Geochemical Conceptual Site Model and Batch-Equilibrium Modeling of Groundwater at Monitoring Well DD, Homestake National Priorities List Site, New Mexico

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Executive Summary

Geochemical and hydrological processes described in detail in this updated report form the basis of a dynamic and complex conceptual-site model for groundwater background in the alluvial aquifer system in San Mateo Creek Basin north of the Homestake Mining Company of California's (Homestake's) National Priorities List (NPL) site (Homestake NPL Site). Approximately 125 billion gallons of mine water (12.672 million gallons/day averaged over 26 years, 0.383 million acre-feet) were pumped from the Westwater Canyon Member of the Morrison Formation and Dakota Sandstone Formation in the Ambrosia Lake area and released to Arroyo del Puerto and San Mateo Creek from 1956 to 1982 (Perkins and Goad 1980, Gallaher and Cary 1986, Weston Solutions, Inc. 2016). Historical (pre-1983) surface-water flow in San Mateo Creek, dominantly consisting of sustained mine-water discharges and treated effluents, acts as a non-point source of recharge to the alluvial aquifer over distances of several kilometers. Groundwater mixing took place after mine-water discharges infiltrated the alluvial aquifer, which is supported by rising water table conditions; solute transients of major ions, nitrate, selenium, and uranium; and a close similarity of major-ion chemistry between historical mine-water discharges and alluvial groundwater north of the Homestake NPL Site. Uranium and other solutes are concentrated in mine-water discharges compared to native alluvial groundwater.

Native groundwater has been reacting with alluvial sediments in San Mateo Creek Basin for thousands of years that most likely produced steady-state conditions with solute concentrations prior to release of voluminous mine-water discharges. Equilibrium conditions likely maintained small variations in solute concentrations in the alluvial aquifer prior to infiltration of mine-water discharges, groundwater mixing, and rising water table conditions observed at several monitoring wells. Stable solute concentrations are observed at alluvial well SMC-08/916 located northeast of the Homestake NPL Site near the eastern boundary of the alluvial aquifer.

Leaching of natural and anthropogenic chemicals from the vadose zone is occurring under rising water table conditions during migration of contaminated groundwater through the alluvium. Increasing saturated thickness in the alluvium is on the order of 3.8 to 5.0 meters (12.6 to 16.5 ft.) since the late 1950s, which has been measured at several alluvial monitoring wells located north of and in proximity to the Homestake NPL Site large tailing pile (LTP), in the lower San Mateo Creek floodplain (Weston Solutions, Inc. 2018). The rising water table in the alluvium north of the LTP likely resulted from (1) surface water recharge consisting of a combination of mine-water discharges, which have infiltrated alluvial sediments along San Mateo Creek and its floodplain, followed by groundwater mixing with native alluvial groundwater; (2) effect of tailing seepage from the unlined LTP and small tailing pile (STP) on the hydraulic gradient of the alluvial

aquifer; and (3) aquifer pumping as part of the Homestake groundwater remediation. Dissolution of gypsum and other soluble salts and desorption of selenium present in the vadose zone is likely occurring under rising water table conditions in the alluvium at wells DD, DD2, Q, P, and R. This leaching process produces a secondary source of groundwater contaminants, such as nitrate, selenium, and sulfate, in the alluvial aquifer north of the Homestake NPL Site.

Sustained surface-water flow allowed a large volume of mine water to recharge the alluvial aquifer over a substantial area of the lower San Mateo Creek floodplain very early in the uranium mining industry's period of discharge operations (1956-1982). Infiltration of mine-water discharges, groundwater mixing, and leaching of soluble solutes from the vadose zone likely produced transient conditions in dissolved concentrations of calcium, sulfate, nitrate, uranium, selenium, and total dissolved solids (TDS) at several upgradient monitoring wells located north of the Homestake NPL Site. Based on transient aqueous geochemical conditions observed at those wells, including the near upgradient background monitoring wells DD, DD2, P, Q, and R, dissolved concentrations of uranium, selenium, nitrate, sulfate, and TDS are not entirely representative of steady-state conditions that are typical of natural groundwater background. Transient geochemical conditions observed at well DD most likely result from a combination of groundwater mixing of infiltrated mine water with native alluvial groundwater, vadose zone leaching, and reactivity of gypsum and calcite.

