GEOCHEMICAL AND ISOTOPIC ASSESSMENT OF REGIONAL
GROUNDWATER FLOW AND AQUIFER CONNECTIVITY IN THE
LISBON VALLEY, UTAH

By

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ABSTRACT

Understanding regional groundwater flow and assessing aquifer connectivity is an important water resource management practice to mitigate migration of contaminants in multiple industries, including the oil and gas and mining sectors. This study focuses on the metal-rich Lisbon Valley of the Paradox Basin in southeastern Utah, where numerous faults may act as conduits or barriers to cross-formational flow. All geochemical and isotopic results show that these distinct aquifers are not strongly hydrologically connected under current natural hydrologic conditions. The upper Burro Canyon Aquifer (BCA) has a calcium-sulfate signature with high TDS and higher concentrations of important ore-forming trace elements, such as Cu, Fe, Co, Mn, and U. Near-zero to negative values of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ are consistent with sulfide oxidation in the mineralized aquifer, however the lack of DO coupled with high concentrations of Fe^{2+} and SO_4^{2-} suggests the aquifer is anoxic, undergoing iron reduction. The BCA has a less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, but higher concentrations of Sr^{2+} , reflective of the carbonate lithology of the aquifer. Corrected radiocarbon ages in the BCA of 3,300-11,000 BP coupled with $\delta^{18}\text{O}$ and δD values in the range of modern precipitation are indicative of recharge occurring during the Holocene. The lower Navajo Aquifer (NA) contains sodium-bicarbonate groundwater with low-to-moderate TDS, while positive values of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ and lower concentrations SO_4^{2-} are characteristic of eolian sandstones; alternatively, low DO and low concentrations of SO_4^{2-} indicates an anoxic environment, which would be conducive to bacterial sulfate reduction, which can also produce positive values of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$. Groundwater in the NA is generally more radiogenic (higher $^{87}\text{Sr}/^{86}\text{Sr}$) than the BCA, but has lower concentrations of Sr^{2+} , characteristic of the higher silicate content of the NA. Corrected radiocarbon ages in the NA of 15,000-36,000 BP, coupled with $\delta^{18}\text{O}$ and δD

values lower than modern precipitation, are indicative of Late Pleistocene recharge, when the climate of the four corners area of the U.S. southwest was 5 to 7°C cooler than today. Principal component analysis (PCA) using major ions and isotopes further affirms the distinct groupings of groundwater observed in the BCA and NA. The regional hydrogeologic model was unable to accurately predict both $\delta^{18}\text{O}$ and groundwater ages, however the trend of increasingly negative $\delta^{18}\text{O}$ values with increasing corrected radiocarbon ages was simulated. Furthermore, the model simulated a shallow fresh groundwater system riding on top of a deeper saline system with limited mixing, with recharge occurring at the La Sal Mountains and flowing southeast to the Lisbon Valley, which is consistent with previous work along with geochemical and isotopic data collected for this study.

1.0 INTRODUCTION

Aquifer connectivity and the potential for cross-formational flow is an issue pertinent to many fields including oil and gas production (e.g., Campbell et al., 2008), mining (e.g., Li et al., 2018), and water resources development and protection (e.g., Johnson et al., 2015; Priestly et al., 2017). For example, understanding regional groundwater flow and assessing aquifer connectivity can aid in the determination of where harmful byproducts of any of the aforementioned activities may end up and how to better protect freshwater resources based on this knowledge.

In geologically complex regions, faulting may lead to the creation of zones of enhanced or reduced permeability that can alter aquifer connectivity across faults and induce cross-formational fluid flow. Depending on the genesis of faulting and whether they are still active, the behavior of faults acting as conduits, barriers, or both can change over time (Caine et al., 1996). For example, permeability may be increased around a fault zone due to secondary fractures that form, as well as brecciation, which may increase permeability initially as breccia is often uncohesive when first formed. On the other hand, permeability around a fault may be decreased by processes such as clay smearing or grain reorientation that can reduce normal flow to a fault by several orders of magnitude. These deformations of the parent rock by faulting subsequently cause permeability to be highly anisotropic around faults (Bense et al., 2013).

Describing fault-flow characteristics have often taken place in two different camps,— structural geologists and hydrogeologists. Typically, structural geologists take a surface-based approach where they map outcrops and measure outcrop characteristics (e.g. orientations of faults, porosity, etc.). This data is then used to synthesize a conceptual

hydrogeologic model, extrapolating how a fault may behave. On the other hand, hydrogeologists take a subsurface-based approach, relying on data collected from arrays of boreholes, but often not directly observing fault characteristics (Bense et al., 2013). By using a suite of geochemical tracers combined with physical hydrogeological conceptions, it may be possible to delineate if cross-formational mixing is occurring and to what extent (Campbell et al., 2008; Johnson et al., 2015; Priestly et al., 2017; Li et al., 2018).

In addition to understanding how hydrologic conditions at LVMC behave in modern times, it is also important to understand the paleohydrology, as these prior conditions are what set the stage for today's current hydrologic conditions. By creating a regional model for groundwater flow and constraining it with isotopic data, the plumbing of the region and why we observe the conditions that we do today may be elucidated. By making these interpretations, it may then be possible to synthesize a better approach to protecting these fossil groundwaters, which have been estimated to dominate 42-85% of groundwater storage in the uppermost 1 km of crust globally (Jasechko et al., 2017).

Extraction of mineralogical and oil and gas resources are an important industry in the Paradox Basin in southeastern Utah and southwestern Colorado, within the greater Colorado Plateau. Mining of copper in the Lisbon Valley began over 100 years ago in 1903 at the Big Indian Mine, however it wasn't until the 1950s and 1960s that extensive exploration with modern techniques began. Because mining is an important industry for the region, it is necessary to not only understand, but also be able to manage the potential impacts to groundwater systems affected by operations.

The Lisbon Valley Mining Company (LVMC) is located in La Sal, Utah, within the Paradox Basin. Currently, LVMC operates using open-pit, heap leach, solvent

extraction-electrowinning (SX-EW) methods, however they are now in the permitting process to expand operations using more modern in-situ recovery (ISR) techniques, which are gaining traction worldwide. The main geologic features in the Lisbon Valley are the Lisbon Valley Anticline (LVA), a northwest-trending, doubly plunging anticline and the Lisbon Valley Fault (LVF), a normal fault off the northeast flank of the anticline. The LVF previously acted as a conduit for mineral-bearing fluids that left the copper deposits in the region (Krahulec, 2006). These copper deposits are found predominantly as oxidized ores located in the Burro Canyon Aquifer (BCA). In order to move forward with permitting processes for ISR, LVMC must show limited communication from the BCA to the lower Navajo Aquifer (NA), which is separated by the Morrison Formation, a confining unit of variable thickness and low permeability. Previous reports that looked at bedrock aquifers in the region have indicated that the NA is one of the most important potable groundwater supplies due to factors such as good water quality and artesian flow in many areas, servicing tens of thousands of people in towns like Blanding, Bluff, La Sal, Moab, Monticello, Montezuma Creek, and the Navajo Indian Reservation (Goode, 1958; Avery, 1986).

This study collected samples and analyzed them for a variety of environmental isotopes, which have never been investigated at LVMC before, including: $\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$ -DIC, $\delta^{34}\text{S}$ - SO_4 , $\delta^{18}\text{O}$ - SO_4 , ^3H , ^{14}C , and $^{87}\text{Sr}/^{86}\text{Sr}$. Additionally, major ion chemistry and trace metals were analyzed, and compared with previously collected hydrologic data in the region. This data was then used to constrain a model for regional groundwater flow. The interpretation of these results was then used to evaluate the following research objectives: (1) assess BCA and NA connectivity in the LVMC area by determining (a) whether unique

geochemical and isotopic signatures in each aquifer exist and (b) the apparent age of groundwater in each aquifer; (2) compare LVMC site hydrogeochemistry to more regional hydrogeochemistry to examine if regional trends in groundwater quality and residence times within the BCA and NA exist; and (3) identify local and regional groundwater flow path(s) and investigate the influence of paleohydrologic conditions on recharge to the BCA and NA.

2.0 BACKGROUND ON PERTINENT ISOTOPES

2.1 Stable Water Isotopes: $\delta^{18}\text{O}$ and δD

Stable water isotopes ($\delta^{18}\text{O}$ and δD) are often used to infer sources of recharge due to the variations in fractionation that occur with changing temperature, altitude, latitude, and continentality (Clark and Fritz, 1997). In this study, temperature and altitude are inferred to be the prominent factors controlling $\delta^{18}\text{O}$ and δD values of precipitation in the study area. When an air mass becomes colder this decrease in temperature causes rainout, a process that drives the precipitation to become progressively more depleted in ^{18}O and D. In general, a decrease in temperature of 1.1 to 1.7°C corresponds to a decrease in $\delta^{18}\text{O}$ of about 1‰. Related to temperature change, when an air mass travels over an area with relief, as the water vapor rises it adiabatically cools by expansion, thus causing rainout to occur and leading to isotopically lighter values of $\delta^{18}\text{O}$ and δD . A decrease in $\delta^{18}\text{O}$ of approximately 0.15 to 0.5‰ per 100-m rise in altitude occurs during orographic rainout (Clark and Fritz, 1997). This lapse rate is consistent with what Wright (2001) reported for the Santa Catalina Mountains in Tucson, Arizona, as well as Hopkins et al. (2014) in the Middle San Pedro Basin in southeastern Arizona.

2.2 Radiogenic Water Isotopes: Tritium

Tritium (^3H) is the radioactive isotope of hydrogen, with a half-life of approximately 12.32 years (Lucas and Unterweger, 2000). Tritium can be a useful age tracer of modern groundwaters due to nuclear weapons testing during the 1950s and 1960s, which introduced large concentrations of ^3H into the atmosphere worldwide. Since the end of weapons testing, bomb ^3H has mostly been washed out of the atmosphere, with

background concentrations returning to ambient conditions. Groundwater that recharged during this period of weapons testing and shortly thereafter, contains elevated concentrations of ^3H (Clark and Fritz, 1997). No long-term ^3H data exists in the immediate vicinity of LVMC, however monthly precipitation data from Albuquerque, New Mexico, ranged from 4.5 to 9.8 TU from 2000 to 2005 (IAEA/WMO, 2019). Additional data from the Tucson Basin in Arizona, indicates that the background ^3H concentration in precipitation in the basin has been relatively stable containing 6 ± 1 TU since 1992 (Eastoe et al., 2004).

2.3 Stable Carbon Isotopes: $\delta^{13}\text{C}$

Carbon-13 ($\delta^{13}\text{C}$) is an important tracer for understanding the role of carbonate evolution in groundwaters due to its large variation in the earth's carbon reservoirs. In this study, the carbon-13 of dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC) was measured to be used in geochemical correction calculations for radiocarbon (^{14}C). Carbon-13 is incorporated into and fractionated by plants multiple times through photosynthesis and carboxylation. Plants generally fall into three different photosynthetic categories: Calvin (C_3), Hatch-Slack (C_4), and Crassulacean acid metabolism (CAM) cycles. C_3 and C_4 type plants will fractionate $\delta^{13}\text{C}$ in a distinct manner. C_3 plants yield a $\delta^{13}\text{C}$ of -24 to -30‰ with an average of about -27‰, and C_4 plants yield a $\delta^{13}\text{C}$ range of -10 to -16‰ with an average of about -12.5‰; CAM plants yield a $\delta^{13}\text{C}$ value that falls within the entire range of C_3 and C_4 plants, but generally somewhere in the middle. After plant matter dies it accumulates and is broken down by aerobic bacteria, which convert most of it back to gaseous CO_2 , further fractionating it by approximately 4‰. As water infiltrates into soils, CO_2 is dissolved and

dissociates in four steps, each slightly fractionating $\delta^{13}\text{C}$. Finally, as groundwater travels through the subsurface, carbonate minerals may dissolve, which adds “dead carbon” ($\delta^{13}\text{C}\text{-DIC} = 0\text{‰}$), thus skewing the value (Clark and Fritz, 1997). The value of $\delta^{13}\text{C}\text{-DIC}$ measured in groundwater can then be used in geochemical correction models, such as Tamers (Tamers, 1967; Tamers and Scharpenseel, 1970; Tamers, 1975) or Fontes and Garnier (1979), that are used for correcting radiocarbon ages.

2.4 Radiogenic Carbon Isotopes: Radiocarbon

Carbon-14 (^{14}C , radiocarbon) is a radioactive isotope with a half-life of approximately 5,730 years. Radiocarbon is produced naturally in the upper atmosphere due to cosmic ray bombardment of ^{14}N . Once formed, atmospheric $^{14}\text{CO}_2$ is incorporated into living biomass through photosynthesis, and into groundwater through CO_2 dissolution. Due to its relatively long half-life, natural production, and ease of incorporation into natural systems, radiocarbon is the leading age tracer for fossil groundwaters, capable of dating groundwaters up to approximately 40,000 years (Clark and Fritz, 1997).

