**TECHNICAL ARTICLE**

# Defining the Extent of Mine-Influenced Groundwater in a Mineralized and Agricultural Area Using Multiple Lines of Evidence

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## Abstract

Mine-influenced groundwater (MIW) at a former copper mine site has affected an alluvial aquifer that also contains groundwater with solutes characteristic of natural mineralization and agricultural activities. Many of the solutes are common to at least two of three potential sources, and some solutes (e.g., sulfate and uranium) are common to all three. This precludes the conventional use of one, or several, characteristic solutes to identify the extent of MIW. So, we used five independent lines of evidence (LOE) to define the extent of MIW in the alluvial aquifer. The five LOE are multivariate statistical analysis of an extensive groundwater analyte suite, groundwater sulfur isotope ($\delta^{34}S_{SO4}$) data, probabilistic calculations of groundwater velocity and flow distance, isotopic ($^3H/^3He$) estimates of groundwater age, and extent of nitrate in groundwater originating from agricultural activities.

**Keywords** Multivariate statistical analysis · Sulfur isotopes · Groundwater age dating

## Introduction

Mine-influenced groundwater (MIW) at a former Anaconda copper mine site (ACMS) is present in an alluvial aquifer that also contains groundwater with solutes characteristic of natural mineralization and agricultural activities. Many of the solutes are common to at least two of the three potential sources, and some (e.g., sulfate and uranium) are common to all three. This precludes the use of only one, or even several, environmental water tracers (Kurukulasuriya et al. 2022) to identify the extent of MIW and the relationship with interconnected groundwater resources.

Groundwater quality at many mine sites is influenced by human activities and naturally occurring processes. As a result, natural or other anthropogenic background water quality can be difficult to distinguish from MIW. This paper presents an analysis of the extent of MIW based on five lines of evidence (LOE): multivariate statistical analysis, analysis of sulfur isotope composition, tritium/helium groundwater age dating, probabilistic calculations of average linear velocity and flow distance, and nitrate as a marker of agricultural impacts. The multiple LOE approach identifies spatially distinct zones of mine-influenced groundwater, naturally mineralized groundwater, and groundwater influenced by agricultural practices. We believe this is the first published use of all five LOE to provide a robust delineation of the extent of MIW and that the methods described in this paper have broad applicability for characterizing the extent of mining-related impacts in groundwater at other sites.

## Site History and Data Sources

The site is a former copper mine and ore processing facility located in central Lyon County, Nevada, USA (Fig. 1). It was operated by various owners from late 1953 to November 1999. Historical activities at the site included the production and use of sulfuric acid and the operation of an alkaline flotation circuit. A solvent extraction electrowinning (SX-EW) plant was also used to process heap leach pad fluids from 1989 to 1999.

Spent process solutions resulting from the beneficiation of oxide ores were conveyed in unlined trenches to the

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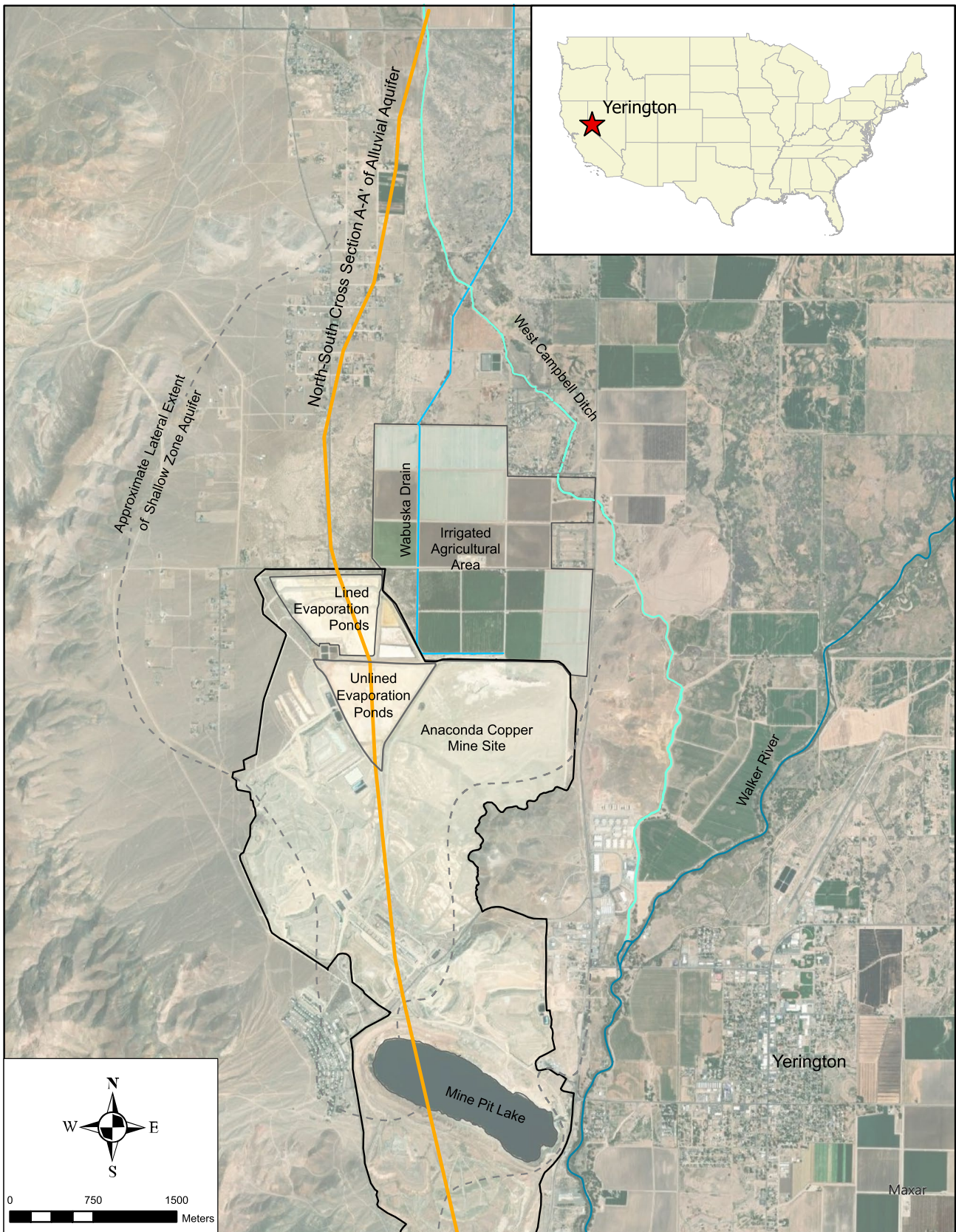
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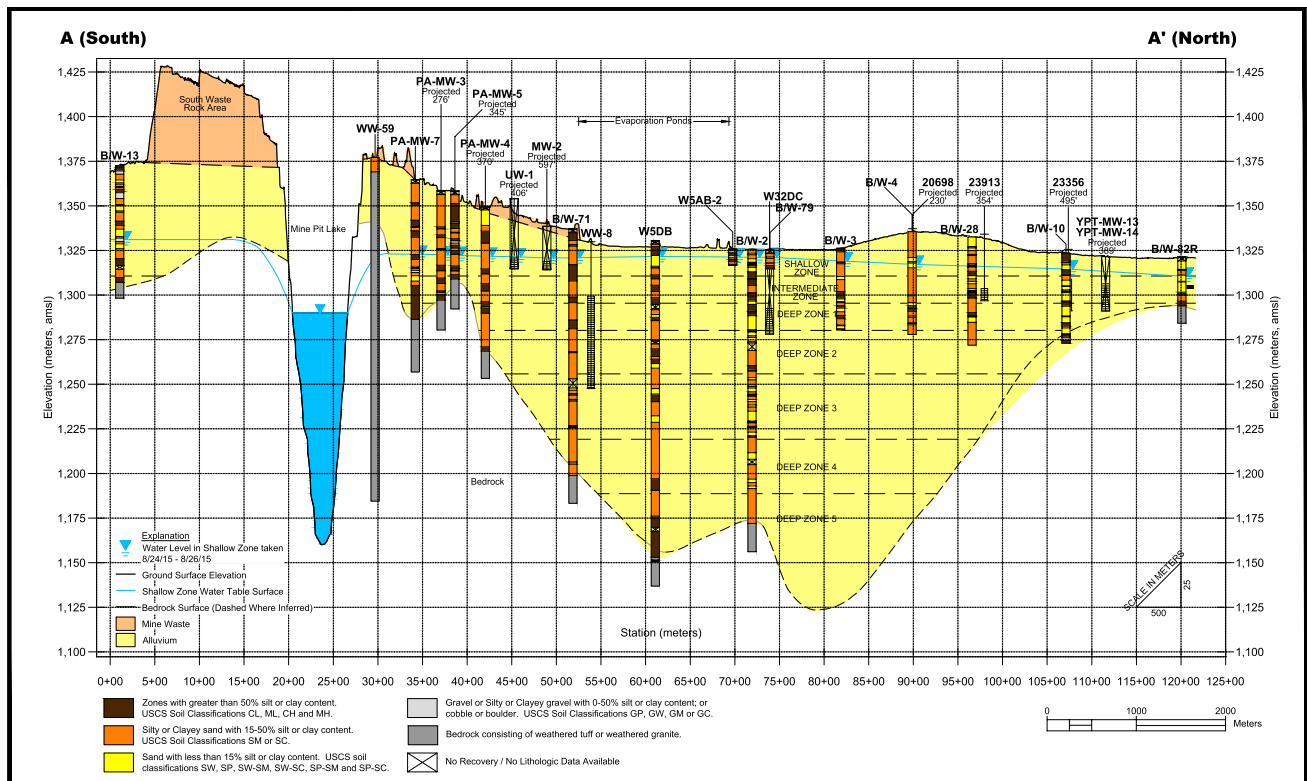
**Fig. 1** Site Location Map

**Fig. 2** North–south Cross-section A-A' of Alluvial Aquifer

unlined evaporation pond (UEP) from 1954 to 1978 and to the lined evaporation pond (LEP) from 1972 to 1978 (Fig. 1). Excess pulp and alkaline recycle process water from sulfide ore flotation were conveyed to the sulfide tailings impoundment. An investigation of the ponds determined that seepage during operation was a primary source of MIW (Copper and Broadbent 2019). Post-operative monitoring indicates that the ponds are not a continuing source of contamination to groundwater. Impacts to groundwater from operation of the ponds included increased acidity (low pH) and increased concentrations of major ions and metals (e.g., sulfate and uranium).

