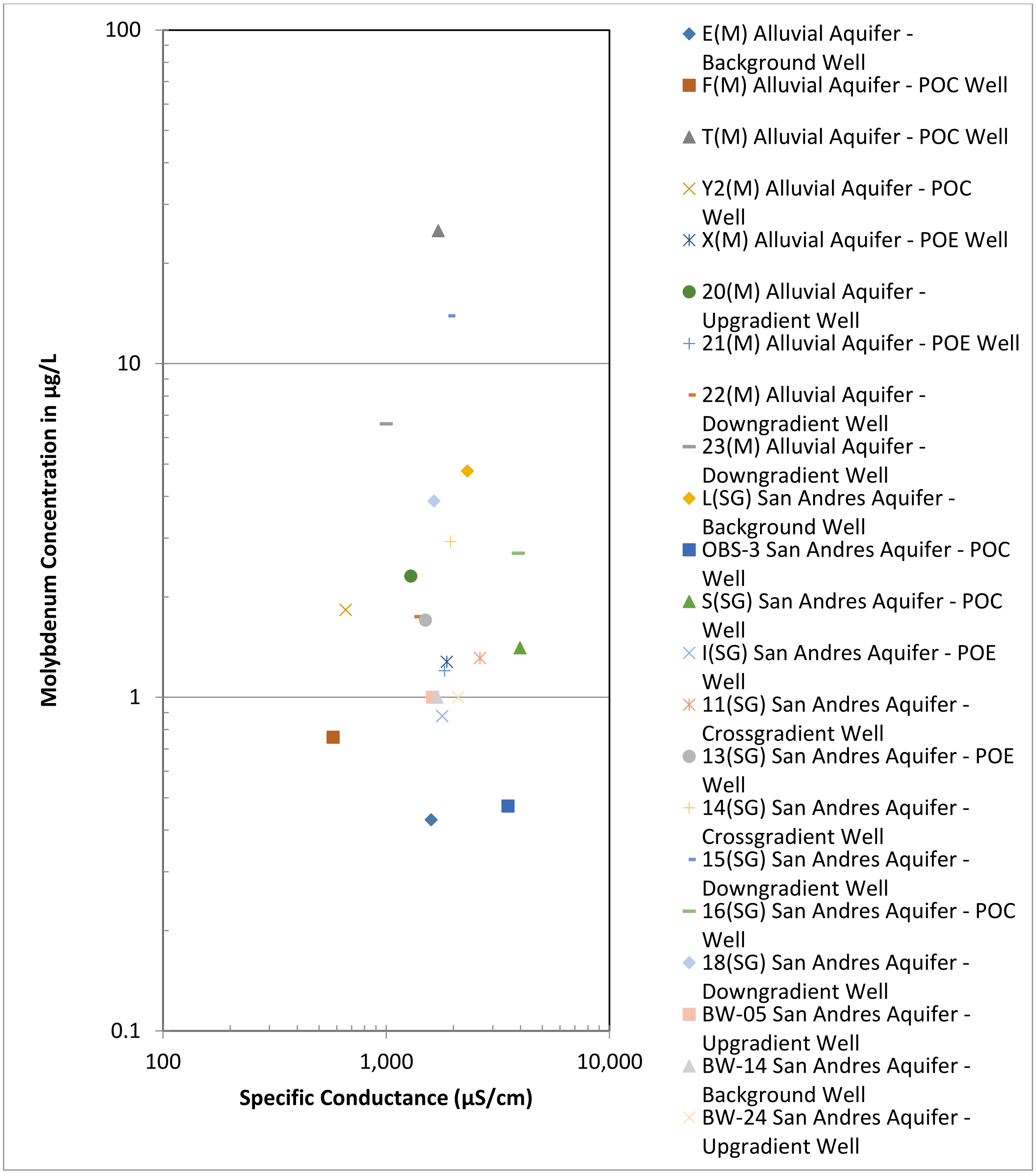


Figure 12. Relationship of Molybdenum Concentration to Specific Conductance

Uranium and Molybdenum Relationship to Dissolved Oxygen

In general, the relationship of uranium and molybdenum concentrations to dissolved oxygen show no overall trends as shown in the log plots of uranium and molybdenum to dissolved oxygen in Figures 13 and 14 respectively. The Mann-Whitney test determined the relationship between uranium and dissolved oxygen to be statistically significant. However, the Mann-Whitney test found no correlation between molybdenum and dissolved oxygen.

As expected, groundwater samples from the alluvial aquifer wells have greater dissolved oxygen concentrations (0.62 – 7.44 mg/L with an average of 3.97 mg/L) than groundwater samples from the San Andres aquifer wells (0.51 – 5.32 mg/L with an average of 1.92 mg/L) which would favor the formation of the soluble species of uranium (VI) and molybdenum.