Uranium(VI) carbonate-carbonato (anion) complexes are excellent tracers to assess groundwater mixing of infiltrated mine water with native oxic groundwater in the alluvial aquifer in San Mateo Creek Basin. These complexes are mobile and do not significantly adsorb onto amorphous ferric hydroxide under circumneutral pH conditions characteristic of the alluvial aquifer in San Mateo Creek Basin. It is recognized that groundwater flow in the alluvium, from north-northeast to south-southwest, is complex in the fluvial sediments characterized by variable, non-isotropic and heterogeneous hydraulic properties and preferred flow paths along one or more buried paleochannels. Based on a simple and first-order binary mixing model of dissolved uranium(VI), approximately 97.11 percent of alluvial groundwater at monitoring well P (1979 - 1980) mixes with 2.89 percent of infiltrated mine water to produce an average dissolved concentration of uranium of 0.165 mg/L measured at well DD from 1997 to 2019. Using the same approach, approximately 89.85 percent of alluvial groundwater at well SMC-08/916 (1997 - 2005) mixes with 10.15 percent of infiltrated mine water to produce average dissolved concentrations of uranium at well DD. These initial mixing ratios provide plausible percentages of native alluvial groundwater impacted from infiltrating mine water north of well DD, which may have occurred at least since 1976.

Partial evaporation of surface water, consisting of mine-water discharges, snowmelt, and storm water, occurred prior to infiltrating through the vadose zone to alluvial groundwater, based on enriched isotopic ratios of δ^2H-H_2O and $\delta^{18}O$-H_2O (Weston Solutions, Inc. 2018). Light or negative $\delta^{34}S$-SO_4 ratios are typically less than -20 per mil measured in alluvial groundwater samples. The $\delta^{34}S$-SO_4 ratios measured in alluvial groundwater are the same as pyrite examined from uranium ore samples collected from the Westwater Canyon Member of the Morrison Formation of Jurassic age (Weston Solutions, Inc. 2018). Less negative $\delta^{34}S$-SO_4 ratios occur along the eastern boundary of the alluvial aquifer at wells SMC-08/916, SMC-10/914, and ND. Oxidative dissolution of trace amounts of framboidal pyrite in alluvial sediments in the area of well DD have also produced depleted $\delta^{34}S$-SO_4 ratios in alluvial groundwater at the Homestake NPL Site, which has mixed with infiltrated sulfate-rich mine water (Arcadis 2018).

Mineralized sediments have been transported over geologic time (greater than 10,000 years) and deposited in the San Mateo Creek Basin (Arcadis 2018, Ulrich et al. 2019). Desorption of uranium(VI) and oxidative dissolution of potential trace uranium(IV) solid phases, including uraninite and coffinite, may provide a secondary or minor source of dissolved uranium measured in alluvial groundwater at well DD, based on results of inconclusive batch-leach tests conducted by Arcadis (2018). Most of the dissolved uranium, typically greater than 0.10 mg/L, measured at wells DD and DD2, however, is likely sourced from infiltrated mine-water discharges containing low mg/L concentrations of dissolved uranium (Perkins and Goad 1980). Dissolved uranium is predicted to occur as ternary calcium uranyl carbonate complexes, which are non-adsorbing or mobile in the alluvial aquifer in the San Mateo Creek Basin.