Data for this evaluation were collected as part of remedial investigations performed under the oversight of the U.S. Environmental Protection Agency and the Nevada Division of Environmental Protection. In total, characterization activities for the site resulted in the drilling and logging of 133 boreholes and 10,000 m of core, the installation of 299 monitor wells, and hydraulic testing of 296 wells. Groundwater monitoring activities included the collection of semi-annual water quality samples from 236 wells, annual water quality samples from 353 wells, and quarterly measurement of water level in 360 wells. The hydrogeologic data are summarized in Copper and Broadbent (2020).

## Hydrogeologic Setting

The site is in Mason Valley, a structural graben in the Basin and Range Province of the western U.S. The graben is filled with unconsolidated deposits derived from the erosion of adjacent mountain blocks, material transported into the valley by the East and West Walker Rivers, and sediment associated with the Pleistocene-age Lake Lahontan. (Huxel and Harris 1969; Reheis 1999). Alluvial fan deposits are generally coarse-grained and poorly sorted and have relatively few inter-bedded clay lenses (Huxel and Harris 1969; Plume 1996 and Mifflin 1988). Alluvium from the East and West Walker Rivers consists of interbedded gravel, sand, silt, and clay. Younger sediments deposited by Lake Lahontan are typically fine-grained (Reheis 1999). The unconsolidated deposits (alluvium) are saturated at depths starting about 5–45 m below ground surface (bgs) and form a locally important alluvial aquifer (Fig. 2). The alluvial aquifer was divided into seven elevation-based zones for the remedial investigation. The LOE evaluation process is detailed herein for the uppermost, shallow zone, which includes the upper 15 m of the aquifer below the water table, but all zones were evaluated.

In the arid environment of western Nevada, percolation of surface water runoff from the Sierra Nevada mountains

to the west is the primary source of recharge to the alluvial aquifer with mountain-front recharge contributing significantly less (Carroll et al. 2010; Huxel and Harris 1969; Myers 2001; Papadopulos & Associates 2014). The amount of recharge derived by infiltration from stream channels, ditches, and flooded agricultural fields varies from year to year depending on several factors including the volume of flow in the Walker River and the volume of water diverted for irrigation. Recharge from precipitation on the valley floor is negligible based on stable isotope data (Brown and Caldwell 2014) and work by Huxel and Harris (1969) and Lopes and Allander (2009a, b).

Prior to mining and agricultural land use, alluvial groundwater in the Mason Valley flowed north parallel to the axis of the valley. Mining activities during the 1960s and 1970s including pumping for water supply that modified the groundwater flow patterns and created a cone of depression northeast of the evaporation ponds (Fig. 3). During this time, groundwater within the cone of depression flowed radially toward the water supply wells while groundwater outside of the cone of depression continued to flow northward. At the end of pumping in 1977, groundwater levels recovered, and northward flow resumed in the area near the evaporation ponds.

The amount of irrigated land northeast of the evaporation ponds increased during the late 1980s. Currently, infiltration of irrigation water creates a mound in the alluvial aquifer that changed the direction of groundwater flow from north to west and northwest near the evaporation ponds (Fig. 4).

The direction of groundwater flow in the alluvial aquifer beneath most of the ACMS is to the northeast, north, or northwest, depending on location and depth within the aquifer. The exception to these general flow trends is in the southern part of the ACMS in the vicinity of the mine pit where there is a potentiometric depression around the pit lake. As a result, there is a groundwater flow divide $\approx 600$ m north of the pit lake. Groundwater south of the divide flows south towards the pit lake. Groundwater north of the divide flows north and was the subject of this evaluation.

## Natural Groundwater Chemistry

The Yerington District includes four porphyry copper deposits that were emplaced during various episodes of plutonism extending from the middle Jurassic to the late Neogene. The deposits include Yerington, Ann Mason, MacArthur, and the Bear (Dilles et al. 2000). The Yerington deposit is Jurassic in age (165–169 million years ago) and was the focus of mining activities at the Site (Dilles et al. 2000). The porphyry body is associated with dike swarms that were emplaced through a granite cupola. A series of Oligocene and early Miocene ignimbrites and lava flows later blanketed the Yerington

area. Subsequent east-dipping normal faulting tilted the section 60–90 degrees west and exposed the mineralized and hydrothermally altered porphyry at the south end of the site (Dilles et al. 2000). Berger et al. (2008) and Cameron et al. (2008) describe the evolution of similar deposits in which the porphyry intrusion and hypogene mineralization were followed by supergene enrichment. Major hydrothermal mineralogy associated with the Yerington deposit includes chalcopyrite, bornite, pyrite, molybdenite, magnetite, hematite, rutile, and chlorite as well as other silicate and calcsilicate minerals. Common secondary minerals include iron(III) hydroxides, manganese(II) hydroxides, jarosite-alunite, geothite, hematite, basaluminite, gypsum, malachite, and phyllosilicates altered by substitution of potassium with trace metals. Rock-water interaction can result in trace metal enrichment, particularly for the more soluble secondary minerals (Halley et al. 2015; Leybourne and Cameron 2010).

Alluvial groundwater at the site contains elevated concentrations of sulfate, uranium, arsenic, and other constituents due to contact with mineralized volcanic tuff and alluvium derived from volcanic tuff. Surface water and groundwater located upstream, upgradient, and cross gradient from the site have similar concentrations of these solutes. This is evidence that the solutes are naturally occurring and are not related to previous mining activities (Benson and Spencer 1983; Brown and Caldwell 2014).

## Agricultural Land Use and Impacts to Groundwater Quality

Mason Valley is the largest agricultural area in the Walker River Basin. It contains some of the most productive land in Nevada (Lopes and Allander 2009a). The total irrigated area in Mason Valley during 2000 was 15,800 ha (39,100 acres), which is equal to about 44% of the valley floor (Lopes and Allander 2009a).

Agricultural irrigation in Mason Valley influences groundwater chemistry and patterns of groundwater flow by: (1) transporting fertilizers and other agricultural chemicals into groundwater; (2) leaching naturally-occurring constituents from the unsaturated zone below irrigated fields and transporting them into groundwater; (3) increasing soil alkalinity, which increases uranium solubility in water that infiltrates to groundwater (Benson and Leach 1979; Nolan and Weber 2015); (4) evapotranspiration of water applied to the fields, which concentrates solutes in infiltrating water; (5) pumping for irrigation, which lowers the water table and modifies the local direction of groundwater flow; and, (6) infiltration from fields and ditches, which increases groundwater levels and modifies the local direction of groundwater flow.

**Explanation:**

- ● Groundwater Well

— Shallow Zone Aquifer Groundwater Contour Meters AMSL (Feet AMSL)