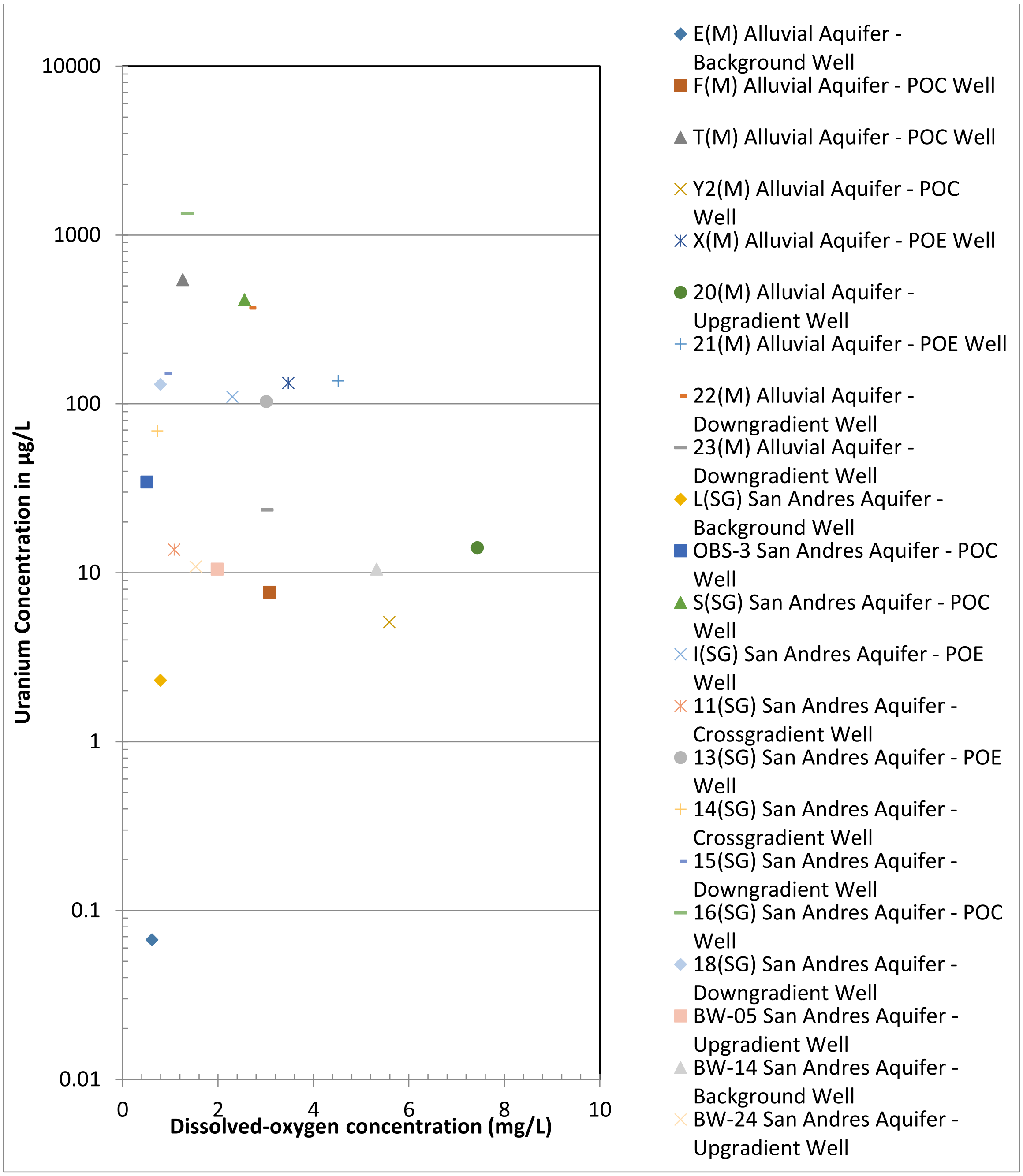


Figure 13. Relationship of Uranium Concentration to Dissolved-Oxygen

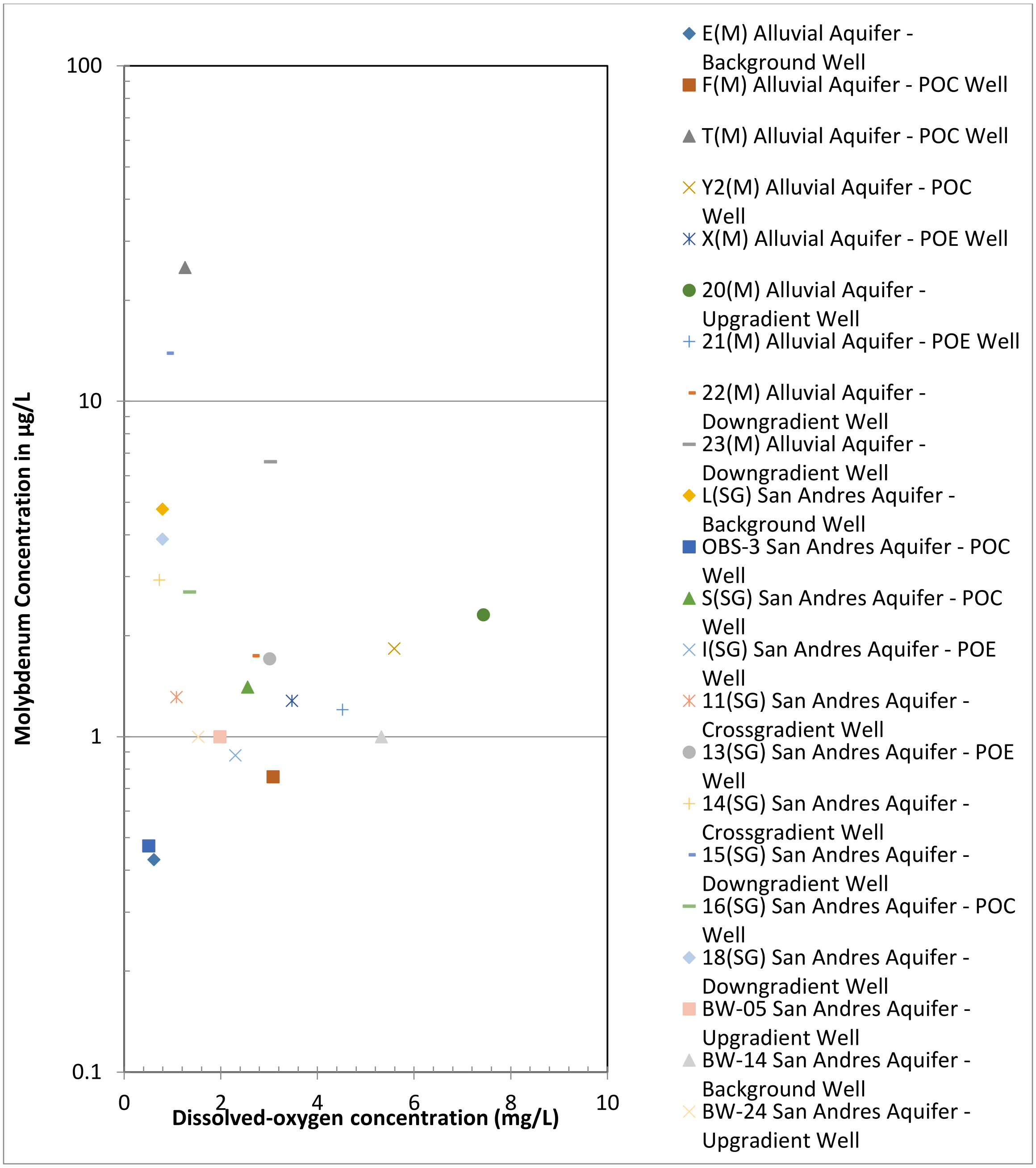


Figure 14. Relationship of Molybdenum Concentration to Dissolved-Oxygen

Uranium Isotopic Data

Figure 15 of activity ratio (AR) values relative to uranium concentrations shows that groundwater samples with uranium concentrations greater than 100 µg/L generally have AR values close to 1.0, indicating the source is from liquid waste and tailings solids produced during uranium mill operations. This correlation between uranium concentration and AR values is in agreement to data analyzed by Zielinski (1997) from a uranium mill in south-central Colorado. The POC wells 16(SG), S(SG), and T(M) with the greatest amounts of uranium at 1345 µg/L, 414 µg/L, and 544 µg/L all had AR values below 1.0 at 0.95, 0.94, and 0.96 respectively.

Activity ratios of ^{234}U/^{238}U in all groundwater samples from the Bluewater site range from near secular equilibrium of 0.94 to a high of 4.5. For the alluvial aquifer background well E(M), uranium concentrations for three of the four sampling events were below detection limits and 0.38 µg/L for one event. Averaging the data with the assumption that uranium concentrations less than the detection limit are assumed equal to one-half of the detection limit results in a uranium concentration of 0.03 µg/L. Concentrations for ^{234}U and ^{238}U were also detected but at were at values that could not be quantified with certainty. As such, the AR for the E(M) well was not used in this analysis. For the remaining alluvial wells, AR values range from 0.96 to 1.54.

The Mann-Whitney test determined the relationship between uranium AR values to uranium concentrations to be statistically significant.

Groundwater samples with uranium concentrations less than 100 µg/L had AR values that range from 1.12 to 4.50. All samples that have AR values greater than 2.13 are from the NMED 2008 groundwater samples. Figure 15 shows a definite trend in which AR values decrease with increasing uranium concentration. Additionally background and up-gradient wells from both the alluvial and San Andres wells demonstrate higher AR values with decreased uranium concentration from this figure. It is also apparent that there are no distinct differences among AR values and uranium concentrations between alluvial and San Andres wells.