Based on batch-equilibrium simulations using the computer program PHREEQC (Parkhurst and Appelo 2013), alluvial groundwater at well DD is in equilibrium with gypsum and dolomite (ordered); is oversaturated with barite, calcite, ferrihydrite, gibbsite, and pyrolusite; and is undersaturated with $CaMoO_4$, carnotite, chalcedony, dolomite (disordered), K-jarosite, rhodocrosite, tyuyamunite, and uraninite. Surface complexation of UO_2^{2+}, uranyl carbonate-carbonato, and oxo-hydroxo adsorbates onto hydrous ferric oxide (HFO), represented by amorphous ferric hydroxide, with well DD groundwater equilibrated with the HFO surface, is minimal based on PHREEQC simulations. Results of the PHREEQC simulations are consistent with elevated dissolved concentrations of uranium measured at this well since 1976. Based on results of PHREEQC simulations, non-complexed or free calcium (Ca^{2+}) concentrated in alluvial groundwater effectively competes with other adsorbates for adsorption sites present on HFO. Results of PHREEQC inverse modeling, consisting of groundwater mixing of native alluvial groundwater (well SMC-08/916) with mine-water discharges, reasonably produce major ion chemistry measured at well DD. A suite of site-specific minerals, including calcite, gypsum, montmorillonite-Ca, kaolinite, illite, plagioclase, biotite, halite, and chalcedony, were used as part of inverse modeling to quantify major ion chemistry at well DD.

1.0 Introduction

The Homestake Mining Company of California's (Homestake's) National Priorities List (NPL) site (hereinafter "Homestake NPL Site") is a former uranium mill and tailing disposal facility located in the lower San Mateo Creek Basin, 8.4 kilometers (km) (5.2 miles) north of Milan, New Mexico (Figure 1). The Site is also a Uranium Mill Tailings Radiation Control Act (UMTRCA) Title II site regulated by the U.S. Nuclear Regulatory Commission (NRC) under Source Material License SUA-1471. The Homestake NPL Site was operated from 1958 to 1990.

The purpose of this report is to evaluate the origin and geochemical dynamics of elevated uranium concentrations measured at Homestake's alluvial monitoring well DD. Concentrations of dissolved uranium typically exceed 0.100 milligrams per liter (mg/L) at well DD, which is one of the locations used to determine background concentrations of inorganic solutes in alluvial groundwater. As part of the evaluation, computer simulations were conducted with the program PHREEQC (Parkhurst and Appelo 2013) to examine uranium and other solute speciation, mineral stability, adsorption, and mixing reactions and processes that could be occurring in the alluvial aquifer in the vicinity of well DD. The input files for computer simulations include groundwater chemistry data collected by Homestake (Arcadis 2018, Ulrich et al. 2019) at several alluvial wells, including well DD, which were sampled during October 2016 when the U. S. Environmental Protection Agency (EPA) was conducting sampling as part of its reassessment of background-water quality at the Homestake NPL Site.