— Mine Site Boundary

— West Campbell Ditch

— Wabuska Drain

— Walker River

- - - Approximate Lateral Extent of Shallow Zone Aquifer

☐ Mine Pit Lake

☐ Irrigated Agricultural Area

☐ Evaporation Ponds

▨ Undifferentiated Granitic, Metamorphic, and Volcanic Bedrock

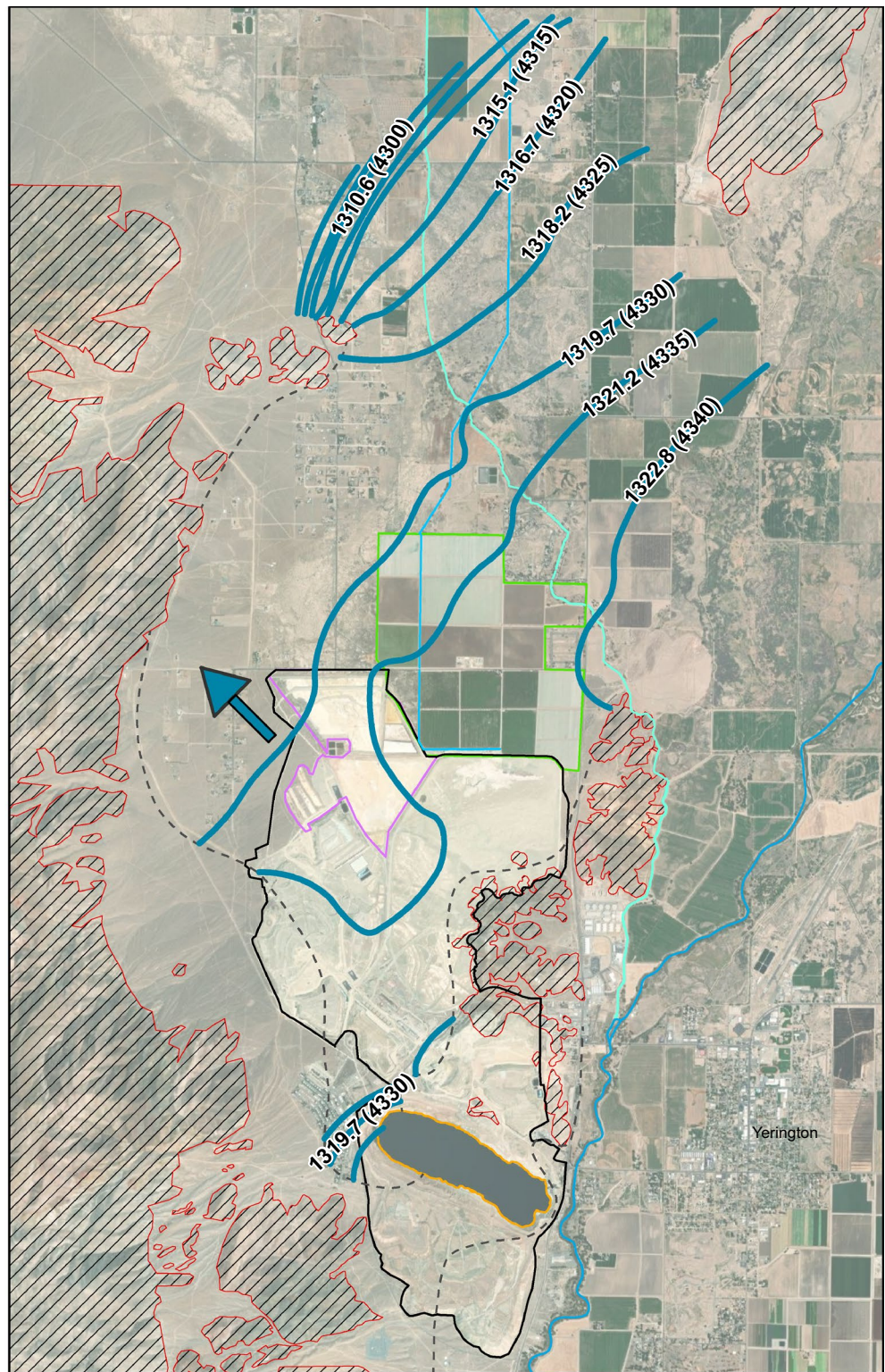Note: Map drawn from water level data in Huxel and Harris, Table 25 (1969)
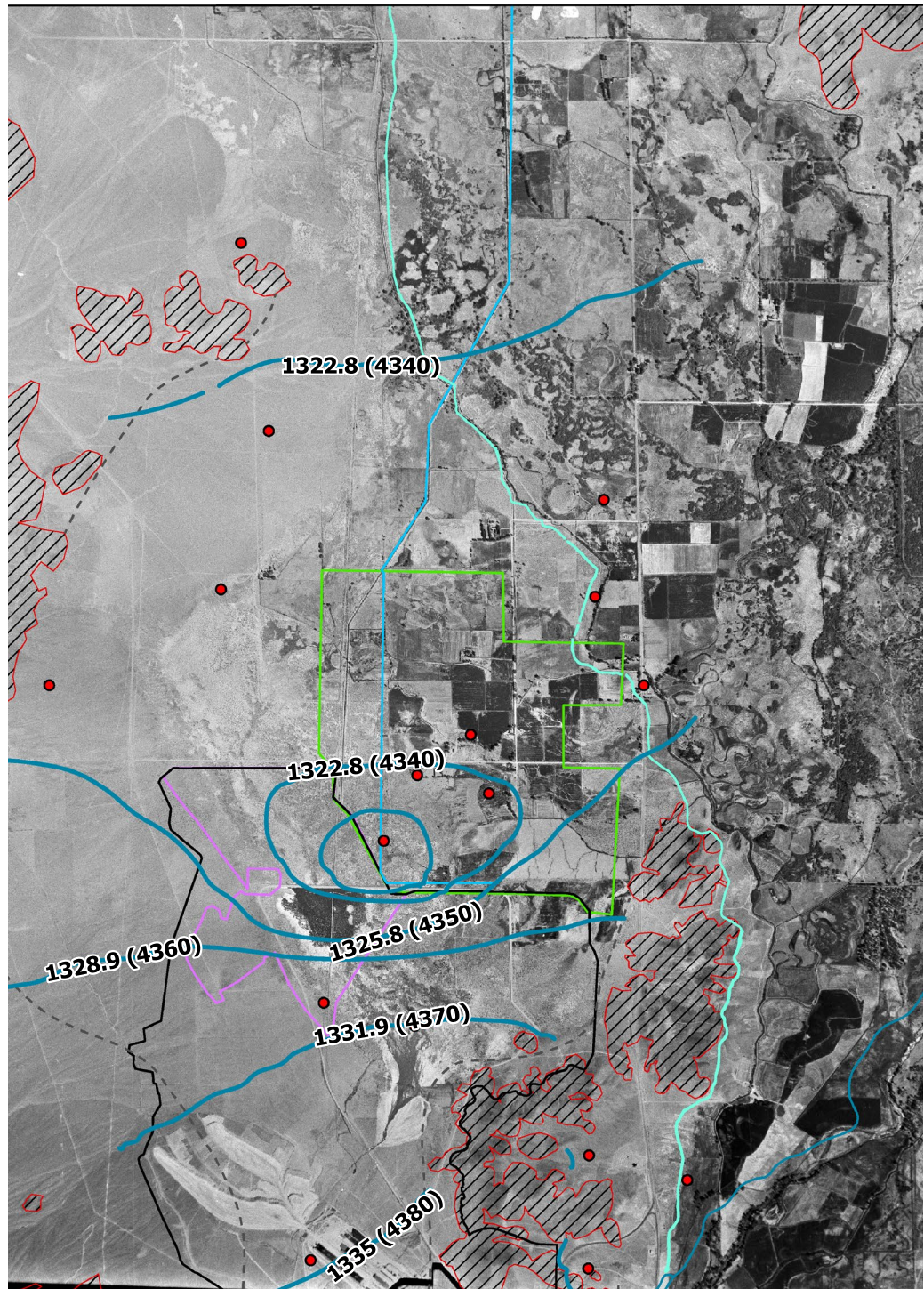
**Fig. 3** Potentiometric Surface Shallow Zone Aquifer (1965–1966)

Agricultural irrigation has increased nitrate, sulfate, uranium, and calcium concentrations in groundwater below and downgradient of fields northeast of the site (Benson and Spencer 1983; Brown and Caldwell 2014). Fertilizer and agricultural amendments are sources of nitrate, sulfate, and calcium. Naturally occurring uranium is mobilized from soil under oxidizing conditions with increasing alkalinity and concentrations of calcium. Increased alkalinity and calcium are key factors that affect the formation of dissolved uranium species that have little tendency to bind to aquifer solids and are easily transported in groundwater (Bernhard et al. 2001).

**Fig. 4** Potentiometric Surface Shallow Zone Aquifer (2018)

Agriculturally influenced trends in concentration for nitrate, sulfate, uranium, and calcium in the shallow alluvial aquifer are shown in Fig. 5. The data are from a well located downgradient of an irrigated field away from potential flow paths from the site. The plots indicate that the average concentrations of the constituents increased
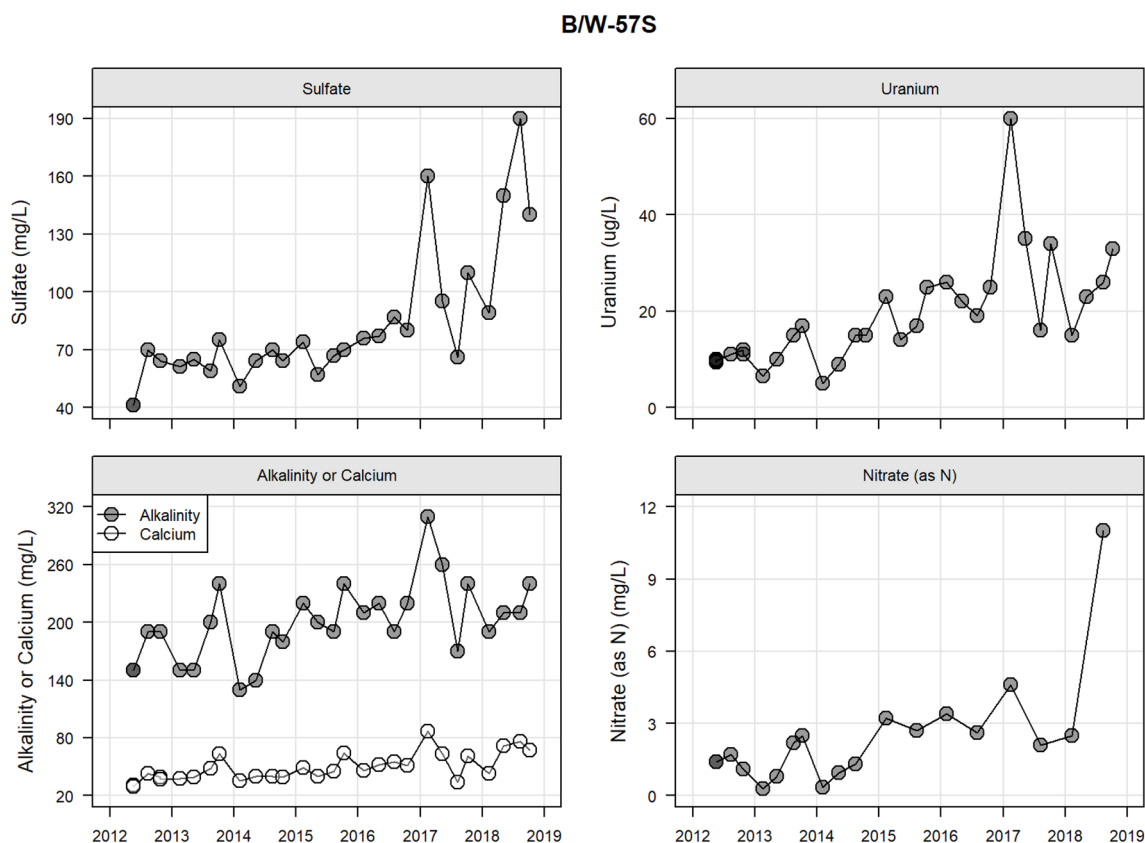
**B/W-57S**



**Fig. 5** Time Series Graphs of Sulfate, Uranium, Alkalinity, Calcium and Nitrate in Well B/W-57S

downgradient of the agricultural area between 2012 and 2018.