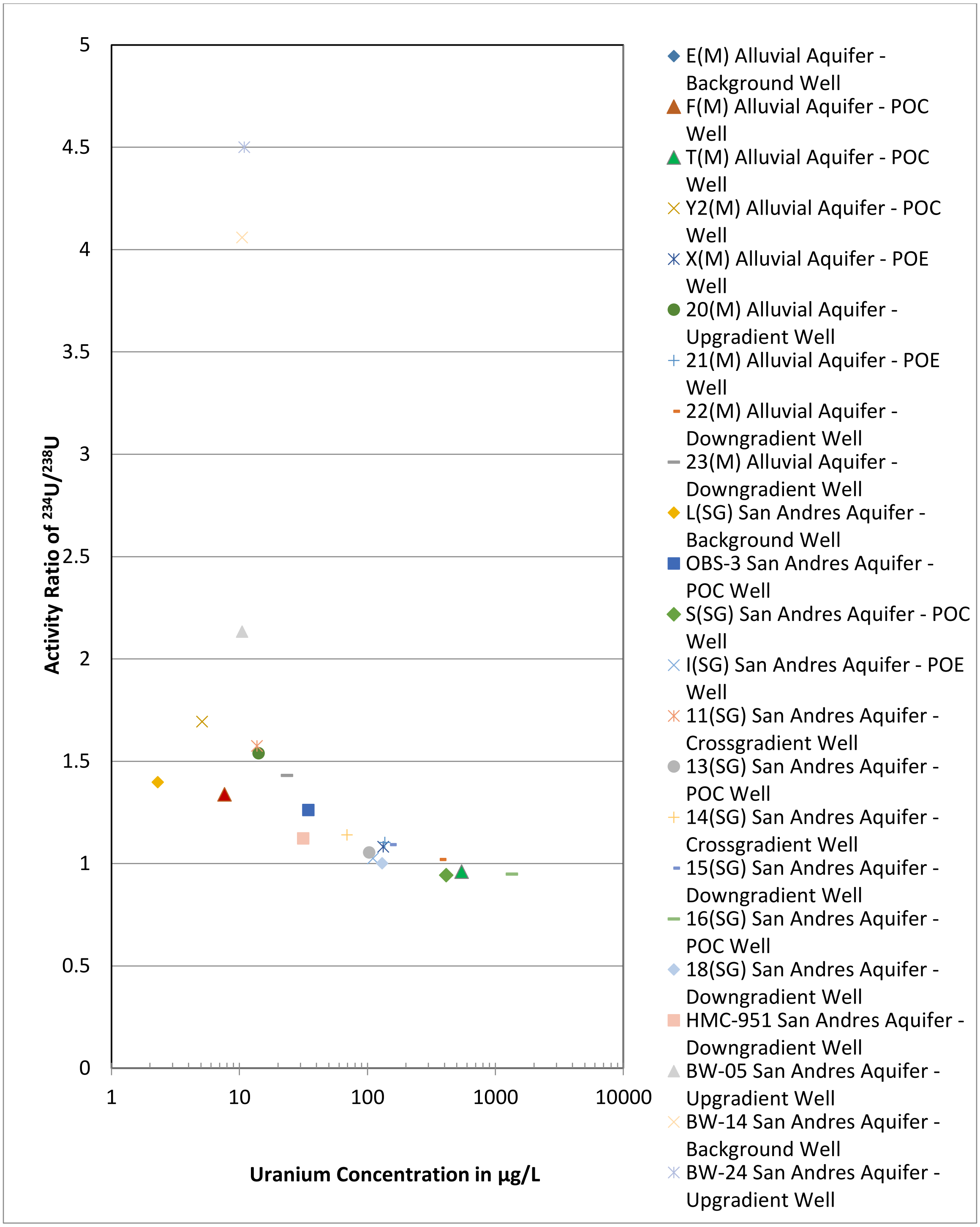


Figure 15. Relationship of $^{234}U/^{238}U$ Activity Ratio to Uranium Concentration

The concentration of molybdenum in Bluewater site groundwater is approximately greater than one order of magnitude less than of uranium. However as previously discussed there appears to be some correlation between molybdenum and uranium concentrations. Although not as apparent as in Figure 15 between the relationship of AR values to uranium, Figure 16 (AR values relative to molybdenum) indicates a relationship similar to that for uranium concentrations. However, the Mann-Whitney test determined the relationship between uranium AR values to molybdenum concentrations as not statistically significant. Well T(M) displays the highest amount of molybdenum and has a low AR value of 0.96. Well OBS-3 has the lowest recorded molybdenum concentration of 0.47 µg/L (other than the E(M) well with an undetermined AR value) and an AR value of 1.26. Additionally background and up-gradient wells from both the alluvial and San Andres wells demonstrate higher AR values with decreased molybdenum concentration from this figure. It is also apparent that there are no distinct differences among AR values and molybdenum concentrations between alluvial and San Andres wells.

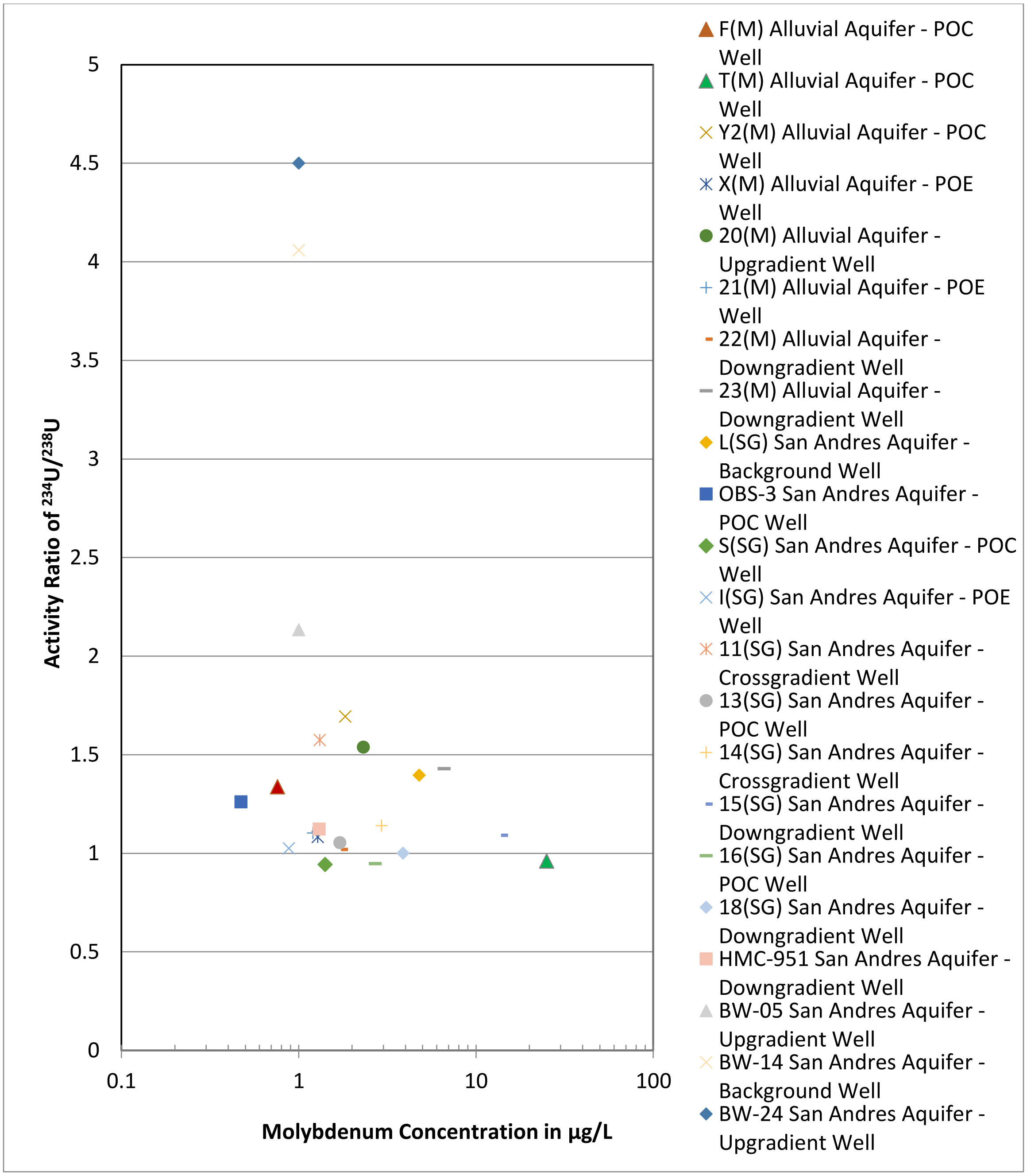


Figure 16. Relationship of $^{234}U/^{238}U$ Activity Ratio to Molybdenum Concentration

The plot of $^{234}U/^{238}U$ AR values to selenium concentrations in Figure 17 shows no identifiable trend and no general differences between the alluvial and San Andres wells. The Mann-Whitney test determined the relationship between uranium AR values to selenium concentrations as not statistically significant. The wells with the greatest selenium concentrations, 16(SG), 21(M), and S(SG) have low AR values within a narrow band between 0.94 – 1.10. Selenium concentrations at the Bluewater site are low with the largest the highest concentration being 15.9 µg/L at well 16(SG). The United States Environmental Protection Agency maximum contaminant level for selenium in drinking water is 50 µg/L.