Depending on the aquifer systems that groundwater resides in, certain correction factors have to be applied to obtain an appropriate groundwater ‘age’ using radiocarbon dating. In carbonate aquifers or other systems with large inputs of carbonate, corrections are made as the dissolution of carbonate minerals adds “dead” ^{14}C to the system. This addition of dead carbon (generally assumed to have $\text{pmc} = 0$) thus arbitrarily lowers the apparent age of the groundwater (Clark and Fritz, 1997). While not specifically researched in this study, radiocarbon has also been used to estimate average recharge rates of an aquifer system (Zhu, 2000).

2.5 Sulfur Isotopes: $\delta^{34}\text{S}$ -SO₄ and $\delta^{18}\text{O}$ -SO₄

Due to biological cycling of sulfur compounds, both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulfate ($\delta^{34}\text{S}$ -SO₄ and $\delta^{18}\text{O}$ -SO₄) can be highly fractionated, the ranges of which can be indicative of aquifer redox conditions. In near-surface environments with oxic conditions, the oxidation of aqueous sulfide to sulfate can be an important source of sulfate in groundwater (Clark and Fritz, 1997). Oxidation of sulfide can occur chemically by O₂ leading to a depletion of $\delta^{34}\text{S}$ -SO₄ of approximately 5‰ (Fry et al, 1988), however oxidation of sulfide can also be biologically mediated leading to larger depletions of up to 20‰ in the resultant sulfate produced (Kaplan and Rittenberg, 1964). The value of $\delta^{18}\text{O}$ of the resultant sulfate will depend on the reaction pathway, but is similar to sulfate from sulfide minerals (Clark and Fritz, 1997). Oxidation of base-metal sulfides (e.g. pyrite, chalcocite) are also subject to oxidation and subsequent fractionation, however to a lesser degree – biologically mediated processes may only lead to a depletion of $\delta^{34}\text{S}$ by 2 to 5.5‰ (Toran and Harris, 1989). The resultant value of $\delta^{18}\text{O}$ is more complicated and is a factor of both atmospheric and water molecule inputs, along with any fractionation that occurs (Krouse, 1980; Longinelli, 1989; Toran and Harris, 1989).

Conversely, while the oxidation of sulfide leads to depletions in $\delta^{34}\text{S}$ -SO₄ and $\delta^{18}\text{O}$ -SO₄, the reduction of sulfate to sulfide via bacteria will lead to the accumulation of residual sulfate with $\delta^{34}\text{S}$ -SO₄ and $\delta^{18}\text{O}$ -SO₄ values that are enriched in the heavier isotope. Resultant fractionation of bacterial sulfate reduction (BSR) is variable and depends on both the environmental conditions as well as the particular bacterial communities involved (Clark and Fritz, 1997). While enrichments of up to 40‰ have been observed (Krouse et

al., 1970), it is more typical to see enrichment factors of up to approximately 25‰ (Clark and Fritz, 1997). The following is a simplified reaction of BSR (Clark and Fritz, 1997):

2.6 Strontium

Strontium-87 (^{87}Sr) is a stable isotope of strontium that has two sources. The first is its production by beta decay of ^{87}Rb (half-life = 4.8×10^{10} years); the second is primordial and produced during nucleosynthesis. Strontium is a divalent ion geochemically similar to Ca^{2+} , and as such will readily substitute into calcium-bearing mineral lattices. Likewise, rubidium is a monovalent ion geochemically similar to K^+ , and as such will readily substitute into potassium-bearing minerals (Clow et al., 1997). These properties of Sr and Rb thus make them ideal tracers in many groundwater systems. As ^{87}Rb decays and the concentration of ^{87}Sr increases, the increasing concentration of ^{87}Sr can be compared to the amount of non-radiogenic ^{86}Sr – the ratio of which can provide insight into water-rock reactions (Campbell et al., 2008; Priestly et al. 2017), trace groundwater movement (Campbell et al., 2008; Priestly et al. 2017), and identify sources of salinity (Brenot et al., 2014).

3.0 STUDY LOCATION

3.1 Climate

Based upon the Köppen classification system, La Sal, UT near LVMC is considered a cold semi-arid (steppe) climate (BSk), intermediate between desert climates and humid climates (Cold, 2019). The annual minimum temperature is 1.4°C, the annual maximum temperature is 15.4°C, and the annual average temperature is 8.4°C. La Sal receives on average 35.8 cm of rainfall and 129.5 cm of snow each year (US Climate Data), however annual rainfall in the mountains can exceed 76 cm (Avery, 1986) and annual snowfall can exceed 3 m (Richmond, 1962). Temperatures during the Late Pleistocene are inferred as being 5 to 7°C cooler than they are today in the four corners area of the U.S. southwest (Philips et al., 1986; Zhu et al., 1998), while summer temperatures during the mid-Holocene were 2 to 4°C warmer than they are today in the nearby Black Mesa Basin in northeastern Arizona (Zhu et al, 1998). During the Late Pleistocene, recharge rates are estimated to be two to three times greater than they are today, however a reduction in recharge rate of about 50% is inferred during the early- to mid-Holocene when summer temperatures were warmer (Zhu et al, 1998).

Vegetation at the study location is divided into three primary vegetation zones. The piyon-juniper (PJ) zone exists at the highest elevations with steeper slopes. Dominant vegetation in the PJ zone includes big sagebrush along with other shrubs, some forbs such as cryptantha, and grasses, such as wheat grass. The second category of vegetation is the sagebrush (SB) zone, which occurs in valley bottoms which have gentler slopes. Sagebrush is almost exclusively the dominant vegetation in this zone, with the exception of some areas containing rabbitbrush where disturbance previously occurred; some native grasses are

present as undergrowth. The third category of vegetation is the grassland/rangeland (GR) zone, which occurs in meadows which were previously cleared in the 1960s and 1970s and have since been reseeded. Dominant vegetation includes wheat grass that was planted after clearing occurred, as well as sagebrush which is starting to grow back (Jackson, 1997).

3.2 Geology

LVMC is located southeast of La Sal, UT near the center of the Paradox Basin, in southeastern Utah and southwestern Colorado in the Colorado Plateau (Figure 1). The Paradox Basin is a northwest-southeast trending evaporitic basin that formed approximately 330 to 310 million years ago (Ma) during the Pennsylvanian. During this period of time, the region was affected by the Uncompahgre Uplift, which formed the westernmost range of the Ancestral Rockies. Concurrently, while this tectonic uplift in the region was occurring, a depression immediately adjacent to this uplift formed – now known as the Paradox Basin (Eby et al, 2003). Following its formation, the Paradox Basin was filled with evaporitic deposits, lain by a restricted seaway that was bounded to the northeast by the Uncompahgre Uplift. Some of these evaporites were deposited in local lows allowing for the accumulation of thick salt beds (Weir and Puffet, 1981). Subsequent burial of these lower-density salts by clastic materials of a higher density, sourced from the adjacent highlands, led to the continued plastic deformation of the salts, with the density difference causing them to rise. The rising of these evaporites has caused the formation of numerous northwest trending anticlines, such as the Moab Anticline, Paradox Anticline, and Lisbon Valley Anticline (Jackson, 1997). Within the Paradox Basin, and just north of the Lisbon Valley are the La Sal Mountains, intrusive igneous laccoliths thought to be

Tertiary in age (31.4 to 26 ma). Further south and slightly west are the Abajo Mountains, another set of intrusive igneous laccoliths generally comparable in age to the La Sals (32 to 20.4 ma) (Sullivan et al, 1991).

The LVMC study area is located in the Lisbon Valley, which likely formed as a result of the partial dissolution and subsequent collapse of an intrusive salt dome (Avery, 1986). The Lisbon Valley is dominated by two major features: the Lisbon Valley Anticline (LVA) and the Lisbon Valley Fault (LVF). The LVA is an elongated salt diapir, approximately 32 km in length. The LVA plunges to the northwest and southeast, with the southeast end affecting the study location (Jackson, 1997; Weir and Puffet 1981). The LVF extends approximately 48 km in length, with the fault zone spreading out in a complex, fan-like structure. Dips within the fault zone are generally northeast at 50 to 60 degrees (Jackson, 1997). Strong deformation of rock on either side of the fault is not seen. Competent units of rock like the Burro Canyon Formation and Dakota Formation on the northeast side of the fault contain numerous fractures within 100 m, but brecciation of rock is limited to within approximately 0.3 m of the fault. On the southwest side, far fewer fractures occur in competent beds, while numerous fractures (possibly tensional joints caused by the LVA) occur in the Glen Canyon Group (Weir and Puffet, 1981).

The two principal aquifers of interest in the Lisbon Valley are the Burro Canyon Aquifer (BCA) and the Navajo Aquifer (NA) (Figure 2). The BCA is an Early Cretaceous unit palynologically dated at approximately 129 to 100 Ma (Tschudy et al., 1984) that is comprised of the Burro Canyon Formation and the Dakota Formation. The Burro Canyon Formation ranges from 24 to 91 m in thickness and consists primarily of sandstone and conglomerates, however localizations of quartzite, mudstone, and thin beds of limestone

are also present. The Dakota Formation is generally 30 m thick and comprised of sandstone and conglomerates, interbedded with carbonaceous mudstone and shale that grade to localized beds of impure coal (Weir and Puffet, 1981). The BCA is capped in sporadic portions by the Mancos Shale, a Late Cretaceous marine shale with interbeds of thin sandstone and siltstone; locally the unit is limey and sandy (Weir and Puffet 1981; Kirby 2008). The Mancos Shale is generally not present where the Burro Canyon Formation or Dakota Formation are exposed, likely due to erosion (Kirby, 2008).

Underlying the BCA is the Morrison Formation, averaging 229 m in thickness, which separates the BCA and NA. The Morrison Formation is Late Jurassic in age (155 to 148 Ma) (Kowallis et al., 1998) and is comprised of the upper Brushy Basin Member and the lower Salt Wash Member. The Brushy Basin Member is comprised of gray to grayish-red mudstone with sparse dark-brown conglomeratic sandstone towards the bottom. The Salt Wash Member is mainly composed of thick lenses of light-brown sandstone interbedded with red mudstone (Weir and Puffet, 1981).

The Glen Canyon Group (referred to in this study as the NA) consists of the Entrada Formation, Navajo Sandstone, Kayenta Formation, and Wingate Sandstone, and is Late Triassic to Early Jurassic in age (196 to 175 Ma) (Lucas et al., 2005). The Entrada Sandstone ranges from 122 to 145 m in thickness and consists of four members in descending order: Moab Members, Slick Rock, Dewey Bridge, and unnamed lower member. The members range from silty-to-fine sandstones to sandstones with medium-to-coarse grains. The Navajo Sandstone ranges from 53 to 183 m in thickness and generally consists of well-sorted, sub-rounded, very fine grains of quartz and feldspar. Often, in

earlier reports for the region, the Dewey Bridge Member has been grouped with the Navajo Sandstone as they are nearly indistinguishable in some areas at the contact.

The Kayenta Formation ranges from 53 to 122 m in thickness and is comprised of similar material of the rest of the Glen Canyon Group. The Kayenta is distinguishable from the rest of the Glen Canyon Group by the presence of siltstone and conglomeratic beds. The Wingate Sandstone is generally 91 m in thickness in the area, and is so well cemented by calcite, it appears to be one massive unit; however, horizontal- and cross-beds of 0.3 to 18 m in thickness exist in this unit (Weir and Puffet, 1981).

3.3 Hydrology

There are no perennial streams in the Lisbon Valley, however due to the topography of the surrounding area, several unnamed ephemeral streams exist within the vicinity of LVMC. A surface water divide exists just east of Centennial Pit, an open-pit area of copper mining at LVMC. This divide causes the area east to be drained by a major ephemeral stream that flows generally southeast, while west of the divide drainage occurs from a different ephemeral stream that flows east and northeast, eventually joining another ephemeral stream. These streams are noted as typically being dry, with flow only occurring after major precipitation events. The nearest perennial stream to LVMC is the Dolores River, located approximately 32 km east (Jackson, 1997).

Fine resolution-scale information on subsurface flow for the region is sparse, however Avery (1986) indicates that flow in the NA in the La Sal, Utah area is confined, while flow north of the site (just south of the La Sal Mountains) would be to the west and southeast due to a groundwater divide. In the BCA, Avery (1986) indicates that flow

generally follows that of surface water: east of La Sal, flow is to the southeast, while on the western peripheries of the La Sal Mountains flow is likely downdip and away. Information provided by LVMC for wells at the mine is generally comparable with data from Avery (1986), suggesting flow paths of both the BCA and NA originate at/near the La Sal Mountains then flow southeast towards to study area.