The sources of irrigation water are wells in the alluvial aquifer and surface water diversions from the Walker River. In years with abundant surface water, more water is diverted and applied to the fields, while groundwater pumping is significantly reduced in years with limited surface water availability. The irrigation wells are screened in the deep zones of the alluvial aquifer to the north and create horizontal and vertical hydraulic gradients towards the irrigation wells when pumped.

## Multiple Lines of Evidence Approach

The delineation of MIW, naturally mineralized groundwater, and agriculturally influenced groundwater was based on the evaluation of five LOEs: multivariate statistical analysis (MSA); sulfur isotope ($\delta^{34}S_{SO4}$) data; probabilistic calculations of groundwater velocity and flow distance; isotopic ($^{3}H/^{3}He$) estimates of groundwater age; and extent of nitrate migration from agricultural activities.

The delineation of MIW by each LOE is shown only for the shallow zone of the alluvial aquifer to illustrate the techniques presented in this paper. However, the LOE were applied to all zones within the alluvial aquifer, as discussed in the Composite Weight of Evidence Evaluation section.

## Multivariate Statistical Analysis

MSA was used to explore groundwater chemistry to identify relationships between groups of analytes and groups of samples. Strong correlations between groups of analytes can be used to distinguish naturally occurring geochemical processes in mineralized areas from anthropogenic impacts related to mining, ore processing, and agriculture. Similarly, strong correlations between groups of samples can be used to determine the spatial extent of different types of groundwater. MSA was used to evaluate groundwater data for the site using both supervised and unsupervised algorithms, as shown in the flowchart (Fig. 6).

Preparation of the dataset included normalization and standardization of analytical data. The normalization process included comparing four different procedures:
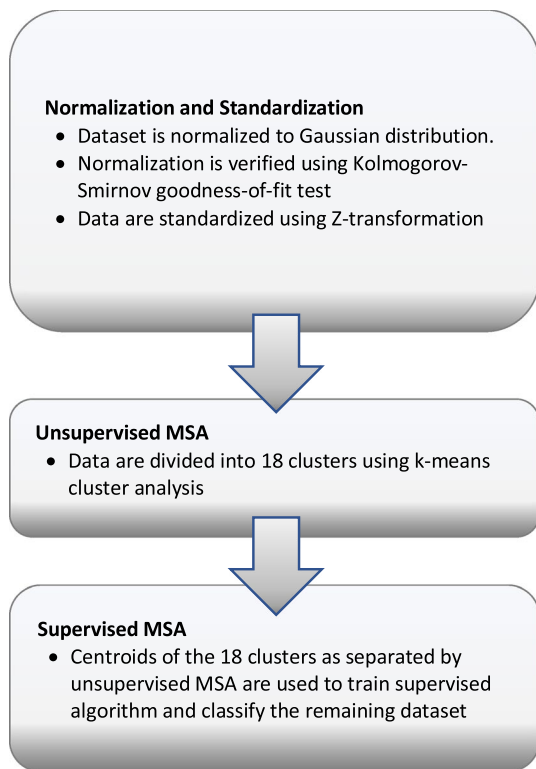
**Fig. 6** Flowchart of Multivariate Statistical Analysis Evaluation

log-normalization, chloride-normalization, TDS-normalization, and $SO_4 + Cl$ normalization and then using the Kolmogorov-Smirnoff (K-S) goodness-of-fit test (Chakravarti et al. 1967) to determine which approach should be applied. The $SO_4 + Cl$ normalization procedure was determined to be the most appropriate based on the lowest sum of K-S scores for all analytes used in the MSA. The standardization process for the dataset followed the Z-score approach, i.e., Z-transformation (Moore et al. 2017).

The unsupervised MSA approach used a k-means cluster analysis with a predetermined optimum number of 18 clusters. The clusters were grouped into three categories, which included MIW, naturally mineralized groundwater, and groundwater influenced by agricultural practices and/or infiltration of Walker River water. The MIW groundwater type is characterized by low pH, low alkalinity, and high metals concentrations (Al, Cd, Co, Cu, Fe, Mn, Ni, and Zn). The naturally mineralized groundwater type is characterized by high pH and elevated concentrations of As, Mo, and V. The agriculturally-influenced groundwater was indicated by elevated nitrate levels. The results of the MSA were used to classify the primary water type for each of the samples, which were grouped by well and used to spatially delineate the boundary of each water type in the shallow zone of the alluvial aquifer (Fig. 7).

## Sulfur Isotope ($\delta^{34}S_{SO4}$) Data

The isotopic signatures of the sulfur in ore from the site, sulfuric acid used to process ore prior to 1970, and naturally mineralized water were used to delineate the leading edge of the MIW released during early mining activities at the site. Because the intent was to delineate only the leading edge of the MIW, this paper does not attempt to distinguish between MIW sulfur isotope signatures attributable to different periods of mining operations at the site.

The initial site operation used sulfur ore from the Leviathan Mine in Alpine County, California, USA to produce sulfuric acid for the process leach solution. The sulfuric acid was produced on site and had a $\delta^{34}S_{SO4}$ signature of $-17.6‰$ (Taylor and Wheeler 1994). In 1961, sulfuric acid production began to transition from Leviathan sulfur ore to other sources, and by 1971 the use of Leviathan sulfur ore was discontinued. The replacement sources of sulfur had heavier isotopic composition than sulfur from the Leviathan Mine (i.e., $\delta^{34}S_{SO4}$ values that were less negative and even quite positive).

The $\delta^{34}S_{SO4}$ values of sulfur in naturally mineralized water at the site range from $-17.12‰$ to $+15.54‰$ and were heavier than sulfur from the Leviathan Mine (Copper and Broadbent 2020). The isotopic composition of sulfide ore from the site is also heavier than Leviathan sulfur and is reported to range from $-4.7‰$ to $-6.3‰$ (Field 1966; Lipske 2003). Although data from the early operational period of the site are not available to document the isotopic composition of the fugitive process solution mixed with groundwater, recent data was used to identify the groundwater samples that were affected by the early releases.

Recent sulfur isotopic data measured in site groundwater samples were statistically evaluated using normal quantile–quantile plots (Q-Q plots). These plots are graphic tools that compare two set of quantiles against each other to evaluate if the data are normally distributed. The analysis was performed by regressing a line through the $\delta^{34}S_{SO4}$ data (y-axis) plotted against theoretical quantiles for a normal distribution that describes the data (x-axis). A single population of normally distributed data will plot along or near the regression line. Different populations with different statistical distributions will deviate from the regression line and plot as trends with different slopes.

A mixture of early process solution ($\delta^{34}S_{SO4} = -17.6‰$) and naturally mineralized groundwater ($\delta^{34}S_{SO4} = -17.12‰$ to $+15.54‰$) would plot as a linear group of negative values at the lower end of the dataset below the inflection point with another population. This population was identified through an iterative process of selecting increasingly narrow isotopic ranges

## Explanation:

- Agriculture/ Walker River Water Type
- Mine-Influenced Groundwater Type
- Naturally Mineralized Type Groundwater

— Northern Extent of Mine-Influenced Ground Water Type (Dashed where Inferred)

- See text for explanation of statistically based water types.