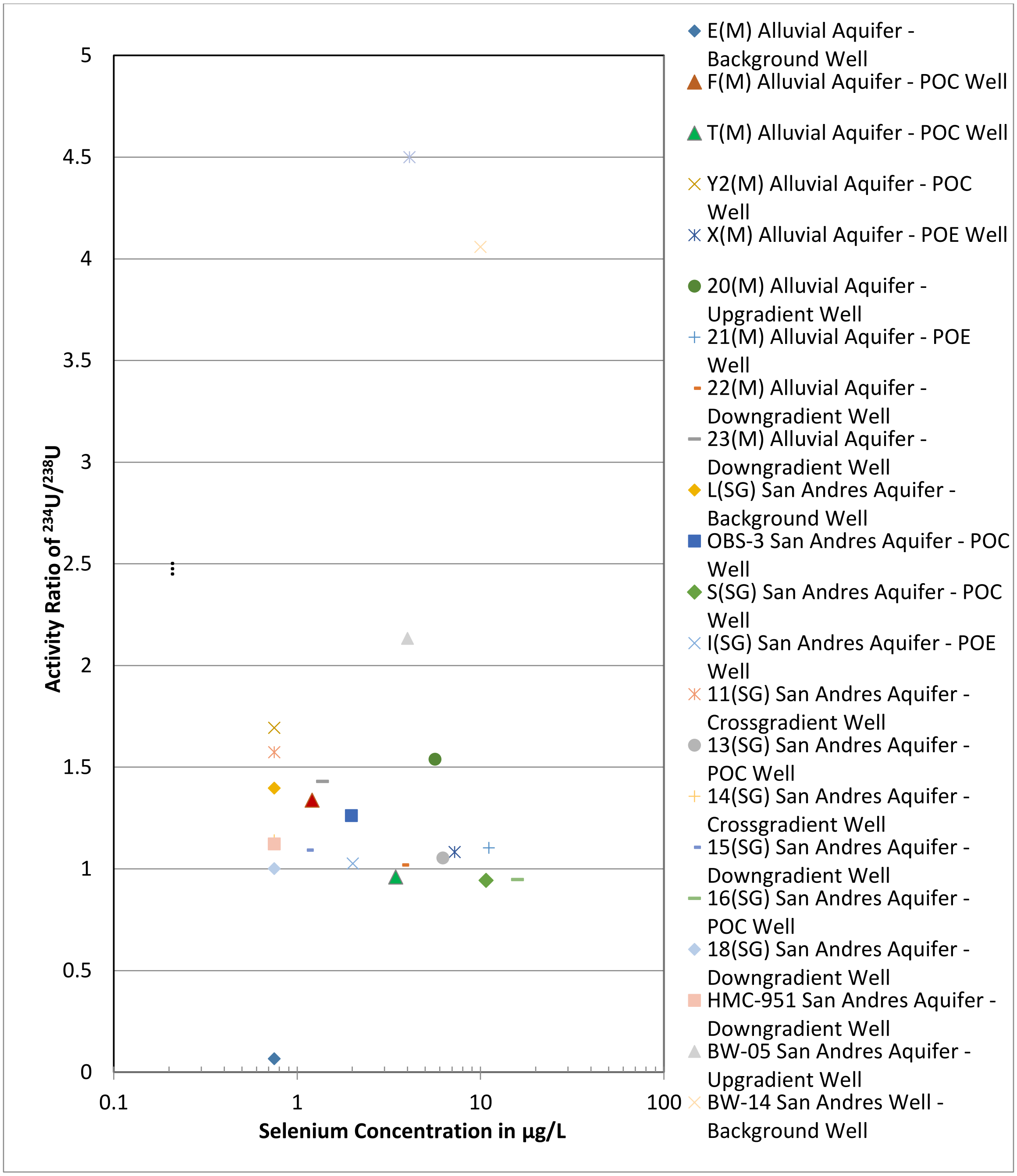


Figure 17. Relationship of $^{234}U/^{238}U$ Activity Ratio to Selenium Concentration

A common method of analysis is to plot the $^{234}U/^{238}U$ activity ratio against the reciprocal of uranium concentration to identify mixing and aquifer water interactions (Osmond, 1992). From Figure 18 some obvious patterns can be recognized. Attenuation from well 16(SG), a POC well with a uranium concentration of 1345 µg/L to the south to well S(SG), a POC well with a uranium concentration of 413.67 µg/L. Attenuation from well 14(SG), a cross-gradient well with a uranium concentration of 69.2 µg/L to the southeast to well HMC-951, a down-gradient well with a uranium concentration of 31.50 µg/L. Wells 11(SG), a cross-gradient well from the San Andres aquifer and 20(M), an up-gradient well from the alluvial aquifer have also most identical uranium concentrations and $^{234}U/^{238}U$ activity ratios at 13.70 µg/L and 14.10 µg/L and 1.57 and 1.54 respectively. The data from these wells is a very good example of background conditions and mixing among the aquifers possibly due to the displacement of the Ambrosia Lake Fault.

Additional attenuation is demonstrated from well 22(M), a down-gradient alluvial well with a uranium concentration of 370.33 µg/L to the southeast to well X(M), a POE well with a uranium concentration of 133 µg/L. The $^{234}U/^{238}U$ activity ratios for this sequence of flow is 1.02 to 1.08.