Recharge to the region is likely dominated by the La Sal Mountains, which rise from a base altitude of approximately 2,133 m to a maximum height of over 3,877 m at Mt. Peale. Recharge from infiltration of precipitation occurs where the BCA and NA crop out, estimated to be approximately 5% of the total average precipitation that falls on the respective formation outcrops ($4.81 \times 10^7 \text{ m}^3$ for the BC and $3.08 \times 10^7 \text{ m}^3$ for the NA). The BCA is present under a layer of alluvium around the flanks of the La Sal Mountains which may enhance recharge. The NA does not crop out around the flanks of the La Sal Mountains; potentiometric well data from Flat Iron Mesa, approximately 34 km northwest of LVMC, indicates that recharge from vertical leakage of overlying formations may occur in the Flat Iron Mesa area (Avery, 1986).

The Mancos Shale is considered a barrier to recharge wherever it is present. Based upon various down-well methods (e.g. packer tests, bailer recovery tests, etc.) conducted around the region, hydraulic conductivity of the BCA ranges from 1.59×10^{-7} to 2.72×10^{-6} m/s; hydraulic conductivity of the Morrison Formation ranges from 1.27×10^{-6} to 3.46×10^{-6} m/s; and hydraulic conductivity of the NA is lower and ranges from 7.06×10^{-8} to 1.20×10^{-6} m/s (Avery, 1986; Jacobs, 1996). Locally, hydraulic conductivity of the BCA ranges from 1.04×10^{-7} to 4.70×10^{-5} m/s; hydraulic conductivity of the Morrison Formation ranges from 5.0×10^{-7} to 5.25×10^{-6} m/s; and hydraulic conductivity of the NA is lower and ranges

from 4.69×10^{-8} to 2.90×10^{-6} m/s. To note, unsaturated portions of the Morrison Formation exist in between the BCA and NA, making it a more effective barrier to vertical flow (Whetstone Associates, 2018).

Previous work indicates that at LVMC, groundwater from the BCA is generally characterized as a Ca-Mg-SO₄ type with near-neutral to alkaline pH and moderately high TDS. Additionally, groundwater in the BCA at LVMC naturally exceeds Utah Groundwater Quality Standards for U, gross alpha, and gross beta particle activity, and also frequently exceeds the standards for As, Al, Fe, and Cd. Long-term monitoring has indicated that mining activities from 2005 to 2018 have not had a negative impact on groundwater quality within the BCA (Whetstone Associates, 2018).

In the NA, groundwater is characterized as an Na-HCO₃ type with near-neutral to alkaline pH and moderate TDS. Gross alpha and gross beta particle activity commonly exceed groundwater quality standards in the NA (Whetstone Associates, 2018). No isotopic data was collected at LVMC prior to this study – only major ion chemistry and some trace elements have been collected. Regional data of major ion chemistry, trace elements, and isotopes are available for the BCA and NA in other parts of Utah and southwestern Colorado (Avery, 1986; Kimball, 1992; Naftz et al., 1997; Truini and Longworth, 2003; Tuttle and Grauch, 2009; Kampman et al., 2014; U.S. Geological Survey, 2016) however no other studies were found immediately adjacent to LVMC.

4.0 METHODS

4.1 Field Methods

Groundwater samples were collected from a total of 19 completed wells and two uncased boreholes at the LVMC over the course of several sampling events in October-November 2017, March 2018, July 2018, and August 2018 (Table 1). Samples at each location were only collected once during this sampling period, however major ion chemistry and metals data extending back decades exists (Whetstone Associates, 2018). From these 21 samples, a full suite of isotope analyses was performed on 11 samples from select locations. Five of these samples were from wells completed in the BCA, while the other six samples were groundwater from wells completed in the NA.

Field instruments were calibrated prior to measuring field parameters. The pH meters (Oakton pH Con 300, Oakton PC 450) were calibrated at each station using a point-slope calibration with 4.1, 7.0, and 10.0 buffer solutions. Electrical conductivity was calibrated prior to the start of the sampling round with 84, 1,413, and 12,880 $\mu\text{S}/\text{cm}$ standard solutions. Water levels were measured using an electronic water level indicator. Measurements were recorded to the nearest 0.3048 cm to the top of the PVC or steel well casing. For consistency, the readings were taken on the north side of the well casing or at a designated measuring point for each well. Because the depth to water exceeds 274 m in several wells, water level measurement can be complicated due to twisting and stretching of the water level indicator cable. Therefore, the minor variations in water levels should not be necessarily interpreted as real (or seasonal) changes for these deeper wells. Monitoring well purging, groundwater sample collection, sample handling, documentation, and analysis were performed in accordance with the Standard Operating Procedure for

Groundwater Sampling (U.S. EPA, 2017). Prior to sampling, a minimum of three casing volumes of water were purged from each well, with the exception of SLV2; SLV2 was bailed dry after approximately one well volume and a sample was collected after water level recovery. Field parameters (pH, temperature, and specific conductance) were measured during purging and recorded on field sampling data sheets.

Samples were collected directly from the pump outlet or were collected directly from the bailer (where applicable). All groundwater samples were filtered through a 0.45- μm nylon filter, except for ^3H , radiocarbon, and sulfate isotope samples ($\delta^{34}\text{S}\text{-SO}_4$ and $\delta^{18}\text{O}\text{-SO}_4$). Sample aliquots for alkalinity, anions, cations, and Sr isotopes were collected into pre-cleaned 30-mL high-density polyethylene (HDPE) bottles with no headspace. Ultra-pure nitric acid was added to cation and Sr isotope samples to keep the pH below 2. Sample aliquots for $\delta^{18}\text{O}$ and δD were collected into two 10-mL glass vials and sealed with crimp tops with no headspace. Aliquots for $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) were collected into 30-mL glass serum vials and sealed with crimp tops with no headspace. Sample aliquots of ^3H were collected into 1-L HDPE bottles with no headspace. Radiocarbon samples were collected into two 500-mL amber glass bottles and sealed with no headspace. Aliquots of sulfate isotopes were collected into 1-L amber HDPE bottles with no headspace and were acidified with 10 drops of ultra-pure nitric acid to prevent bacterial sulfate reduction. All samples were stored on ice in the field and refrigerated in the laboratory to remain at or below 4°C .

4.2 Laboratory Methods

Alkalinity, cations, anions, and $\delta^{18}\text{O}/\delta\text{D}$ analyses were performed at the University of Arizona's Department of Hydrology and Atmospheric Sciences. Alkalinity was performed by the Gran-Alk titration method as described by Gieskes and Rogers (1973) (precision $\pm 0.6\%$). Using this method, it was assumed that carbonate alkalinity is equal to the titration alkalinity, as organic acids and hydrogen sulfide were not present in meaningful concentrations. Major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Sr^{2+} , Ba^{2+} , Si, B, and total Mn, Fe, Zn, and Al) were analyzed (precision $\pm 3\%$) using a Perkin-Elmer Optima 5300DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Major anions (SO_4^{2-} , Cl^- , F^- , Br^- , NO_2^- , and NO_3^-) were analyzed (precision $\pm 2\%$) using a Dionex Ion Chromatograph (IC) model ICS-3000 using an AS23 analytical column. USGS reference standard M216 was used. Charge balances for all samples were within 5%. Stable water isotopes ($\delta^{18}\text{O}$ and δD) were analyzed (precision $<0.08\text{‰}$ and $<0.9\text{‰}$, respectively) using a Los Gatos Research Laboratory Isotope Analyzer model LWIA-24d with 4th generation cavity enhanced adsorption.

Tritium, $\delta^{34}\text{S}$ of dissolved sulfate ($\delta^{34}\text{S}\text{-SO}_4$), $\delta^{18}\text{O}$ of dissolved sulfate ($\delta^{18}\text{O}\text{-SO}_4$), and $\delta^{13}\text{C}\text{-DIC}$ analyses were performed at the University of Arizona's Department of Geosciences Environmental Isotopes Laboratory (EIL). Tritium was analyzed (detection limit = 0.4 TU) using a Quantulus 1220 Spectrometer in an underground counting laboratory using electrolytic enrichment and liquid scintillation decay counting methods (Theodorsson, 1996). Samples were enriched by a factor of about nine and subsequently mixed 1:1 with an Ultimagold Low Level Tritium Cocktail and counted for 1,500 minutes. Standardization is based on international standard OGS-1.

For the sulfur isotopes of sulfate, $\delta^{34}\text{S}\text{-SO}_4$ was analyzed (precision $\pm 0.15\text{‰}$) using a ThermoQuest Finnigan Delta Plus XL instrument. First, BaSO_4 was precipitated out of the groundwater samples, which were subsequently combusted at 1030°C with O_2 and V_2O_5 using an elemental analyzer (Costech) coupled to the mass spectrometer. Standardization is based on international standards OGS-1 and NBS123, and several other sulfide and sulfate materials that have been compared between laboratories. For the oxygen isotope of sulfate, $\delta^{18}\text{O}\text{-SO}_4$ was analyzed (precision $\pm 0.40\text{‰}$) using a Thermo Electron Delta V instrument. Samples were combusted with excess carbon at 1350°C using a thermal combustion elemental analyzer (ThermoQuest Finnigan) coupled to the mass spectrometer. Standardization is based on international standard OGS-1. Stable carbon isotope analysis of dissolved inorganic carbon ($\delta^{13}\text{C}\text{-DIC}$) was analyzed (precision $\pm 0.2\text{‰}$) using a ThermoQuest Delta Plus XL coupled with a Gasbench automated sampler. Samples were reacted for > 1 hour with phosphoric acid at room temperature in Exetainer vials previously flushed with He gas. Standardization is based on NBS-19 and NBS-18.

Radiocarbon samples were measured at the University of Arizona's Accelerator Mass Spectrometer (AMS) Laboratory. Samples were analyzed (detection limit = 0.2 pmc) using a National Electrostatics Corp. tandem accelerator mass spectrometer. Carbon dioxide was extracted from samples by acid hydrolysis and was then reduced to graphite that was made into targets for accelerator mass spectrometry. Radiocarbon ages presented by the lab are uncorrected.

Trace elements and the strontium isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) of samples were measured at the University of Texas at El Paso's Center for Earth and Environmental Isotope Research (CEEIR) Laboratory. Trace element concentrations were measured with a

Thermo Fisher iCap RQ ICP-MS instrument. The NIST water standard (NIST 1640a reference material) and USGS standards were used to assess accuracy. Analytical error was between 1 and 11%. To measure $^{87}\text{Sr}/^{86}\text{Sr}$, groundwater samples first had to be prepared. Approximately 25-mL of groundwater samples were evaporated to dryness; the dry samples were re-dissolved in 3.5 N HNO_3 then separated and purified through Sr-Spec resin. The purified samples and strontium standard (SRM 987) were measured for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios on a MC-ICP-MS using the standard-sample bracketing method (Konter and Storm, 2014). About 200 mg of rock standard BCR2 was acid-digested in HNO_3 -HF and HCl - H_3BO_3 then separated through Sr-Spec resin. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in BCR2 reported values of 0.705019 ± 4 (2σ ; $N=5$) consistent with averages reported in other studies (Raczek et al., 2003). Blanks are negligible for Sr analysis (~ 82 pg).

4.3 Radiocarbon Age Corrections

Radiocarbon values reported by the AMS laboratory were corrected to account for geochemical reactions occurring in the subsurface, such as carbonate mineral dissolution, that can add dead carbon (0 pmc ^{14}C) to the groundwater and artificially increase the apparent groundwater ‘age’ (Clark and Fritz, 1997). To make these corrections, NetpathXL (Parkhurst and Charlton, 2008), a revised version of NETPATH (Plummer et al., 1994), was used. NetpathXL employs the revised Fontes and Garnier model of Han and Plummer (2013) and performs basic inverse modeling, based upon the major ion chemistry, $\delta^{13}\text{C}$ -DIC, and radiocarbon values. The program then plots sample points on a graph, which depending on where the samples plot, indicates whether the Tamers model, gas exchange model, or solid exchange model should be used in radiocarbon age

corrections. In this study, the $\delta^{13}\text{C}$ of soil CO_2 was assumed to be -22‰ based upon a study conducted in western Utah and the Basin and Range and Colorado Plateau transition zone (Hart et al. 2010).

4.4 Principal Component Analysis

Principal component analysis (PCA) was completed using XLSTAT (XLSTAT, 2019), a statistical analysis program, to explore the relationships of aquifer geochemistry. PCA has been used previously in groundwater and surface water mixing problems (Christopherson and Hooper, 1992; Liu et al., 2004). To note, all wells with no results for any given analysis were removed, because non-zero values must be present in order to conduct PCA; 325 and LV-41-75 were also removed due to the fact that their corrected radiocarbon ages indicate that they are “modern” water but cannot specify a more precise age. PCA was conducted on nine select wells from the BCA and NA, analyzing 12 major ions and isotopes (HCO_3^- , SO_4^{2-} , Cl^- , F^- , Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Sr^{2+} , $\delta^{18}\text{O}$, $\delta^{34}\text{S}$ - SO_4 , and corrected radiocarbon ages).