— Mine Site Boundary

— West Campbell Ditch

— Wabuska Drain

— Walker River

- - - Approximate Lateral Extent of Shallow Zone Aquifer

☐ Mine Pit Lake

☐ Irrigated Agricultural Area

☐ Evaporation Ponds

▨ Undifferentiated Granitic, Metamorphic, and Volcanic Bedrock
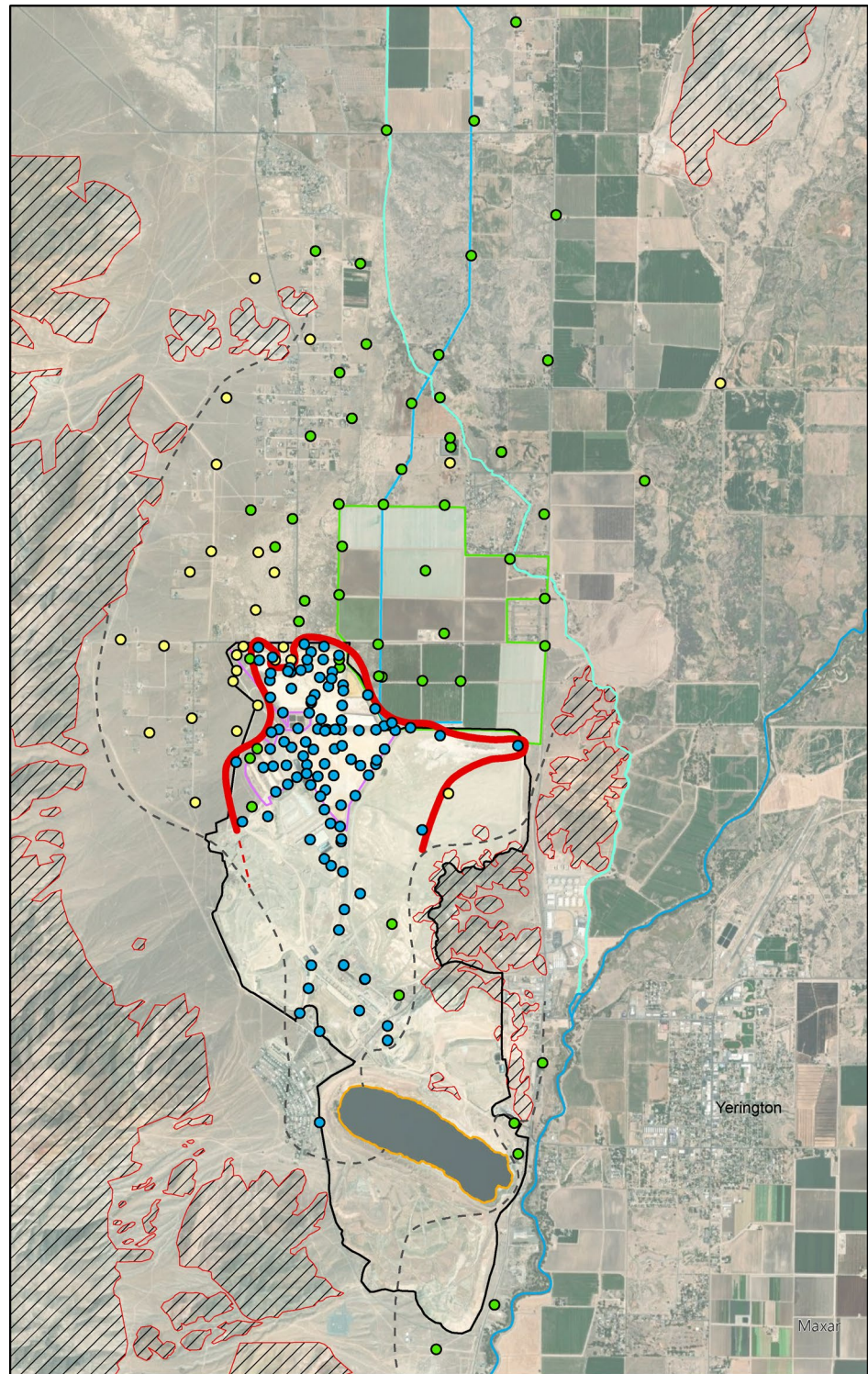


**Fig. 7** Distribution of Statistically Based Water Types in Shallow Zone Aquifer

from the lower values of the dataset, generating Q-Q plots, and assessing which plots best approximated the regression line (Fig. 8). The plot for all data from the site has several segments with different slopes that indicate the presence of multiple populations. The plots for subsets of data become increasingly linear for smaller subsets at

Quantile-Quantile Plots of δ³⁴S$_{SO4}$ Data
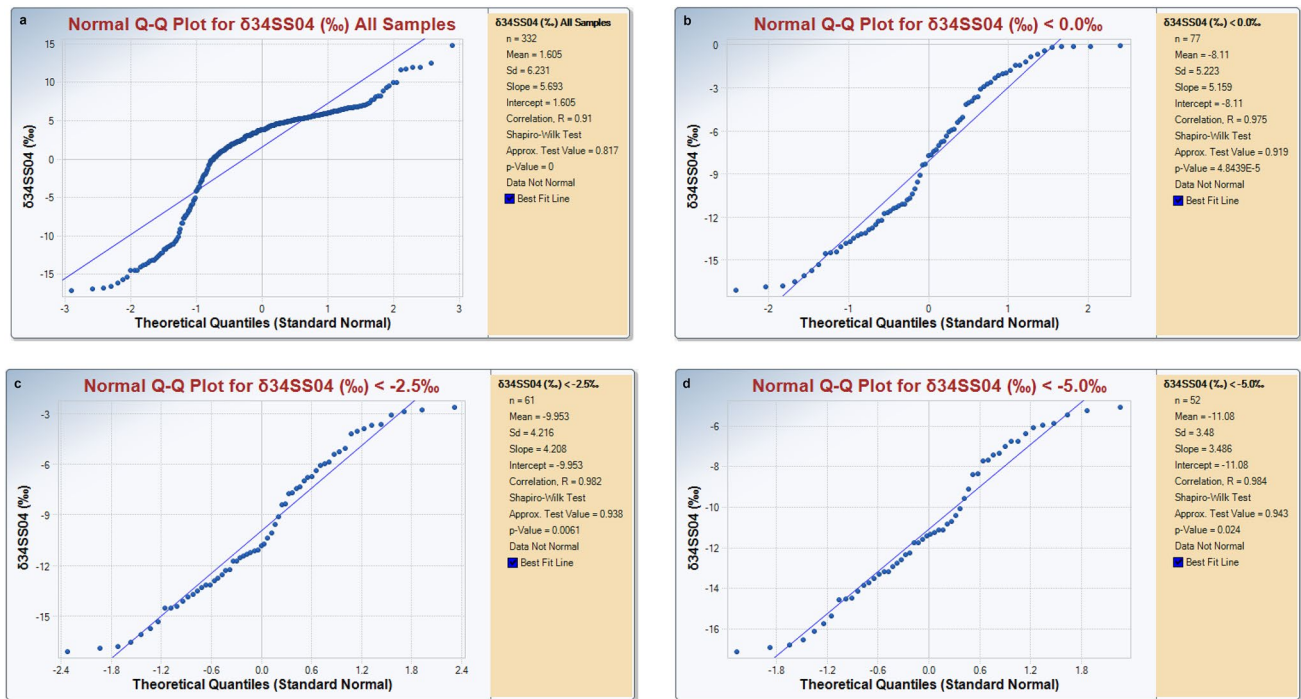
**Fig. 8** Quantile–Quantile Plots of $\delta^{34}S_{SO4}$ Groundwater Data

the lighter end of the range. The results of the analysis indicate that the subset of samples with $\delta^{34}S_{SO4}$ values less than $-5‰$ best approximates a single normally-distributed population representative of a mixture of pre-1970 process solution and naturally mineralized groundwater. Partial oxidation and exchange between sulfide ore and aqueous sulfate can lead to higher $\delta^{34}S_{SO4}$ values in the dissolved sulfate in comparison to the sulfide ore (Thode 1970). It is unknown whether and to what extent such processes may have influenced the isotopic composition of sulfate in the mixture of pre-1971 process solution and naturally mineralized groundwater. Such effects may have been minor because only sulfates, and not sulfides, were mixed in the subsurface. However, the use of isotopic data less than $-5‰$ $\delta^{34}S_{SO4}$ to identify the early release of process solution was effective because there were no other sources of such negative isotopic signatures. As previously stated, replacement sources of sulfur to make sulfuric acid were less negative than $-5‰$ $\delta^{34}S_{SO4}$ and even quite positive. Based on this analysis, the sulfur isotope data were contoured and the $-5‰$ $\delta^{34}S_{SO4}$ contour line was used to delineate the extent of MIW related to the early release of process solution (Fig. 9).

## Groundwater Velocity and Flow Distance Estimates

Water level and hydrologic testing data from remedial investigations of the site were used in average linear velocity calculations of groundwater flow to estimate potential transport distances of MIW from the evaporation ponds. This LOE used a Monte Carlo simulation of the transport distances based on the following equation:

$$v = Ki/n_e$$

where: $v$ = average linear velocity, $K$ = hydraulic conductivity, $i$ = hydraulic gradient, and $n_e$ = effective porosity.