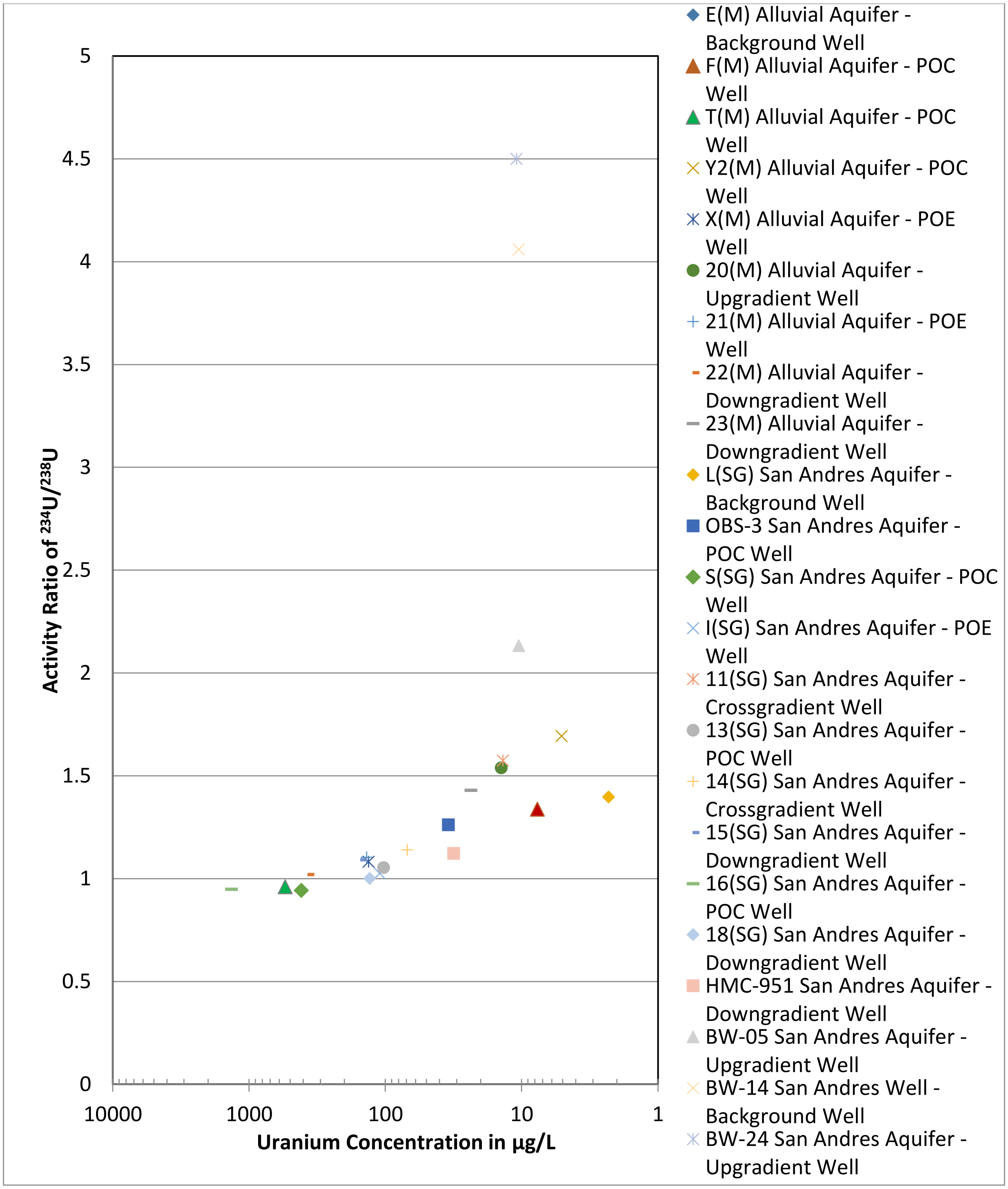


Figure 18. Relationship of $^{234}U/^{238}U$ Activity Ratio to the Reciprocal of Uranium Concentration

Water Fractionation

In general, water from both the San Andres and alluvial aquifers falls on the Albuquerque Local MWL as shown in Figure 19. The actual location of the data of the data points along the Albuquerque Local MWL is affected by temperature as well as continental, elevation and latitude effects. For instance, a well-mixed, groundwater dominated system will not vary much isotopically as is shown by the tight grouping of data points in the figure, while a system (or source) receiving seasonal input (event water) will vary considerably more. Isotopically heavier precipitation occurs as rain (typically ~ -3‰ - 0‰ for δ ^{18}O), while snow is dramatically lighter (~ -20‰ for δ ^{18}O). Warm regions are characterized by more enriched (positive) values of hydrogen and oxygen isotopes and cooler regions characterized by more depleted (negative) values.

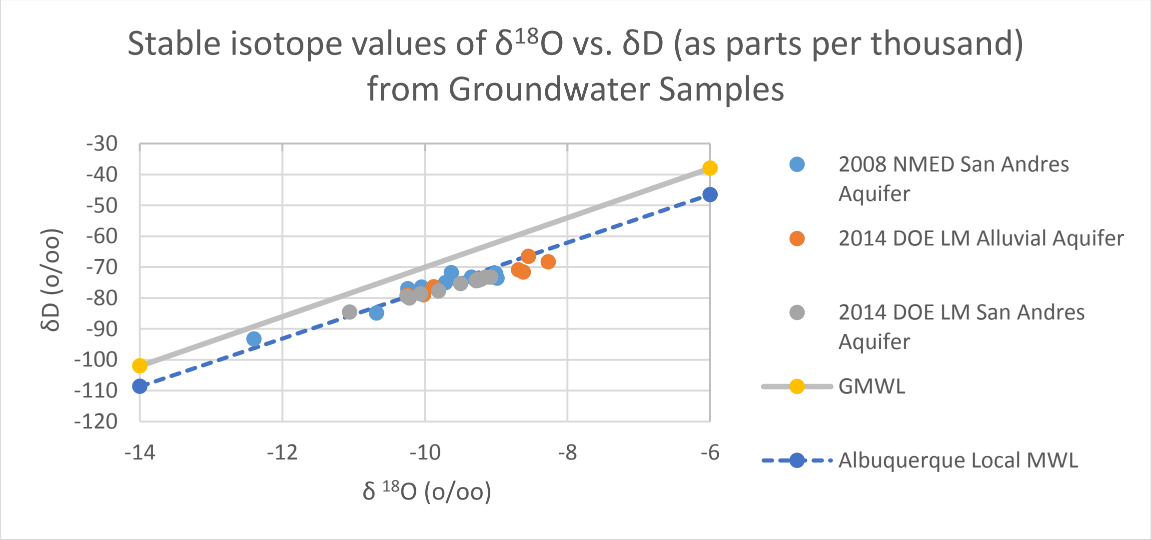


Figure 19. Stable Isotope Values from Groundwater Samples

The 2014 DOE LM alluvial aquifer data is slightly more enriched in ^{2}H and ^{18}O than the San Andres aquifer data suggesting more repeated isotopic fractionation during a succession of precipitation and evaporation events. The samples that fall below the MWL are the result from evaporation due to the processing of uranium where it went through a mill circuit and then into an evaporation pond.

The general trend for δ ^{18}O samples collected from both the San Andres and alluvial aquifers is that background wells BW-14 and L(SG) are less enriched (between-12 and -11‰), with the δ ^{18}O composition becoming progressively more enriched along the transect, indicating evaporation down-gradient of the mill site and mixing with other evaporated waters. The down-gradient well 22(M) and POC well F(M) were the most enriched wells at approximately -8‰ δ ^{18}O. As with ^{18}O, high ^{2}H concentrations are observed in strongly evaporated surface waters. The down-gradient well 22(M) and POC well F(M) had δ D (‰) values of -66.56 and -68.33 respectively whereas the background wells BW-14 and L(SG) had much lower δ D (‰) values of -93.3 and -84.61 respectively.

Tritium

The water samples collected as part of this investigation can generally be characterized as being modern with tritium values ranging from undetected (less than 2.43 pCi/L) at well 14(SG) to 11.7 pCi/L at well F(M). The average value of tritium for the alluvial wells is 7.81 pCi/L. The average value of tritium from the San Andres wells was 6.88 pCi/L, this assumes a value of 1.22 pCi/L (equal to one-half the detection limit) for well 14(SG) for which tritium was undetected. Based on the ^3H concentrations there are no significant differences between San Andes and alluvial aquifers and it can be assumed that with the water being modern, groundwater recharge occurred within the last 5 to 10 years.

5 DISCUSSION

The Bluewater site includes the alluvial and San Andres aquifers that have been contaminated from uranium milling operations from the leaching of tailings. The alluvial aquifer in the Bluewater area includes saturated subsurface flow within the alluvium and overlying Bluewater Basalt. Recharge to the alluvial aquifer is from direct precipitation, infiltration from occasional surface water flow and from upward leakage by the San Andres aquifer. Recharge to the San Andres aquifer occurs at formation outcrops in the Zuni Mountains southwest of the Bluewater site by either direct precipitation or from surface runoff events.

This investigation utilized isotopic techniques to determine the origin of the aquifer groundwater, the interaction of groundwater movement among the aquifers and the impact to groundwater quality due to anthropogenic influence. The source of data used in this investigation is from DOE's LM program and data collected by NMED as part of their 2010 study. DOE (2014) estimated that a uranium concentration of 10 µg/L is representative of background conditions in both aquifers. Data from NMED (2010) for up-gradient and background wells completed in the San Andres aquifer provides an estimate of 10-11 µg/L of uranium.