4.5 Hydrogeologic Modeling

To better understand the mechanisms responsible for the composition of the environmental isotopic data collected as part of this study, a regional cross-sectional hydrologic model was constructed to characterize the Pleistocene to modern groundwater flow patterns from the La Sal Mountains to the Lisbon Valley (Figure 13). We hypothesize that groundwater flow originates in the La Sal Mountains, is driven by topography, and discharges into Lisbon Valley, the regional topographic low. Due to the presence of saline

brines and evaporite units within Lisbon Valley, it is difficult to speculate on the depth of circulation without variable-density hydrologic modeling. The northwest-southeast cross-sectional model was constructed perpendicular to published water table contours from Avery (1986), as well as available data from LVMC (Whetstone Associates, 2018) (Figure 12).

We used the code *FEMOC* (Person et al. 2007; Pepin et al. 2015), which solves for variable-density groundwater flow, heat, and solute transport along a 36 km long transect (Figure 13). Each transport equation (groundwater flow, heat, solute, groundwater residence times, isotopic transport and fluid-rock exchange) was solved sequentially. An equation of state relating density and viscosity to changes in temperature, pressure and salinity coupled the groundwater flow, heat and solute transport equations (Batzle and Wang, 1992) was used. The governing transport equations are presented in Pepin et al. (2015) and Person et al. (2007) for isotopic transport. To compute the isotopic composition of the solid phase, we assumed a uniform mineralogy for each hydrostratigraphic unit consisting of quartz, anorthite, muscovite, biotite, hornblende, and quartz. Initial fluid isotopic composition was determined based on rock composition and temperature using an equilibrium isotopic exchange coefficient. Fluid-rock exchange was minimal at the low temperatures ($<160^{\circ}\text{C}$) for these simulations. We solve for groundwater residence times using the advection-dispersion equation presented in Goode (1996). All transport equations were solved using the finite element method. Due to the potential for grid dispersion influencing groundwater residence times, we compared nodal solutions of groundwater age to advective groundwater ages using a reverse particle tracking algorithm. Particles were introduced at nodes adjacent to the well screens sampled at LVMC and

tracked through the flow field back up into the La Sal Mountains (Figure 18). Particle tracking along flow paths also permitted the determination of the elevation of recharge, which was in turn used to estimate the $\delta^{18}\text{O}$ value of recharge associated with the simulated groundwater residence time. We compared the particle recharge isotopic composition to the nodal solution to the advective-dispersive isotopic transport/exchange equation.

This model consisted of 12 hydrostratigraphic units (Table 6a). The Lone Wolf and Lisbon Valley fault zones were included within the model. We used typical properties for the sandstone, shale, limestone, and evaporite units (Table 6a), taking into account available permeability data for the BCA and NA (Avery, 1986; Jacobs Engineering Group 1996). Stratigraphic offsets caused by the LVF were included in the model. The mesh was composed of 2,486 nodes and 5,466 triangular elements. Characteristic element size in the x-direction varied between about 100-500 m and 50-150 m in the z-direction. We present three simulations here. The permeability of the hydrostratigraphic units is presented in Table 6a.

For groundwater flow, regional water table values were compiled from Avery (1986) and from LVMC (Whetstone Associates, 2018) to specify present-day water table conditions along the top of the model domain (Figure 14a). Water tables reached the land surface within the La Sal mountains over much of the cross-section. During the last glacial maximum (LGM), the imposed water table reached over 3,120 m but fell to 2,400 m at present day. We allowed heads to increase within the recharge area by about 30% in the La Sal Mountains during Pleistocene times in order to account for cooler and wetter conditions (Figure 14a; Putman and Broecker, 2017). The isotopic composition ($\delta^{18}\text{O}$) of the recharge varied with elevation between -12.8 to -16‰ between Lisbon Valley and the

La Sal Mountains, respectively. To account for a 5 to 7°C colder climate in the four corners region of the southwest during the LGM (Philips et al, 1986; Zhu et al., 1998), $\delta^{18}\text{O}$ was reduced by about 5.5‰ between recent to LGM times, based upon an approximate decrease in $\delta^{18}\text{O}$ of 1‰ per a 1.1 to 1.7°C decrease in temperature (Clark and Fritz, 1997); Figure 15 presents a time series of the imposed isotopic composition of the recharge through time (after Hansen et al. 2017). We imposed a groundwater age of 0 years at the land surface/water table. An initial salinity concentration gradient of 25 mg/L/m was set for the shallow aquifer; elements within the Paradox Formation were set at 300,000 mg/L.

For groundwater flow, solute transport, isotope transport, and groundwater residence times, the sides and bottom of the model domain were specified as no-flux boundaries. The no-flux boundary on the northern end represents the groundwater divide that exists at the La Sal Mountains, while the no-flux boundary on the southern side is proximal to the regional topographic low (Lisbon Valley). For heat transport, a specified temperature boundary condition was assigned across most of the top of the solution domain at the water table. Temperature decreased with elevation using a lapse rate of 0.006 °C/m. Assigned water table temperatures ranged from 9.3°C at the La Sal Mountains to 12°C within LVMC, which falls within the range of mean annual minimum and maximum air temperatures in La Sal (US Climate Data). Along the base of the solution domain, a basal heat flux of 60 mW m⁻² was assigned. Initial subsurface temperatures were assumed to increase linearly with depth using a 30°C km⁻¹ temperature gradient that is representative of the region (Henrikson and Chapman, 2002). All model simulations were run for 1 million years using a timestep of 100 years to reach steady-state conditions in order to eliminate the influence of initial conditions.

Aquifer permeabilities can vary by several orders of magnitude (Freeze and Cherry, 1979). As part of a sensitivity study, the permeability of the NA and BCA were varied between 10^{-13} and $8 \times 10^{-13} \text{ m}^2$. The permeability and porosity for the best-fit model (Run 5; Figure 13) for the BCA were $5 \times 10^{-12} \text{ m}^2$ and 0.20, respectively, while in the NA permeability was set to $1 \times 10^{-13} \text{ m}^2$ and porosity was set to 0.10 (Table 6a). Model output from the three simulations are described below. Thermal transport and petrophysical parameters that were assigned to all hydrostratigraphic units were held constant (Table 6b).

5.0 RESULTS

5.1 Field Parameters

Field parameters of groundwater samples were measured at 21 well and borehole sites (Table 2). Temperature ranged from 12.9 to 14.4°C in samples from the Mancos Shale, from 11.1 to 20.8°C in the BCA, and from 17.6 to 24.8°C in the NA. pH ranged from 6.83 to 7.87 in the Mancos Shale, with an average of 7.21; from 6.54 to 9.01 in the BCA, with an average of 7.01; and from 6.80 to 8.77 in the NA, with an average of 7.20. EC in the Mancos Shale ranged from 629 to 6,690 $\mu\text{S}/\text{cm}$, with an average of 2,791 $\mu\text{S}/\text{cm}$; from 875 to 2,100 $\mu\text{S}/\text{cm}$ in the BCA, with an average of 1509 $\mu\text{S}/\text{cm}$; and from 617 to 1,345 $\mu\text{S}/\text{cm}$ in the NA, with an average of 848 $\mu\text{S}/\text{cm}$.

5.2 Alkalinity

Twelve groundwater samples were analyzed for alkalinity (Table 3). In the BCA, alkalinity ranged from 202 mg/L (well PW-9) to 743 mg/L (borehole 325). In the NA, alkalinity had a smaller range, from 217 mg/L (LV-41-75) to 390 mg/L (MW97-11). Given that a majority of samples had neutral to near-neutral pH, bicarbonate (HCO_3^-) is assumed to be the dominant constituent of alkalinity, with one exception. Field measured pH at PW-9 was 9.01, which suggests that carbonate (CO_3^{2-}) may be a minor component to alkalinity at this sample location.

5.3 Major Ions

In general, Ca^{2+} , Na^+ , Mg^{2+} , SO_4^{2-} , and HCO_3^- were the dominant ions in the sampled groundwaters (Table 3). In the BCA, groundwaters were generally characterized as a Ca-Mg- SO_4 type. Ca^{2+} ranged from 41.9 to 223 mg/L, Mg^{2+} ranged from 18.9 to 96.4 mg/L, and SO_4^{2-} ranged from 72.6 to 866 mg/L. In the NA, groundwaters were generally characterized as a Na- HCO_3^- type. Na^+ ranged from 11.4 to 216 mg/L, while HCO_3^- ranged from 217 to 390 mg/L. Further distinction is made by the low concentrations of Cl^- present in the BCA (14.9 to 32.8 mg/L) compared to higher concentrations of Cl^- in the NA (18.0 to 122 mg/L), and the aforementioned high concentrations of SO_4^{2-} in the BCA (72.6 to 990 mg/L) compared to low concentrations of SO_4^{2-} in the NA (14.8 to 147 mg/L). Total dissolved solids (TDS) in the BCA ranged from 950 to 1,898 mg/L, with an average of 1,424 mg/L, while TDS in the NA was lower, ranging from 337 to 892 mg/L, with an average 650 mg/L.

5.4 Trace Elements

In general ore-forming trace elements such as Cu, Fe, Co, Mn, and U were found, on average, in higher concentrations in the BCA than in the NA. Additionally, trace element Rb was generally observed at higher concentrations in the BCA than the NA. Conversely, other trace elements such as V, Ni, Zn, and Ba were found at higher concentrations in the NA than the BCA on average. Al and As were found at generally comparable concentrations in the two aquifers. Of note, As exceeded the U.S. EPA's drinking water standard for As (10 $\mu\text{g/L}$) in BCA well PW-4 (35.1 $\mu\text{g/L}$) and NA wells PW-7 (22.7 $\mu\text{g/L}$) and MW97-13 (10.7 $\mu\text{g/L}$). Additionally, exceedances of the U.S.

EPA's drinking water standard for U (30 µg/L) were observed at BCA wells PW-3 (41 µg/L) and PW-4 (86 µg/L).

5.5 Stable Isotopes

Stable isotopes of water ($\delta^{18}\text{O}$ and δD) were measured at 19 wells (Table 5). All samples generally plotted along the Utah Meteoric Water Line (UT MWL) where $\delta\text{D} = (\delta^{18}\text{O} * 6.7) - 12.6$, as reported in Kendall and Coplen (2001). As such, further presentation of results will be limited to $\delta^{18}\text{O}$. In the Mancos Shale, $\delta^{18}\text{O}$ values ranged from -14.2 to -13.5‰; in the BCA, $\delta^{18}\text{O}$ values ranged from -16.5 to -10.2‰; in the NA, $\delta^{18}\text{O}$ values ranged from -17.4 to -13.5‰.

Stable carbon isotopes of dissolved inorganic carbon ($\delta^{13}\text{C-DIC}$) were measured at 19 wells (Table 5). In the Mancos Shale, $\delta^{13}\text{C-DIC}$ values ranged from -8.9 to -3.3‰. In the BCA, $\delta^{13}\text{C-DIC}$ values ranged from -9.5 to +7.9‰, with the observed value of +7.9‰ being the only positive $\delta^{13}\text{C-DIC}$ value measured in the study area. In the NA, $\delta^{13}\text{C-DIC}$ values ranged from -17.1 to -6.1‰.

Stable sulfur and oxygen isotopes of sulfate ($\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$) were measured at 12 wells (Table 5). In the Mancos Shale sample, $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ were -1.2‰ and -0.3‰, respectively. In the BCA, values of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ ranged from -8.1 to +15.9‰ and -5.8 to +7.64‰, respectively. One sample from the BCA, borehole 325, formed an insufficient amount of BaSO_4 precipitate during laboratory preparations, and thus was unable to be analyzed. In the NA, $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ ranged from +3.8 to +8.9‰ and -2.0 to +5.7‰, respectively.

5.6 Strontium Isotopes

The ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ was measured at 12 wells (Table 5). In the BCA, the strontium isotope ratio ranged from 0.70924 to 0.70947, with an average of 0.70935. In the NA, strontium isotope ratios were slightly more radiogenic than the BC and ranged from 0.70920 to 0.70970, with an average of 0.70951.

5.7 Age Tracers

Tritium was measured at 11 wells (Table 5). In the BCA, ^3H was below the detection limit (0.4 TU [November 2017], 0.5 TU [September 2018]) in three out of five wells; the two detections reported were 1.0 and 1.5 TU. In the NA, ^3H was non-detect in four out of six wells. In two of the wells, ^3H was reported at the method detection limit of 0.5 TU. As such, these detections will henceforth be considered as non-detections.