The simulation was performed for 2500 realizations using random values based on probability distributions for the input parameters (Table 1 and Fig. 10). Hydraulic conductivity data for the analysis were derived from constant-rate discharge and recovery tests performed in eight wells near the evaporation ponds. The wells were pumped for 4 days each at discharge rates ranging from less than 4–53 L/min (1–14 gpm). Hydraulic conductivity estimates for the tests are log-normally distributed and ranged from 0.2 to 9.5 m/day (0.6–31 ft/day) based on drawdown and recovery water level data from the pumped wells and observation
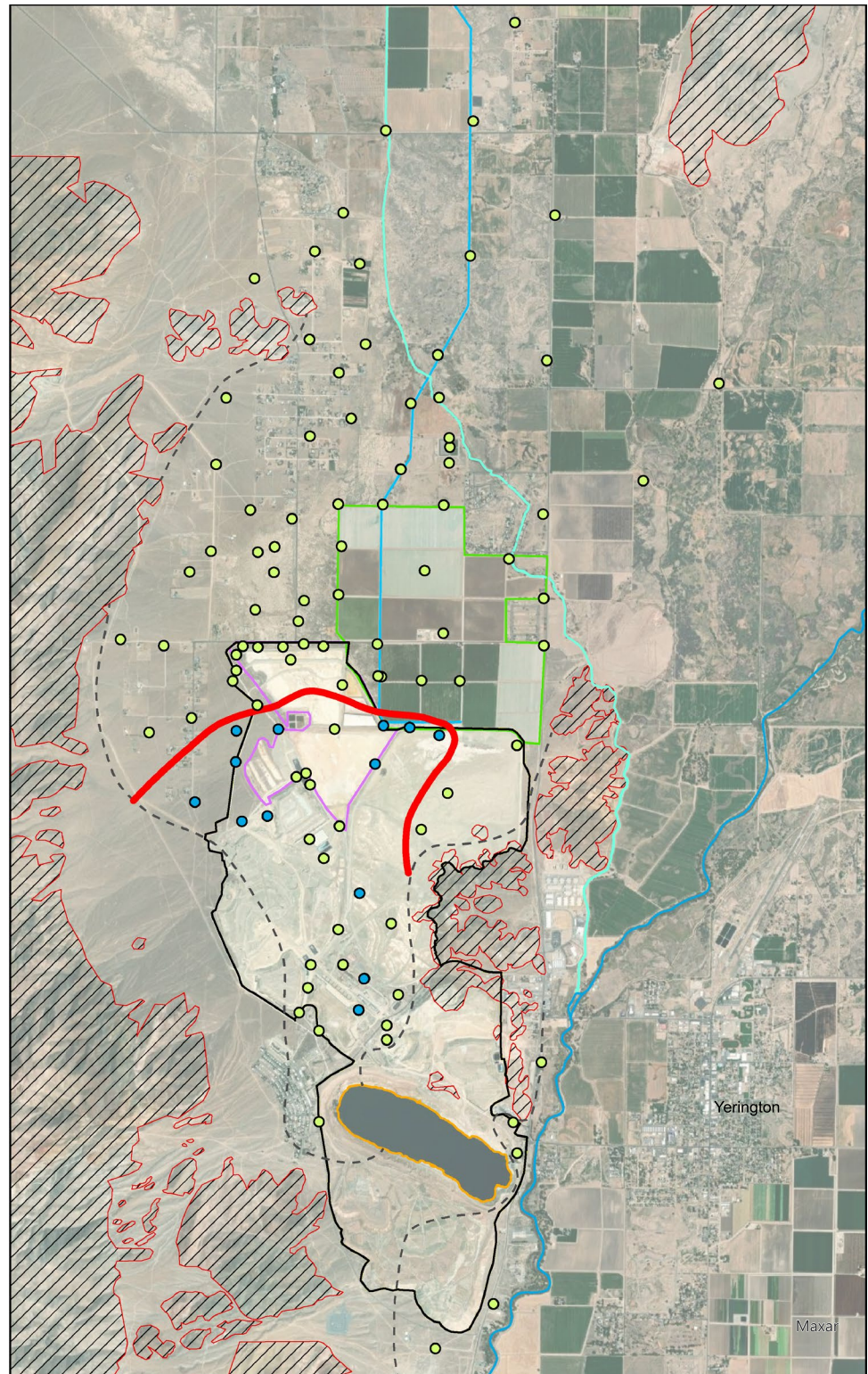
**Fig. 9** Distribution of $\delta^{34}S_{SO4}$ in Shallow Zone Aquifer

**Table 1** Input Parameters for Groundwater Travel Distance Calculation

| Parameter | Time period | Distribution type | Mean (or constant) value | Standard deviation |
|---|---|---|---|---|
| Hydraulic conductivity (K) m/s (ft/day) | 1954–2014 | Log-normal | $3.12 \times 10^{-5}$ (8.83) | $2.89 \times 10^{-5}$ (2.5) |
| Effective porosity ($n_e$) | 1954–2014 | Normal | 0.15 | 0.05 |
| Hydraulic gradient (i) Northerly flow direction | 1954–1976 | Normal | 0.0015 | 0.0005 |
| | 1977–1986 | Constant | 0.0013 | – |
| | 1987 | Constant | 0.001 | – |
| | 1988 | Constant | 0.0008 | – |
| | 1989 | Constant | 0.0006 | – |
| | 1990 | Constant | 0.0004 | – |
| | 1991 | Constant | 0.002 | – |
| Hydraulic gradient (i) Northwest flow direction | 1992–2014 | Normal | 0.00046 | 0.00007 |
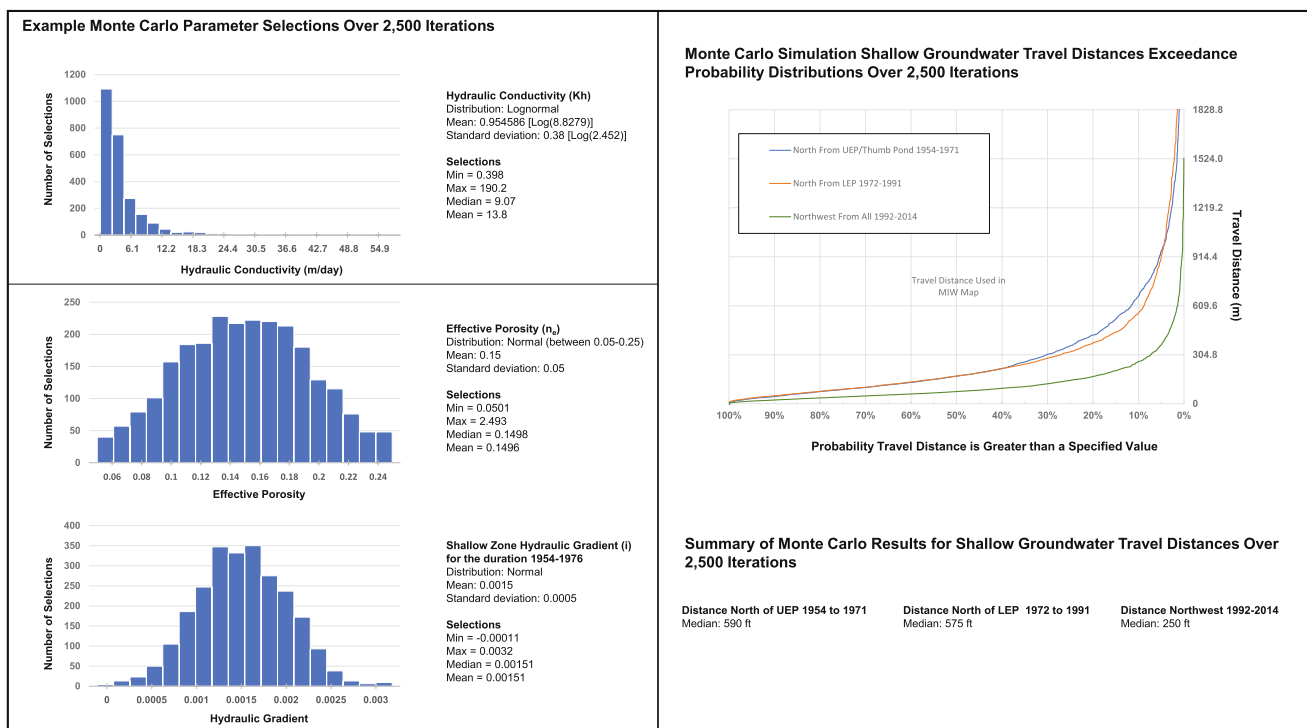


**Fig. 10** Monte Carlo Simulations of Groundwater Travel Distances, Shallow Zone Aquifer

wells (n = 24). The values for effective porosity were assumed to be normally distributed and were based on the dominant characteristics of the more permeable intervals within the shallow aquifer.

Groundwater flow directions and hydraulic gradients for the analysis were based on water level measurements and potentiometric surface maps for the period from 1954 to 2014. Prior to the start of mining operations in 1953, the groundwater flow direction at the site was down valley to the north. Pumping for mine water supply between 1953

and 1977 decreased water levels in the alluvial aquifer north and northeast of the evaporation ponds creating a cone of depression and increasing the northward hydraulic gradient between the ponds and the closest water supply well (Fig. 3). The flow direction in the agricultural area northeast of the evaporation ponds was south to southwest.

Mine water supply pumping ended in 1977 and water levels in the aquifer rebounded, resuming northward flow in the agricultural area northeast of the site. Expansion of agricultural land use during the late 1980s and increased irrigation

of previously unfarmed land directly east and northeast of the evaporation ponds resulted in mounding of the water table and a change in the direction of shallow groundwater flow near the ponds from north to northwest by about 1992. This northwest pattern of flow continues to the present (Fig. 4). The flow direction and hydraulic gradients used in the Monte Carlo simulation are summarized in Table 1. Groundwater flow in the deep alluvial aquifer is influenced by pumping of distant irrigation wells to the north of ACMS. When pumped, these wells create a downward gradient that can dissipate some of the mounds observed in the shallow aquifer created by infiltration of irrigation water.

The Monte Carlo simulation considered transport from two sources, the UEP and the LEP. The UEP operated from approximately 1954 to 1978. The LEP operated from 1972 to 1978. The transport direction in the aquifer prior to 1992 was northward. Starting in 1992, the transport direction was simulated to the northwest, reflecting the dominant influence of irrigation in the agricultural areas. The resulting output from the Monte Carlo simulation provides a probabilistic description of potential groundwater travel distances during the evaluated time frames. The distributions of hydraulic conductivity, hydraulic gradient, and effective porosity values selected for the Monte Carlo simulations are shown in the left panel of Fig. 10. The x-axis of the graph in the right panel of Fig. 10 is the probability that the travel distance is greater than the distance indicated on the y-axis. For example, the 50% probability value for travel from the UEP in the period circa 1954 to 1972 is 180 m (590 ft) from the northern edge of the UEP. There is a 50% probability that the actual travel distance was less than 180 m (590 ft) and a 50% probability that the travel distance was greater than 180 m (590 ft). We assigned the 50% probability travel distance as the most likely estimate. The 50% probability travel distances and directions for MIW from the two sources between 1954 and 2014 are shown in Fig. 11. The northward trending travel area from circa 1954 to 1972 is shown in dark blue, the northward trending travel area 1972 to 1991 is shown in medium blue, and the northwestward trending travel area 1991 to 2014 is shown in light blue.