The structural geology at the Bluewater site includes a number of faults and a mineralized zone that is believed to extend well below the main tailings and carbonate tailings impoundments and laterally along fault zones. It is thought that this mineralized zone is the source of uranium through solid phase dissolution for the alluvial and San

Andres aquifers at the Bluewater site and that the faults serve as both conduits for flow between the aquifers and as impediments to flow.

Analysis of uranium and chemical data suggest that groundwater from the two aquifers have similar water quality characteristics but are distinctly unique from separate geological units prior to entering the Bluewater disposal site. This is implied from the average alluvial aquifer specific conductance being about 64 percent as that of the San Andres aquifer. Additionally the dissolved oxygen values for alluvial water are higher than the San Andres aquifer. This suggests limited mixing among the aquifers, with the alluvial aquifer water receiving the most recent recharge.

The San Andres and alluvial aquifer wells that are located west and northwest of the main tailings cell are representative of background or up-gradient conditions based on groundwater flow directions established by DOE from hydraulic head data. The USEPA set the maximum contaminant level of uranium in community water supplies at 30 µg/L. All wells designated by DOE and NMED as background and up-gradient are below the maximum contaminant level for uranium.

Within the Bluewater site area there is a wide range of uranium concentrations among the Bluewater wells. As expected the lowest values occur at the alluvial aquifer background well E(M) and the San Andres aquifer background well L(SG) with uranium concentrations of 0.03 µg/L and 2.7 µg/L respectively. The highest concentration of uranium at 1345 µg/L occurred at Well 16(SG), a POC well completed in the San Andres aquifer located directly east and down-gradient of the main tailings cell. Well T(M) had the second highest concentration of uranium at 543.5 µg/L which exceeds the ACL for a POC alluvial well.

In general, molybdenum is considered low for water collected in proximity to a uranium mill tailing site with the range among all Bluewater wells being between 0.43 µg/L at the E(M) alluvial aquifer background well to 25.05 µg/L at the T(M) San Andres aquifer POC well. From this investigation it is apparent that there is a positive correlation between uranium and molybdenum, with the greatest uranium and molybdenum concentrations occurring at the POC well (located directly east and down gradient of the main tailings cell) and down-gradient wells for both aquifers.

There are no distinct differences in uranium and molybdenum concentrations among the alluvial and San Andres aquifers. Both aquifers have background wells with low uranium and molybdenum concentrations and higher concentrations of these constituents down gradient. There is some positive correlation between uranium and specific conductance with the highest specific conductance occurring along with the highest uranium value. However no correlation between specific conductance and molybdenum was observed and this may be due to the overall low molybdenum values of the Bluewater wells.

The isotopic groundwater signatures evaluated in this investigation were very useful in discriminating between uranium mill derived groundwater and water with no know anthropogenic influence as well as the extent of uranium contamination and the interaction of groundwater movements among the alluvial and San Andres aquifers.

The uranium isotopic composition ($^{234}U/^{238}U$) of groundwater from the alluvial and San Andres aquifers near the Bluewater mill show variable uranium contamination with distinct mill site derived environmental isotopic signatures. Findings from this investigation by evaluating tritium concentrations, isotopic fractionation, and $^{234}U/^{238}U$ activity ratios were in agreement to the chemical analysis previously discussed and include some additional items of interest as follows:

- Common properties of the two aquifers include nearly identical and low values of tritium which indicates that mixing could be occurring or recharge and aquifer transmissivities are aligned such that groundwater among the aquifers is of similar age. 2014 tritium levels in groundwater from both aquifers suggests that the waters are modern with recharge occurring within the last 5 to 10 years.
- For alluvial aquifer wells, uranium activity ratios values range from 0.96 to 1.54. For samples with activity ratio values close to 1.0, the uranium concentrations were found to be greater than 100 µg/L. The correlation between uranium concentration and activity ratio values is in agreement to the study by Zielinski (1997). Comparing uranium activity ratios values to molybdenum and selenium concentration displays a similar relationship as that of activity ratio values to uranium.
- There are no distinct differences between activity ratio values to uranium, molybdenum, and selenium concentrations between the alluvial and San Andres aquifers.

- Plotting the $^{234}U/^{238}U$ activity ratio against the reciprocal of uranium concentration has identified some interesting findings with regards to groundwater flow directions and uranium background concentrations.
    - Attenuation of San Andres aquifer water is occurring east of the main tailings cell to the south.
    - Attenuation of San Andres aquifer water is occurring south of the main tailings cell to the southeast. This is in general agreement with flow directions determined from previous studies conducted at the Bluewater site.
    - Attenuation of alluvial aquifer water is occurring south of the main tailings cell to the southeast. This is in general agreement with flow directions determined from previous studies conducted at the Bluewater site. The uranium concentration in the alluvial aquifer appears to decrease with flow distance from the mill site to the southeast.
    - The background uranium concentration based on the activity ratio and uranium concentration are the same for both the alluvial and San Andres aquifers at concentrations up to about 14 µg/L and may indicate mixing among the aquifers possibly due to the displacement of the Ambrosia Lake Fault.
- Although the uranium concentrations of uranium and other constituents are similar for the San Andres and alluvial aquifers, isotopic fractionation suggests separate water identities and limited mixing. Down-gradient of the main tailings

cell, water from both aquifers is more enriched suggesting influences due to the processing of uranium and increased evaporation.

- The alluvial aquifer water is slightly more enriched in ^{2}H and ^{18}O than the San Andres aquifer suggesting more repeated isotopic fractionation during a succession of precipitation and evaporation events and is an indication that the alluvial aquifer in the vicinity of the Bluewater site has mixed with water beneath the main tailings impoundment whose origins may be from the evaporation pond used during the milling process.
- The range of $\delta\ ^{18}O$ and δ D is comparable to those measured in central to northwestern New Mexico. The relationship between ^{2}H and ^{18}O ratios of water from the alluvial and San Andres aquifers at the Bluewater site is similar to Craig's (1961) and the Albuquerque Local MWL. Groundwater from the Bluewater site represents present climatic conditions.

6 CONCLUSION

The purpose of this study was to develop an understanding of the Bluewater site's groundwater resources with regards to the extent of contamination and to use chemical and isotopic signatures to distinguish between uranium mill related and naturally occurring groundwater constituents.

The uranium isotopic composition of groundwater from the alluvial and San Andres aquifers near the mill tailings cell at the Bluewater site indicates that uranium milling operations are the source of contamination. Evaluating uranium isotope data against dissolved uranium concentration provided an effective tool for assessing the mixing of groundwater and extent of contamination from uranium milling operations.

This thesis serves to set the precedent and foundation for subsequent studies by improving the current understanding of the nature and extent of groundwater contamination in the study area. $^{234}U/^{238}U$ activity ratios are a valuable addition to integrated studies of contaminant migration at uranium mill sites and offer the added benefit for understanding mixing and precipitation processes. By understanding the background conditions and the distribution of uranium contamination at the Bluewater site, further laboratory investigations made in batch and column experiments using collected groundwater, soil, and sediments samples from the study area will help to better understand the geochemical reactions that affect contaminant transport at the Bluewater site.