Radiocarbon was measured at 11 wells (Table 5). NetpathXL (Parkhurst and Charlton, 2008) indicated that all of the samples, except for one, should use the revised Fontes and Garnier solid exchange model (Han and Plummer, 2013) for calculating corrected radiocarbon ‘ages’; it was indicated that sample PW-8 should use the Tamers model (Tamers, 1967; Tamers and Scharpenseel, 1970; Tamers, 1975) for ‘age’ corrections. To note, several other samples were close to falling within the region to use the Tamers model. This, coupled with the fact that the difference between the Fontes and Garnier age and the Tamer age produced for PW-8 was small, all ages will subsequently be reported using the Fontes and Garnier solid exchange model for consistency. In the BCA, corrected radiocarbon ages indicated groundwaters ranged from modern to 11,000 BP. In the NA, corrected radiocarbon ages indicated that groundwaters ranged from

modern to 36,000 BP. Each aquifer had a single sample that radiocarbon data indicated as being “modern”; these samples are discussed further below. Excluding each of these ‘modern’ samples, corrected radiocarbon ‘ages’ for the BCA and NA ranged from 3,300 to 11,000 and 15,000 to 36,000 BP, respectively.

5.7 Principal Component Analysis

PCA from 9 select wells from the BCA and NA, analyzing 12 major ions and isotopes, yielded the first two principal axes explaining 77.84% of the variability of the data (Figure 11). In general, most BCA wells plot on the righthand side with acute angles between the well points and analyte vectors indicating that BCA wells can be characterized by and have larger concentrations of Ca^{2+} , Mg^{2+} , K^+ , Sr^{2+} , HCO_3^- , and SO_4^{2-} and more positive $\delta^{18}\text{O}$ values. Groundwater from the NA plots on the left-hand side, with a typical geochemical signature better explained by Na^+ , Cl^- , and F^- concentrations, positive $\delta^{34}\text{S}$ - SO_4 values, and older corrected radiocarbon ages.

5.8 Hydrogeologic Modeling

We ran six model runs using different boundary conditions and permeability values for the fault zone, BCA, and NA. The first three model runs assumed a static water table configuration consistent with modern water table contour maps (not shown). Model runs 4-6 considered temporally varying water table elevations, isotopic composition of recharge, and land surface temperatures. Computed hydraulic heads, flow patterns, temperatures and concentrations did not vary significantly between simulations and we only present spatial contour plots from one model run below (Run5).

For model Run 5, simulated flow patterns and groundwater streaklines indicate that a shallow topographically driven flow system exists with flow from the La Sal Mountains to Lisbon Valley (Figure 13b). Recharge rates between the last glacial maximum (LGM, 21,000 BP) to modern varied between about 0.3 to 0.58 m/year within the La Sal Mountains. The shallow, topographically driven flow system extends about 1 km deep across the transect; the thickness of the freshwater zone is greater beneath the La Sal Mountains. Salinities increased dramatically with depth below 1 km (Figure 13d), with a mixing zone about 200 m wide marking the transition to the deeper convective flow system (Figure 13b). The initial salinity gradient was set at 23 mg/L/m. Higher concentrations developed adjacent to the Paradox Formation. Paradox Formation elements had concentrations set to 300,000 mg/L. Thermal convection cells formed within the crystalline basement beneath the La Sal Mountains. Maximum vertical flow rates within the deeper convective system beneath the La Sal Mountains were about 0.2 m/year. Due to the shallow nature of the freshwater flow system, thermal convection was minimal (Figure 13c). Simulated groundwater age varied laterally and with depth across the model transect, with Late Pleistocene groundwater ages computed for the shallow, freshwater system (Figure 13e). Groundwater isotopic composition ($\delta^{18}\text{O}$) varied laterally and was sensitive to the permeability conditions used.

Particle trajectories from the nodes closest to the LVMC monitoring wells sampled back to the La Sal Mountains are also shown in Figure 18. Hydraulic head and salinity profiles from the northern edge of Lisbon Valley are plotted in Figure 17. Simulated heads increase with depth, which is inconsistent with field observations. Computed advective groundwater ages and $\delta^{18}\text{O}$ composition at the time of recharge for the best fit simulation

are shown in Figure 13. Groundwater age, salinity, and temperature were not very sensitive to permeability values used, however the isotopic composition of the groundwater was sensitive to permeability values used (Figure 16). Computed nodal isotopic composition of groundwater was out of phase with recharge isotopic composition of groundwaters (Figure 15). Computed and observed head and salinity versus depth are presented in Figures 18a-b within Lisbon Valley. Observed heads (circles) in Figure 17a indicate Lisbon Valley is a recharge area, however the simulated heads from a profile extracted from Run 5 along the northern side of Lisbon Valley indicate groundwater discharge conditions. The regional model overpredicted salinity conditions by at least an order of magnitude (Figure 17b).

We used a particle tracking algorithm to track flow paths from wells up into the La Sal Mountains (Figure 18). Particle trajectories were found to be sensitive to the permeability of the BCA and NA. In some instances, particle tracking suggests that groundwater moves from the La Sal Volcanics into the underlying Cutler Formation and then up into the NA.

6.0 DISCUSSION

The geochemical and isotopic results were integrated with physical hydrogeologic observations and groundwater flow and solute transport modeling to: (1) assess BCA and NA connectivity in the LVMC area by determining (a) whether unique geochemical and isotopic signatures in each aquifer exist and (b) the apparent age of groundwater in each aquifer; (2) compare LVMC site hydrogeochemistry to more regional hydrogeochemistry to examine if regional trends in groundwater quality and residence times within the BCA and NA exist; and (3) identify local and regional groundwater flow path(s) and investigate the influence of paleohydrologic conditions on recharge to the BCA and NA.

6.1 Local to Regional Aquifer Quality and Hydraulic Connectivity

6.1.1 Solute Chemistry and Residence Time

Major ion chemistry, trace metals, solute isotopes, and age tracers can be indicative of whether mixing is occurring between two aquifers, because if mixing were occurring, one would expect the values of these geochemical parameters of each water to be similar and/or follow a mixing trend (Campbell et al., 2008; Johnson et al., 2015; Priestly et al., 2017; Li et al., 2018). The unique geochemical and isotopic signatures of each aquifer at LVMC, and lack of mixing trends between aquifer endmember compositions, suggests that limited cross-formational flow is occurring between the BCA and the NA.

Groundwater in the BCA is a Ca-Mg-SO₄ type water, while NA wells generally plot as an Na-HCO₃ type water (Figures 6a-d). PCA of 12 major ions (SO₄²⁻, HCO₃⁻, Na⁺, Ca²⁺, Mg²⁺, K⁺, Sr²⁺, Cl⁻, F⁻), isotopes ($\delta^{18}\text{O}$, $\delta^{34}\text{S-SO}_4$), and corrected radiocarbon ages of groundwater samples from the BCA and NA (Figure 11) further highlights the distinct

groupings of the BCA and NA found at LVMC. In addition, BCA wells, on average had higher concentrations of important ore-forming trace elements, such as Cu, Fe, Co, Mn, and U, than the NA (Tables 4, 7).

Several other studies have assessed aquifer water quality and/or connectivity of the BCA and NA in other parts of southeastern Utah, as well as southwestern Colorado (Avery, 1986; Spangler et al., 1996; Naftz et al., 1997; Zhu et al., 2000; Kirby, 2008) and provide the basis for a spatial comparison of the BCA and NA. Results from these other studies shows that hydrochemistry of the BCA and NA varies depending on locality. Avery (1986) indicates that the BCA in much of the region is a Ca-HCO₃ type with a moderately low TDS (< 500 mg/L), however in some areas such as Montezuma Creek or Blanding, Utah, groundwater from the BCA is more saline (up to 2,890 mg/L TDS) with an Na-HCO₃ or Ca-Mg-SO₄ type signature, the latter of which would be consistent with groundwater chemistry observed at LVMC. In the NA, Avery (1986) indicates that groundwater ranges from a Ca-HCO₃ to Na-Cl-SO₄ and is low in TDS (< 250 mg/L), but generally increases in TDS along flow paths. In other areas, such as Montezuma and Aneth, UT, the NA is observed as brackish in some wells (up to 8,640 mg/L TDS). This deterioration in chemical quality may be due to upward flow of more saline groundwater from the underlying Cutler and Hermosa formations, or due to contamination from the oil/gas industry because of unplugged or poorly plugged test holes or leaking water injection wells (Avery, 1986). Deterioration in water quality to this degree in the NA is not observed at LVMC.

Furthermore, distinct groupings of BCA and NA wells at LVMC and more regionally were observed in stable water isotope analyses and corrected radiocarbon ages (Figures 10, 11a-b), which are suggestive of recharge occurring at different times for the

two aquifers. All groundwater samples from LVMC analyzed in this study plotted along the Utah meteoric water line (Kendall and Coplen, 2001), suggesting that waters of the BCA and NA are meteoric in origin. BCA wells at LVMC plotted with a wide range of $\delta^{18}\text{O}$ and δD values generally within the range of modern surface waters of the region (Gardner, 2004; Bowen, 2017). Coupled with corrected radiocarbon ages of 3,300 to 11,000 BP, these values are consistent with groundwater in the BCA recharging during the Holocene. The one exception is borehole 325, which will be discussed further below.

In the NA, five of six samples plotted with $\delta^{18}\text{O}$ and δD values lower than any of the other samples collected from LVMC for this study. The one exception in the NA is from borehole LV-41-75, which is the only sample from the NA collected from an unconfined portion of the aquifer that is open to the atmosphere. Of note, samples from the NA were isotopically lighter than modern composite snow samples collected from the Abajo Mountains (Spangler, 1996) to the southwest of the study area, which would suggest that groundwater in the NA recharged when the climate was cooler (Clark and Fritz, 1997; Zhu et al., 1998). This is consistent with corrected radiocarbon ages in the NA, which ranged from 15,000 to 36,000 BP, which would suggest that groundwater in the NA recharged during the Late Pleistocene.

The low $\delta^{18}\text{O}$ and δD values of NA samples coupled with corrected radiocarbon ages that date to the Late Pleistocene are consistent with other results from the Colorado Plateau in the nearby San Juan and Black Mesa basins, where climatic conditions of the Late Pleistocene were inferred to be 5 to 7°C cooler than modern temperatures for the region (Philips et al. 1986; Zhu et al., 1998). The studies by Philips et al. (1986) and Zhu et al. (1998) additionally indicate that recharge during summer months may have been

lower, however recharge was greater during the winter months of the Late Pleistocene, leading to recharge rates two to three times greater than modern rates.

Regionally, stable water isotopes and corrected radiocarbon ages for the NA south of LVMC in the Black Mesa Basin of northeastern Arizona (Zhu, 2000) were compared to the results from LVMC. In the plot of δD versus $\delta^{18}O$ (Figure 9), groundwater samples from the NA from Zhu (2000) are, in general, isotopically heavier than the samples collected at LVMC. This difference in observed δD and $\delta^{18}O$ values is likely due to recharge for LVMC occurring at a higher elevation than recharge at the Black Mesa Basin (Clark and Fritz, 1997). Two distinct groupings exist in Zhu's data: 1) groundwater with a corrected radiocarbon age of less than 11,000 BP (Holocene recharge) that exhibits isotopically heavier δD and $\delta^{18}O$ values; and 2) groundwater with a corrected radiocarbon age greater than 11,000 BP (Late Pleistocene recharge) that has isotopically lighter δD and $\delta^{18}O$ values. These two distinct groupings of groundwater are further highlighted in the plot of corrected radiocarbon age versus $\delta^{18}O$ (Figure 10a). The results from Zhu (2000) are thus consistent with the findings of this study.

6.1.2 Isotopic indicators of different water-rock reactions in each aquifer

The values of sulfate and strontium isotopic ratios from the BCA and NA at LVMC suggest distinct water-rock reactions occurring within each aquifer, consistent with their differing lithologies, with no indication of mixing. In three of four BCA samples, as well as the one Mancos Shale sample, $\delta^{34}S-SO_4$ and $\delta^{18}O-SO_4$ values plot within the typical range of sulfide oxidation (Figure 7a). The results of the sulfate isotopes for the BCA are consistent with the fact that chalcocite (copper sulfide ore deposit), as well as azurite and

malachite (copper carbonate minerals), are predominantly found in the BCA (Jackson, 1997). The generally higher concentrations of trace metals in BCA samples supports the oxidation and release of these trace metals from mineralized zones within the BCA, however the lack of DO coupled with high concentrations of SO_4^{2-} and Fe^{2+} suggests that aquifer is anoxic, but still undergoing iron reduction (i.e. sulfate reduction has yet to occur). On the other hand, five of the six NA samples plot within the atmospheric deposition and soil sulfate regions, consistent with the NA being an eolian formation (Figure 7a). Alternatively, the observed values in the NA could also be attributed to this confined aquifer exhibiting reducing conditions; in an anoxic environment such as this, BSR may occur and would produce more positive $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ values (Clark and Fritz, 1997; Krouse et al., 1970). If BSR was occurring, one would expect to see strongly positive values of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$, decreased concentrations of SO_4^{2-} (Figure 7b), and increased concentrations of HCO_3^- , as explained by [rxn. 1]. NA wells exhibit positive $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ and much lower concentrations of SO_4^{2-} compared to the BCA, but the BCA generally has higher concentrations of HCO_3^- , however this may in part be due to the poorer water quality of the BCA in general.