## Isotopic ($^3$H/$^3$He) Estimates of Groundwater Age

Tritium/helium ($^3$H/$^3$He) age-dating of groundwater samples collected in 2012 and 2014 was used as a LOE to distinguish older naturally mineralized groundwater from MIW that contains a component of younger mine or process water and entered the aquifer after the start of operations, circa 1954. The $^3$H/$^3$He method can be used to estimate the age of groundwater that recharged to the aquifer within about the last 60 years. The age dates are not significantly affected by mixing with groundwater recharged prior to the start of nuclear weapons testing in 1951 because the $^3$H and $^3$He concentrations in older water are several orders of magnitude less than in modern water (Cook and Herczeg 2000). A limitation of this LOE is that it cannot be used to differentiate MIW from naturally mineralized water that contains a component of natural recharge that occurred within the last 60 years.

Tritium occurs from natural and anthropogenic sources (Clark and Fritz 1997). Naturally occurring tritium is formed in the upper atmosphere by the bombardment of nitrogen atoms by cosmic radiation where:

$$^{14}_{7}N + ^1_0n \rightarrow ^{12}_6C + ^3_1H$$
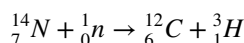
It combines with oxygen to form water and decays by beta release to form helium:

$$^3H + O_2 \rightarrow ^3 HO_2 \rightarrow^1 H^3HO$$

$$^3H \rightarrow^3 He + \beta^-$$
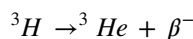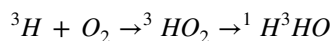
Natural tritium levels in precipitation are low and are a function of equilibrium between production in the upper atmosphere, radioactive decay, and losses by rain out. Anthropogenic tritium (bomb tritium) is several orders of magnitude more abundant and is primarily related to nuclear weapons testing between 1951 and 1962. Smaller amounts of tritium are currently being released by nuclear power plants and other sources. Prior to 1951, the average tritium concentration in precipitation ranged from about 2 to 8 TU. Peak concentrations in precipitation during 1963 approached 6000 TU (Clark and Fritz 1997).

The $^3$H/$^3$He age dates for groundwater samples from the site were based on the helium isotope mass balance, which was used to determine the amount of tritiogenic $^3$He from radioactive decay of $^3$H. (Schlosser et al. 1988, 1989). $^3$H and $^3$He are virtually inert in groundwater and are unaffected by other solutes and contamination from most sources. The $^3$H/$^3$He "clock" starts after water enters the aquifer and is completely isolated from the gas phase (Solomon and Cook 2000). The age dates can be reset by exposure to the atmosphere.

Based on this analysis, it follows that groundwater recharged to the alluvial aquifer prior to 1954 is not MIW. The results of the study are shown on Fig. 12. Groundwater with age dates greater than 60 years is primarily located on the western side of the valley northwest of the site.

**Fig. 11** Monte Carlo Estimate of Groundwater Travel Distances in Shallow Zone Aquifer

Explanation:

- ○ Groundwater Recharged After 1954
- ○ Groundwater Recharged Prior to 1954
- —— Mine Site Boundary
- —— West Campbell Ditch
- —— Wabuska Drain
- —— Walker River
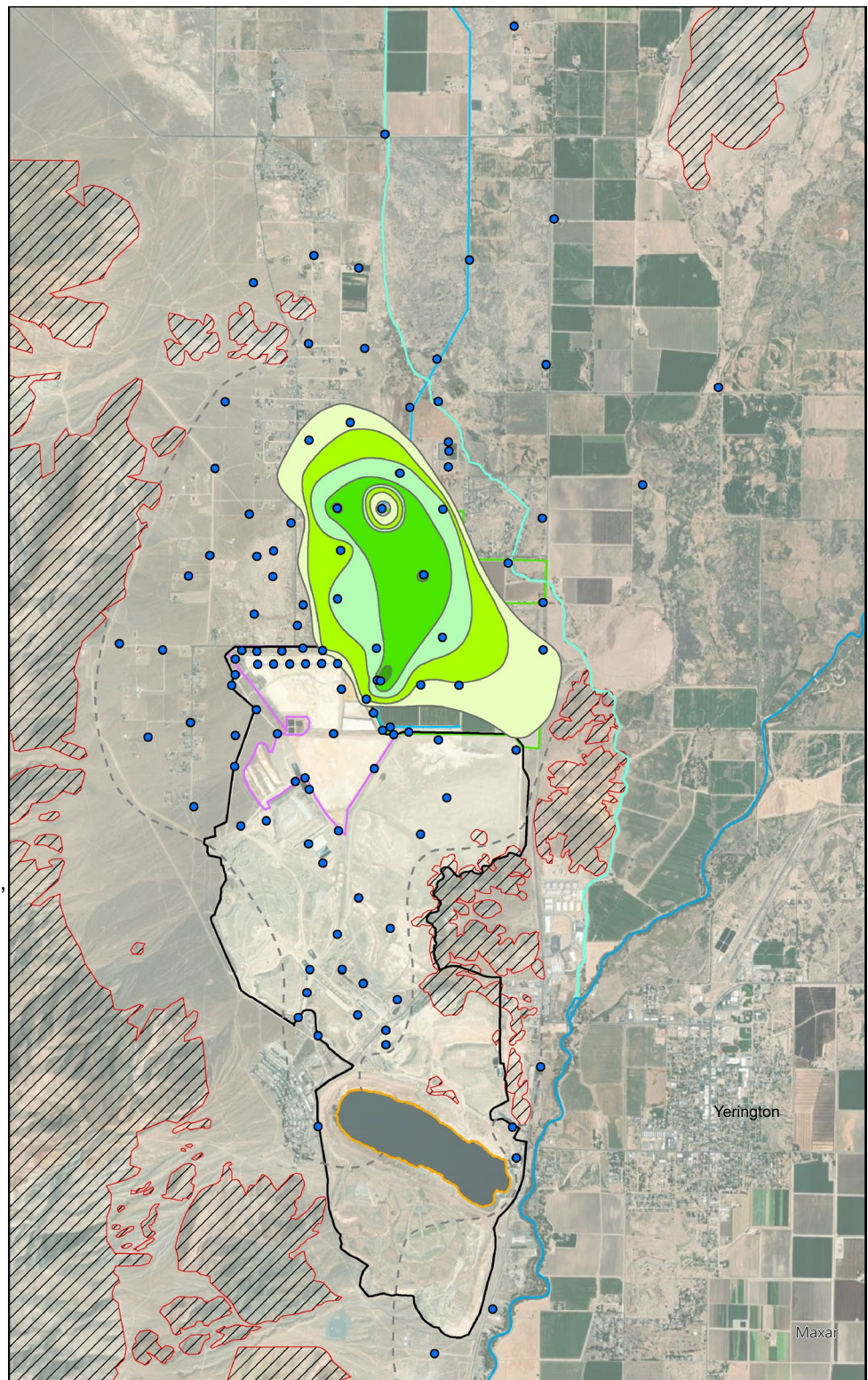- - - - Approximate Lateral Extent of Shallow Zone Aquifer
- Groundwater Recharged Prior to 1954
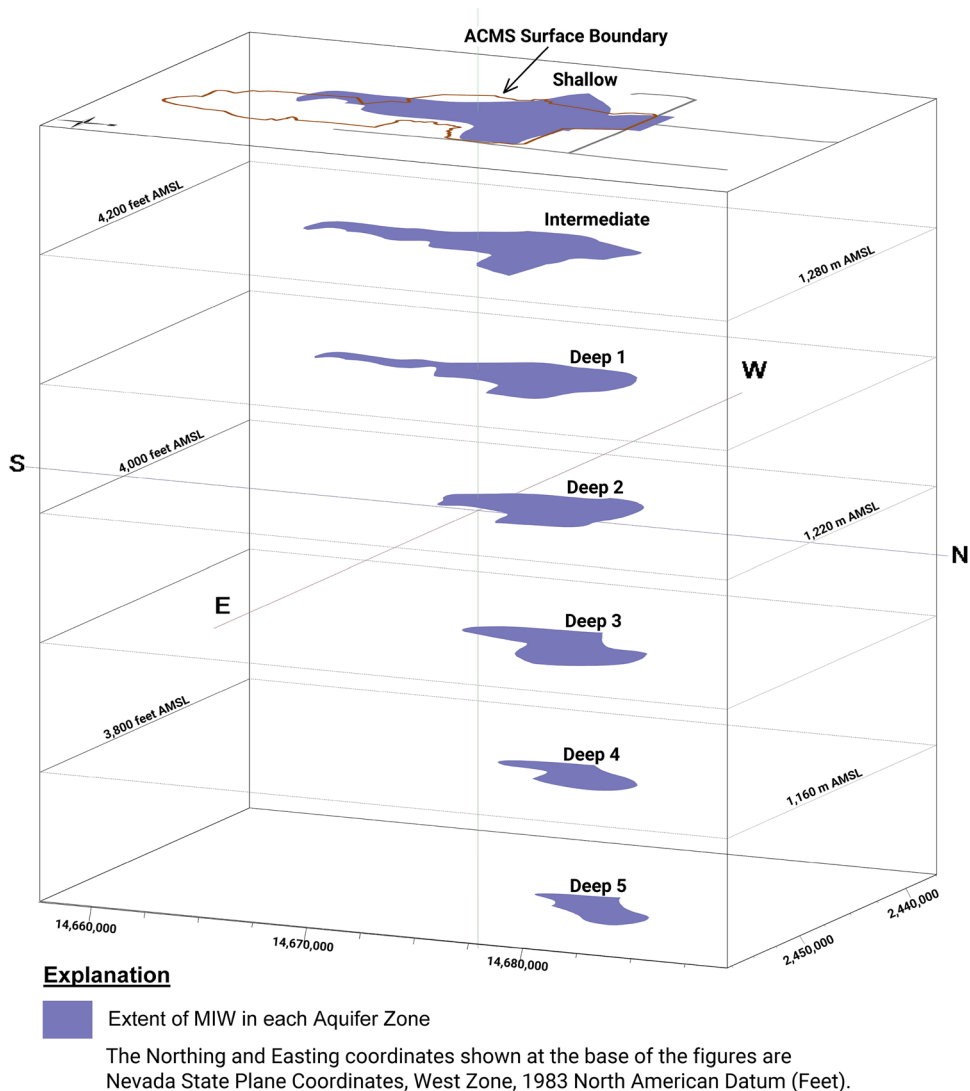- Mine Pit Lake
- Irrigated Agricultural Area
- Evaporation Ponds
- Undifferentiated Granitic, Metamorphic, and Volcanic Bedrock
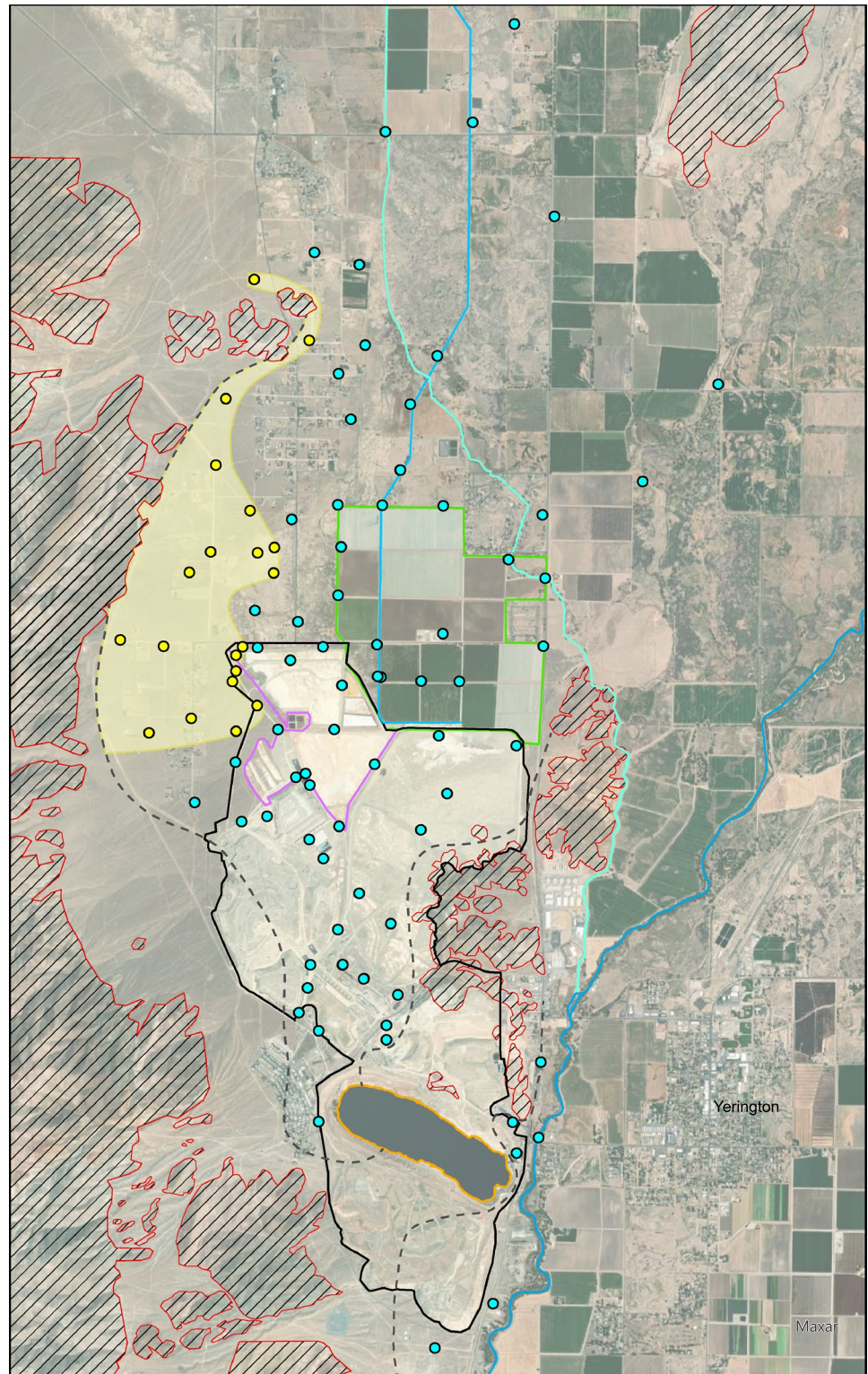
**Fig. 12** Extent of Shallow Zone Alluvial Groundwater Recharged Before 1954