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APPENDIX I

Mann-Whitney Test Calculations

U x Mo

13.7	1.31	0.03	1		1		2	
103.25	1.71	0.43	2		17		3	
69.2	2.93	0.47	3		23		4	
151.5	13.92	0.76	4		25		5	
1345	2.7	0.88	5		26		6	
130.5	3.88	1	6		27		7	
14.1	2.31	1	7		28		8	
137	1.2	1	8		29		9	
370.33	1.74	1.2	9		31		10	
23.55	6.6	1.28	10		32		11	
0.03	0.43	1.31	11		34		12	
7.66	0.76	1.31	12		35		13	
31.5	1.31	1.41	13		36		14	
110.2	0.88	1.71	14		37		15	
2.31	4.77	1.74	15		38		16	
34.53	0.47	1.83	16		39		18	
413.67	1.41	2.31	17		40		19	
543.5	25.05	2.31	18		41		20	
133	1.28	2.7	19		42		21	
5.11	1.83	2.93	20		43		22	
10.5	1	3.88	21		44		24	
10.5	1	4.77	22		45		30	
10.9	1	5.11	23		46		33	
U	Mo	6.6	24					
		7.66	25	R1=	759	R2=	322	
		10.5	26	n1=	23	n2=	23	
		10.5	27					
		10.9	28		μU=		n1*n2/2	264.5000
		13.7	29					
		13.92	30		σU=		(n1*n2*(N+1)/12)^0.5	45.5183
		14.1	31					
		23.55	32		U=		n1*n2+(n1(n1+1)/2)-R1	46.0000
		25.05	33					
		31.5	34		U'=		n1*n2-U	483.0000
		34.53	35					
		69.2	36					
		103.25	37		Zc=		(U'-μU)/σU	4.8003
		110.2	38					
		130.5	39					
		133	40					
		137	41					
		151.5	42			t0.05(1),∞= Z0.05(1)=1.644	see table B.3 α=0.05one tail, v=∞	
		370.33	43					
		413.67	44			Zc=	>	1.6440
		543.5	45			Reject Ho		
		1345	46					

U x Specific Conductance

13.7	2627	0.03	1		1		23	
103.25	1500	2.31	2		2		24	
69.2	1944	5.11	3		3		25	
151.5	1907	7.66	4		4		26	
1345	3905	10.5	5		5		27	
130.5	1638	10.5	6		6		28	
14.1	1289	10.9	7		7		30	
137	1827	13.7	8		8		31	
370.33	1343	14.1	9		9		32	
23.55	1000	23.55	10		10		33	
0.03	1588	31.5	11		11		34	
7.66	577	34.53	12		12		35	
31.5	1240	69.2	13		13		36	
110.2	1784	103.25	14		14		37	
2.31	2308	110.2	15		15		38	
34.53	3511	130.5	16		16		39	
413.67	3975	133	17		17		40	
543.5	1709	137	18		18		41	
133	1870	151.5	19		19		42	
5.11	658	370.33	20		20		43	
10.5	1613	413.67	21		21		44	
10.5	1688	543.5	22		22		45	
10.9	2101	577	23		29		46	
U	Spec. Cond.	658	24					
		1000	25	R1=	282	R2=	799	
		1240	26	n1=	23	n2=	23	
		1289	27					
		1343	28		μU=		n1*n2/2	264.5000
		1345	29					
		1500	30		σU=		(n1*n2*(N+1)/12)^0.5	45.5183
		1588	31					
		1613	32		U=		n1*n2+(n1(n1+1)/2)-R1	523.0000
		1638	33					
		1688	34		U'=		n1*n2-U	6.0000
		1709	35					
		1784	36					
		1827	37		Zc=		(U'-μU)/σU	-5.6790
		1870	38					
		1907	39					
		1944	40					
		2101	41					
		2308	42			t0.05(1),∞= Z0.05(1)=1.644	see table B.3 α=0.05one tail, ν=∞	
		2627	43					
		3511	44			Zc=	<	1.6440
		3905	45			Accept Ho		
		3975	46					

Mo x Specific Conductance

1.31	2627	0.43	1		1		24	
1.71	1500	0.47	2		2		25	
2.93	1944	0.76	3		3		26	
13.92	1907	0.88	4		4		27	
2.7	3905	1	5		5		28	
3.88	1638	1	6		6		29	
2.31	1289	1	7		7		30	
1.2	1827	1.2	8		8		31	
1.74	1343	1.28	9		9		32	
6.6	1000	1.31	10		10		33	
0.43	1588	1.31	11		11		34	
0.76	577	1.41	12		12		35	
1.31	1240	1.71	13		13		36	
0.88	1784	1.74	14		14		37	
4.77	2308	1.83	15		15		38	
0.47	3511	2.31	16		16		39	
1.41	3975	2.7	17		17		40	
25.05	1709	2.93	18		18		41	
1.28	1870	3.88	19		19		42	
1.83	658	4.77	20		20		43	
1	1613	6.6	21		21		44	
1	1688	13.92	22		22		45	
1	2101	25.05	23		23		46	
Mo	Spec. Cond.	577	24					
		658	25	R1=	276	R2=	805	
		1000	26	n1=	23	n2=	23	
		1240	27					
		1289	28		µU=		n1*n2/2	264.5000
		1343	29					
		1500	30		σU=		(n1*n2*(N+1)/12)^0.5	45.5183
		1588	31					
		1613	32		U=		n1*n2+(n1(n1+1)/2)-R1	529.0000
		1638	33					
		1688	34		U'=		n1*n2-U	0.0000
		1709	35					
		1784	36					
		1827	37		Zc=		(U'-µU)/σU	-5.8108
		1870	38					
		1907	39					
		1944	40					
		2101	41					
		2308	42			t0.05(1),∞= Z0.05(1)=1.644	see table B.3 α=0.05one tail, ν=∞	
		2627	43					
		3511	44			Zc=	<	1.6440
		3905	45			Accept Ho		
		3975	46					

U x Dissolved Oxygen

13.7	1.09	0.03	1		1		2	
103.25	3.01	0.51	2		14		3	
69.2	0.73	0.62	3		23		4	
151.5	0.89	0.73	4		27		5	
1345	1.36	0.79	5		28		6	
130.5	0.79	0.79	6		29		7	
14.1	7.44	0.89	7		30		8	
137	4.52	1.09	8		31		9	
370.33	2.67	1.26	9		32		10	
23.55	3.03	1.36	10		33		11	
0.03	0.62	1.53	11		34		12	
7.66	3.08	1.98	12		35		13	
31.5	4.01	2.3	13		36		15	
110.2	2.3	2.31	14		37		16	
2.31	0.79	2.56	15		38		17	
34.53	0.51	2.67	16		39		18	
413.67	2.56	3.01	17		40		19	
543.5	1.26	3.03	18		41		20	
133	3.47	3.08	19		42		21	
5.11	5.59	3.47	20		43		22	
10.5	1.98	4.01	21		44		24	
10.5	5.32	4.52	22		45		25	
10.9	1.53	5.11	23		46		26	
U	DO	5.32	24					
		5.59	25	R1=	768	R2=	313	
		7.44	26	n1=	23	n2=	23	
		7.66	27					
		10.5	28		μU=		n1*n2/2	264.5000
		10.5	29					
		10.9	30		σU=		(n1*n2*(N+1)/12)^0.5	45.5183
		13.7	31					
		14.1	32		U=		n1*n2+(n1(n1+1)/2)-R1	37.0000
		23.55	33					
		31.5	34		U'=		n1*n2-U	492.0000
		34.53	35					
		69.2	36					
		103.25	37		Zc=		(U'-μU)/σU	4.9980
		110.2	38					
		130.5	39					
		133	40					
		137	41					
		151.5	42			t0.05(1),∞= Z0.05(1)=1.644	see table B.3 α=0.05one tail, v=∞	
		370.33	43					
		413.67	44			Zc=	>	1.6440
		543.5	45			Reject Ho		
		1345	46					