Regionally, isotopes of sulfate of groundwater and rock for the BCA and NA have a large range of values, varying spatially (Kimball, 1992; Tuttle and Grauch, 2009; U.S. Geological Survey, 2016). Data accessed from the USGS's National Water Information System (NWIS) for the BCA had values of $\delta^{34}\text{S-SO}_4$ that were all positive, ranging from +2.98 to +12.24‰. These values are not consistent with values observed at LVMC and may be due to reducing environmental conditions being present at these locations, instead of the typical sulfide oxidation values observed at LVMC. Compiled data (Kimball, 1992;

U.S. Geological Survey, 2016) shows that the NA in other areas has $\delta^{34}\text{S-SO}_4$ values that range from -14.87 to +9.70‰. This again shows that aquifer conditions are not uniform spatially, however this is not unexpected. Ranges of values of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ for rock samples from the Mancos Shale, Dakota Sandstone, and a gypsum mine in southwestern Colorado (Tuttle and Grauch, 2009) are plotted as yellow boxes on the graph of $\delta^{18}\text{O-SO}_4$ versus $\delta^{34}\text{S-SO}_4$ (Figure 7a). Strong negative values are observed in $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ in the Mancos Shale rock samples and are not consistent with the single Mancos Shale groundwater sample from LVMC, which had slightly negative values. Values of $\delta^{34}\text{S-SO}_4$ of rock samples from the Dakota Sandstone are generally near-zero to negative, which is consistent with values observed from BCA groundwater samples at LVMC, while $\delta^{18}\text{O-SO}_4$ of the Dakota Sandstone encompasses a broader range. The values of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ obtained from gypsum samples are strongly positive and are not consistent with any of the groundwater samples collected in this study. However, while five of the six NA samples fell in the ranges of atmospheric deposition and/or soil sulfate (Figure 7a), typical of an eolian sandstone, they did fall in between the ranges of observed values for the Dakota Sandstone and gypsum samples, which may suggest that groundwater in the NA carries a signature of mixing between these two endmembers. If this were the case, the dissolution of the gypsum endmember would lead to high concentrations of SO_4^{2-} in solution, which was not observed at any NA sample location.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios observed in groundwater from the BCA and NA are consistent with the rock and mineral types present within each formation. The BCA is a stream-lain deposit, which has notable laminations of limestone and shale, whereas the NA is an eolian formation with less carbonate-type rocks than the BCA (Weir and Puffet, 1981). In

general, carbonates are found to have a lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, but more readily weather, whereas silicates are found to have a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, but are more resistant to weathering (Edmond, 1992; Bickle et al. 2001). These characteristic traits are observed at LVMC; a lower $^{87}\text{Sr}/^{86}\text{Sr}$ signature with higher $[\text{Sr}^{2+}]$ in the BCA, but higher $^{87}\text{Sr}/^{86}\text{Sr}$ signature in the NA with lower $[\text{Sr}^{2+}]$. Concentrations of Ca^{2+} , K^{+} , and Rb^{+} were typically higher in the BCA and are consistent with the carbonate lithology; because Sr^{2+} readily substitutes with Ca^{2+} , and relatively soluble carbonate minerals are present in the aquifer, this may explain the higher concentrations of Sr^{2+} observed in the BCA.

Additional data for strontium isotopes of groundwater within the BCA are not available for the region. However, data does exist for fresh groundwater of the NA (Naftz et al., 1997), as well as from one rock sample from the BCA (Truini and Longworth, 2003) and numerous rock and mineral samples from the NA (Naftz et al., 1997; Truini and Longworth, 2003; Kampman et al., 2014). Groundwater in the NA had an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio that ranged from 0.70860 to 0.71063 with an average of 0.70972, and Sr^{2+} concentrations that ranged from 0.03 to 20 mg/L with an average of 4.19 mg/L (Figure 8). It is apparent that the range of values reported for groundwater in the NA encompasses all the values reported for the BCA and NA at LVMC; the average of the data set, while higher in Sr^{2+} concentration, is however consistent with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio observed in the NA (i.e. more radiogenic than the BCA). The one rock sample from the BCA had an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71931 (Truini and Longworth, 2003), while the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the NA ranged from 0.70737 to 0.73301, with an average of 0.71378 (Naftz et al., 1997; Kampman et al., 2014). The average value of the NA being less radiogenic than the BCA is not consistent with data

from LVMC or the other referenced studies, however only having a single sample from the BCA does not provide an adequate spread of data to compare to.

6.1.3 *Anomalous groundwater samples*

Within the BCA and NA at LVMC there were select wells that did not exhibit geochemical signatures typical of their respective aquifer. Two BCA wells had geochemical signatures that did not look like a BCA or NA type water (PW-9 and borehole 325), while one NA sample (borehole LV-41-75) had a geochemical signature that differed from the other NA samples. At PW-9, the water carried a Na-SO₄ signature, which at first glance may suggest upward leakage from the NA, and thus a connection between the BCA and NA. Upon further analysis however, the addition of geochemical results of nearby Mancos Shale well 94MW6 shows that PW-9 has a geochemical signature nearly identical to 94MW6. Based upon this observation, it is possible that downward leakage from the Mancos Shale into the BCA is occurring within this area of the mine. Further evidence of downward leakage from the Mancos Shale is found in PW-9, being one of two sample locations with detections of ³H (1.5 TU), which indicates some modern water may be mixing with the older Holocene groundwater. The geochemistry at PW-9 is unique in that the most positive $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ values (+15.9‰ and +7.6‰, respectively) were reported at this location. One explanation for these results may be the occurrence of BSR at this location. In addition to the highest positive values of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ observed at the mine, PW-9 also exhibits the second lowest concentration of SO₄²⁻ of all BCA wells analyzed. However, PW-9 exhibits the lowest concentration of HCO₃⁻ of all wells analyzed. Given this discrepancy in what would be expected during BSR, and the fact that the geochemical signature of PW-9 is nearly identical to that of 94MW6, it is

possible that BSR is not occurring at this well, and PW-9 is merely inheriting the signature of the overlying Mancos Shale due to downward leakage. Without additional isotopic results from the Mancos Shale however, the results are inconclusive.

The sample from borehole 325 exhibits a geochemical signature dominated by Na^+ and HCO_3^- , the concentrations of both being higher than any other well sampled. Additionally, 325 is the only sample to exhibit a positive $\delta^{13}\text{C}$ -DIC value (+7.9‰). In general, the only way to obtain such positive $\delta^{13}\text{C}$ -DIC values in groundwater is due to the occurrence of methanogenesis; a simplified pathway-independent reaction for methanogenesis (Clark and Fritz, 1997) is as follows:

In addition to the positive $\delta^{13}\text{C}$ -DIC value exhibited, methanogenic groundwater should also have increased concentrations of HCO_3^- due to the production of CO_2 ; additionally, because methanogenesis occurs lower on the redox ladder than sulfate reduction, one would expect minimal concentrations of sulfate present (Clark and Fritz, 1997). This is in fact the case, as 325 had the highest concentration of HCO_3^- of all wells sampled and the lowest concentration of SO_4^{2-} of any BCA well sampled (second lowest overall). Additional evidence of the possibility of methanogenesis occurring is the presence of several coal beds noted in the bore log (Figure 21, Appendix C) of 325, as coal beds are conducive to supporting the type of microbial communities involved in this reaction (e.g., Schweitzer et al., 2018).

NA sample borehole LV-41-75 had stable water isotope values that fell in the middle of the range of values reported from the BCA, whereas the other five NA samples had stable water isotope values that were isotopically lighter than all other samples (Figure

9). Major ion chemistry for LV-41-75 also differed, characterized as a Ca-HCO₃ type water, plotting far left on the piper diagram (Figure 6) and not looking comparable to any other sample. Furthermore, the plot of $\delta^{18}\text{O-SO}_4$ versus $\delta^{34}\text{S-SO}_4$ (Figure 7a) indicates that LV-41-75 falls within the range of sulfide oxidation, a characteristic of BCA wells. Finally, the corrected radiocarbon age for LV-41-75 suggests “modern” water, however ³H was non-detect suggesting submodern water; a corrected radiocarbon age of modern but ³H that is non-detect suggests groundwater at LV-41-75 recharged sometime within the last 500 years or so. The culmination of all these observations at LV-41-75 are consistent with the fact that due to large vertical displacement along a fault (Figure 4), LV-41-75 is the only NA sample collected from an unconfined portion of the aquifer, subjected to oxidizing conditions.

6.2 Local and Regional Groundwater Flow

6.2.1 Local Groundwater Flow

Local-scale groundwater flow at LVMC is complex. Previous work completed at LVMC (Whetstone Associates, 2018) indicates that lateral flow in the BCA is limited to short distances due to geologic structures (i.e. faults; Figures 4-5), which prevent flow and compartmentalize the aquifer into many disconnected blocks. The report indicates that some groundwater flows downward from the BCA to the NA through localized faults or high angle fractures. The distinct values of isotopic composition of BCA and NA groundwater collected for this study seemingly indicate that if these connections are present, communication still appears to be limited.

The report from Whetstone Associates (2018) indicates that substantial compartmentalization is also observed in the NA due to offset along faults, juxtaposing high and low permeable units against one another. This compartmentalization along with low permeability fault gouge is inferred as causing faults to behave as barriers to horizontal flow in the NA. Whetstone Associates (2018) indicate that the apparent direction of groundwater flow in the NA below LVMC is to the northeast. Geochemical and isotopic data do not parse out this observed flow direction, however this may be due to the few number of samples collected from the NA and/or the substantial amount of compartmentalization of the NA. More isotopic data from additional sample locations would need to be collected from both the BCA and NA to better characterize local groundwater flow at LVMC due to the geologically complex structures that exist at LVMC.

6.2.2 *Regional Groundwater Flow*

Suspected regional groundwater flow based upon water table contours from Avery (1986), was from the La Sal Mountains flowing southeast to LVMC. Based upon the low observed salinities in groundwater samples combined with $\delta^{18}\text{O}$ values representative of Holocene and Late Pleistocene recharge, the fresh groundwater system is meteoric in origin, and appears to be riding on top of a deeper saline system. These inferences are further reinforced by the model which shows the freshwater system extending approximately 1 km in depth and not strongly mixing with the lower saline system (Figure 13d). In a plot of corrected radiocarbon age versus hydraulic head (Figure 10b) a strong correlation between decreasing hydraulic head and increasing corrected radiocarbon age is observed, suggestive of the occurrence of regional lateral flow occurring. In the regional

model, reverse particle tracking shows the particles placed in the nodes nearest the wells of LVMC have trajectories that trace back to the La Sal Mountains (Figure 18), further corroborating a regional flow system.

In samples collected from LVMC, the BCA had younger corrected radiocarbon ages and isotopically heavier $\delta^{18}\text{O}$ values suggestive of Holocene recharge, while the NA had older corrected radiocarbon ages and isotopically lighter $\delta^{18}\text{O}$ values suggestive of Late Pleistocene recharge (Figure 10a). We compared computed advective and advective-dispersive groundwater ages and $\delta^{18}\text{O}$ composition in Figure 19 for three different model runs. The advective ages based on reverse particle tracking and isotopic composition of the recharge were able to reproduce, in general, the observed trend of increasingly negative $\delta^{18}\text{O}$ with increasing age. The simulated ages from the advective model were however unable to reproduce the wide range of ages observed from groundwater collected from LVMC. Solutions to the advection-dispersion equation produced a wider range of ages like those that are observed, but resulted in a narrow range of simulated isotopic composition (Figure 19).

The best fit simulation (Run 5) produces a trend of more negative $\delta^{18}\text{O}$ values with increasing age that is, in broad terms, consistent with well data (Figure 19), however the advective ages from this run were all Holocene in age ($< 11,000$ BP). These simulated ages are not consistent with any of the observed corrected radiocarbon ages from the NA at LVMC (all NA ages $\geq 15,000$ BP). Finally, the model predicted that the Lisbon Valley would be an area of discharge, which is inconsistent with observed hydraulic head measurements at LVMC which indicate the Lisbon Valley is an area of recharge (Figure 17a). While aquifer dewatering occurs at the mine, historic data does not show large

discrepancies between the amount in drawdown between the BCA and NA that could account for this difference between simulated versus observed flow conditions. One hypothesis is that the Lisbon Valley is being affected by the southern no-flow boundary dictated in the model, that when combined with Lisbon Valley being the topographic low, causes the Lisbon Valley to be an area of discharge. While additional water table elevations are not available immediately adjacent to the Lisbon Valley, there is data from Slick Rock, Colorado (approximately 45 km SE; Jacobs Engineering Group, 1996) that indicates hydraulic head in both the BCA and NA are approximately 100 m lower in each when compared to data from the mine. It is possible that regional flow continues through the Lisbon Valley, heading towards and potentially discharging to the Dolores River. Future work could include extending the transect to the Slick Rock area, or replacing the current no-flow boundary at the southern end of the model with a reasonable constant head or specified flux boundary to allow the potential flow of water to continue through the Lisbon Valley area.