**Fig. 13** Extent of Elevated Nitrate in Shallow Zone Aquifer from Agricultural Activities

## Extent of Nitrate Migration from Agricultural Activities

Nitrate is used as a tracer of agricultural influenced groundwater because fertilizers containing nitrate are applied on the fields north of the Site. Nitrate is a not a constituent related to the previous mining operation. A pronounced nitrate plume occurs in groundwater below the agricultural fields northeast of the evaporation ponds (Fig. 13). The maximum concentration near the center of the plume exceeds 40 mg/L. Most shallow wells in alluvium below the fertilized and irrigated fields have nitrate concentrations greater than 10 mg/L. The configuration of the nitrate plume reflects, in part, the groundwater flow pattern created by the infiltration of irrigation water from the fields.

Groundwater flow directions below and near the agricultural fields are dominated by the infiltration of irrigation water. The average delivery of irrigation water to the fields is about 1.2 m/year (4 ft/year) and the average crop consumption is about 0.9 m/year (3 ft/year; S.S. Papadopulos & Associates 2014), so the average infiltration to groundwater below the fields is about 0.3 m/year (1 ft/year) or about 25% of the irrigation water delivered to the fields. The infiltration of irrigation water during the last 30 years has been sufficient to displace all of the water in the shallow zone below the fields and the current groundwater quality is dominated by the chemistry of the irrigation water applied to the fields.

Groundwater monitoring data indicate that nitrate concentrations within the site boundary are generally less than 1 mg/L, and therefore, elevated nitrate concentrations are useful as a LOE to determine the extent of agricultural influenced groundwater (Fig. 13). Based on review of available monitoring data and the patterns of flow caused by infiltration of irrigation water, 5 mg/L of nitrate was selected as a conservative criterion to define areas of agriculturally influenced groundwater without overlapping mining related impacts.

## Composite Weight of Evidence Evaluation

The LOEs discussed in this paper can be grouped into two broad categories: evidence that indicates the presence of MIW and evidence that excludes the presence of MIW. LOEs that indicate the presence of MIW include mining-related water types defined by MSA, groundwater with $\delta^{34}S_{SO4}$ values less than $-5‰$, and the 50% probability groundwater travel distance estimate. The MSA LOE is based on evaluation of 34 analytes in 399 samples and provides a quantitative approach for determining what is and what is not MIW. The sulfur isotope LOE fingerprints groundwater affected by the initial releases of process solution from the site. The probabilistic groundwater travel distance LOE indicates areas that are statistically likely to have MWI based on the hydraulic characteristics of the aquifer. LOEs that define areas in which MIW is not present include $^3H/^3He$ age dates of groundwater older than 60 years and elevated nitrate concentrations greater than 5 mg/L, which are characteristic of groundwater that has been displaced by the infiltration of irrigation water. The areas defined in the shallow zone of the alluvial aquifer by the five LOEs for this study are shown on Fig. 14. Overall, the travel distances of MIW in the shallow zone reflect the little recharge that occurred within the ACMS since operations ended, the associated relatively flat horizontal hydraulic gradients compared to the gradients in the irrigated agricultural areas to the north, and downward vertical hydraulic gradients (discussed below).

The five LOE methodology was also applied to deeper zones in the alluvial aquifer. The results of the composite weight of evidence evaluation of the extent of MIW for all zones are shown in Fig. 15. MIW occurs in the deep zones of the alluvial aquifer and the MIW areas become smaller with depth. The deep zones of MIW reflect the effects of the downward hydraulic gradients created by the historical operation of mine supply and irrigation wells located immediately north of ACMS. These wells are no longer active. The furthest location of MIW from ACMS is in the deepest zone and is approximately 1300 m northeast of the ACMS boundary.

## Conclusions

The LOE approach described in this paper proved to be a useful tool for delineating MIW at this site and for differentiating areas of the aquifer where MIW is present from other areas where groundwater quality has been affected by naturally occurring mineralization and agricultural land use practices. The multiple LOE approach may be useful at other mine sites where groundwater quality is influenced by various complex factors and MIW does not exhibit a unique environmental water tracer signature, making it difficult to differentiate natural ambient water quality from groundwater that has been impacted by mining or other human activities. The multiple LOE approach likely would need to be adapted for site-specific processes, land use and geologic/mineralogic characteristics to distinguish areas of mining-related impacts from naturally mineralized water and areas affected by other anthropogenic activities.

**Fig. 14** Extent of MIW in Shallow Zone Based on Five Independent Lines-of-Evidence

**Fig. 15** Stacked Maps of the Extent of MIW in Each Aquifer Zone



**Explanation**

Extent of MIW in each Aquifer Zone

The Northing and Easting coordinates shown at the base of the figures are Nevada State Plane Coordinates, West Zone, 1983 North American Datum (Feet).

**Data Availability** The data evaluated in this paper can be found in the document titled 20200414 OU-1_RI_REPORT_FINAL the Public Records folder of the following website: https://ndep.nv.gov/land/abandoned-mine-lands/anaconda-home/anacondasite-docs.

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