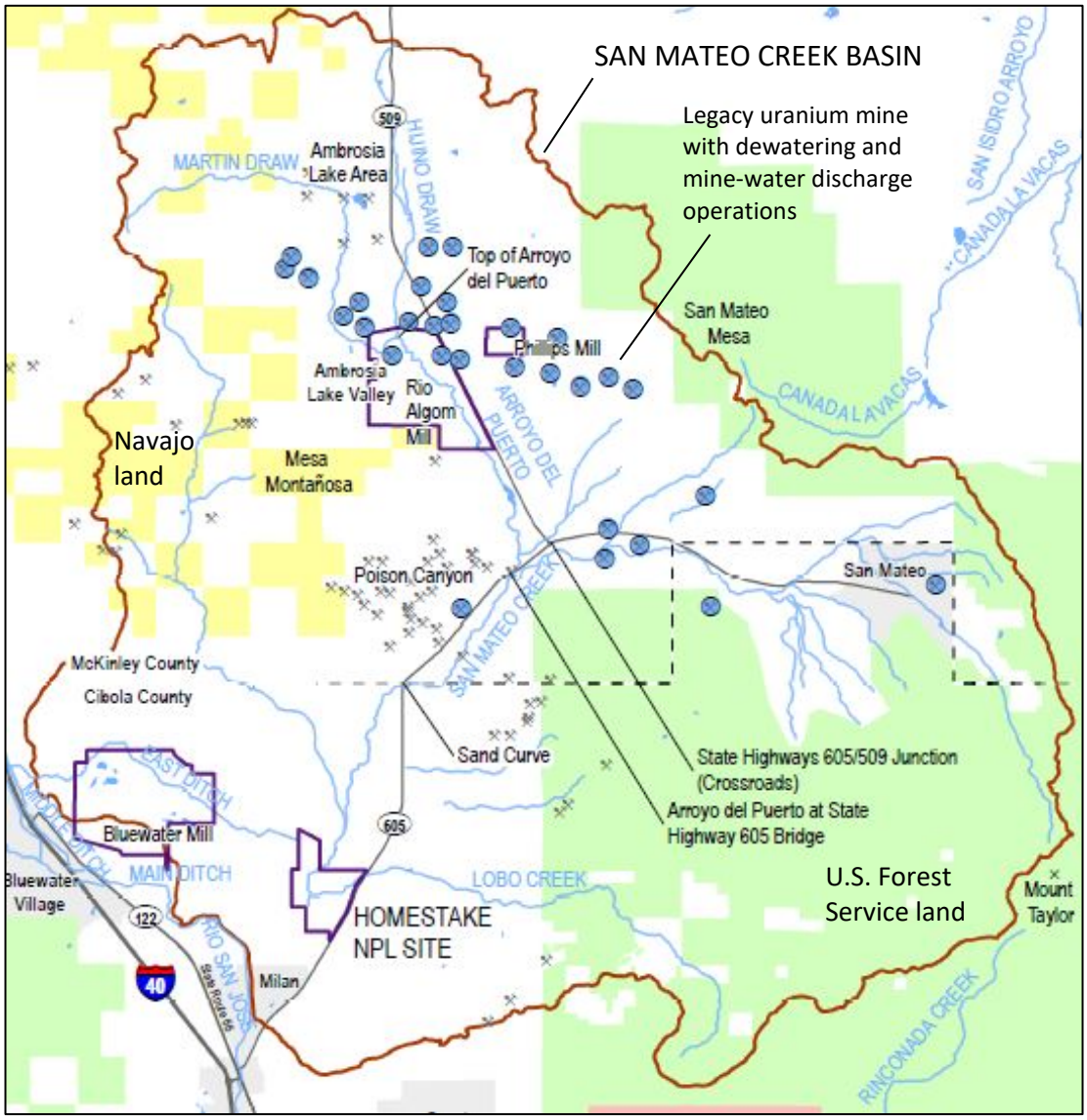

Figure 1. Site location map (modified from Figure A1-3, Weston Solutions, Inc. 2018).

2.0 Site Conditions

Groundwater contamination resulting from legacy uranium mining and milling operations occurs in the alluvium in the San Mateo Creek Basin, located in Cibola and McKinley Counties, New Mexico (EPA 1975, Gallaher and Cary 1986, Weston Solutions, Inc. 2018). Primary and secondary contaminant sources likely impacting alluvial sediments and groundwater in upper San Mateo Creek Basin north of the Homestake NPL Site include: (1) historical mine-water discharges from mines operated in the Ambrosia Lake valley beginning in 1956 and continuing to 1982; (2) leaching of natural and anthropogenic chemicals from the vadose zone during rising water table conditions as mixed groundwater (mine-water discharges and native alluvial groundwater) migrates along flow paths in the alluvium; (3) migration of acidic tailing leachate plumes from unlined tailing impoundments in the Ambrosia Lake valley; and (4) metal- and

radionuclide-contaminated sediments and surface water transported along Arroyo del Puerto and San Mateo Creek during baseflow and seasonal storm events occurring over decades (EPA 1975, EPA 1980, Gallaher and Cary 1986, and Weston Solutions, Inc. 2018).