A number of simplifying assumptions were made for the model, which when combined with the coarseness of the model, may be what leads to the discrepancy between observed corrected radiocarbon ages and simulated advective ages and the lack of ability to “match” the older observed NA ages from LVMC. Additionally, it must be noted that the model is an idealized 2D representation of a more complex 3D system, so it is not unexpected that some of these complexities that exist within the flow system were not able to be represented.

7.0 CONCLUSIONS

1) Major ion chemistry at LVMC indicates that the BCA and NA have distinct geochemical signatures. In general, groundwater from the BCA was a Ca-Mg-SO₄ type water with high TDS and near-neutral pH, while groundwater from the NA was a Na-HCO₃ type with low-to-moderate TDS and slightly more alkaline pH. Additionally, analysis of trace elements showed that locally the BCA generally had higher concentrations of important ore-forming elements such as Mn, Fe, Co, Cu, and U – these results provided further characterization of BCA and NA water types.

2) All isotopic analyses indicated that LVMC the BCA and NA have distinct water compositions. The BCA near-zero to negative $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ values and a less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, while the NA had generally positive $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ values and a more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The isotopic results show that they can be used to bolster the characterization of water type within each aquifer by identifying pertinent water-rock reactions.

3) Stable water isotopes and corrected radiocarbon ages for groundwater samples from LVMC provided further insight into aquifer characterization. Isotopically heavier values of $\delta^{18}\text{O}$ and δD in the BCA coupled with corrected radiocarbon ages for the BCA ranged from 3,300 to 11,000 years BP are consistent with Holocene recharge. In the NA, isotopically lighter $\delta^{18}\text{O}$ and δD values coupled with corrected radiocarbon ages for the NA ranged from 15,000 to 36,000 years BP are consistent with Late Pleistocene recharge. Tritium was generally non-detect at the site; two BCA wells where low-level detections

were observed may indicate the presence of some modern water mixing with the fossil water.

4) All aforementioned conclusions suggest that minimal communication is occurring between the BCA and NA at LVMC. It is possible that in the future with changing climate (e.g. lower or higher regional water tables) or due to mining activities (e.g. dewatering) that these conditions could change. The distinct water types that occur in each aquifer, along with large differences in hydraulic head observed within the same aquifer, but on either side of a fault, suggests that faults that are perpendicular to flow exhibit low permeability zones and act as barriers to flow; generally increasing corrected radiocarbon age with decreasing hydraulic head is consistent with regional flow, suggesting that faults that are parallel to flow act as conduits, however the irregular distribution of corrected radiocarbon ages suggests complex flow paths. Additional data would be required to assess flow paths at a finer resolution.

5) While the regional groundwater model was not able to successfully “match” values of both $\delta^{18}\text{O}$ and groundwater age to observed values, it was able to generally capture the trend of increasingly negative values of $\delta^{18}\text{O}$ with increasing age. Furthermore, the model simulated a shallow fresh groundwater flow system originating at the La Sal Mountains and flowing towards the Lisbon Valley, with limited interaction with the deeper saline system below, consistent with geochemical and isotopic data collected from LVMC. In all, the regional groundwater model seemingly corroborates the hypothesis that recharge for the Lisbon Valley is meteoric in origin and occurs around the La Sal Mountains.

6) This study demonstrated the utility of the multi-tracer approach in providing a thorough characterization of stacked aquifers and evaluation of potential mixing. PCA analysis showed that in the instance of this study location, however, major ion chemistry is adequate in defining BCA and NA groundwater types and whether mixing is occurring. Furthermore, the data collected in this study provides a baseline characterization of environmental conditions before ISCR takes place. In the future, if ISCR operations occur, a tiered analytical approach could be taken, in addition to regular monitoring of major ion chemistry and hydraulic gradients. If major ion chemistry began to look similar between the BCA and NA, and communication between the aquifers was suspected, additional tracers (e.g., $\delta^{18}\text{O}$, $\delta^{34}\text{S-SO}_4$, radiocarbon) could be measured to more definitively examine if cross-formational flow was occurring.

APPENDIX A: TABLES

Table 1: Well Details

Well ID	Sampling Date	Latitude	Longitude	TOC Elevation (m)	Depth (m)	Formation
SLV2	11/2/2017	38.14856	-109.14183	1944.6	unknown	Mancos
94MW6	11/2/2017	38.12372	-109.08806	1916.6	unknown	Mancos
LS-243	3/14/2018	38.10688	-109.09547	1937.6	121.9	Mancos
WILCOX	10/31/2017	38.10526	-109.05534	1889.8	46.0	Dakota
PW-1	10/31/2017	38.15100	-109.13995	1940.6	109.7	Burro Canyon
PW-2	11/1/2017	38.15148	-109.13867	1950.1	228.6	Burro Canyon
PW-3	11/1/2017*	38.14729	-109.13597	1948.3	147.8	Burro Canyon
PW-4	8/1/2018	38.15263	-109.14210	1936.0	129.5	Burro Canyon
PW-9	11/1/2017	38.12116	-109.09063	1920.3	157.0	Burro Canyon
PW-12	11/1/2017*	38.12490	-109.12121	1968.7	304.8	Burro Canyon
MW96-7A	11/1/2017	38.14576	-109.13056	1965.9	364.2	Burro Canyon
98R4	11/1/2017	38.15541	-109.14478	1937.9	138.7	Burro Canyon
98R7	11/2/2017	38.15165	-109.14013	1940.2	102.1	Burro Canyon
325	8/23/2018	38.12001	-109.10598	1940.9	158.5	Burro Canyon
PW-7	8/21/2018	38.12493	-109.11143	1943.2	462.7	Navajo
PW-8	10/31/2017*	38.14782	-109.13432	1954.3	474.0	Navajo
PW-11	11/1/2017*	38.12608	-109.10066	1929.8	457.2	Navajo
MW97-11	8/22/2018	38.13831	-109.13161	2014.0	338.3	Navajo
MW97-13	8/21/2018	38.12695	-109.10746	1950.3	438.9	Navajo
MW06-15	11/2/2017	38.15727	-109.14010	1941.3	274.3	Navajo
LV-41-75	8/23/2018	38.11587	-109.11999	2026.2	176.2	Navajo

Notes: TOC = top of casing; *samples had ⁸⁷Sr/⁸⁶Sr and trace metals collected on 8/1/2018

Table 2: Field Measurements

Well ID	Formation	Temperature (°C)	pH	Specific Conductance (μS/cm)
SLV2	MS	13.6	7.87	629
94MW6	MS	12.9	6.83	6690
LS-243	MS	14.4	7.65	1054
WILCOX	BCA	13.2	6.54	2100
PW-1	BCA	15.5	7.06	1086
PW-2	BCA	15.9	6.87	1888
PW-3	BCA	16.0	6.69	1718
PW-4	BCA	14.7	6.75	1969
PW-9	BCA	14.1	9.01	1220
PW-12	BCA	20.7	7.10	1470
MW96-7A	BCA	13.5	8.27	1976
98R4	BCA	17.1	7.72	1074
98R7	BCA	11.1	7.86	875
325	BCA	20.8	7.14	1228
PW-7	NA	24.1	6.80	617
PW-8	NA	24.8	7.49	1133
PW-11	NA	24.4	7.77	925
MW97-11	NA	19.6	7.95	931
MW97-13	NA	18.8	6.99	610
MW06-15	NA	17.6	8.77	1345
LV-41-75	NA	20.3	6.93	378

Notes: MS = Mancos Shale, BCA = Burro Canyon Aquifer, NA = Navajo Aquifer

Table 3: Major Ions

Well ID	Formation	SO ₄	Alkalinity	Cl	F	Br	NO ₂	NO ₃	Na	Ca	Mg	K	Sr
Unit		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
94MW6*	MS	3,580	1,330	86.3	0.56		< 0.01	< 0.02	1,870	154	105	19	
LS-243	MS	178	437	14.0	0.83	ND	ND	0.56	203	25.4	12.4	8.98	1.61
PW-3	BCA	676	411	18.4	0.42	0.32	< 0.1	< 1.1	64.2	223	82.2	11.0	14.0
PW-4	BCA	990	374	15.6	0.27	0.47	ND	ND	46.0	368	89.2	6.06	8.34
PW-9	BCA	445	202	14.9	0.69	0.22	< 0.1	< 1.1	238	16.8	20.0	10.6	1.91
PW-12	BCA	515	382	17.5	0.48	0.36	< 0.1	< 1.1	157	132	46.8	11.0	5.01
MW96-7A	BCA	866	383	22.1	0.34	0.31	< 0.1	< 1.1	112	227	96.4	11.4	7.87
325	BCA	72.6	743	32.8	0.83	0.42	< 0.25	6.40	271	41.9	18.9	12.9	2.83
PW-7	NA	85.8	262	73.6	0.58	0.36	< 0.21	< 0.11	101	41.6	17.3	7.67	2.32
PW-8	NA	105	381	122	2.58	0.25	< 0.1	< 1.1	216	22.1	17.0	10.2	1.41
PW-11	NA	90.0	252	120	0.58	0.41	< 0.1	< 1.1	122	45.8	19.9	8.56	2.72
MW97-11	NA	147	390	108	0.56	0.35	< 0.22	0.17	144	66.6	24.7	7.98	2.49
MW97-13	NA	85.4	258	45.4	0.61	0.28	< 0.23	< 0.11	72.0	48.8	16.7	6.28	1.97
LV-41-75	NA	14.8	217	18.0	0.25	0.40	< 0.24	3.72	11.4	52.7	17.1	1.54	0.31

Notes: Alkalinity is assumed to be dominated by HCO₃⁻; ND = non-detect; < = less than detection limit; *data from Whestone Associates (2018)

Blank = not analyzed; MS = Mancos Shale, BCA = Burro Canyon Aquifer, NA = Navajo Aquifer

Table 4: Trace Elements

Well ID	Formation	Al	V	Mn	Fe	Co	Ni	Cu	Zn	As	Rb	Ba	U
Unit		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
PW-3	BCA	143	ND	188	1234	1.30	1.07	ND	204	0.933	9.00	20.0	41
PW-4	BCA	111	ND	904	9883	6.94	3.81	ND	60.0	35.1	6.00	9.00	86
PW-9	BCA	33.1	ND	10.6	1.97	0.034	1.22	0.703	5.81	0.513	5.81	7.59	0.101
PW-12	BCA	172	ND	411	1382	4.45	3.82	ND	87.0	3.05	9.00	15.0	13.0
MW96-7A	BCA	12.4	ND	45.9	41.7	0.690	9.37	2.59	15.6	0.162	10.7	13.9	2.93
325	BCA	7.78	0.195	76.7	21.0	0.407	12.6	5.45	5.07	0.585	5.00	85.1	12.5
PW-7	NA	177	ND	38.0	339	ND	0.412	ND	13.0	22.7	4.00	44.0	0.700
PW-8	NA	158	ND	14.0	ND	ND	0.464	ND	ND	0.416	6.00	46.0	0.011
PW-11	NA	129	ND	43.0	1840	ND	ND	ND	ND	6.51	7.00	46.0	ND
MW97-11	NA	6.61	0.242	184	18.6	6.72	328	0.337	289	1.27	4.10	35.6	11.9
MW97-13	NA	6.69	0.014	169	237	0.313	2.63	0.210	203	10.7	4.23	405	0.731
LV-41-75	NA	5.89	0.659	0.423	8.07	0.010	2.65	0.897	5.23	0.081	1.16	288	1.28

Notes: ND = non-detect; MS = Mancos Shale, BCA = Burro Canyon Aquifer, NA = Navajo Aquifer

Table 5: Isotopes

Well ID	Formation	$\delta^{18}\text{O}$	δD	$\delta^{13}\text{C-DIC}$	$\delta^{34}\text{S-SO}_4$	$\delta^{18}\text{O-SO}_4$	$^{87}\text{Sr}/^{86}\text{Sr}$	^3H	^{14}C		
Unit		‰	‰	‰	‰	‰	--	TU	pmc	Uncorrected Age BP	Corrected Age BP
SLV2	MS	-14.2	-108	-8.9							
94MW6	MS	-13.4	-107	-3.3							
LS-243	MS				-1.2	-0.3					
WILCOX	BCA	-13.0	-97	-8.9							
PW-1	BCA	-15.6	-119	-8.7							
PW-2	BCA	-10.2	-82	-2.9							
PW-3	BCA	-12.6	-95	-4.3	-8.1	-5.8	0.70946	< 0.8	13.6	16,000	3,300
PW-4	BCA						0.70947				
PW-9	BCA	-14.6	-110	-8.2	15.9	7.6	0.70924	1.5	12.7	17,000	8,900
PW-12	BCA	-14.8	-111	-7.0	0.1	-2.3	0.70932	1.0	8.4	20,000	11,000
MW96-7A	BCA	-12.9	-97	-1.6	-1.7	-3.2	0.70936	< 0.5	7.7	21,000	4,000
98R4	BCA	-15.3	-114	-7.4							
98R7	BCA	-16.5	-124	-9.5							
325	BCA	-15.9	-119	7.9	*	*	0.70926	< 0.6	1.7	33,000	modern
PW-7	NA	-17.0	-128	-8.4	6.3	4.0	0.70963	0.5	3.6	27,000	19,000
PW-8	NA	-17.0	-128	-10.0	4.0	3.2	0.70920	< 0.6	0.5	42,000	36,000
PW-11	NA	-17.0	-128	-8.8	8.9	5.7	0.70970	< 0.5	1.9	32,000	25,000
MW97-11	NA	-17.2	-129	-6.1	3.8	4.0	0.70935	0.5	2.4	30,000	21,000
MW97-13	NA	-17.4	-130	-6.7	4.0	2.5	0.70958	< 0.5	5.0	24,000	15,000
MW06-15	NA	-16.6	-126	-17.1							
LV-41-75	NA	-13.5	-102	-7.0	4.2851	-2.04	0.70960	< 0.8	54	4,900	modern