Mo x Dissolved Oxygen

1.31	1.09	0.43	1		1		3	
1.71	3.01	0.47	2		2		4	
2.93	0.73	0.51	3		6		5	
13.92	0.89	0.62	4		9		7	
2.7	1.36	0.73	5		11		8	
3.88	0.79	0.76	6		12		10	
2.31	7.44	0.79	7		13		14	
1.2	4.52	0.79	8		15		16	
1.74	2.67	0.88	9		17		20	
6.6	3.03	0.89	10		18		22	
0.43	0.62	1	11		19		26	
0.76	3.08	1	12		21		27	
1.31	4.01	1	13		23		29	
0.88	2.3	1.09	14		24		30	
4.77	0.79	1.2	15		25		33	
0.47	0.51	1.26	16		28		34	
1.41	2.56	1.28	17		31		35	
25.05	1.26	1.31	18		32		36	
1.28	3.47	1.31	19		37		38	
1.83	5.59	1.36	20		40		39	
1	1.98	1.41	21		43		41	
1	5.32	1.53	22		45		42	
1	1.53	1.71	23		46		44	
Mo	DO	1.74	24					
		1.83	25	R1=	518	R2=	563	
		1.98	26	n1=	23	n2=	23	
		2.3	27					
		2.31	28		μU=		n1*n2/2	264.5000
		2.56	29					
		2.67	30		σU=		(n1*n2*(N+1)/12)^0.5	45.5183
		2.7	31					
		2.93	32		U=		n1*n2+(n1(n1+1)/2)-R1	287.0000
		3.01	33					
		3.03	34		U'=		n1*n2-U	242.0000
		3.08	35					
		3.47	36					
		3.88	37		Zc=		(U'-μU)/σU	-0.4943
		4.01	38					
		4.52	39					
		4.77	40					
		5.32	41					
		5.59	42			t0.05(1),∞= Z0.05(1)=1.644	see table B.3 α=0.05one tail, ν=∞	
		6.6	43					
		7.44	44			Zc=	<	1.6440
		13.92	45			Accept Ho		
		25.05	46					

^{234}U/^{238}U Activity Ratio x U

13.7	1.57	0.03	1		1		2	
103.25	1.05	0.94	2		22		3	
69.2	1.14	0.95	3		25		4	
151.5	1.09	0.96	4		26		5	
1345	0.95	1	5		27		6	
130.5	1	1.02	6		28		7	
14.1	1.54	1.03	7		29		8	
137	1.1	1.05	8		30		9	
370.33	1.02	1.08	9		31		10	
23.55	1.43	1.09	10		32		11	
0.03		1.1	11		33		12	
7.66	1.34	1.12	12		34		13	
31.5	1.12	1.14	13		35		14	
110.2	1.03	1.26	14		36		15	
2.31	1.4	1.34	15		37		16	
34.53	1.26	1.4	16		38		17	
413.67	0.94	1.43	17		39		18	
543.5	0.96	1.54	18		40		19	
133	1.08	1.57	19		41		20	
5.11	1.69	1.69	20		42		21	
10.5	2.13	2.13	21		43		23	
10.5	4.06	2.31	22		44		24	
10.9	4.5	4.06	23		45			
U	234U-238U	4.5	24					
		5.11	25	R1=	758	R2=	277	
		7.66	26	n1=	23	n2=	22	
		10.5	27					
		10.5	28		μU=		n1*n2/2	253.0000
		10.9	29					
		13.7	30		σU=		(n1*n2*(N+1)/12)^0.5	44.0416
		14.1	31					
		23.55	32		U=		n1*n2+(n1(n1+1)/2)-R1	24.0000
		31.5	33					
		34.53	34		U'=		n1*n2-U	482.0000
		69.2	35					
		103.25	36					
		110.2	37		Zc=		(U'-μU)/σU	5.1996
		130.5	38					
		133	39					
		137	40					
		151.5	41					
		370.33	42			t0.05(1),∞= Z0.05(1)=1.644	see table B.3 α=0.05one tail, v=∞	
		413.67	43					
		543.5	44			Zc=	>	1.6440
		1345	45			Reject Ho		
			46					

^{234}U/^{238}U Activity Ratio x Mo

1.31	1.57	0.43	1		1		5	
1.71	1.05	0.47	2		2		6	
2.93	1.14	0.76	3		3		7	
13.92	1.09	0.88	4		4		11	
2.7	0.95	0.94	5		8		12	
3.88	1	0.95	6		9		13	
2.31	1.54	0.96	7		10		14	
1.2	1.1	1	8		20		15	
1.74	1.02	1	9		22		16	
6.6	1.43	1	10		23		17	
0.43		1	11		24		18	
0.76	1.34	1.02	12		27		19	
1.31	1.12	1.03	13		32		21	
0.88	1.03	1.05	14		33		25	
4.77	1.4	1.08	15		34		26	
0.47	1.26	1.09	16		36		28	
1.41	0.94	1.1	17		37		29	
25.05	0.96	1.12	18		38		30	
1.28	1.08	1.14	19		39		31	
1.83	1.69	1.2	20		42		35	
1	2.13	1.26	21		43		40	
1	4.06	1.28	22		44		41	
1	4.5	1.31	23		45			
Mo	234U-238U	1.31	24					
		1.34	25	R1=	576	R2=	459	
		1.4	26	n1=	23	n2=	22	
		1.41	27					
		1.43	28		μU=		n1*n2/2	253.0000
		1.54	29					
		1.57	30		σU=		(n1*n2*(N+1)/12)^0.5	44.0416
		1.69	31					
		1.71	32		U=		n1*n2+(n1(n1+1)/2)-R1	206.0000
		1.74	33					
		1.83	34		U'=		n1*n2-U	300.0000
		2.13	35					
		2.31	36					
		2.7	37		Zc=		(U'-μU)/σU	1.0672
		2.93	38					
		3.88	39					
		4.06	40					
		4.5	41					
		4.77	42			t0.05(1),∞= Z0.05(1)=1.644	see table B.3 α=0.05one tail, ν=∞	
		6.6	43					
		13.92	44			Zc=	>	1.6440
		25.05	45			Reject Ho		
			46					

$^{234}U/^{238}U$ Activity Ratio x Se

0.75	1.57	0.75	1		1		8	
6.23	1.05	0.75	2		2		9	
0.75	1.14	0.75	3		3		10	
1.14	1.09	0.75	4		4		11	
15.9	0.95	0.75	5		5		12	
0.75	1	0.75	6		6		13	
5.66	1.54	0.75	7		7		14	
11.1	1.1	0.94	8		19		15	
3.77	1.02	0.95	9		21		16	
1.38	1.43	0.96	10		24		17	
0.75		1	11		24		18	
1.21	1.34	1.02	12		30		20	
0.75	1.12	1.03	13		31		22	
2.01	1.03	1.05	14		33		23	
0.75	1.4	1.08	15		34		25	
1.98	1.26	1.09	16		35		26	
10.72	0.94	1.1	17		37		27	
3.46	0.96	1.12	18		39		28	
7.23	1.08	1.14	19		40		29	
0.75	1.69	1.14	20		41		32	
4	2.13	1.21	21		42		36	
10	4.06	1.26	22		43		38	
4.1	4.5	1.34	23		45			
Se	234U-238U	1.38	24					
		1.4	25	R1=	566	R2=	449	
		1.43	26	n1=	23	n2=	22	
		1.54	27					
		1.57	28		µU=		n1*n2/2	253.0000
		1.69	29					
		1.98	30		σU=		(n1*n2*(N+1)/12)^0.5	44.0416
		2.01	31					
		2.13	32		U=		n1*n2+(n1(n1+1)/2)-R1	216.0000
		3.46	33					
		3.77	34		U'=		n1*n2-U	290.0000
		4	35					
		4.06	36					
		4.1	37		Zc=		(U'-µU)/σU	0.8401
		4.5	38					
		5.66	39					
		6.23	40					
		7.23	41					
		10	42			t0.05(1),∞= Z0.05(1)=1.644	see table B.3 α=0.05one tail, v=∞	
		10.72	43					
		11.1	44			Zc=	<	1.6440
		15.9	45			Accept Ho		
			46					