The former Homestake mill used a solution of sodium bicarbonate (0.35 molar, M)/sodium carbonate (0.08 M) to dissolve uranium from limestone and sandstone-hosted uranium ore primarily consisting of uraninite (UO_2), coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$), carnotite ($K(UO_2)_2V_2O_8 \cdot 3H_2O$), and tyuyamunite ($Ca(UO_2)_2V_2O_8 \cdot 5\text{-}8H_2O$) (Merritt 1971). The ore grade averaged 0.21 percent U_3O_8 and the resulting ore leachate averaged 0.011 percent U_3O_8 (131 µM) (Merritt 1971). The alkaline leaching of the ore was followed by ammonia precipitation of yellow cake (Weston Solutions, Inc. 2018). The alkaline milling process produced a basic pH (>10), high TDS tailing raffinate (wastewater) that was discharged to the two unlined surface impoundments, the LTP and STP, located on site. Since 1977, contaminated groundwater in the alluvium and in the underlying Triassic Chinle Group bedrock aquifers at the Homestake NPL Site has been undergoing remediation by injection of non-contaminated water combined with pump and treat technologies and evaporation. Other components of the remediation system include injection and extraction wells, infiltration trenches, a reverse osmosis (R.O.) plant, zeolite pilot and full-scale treatment systems, lined evaporation ponds for passive and forced (spray) evaporation, and lined collection ponds for recycling water to the R.O. plant.

The key contaminants in alluvial and bedrock groundwater include chloride, molybdenum, nitrate, radium-226, radium-228, selenium, sulfate, thorium-230, and uranium (Homestake 2019). The Chinle Group is comprised of three separate aquifers designated as the Upper, Middle, and Lower Chinle aquifers, which subcrop to the alluvium. They are recharged by alluvial groundwater in some locations and discharge to the alluvium in other locations within San Mateo Creek Basin. Groundwater-flow paths and contaminant distributions in the alluvium and Chinle aquifers south of the LTP are complex due to the hydrostratigraphy, structural geology, and 44 years of on-site remediation efforts (Homestake 2019).

Two lined evaporation ponds (ponds 3A and 3B; collectively referred to as EP-3) were constructed in 2011 to store brine solutions transferred from evaporation ponds 1 and 2 and reclaimed seepage from the LTP, which are concentrated in uranium, sulfate, sodium, total carbonate alkalinity, chloride, molybdenum, and other solutes (Homestake database). Initial water quality sampling of EP-3 occurred in August 2011. EP-3 is located 0.8 km (0.4 mile) north-northwest of the LTP and immediately west of wells DD and DD2 (Figure 2). Several additional monitoring wells (DD3, DD4, DD5, DD6, and DD7) were completed in the alluvium near EP-3 in 2017. These new wells, combined with wells DD and DD2, comprise a monitoring-well leak detection system for EP-3. Wells DD6 and DD7 are dry, while groundwater is present in wells DD3, DD4, and DD5. Groundwater chemistry at wells DD3, DD4, and DD5 is reflective of mixed groundwater, not the high-ionic strength brine water stored in EP-3 (Homestake database). At evaporation pond 3A, concentrations (in mg/L, except for total carbonate alkalinity, mg $CaCO_3$/L) of total carbonate alkalinity, chloride, sulfate, and uranium vary from 18,600 to 81,500; 6,720 to 149,000; 11,600 to 42,000; and 109 to 2,680, respectively (Homestake database). At wells DD3, DD4, and DD5, concentrations (in mg/L, except for total carbonate alkalinity, mg $CaCO_3$/L) of total carbonate alkalinity, chloride, sulfate, and uranium range from 209 to 299; 61 to 147; 1,200 to 2,120; and 0.084 to 0.244, respectively (Homestake database). The wells were sampled between August 2017 and March 2019 (Homestake database) and well DD3, located immediately northeast of EP-3, has lower dissolved concentrations of uranium

compared to wells DD4 and DD5. It is not known, however, if industrial discharges previously occurred in the area prior to construction of EP-3, which could have resulted in localized groundwater contamination in the vicinity of wells DD and DD2. Such potential discharges are unlikely to have occurred, based on groundwater chemistry at wells DD and DD2.

A detailed geochemical conceptual site model (CSM) is presented in this report. This CSM focuses on historical (pre-1983) infiltrating surface water (mine-water discharges and irrigation water), native and contaminated alluvial groundwater, groundwater mixing, rising water table conditions, and groundwater remediation at the LTP. Geochemical processes are discussed that influence the fate and transport of calcium, sulfate, uranium, and other solutes in the alluvial aquifer system in the San Mateo Creek Basin at and north of the Homestake NPL Site.