Notes: ND = non-detect; < = less than detection limit; italicized values at the detection limit, considered non-detect

* = insufficient precipitate formed, analysis could not be run; MS = Mancos Shale, BCA = Burro Canyon Aquifer, NA = Navajo Aquifer

Table 6a: Hydrostratigraphic Properties

Unit #	Unit Name	Run 4		Run 5 (Base Run)		Run 6		ϕ
		$k_x (m^2)$	$k_z (m^2)$	$k_x (m^2)$	$k_z (m^2)$	$k_x (m^2)$	$k_z (m^2)$	
1	La Sal Volcanics	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15	0.05
2	Crystalline Basement	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15	0.05
3	RedWall Limestone	1.00E-13	1.00E-14	1.00E-13	1.00E-14	1.00E-13	1.00E-14	0.1
4	Paradox Salt Member	1.00E-20	1.00E-20	1.00E-20	1.00E-20	1.00E-20	1.00E-20	0.01
5	Honaker Trail fm	1.00E-14	1.00E-15	1.00E-14	1.00E-15	1.00E-14	1.00E-15	0.1
6	Cutler Formation	1.00E-13	1.00E-14	1.00E-13	1.00E-14	1.00E-13	1.00E-14	0.1
7	Triassic (Chinle Fm, Moenkope)	1.00E-14	1.00E-16	1.00E-14	1.00E-16	1.00E-14	1.00E-16	0.05
8	Triassic Navajo Aquifer	2.00E-13	2.00E-14	1.00E-13	1.00E-14	2.00E-13	2.00E-14	0.1
9	Morrison Formation	1.00E-18	1.00E-19	1.00E-18	1.00E-19	1.00E-18	1.00E-19	0.05
10	Burro Canyon Aquifer	2.00E-13	2.00E-14	5.00E-12	5.00E-13	8.00E-13	8.00E-14	0.2
11	Mancos Shale	1.00E-16	1.00E-17	1.00E-16	1.00E-17	1.00E-16	1.00E-17	0.2
12	Fault Zone	5.00E-13	5.00E-12	5.00E-13	5.00E-12	2.00E-14	2.00E-13	0.05

Table 6b: Model Parameters

Parameter	Value	Unit
Longitudinal Dispersivity	10	m
Transverse Dispersivity	1	m
Solute & Thermal Diffusivity	0.0035	m ² /year
Thermal Conductivity Solids	2.5	W/m°C
Thermal Conductivity Fluids	0.58	W/m°C

APPENDIX B: FIGURES

Figure 1: Map of the study area showing the locations of wells sampled created using ArcMap 10.6.1). The inset map shows the location of LVMC within the Colorado River Basin. Note that the Wilcox well (approximately 5.9 km east of LV-41-75) and borehole LS-243 (approximately 2.4 km southeast of LV-41-75) are not pictured.

Figure 2: Stratigraphic column for LVMC (modified from Whetstone Associates, 2018).

Figure 3: Map of the locations of cross-sections B-B' and F-F' along with locations of pertinent wells.

Figure 4: Cross-section B-B' with pertinent wells that are the least lateral distance from the cross-section plotted. Green indicates completion in the Mancos Shale, blue in the BCA, and red in the NA.

Figure 5: Cross-section F-F' with pertinent well that are the least lateral distance from the cross-section plotted. Blue indicates completion in the BCA and red in the NA. Note distortion that occurs at LV-41-75 (it is not actually completed in the BCA), due to large offset caused by a fault immediately adjacent to the borehole (see Figure 4).

Figure 6: a) Piper diagram for the 13 wells analyzed for major ion chemistry. In addition to these 13 wells, location 94MW6 (data from Whetstone Associates, 2018) was plotted as well to include a characteristic Mancos Shale sample, b) stiff diagram for 94MW6, c) stiff diagram for MW96-7A, and d) stiff diagram for PW-11. Note that the scale for b is different than c and d.

Figure 7: **a)** plot of $\delta^{18}\text{O-SO}_4$ versus $\delta^{34}\text{S-SO}_4$ from 11 select locations. Typical ranges of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ attributed to different environmental sulfate sources are plotted as the shaded grey boxes (Mayer, 2007). Ranges of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ found in various rock samples east of the study area (Tuttle and Grauch, 2009) are plotted as shaded yellow boxes; **b)** plot of SO_4 versus $\delta^{34}\text{S-SO}_4$ from 11 select locations. A range of additional values for the BCA are plotted in the narrower grey box and were gathered from the USGS's National Water Information System (U.S. Geological Survey, 2016). A range of values from the NA are plotted as the wider grey box, collected from Kimball (1992).

Figure 8: Plot of Sr versus the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for 12 select locations. The grey shaded box indicates a range of values for groundwater from the NA obtained by Naftz et al. (1997). The pink triangle is an idealized average of the data from Naftz et al. (1997).

Figure 9: Plot of stable water isotopes from 21 sample locations. Values of $\delta^{18}\text{O}$ and δD for groundwater samples collected from the NA in the Black Mesa Basin in northeastern Arizona and reported by Zhu (2000) are plotted as empty black circles and triangles, and represent Holocene and Late Pleistocene groundwaters south of the study area. A range for composite snow samples from the Abajo Mountains are shown as the orange arrow (Spangler, 1996); a range for samples from the Colorado River are shown as the pink arrow (Gardner, 2004; Bowen, 2017); and a range for other regional surface waters shown as the purple arrow (Bowen, 2017) are also plotted.

Figure 10: a) plot of $\delta^{18}\text{O}$ versus corrected radiocarbon ages for 11 select locations and b) plot of corrected radiocarbon ages versus hydraulic head for 8 select location. Samples 325 and LV-41-75 are excluded from the diagram as they had a 'modern' corrected radiocarbon age; the water level at PW-8 was not measured at the time of sampling.

Figure 11: PCA plot for 9 select sample locations from the BCA and NA including 12 major ions and isotopes. The first two principal axes explain 77.84% of the variability.

Figure 12: Modified regional water table contour map for the NA (Avery, 1986). The purple dashed line indicates the northwest-southeast transect used for the groundwater flow model.

Figure 13: **a)** Hydrostratigraphic units used in cross-sectional model (properties listed in Table 6a), **b)** computed freshwater hydraulic heads and streaklines (groundwater flow lines), **c)** computed temperatures, **d)** salinity distribution, and **e)** mean groundwater residence times (in thousands of years) from model Run 5. See Table 6a for hydrologic properties of Runs 4-6.

Figure 14: a) Imposed changes in water table elevation boundary conditions between Late Pleistocene glacial maximum (Pleis.) and modern conditions; and **b)** changes in $\delta^{18}\text{O}$ composition of groundwater recharge across model domain between glacial maximum and modern conditions.

Figure 15: Temporal variations in the isotopic composition of La Sal Mountains recharge during the past 1 million years (after Hansen et al. 2017) and computed groundwater isotopic composition of Lisbon Valley node closest to BCA well PW-9.

Figure 16: Computed groundwater $\delta^{18}\text{O}$ (in ‰) values for model Runs 4-6. The white circle is the node closest to BCA well PW-9 (node 1681). Simulated isotopic composition through time for this node, is presented in Figure 15.

Figure 17: **a)** computed (line) and observed (circles) freshwater heads (m) and **b)** salinity (ppt) versus depth (m) for Lisbon Valley. Simulated values are from Run 5 from the node closest to BCA well PW-9.

Figure 18. Particle trajectories from Lisbon Valley well heads to recharge area in the La Sal Mountains for model Runs 4-6.

Figure 19: **a)** comparison of advective groundwater age and $\delta^{18}\text{O}$ for three simulations (Runs 4, 5, and 6 in red, green, blue, respectively) and observed data from LVMC wells (black); and **b)** comparison of advective-dispersive groundwater age and $\delta^{18}\text{O}$ for the three simulations and observed data from LVMC wells. See Table 6a for transport parameters used in model runs.

APPENDIX C:

SUPPLEMENTARY

DATA

Table 7a: Trace Elements

Well ID	Formation	Be	B	P	Cr	Ga	Se	Rb	Ag	Cs	La	Ce	Pr	Nd
Unit		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
PW-3	BCA	3.54	355	ND	0.834	ND	ND	9.00	ND	0.099	ND	ND	ND	ND
PW-4	BCA	3.42	342	ND	0.573	ND	ND	6.00	ND	0.093	ND	ND	ND	ND
PW-9	BCA	0.03	310	217	0.047	0.025	ND	5.81	0.001	0.017	0.003	0.005	0.001	0.003
PW-12	BCA	2.56	306	ND	0.323	ND	ND	9.00	ND	0.148	ND	0.009	ND	ND
MW96-7A	BCA	0.07	765	235	0.067	0.029	0.028	10.7	ND	0.085	0.013	0.030	0.002	0.011
325	BCA	0.02	233	207	0.070	0.009	0.051	5.00	0.006	0.049	0.005	0.007	0.001	0.003
PW-7	NA	0.85	320	ND	0.805	ND	ND	4.00	ND	0.043	ND	0.007	ND	ND
PW-8	NA	2.73	585	ND	0.072	0.039	ND	6.00	ND	0.021	ND	ND	ND	ND
PW-11	NA	3.58	260	ND	0.865	ND	ND	7.00	ND	0.052	ND	ND	ND	ND
MW97-11	NA	0.04	202	272	0.164	0.005	0.304	4.10	0.013	0.027	0.012	0.041	0.002	0.009
MW97-13	NA	0.03	114	239	0.089	0.010	ND	4.23	0.024	0.043	0.010	0.011	0.001	0.004
LV-41-75	NA	0.01	23.4	214	0.412	0.003	0.736	1.16	0.013	0.020	0.009	0.007	0.002	0.010

Notes: ND = non-detect; MS = Mancos Shale, BCA = Burro Canyon Aquifer, NA = Navajo Aquifer

Table 7b: Trace Elements

Well ID	Formation	Sm	Eu	Gd	Dy	Ho	Er	Tm	Yb	Lu	Tl	Pb	Th
Unit		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
PW-3	BCA	0.009	ND	ND	ND	ND	0.011	ND	ND	ND	0.003	ND	ND
PW-4	BCA	ND	ND	0.020	ND	0.004	0.003	ND	0.005	ND	0.019	ND	ND
PW-9	BCA	4.78E-04	ND	2.91E-04	0.001	2.83E-04	0.001	8.44E-05	0.001	2.25E-04	0.001	ND	0.018
PW-12	BCA	ND	ND	ND	ND	ND	ND	ND	0.010	ND	0.052	ND	ND
MW96-7A	BCA	0.003	0.001	0.001	0.002	4.01E-04	0.002	2.32E-04	0.003	4.18E-04	0.002	2.30E-03	0.018
325	BCA	0.001	0.003	0.001	0.001	1.18E-04	2.77E-04	6.33E-05	0.001	1.29E-04	0.001	ND	ND
PW-7	NA	ND	ND	0.005	ND	ND	ND	ND	0.015	ND	ND	ND	ND
PW-8	NA	ND	ND	ND	ND	0.001	0.003	ND	0.005	ND	ND	ND	ND
PW-11	NA	ND	ND	0.013	ND	ND	0.003	ND	ND	ND	ND	ND	ND
MW97-11	NA	0.003	0.002	0.001	0.003	0.001	0.002	1.69E-04	0.001	1.61E-04	0.006	ND	ND
MW97-13	NA	0.002	0.012	0.001	2.93E-04	4.25E-04	0.001	4.22E-05	0.002	2.25E-04	0.001	ND	ND
LV-41-75	NA	0.004	0.008	0.004	0.004	0.001	0.003	2.11E-04	0.002	2.25E-04	0.002	ND	ND

Notes: ND = non-detect; MS = Mancos Shale, BCA = Burro Canyon Aquifer, NA = Navajo Aquifer

Figure 20: Drill log for borehole 325.

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