Alluvial monitoring well DD is one of several groundwater sampling stations located north and hydraulically upgradient of the LTP that have been defined by Homestake as "near-upgradient" background alluvial monitoring wells with no influence of uranium mining activity[1] (Figure 2). These near-upgradient background wells were used to establish Groundwater Protection Standards under the NRC Source Materials License SUA-1471 (NRC 2006a). Groundwater sampled from well DD contains dissolved concentrations of uranium in excess of 0.100 mg/L (Homestake database).[2] Other selected near-upgradient background monitoring wells (P, P1, P2, P3, P4, and ND) have concentrations of dissolved uranium generally less than 0.040 mg/L, suggesting that dissolved uranium measured in groundwater at well DD and the other DD-series wells is unique in origin. Uranium and other solutes (nitrate, calcium, and sulfate) measured at well DD have likely been derived from (1) anthropogenic sources, consisting of native alluvial groundwater mixed with mine-water discharges released to Arroyo del Puerto in the Ambrosia Lake valley since the mid-1950s and unidentified local sources (Weston Solutions, Inc. 2018), and (2) natural sources, including mineralized sediments originally sourced from outcropping bedrock formations (such as the uranium-bearing Westwater Canyon Member and Brushy Basin Member of the Morrison Formation) north of the Homestake NPL Site (Arcadis 2018, Ulrich et al. 2019). Rising water table conditions resulting from infiltration and mixing of mine-water discharges with native alluvial groundwater, the hydraulic effect of tailing seepage from the LTP and STP, and aquifer pumping by Homestake enhances leaching of natural and anthropogenic chemicals (nitrate, selenium, sulfate, and TDS) from the vadose zone.

2.1 Historical Mine-water Discharges

Mine-water discharges transported to lower San Mateo Creek Basin as surface flow recharged and contaminated the alluvial aquifer (EPA 1975, Gallaher and Cary 1986). Perkins and Goad (1980, page 22, Phillips Uranium Company exhibit) provide a total pumping of 195,920 gallons/minute (GPM), or 282,124,800 gallons/day (GPD), for mine dewatering that occurred in the Ambrosia Lake area from 1956 to 1978. Gallaher and Cary (1986), using pumping rates provided by Perkins and Goad (1980) and data obtained from 1979 to 1982, calculate mine

[1] "…uranium concentrations used in the background analyses completed for the Site in 2004 have not been affected by up-gradient mining, and the background levels for uranium are considered representative of local natural conditions…" (Homestake Mining Company and Hydro-Engineering LLC, 2015, p. 1-2).

[2] Groundwater samples collected from the other DD-series monitoring wells (DD2, DD3, DD4, and DD5), located near DD and EP-3, also have dissolved concentrations of uranium in excess of 0.100 mg/L, but these wells were installed after the Groundwater Protection Standards were established in 2006 and, therefore, were not used in the background calculations.

dewatering operations that varied from 0.720 million gallons/day (MGD) to 16.704 MGD in the Ambrosia Lake area from 1956 to 1982. Cumulatively, an estimated 125 billion gallons of mine water (12.672 MGD averaged over 26 years, 0.383 million acre-feet) were pumped from the Westwater Canyon Member of the Morrison Formation and Dakota Sandstone Formation (Perkins and Goad 1980, Gallaher and Cary 1986) in the Ambrosia Lake area and released to Arroyo del Puerto and San Mateo Creek from 1956 to 1982. From this high volume of aquifer dewatering, billions of gallons of mine water were discharged from 1956 to 1982 to surface drainages flowing into Arroyo del Puerto and San Mateo Creek, transforming ephemeral drainages into perennial streams. Gallaher and Cary (1986) report that 2.16 MGD of mine-water discharge flowed in San Mateo Creek south from the area of the NM State Highways 605 and 509 junction (Crossroads area) for 4.8 km (3 miles) from 1979 to 1981. An historical aerial photograph of San Mateo Creek at Sand Curve[3] taken in October 1958 shows what appears to be surface water, flowing over the banks of the creek channel, as it is transported into the lower floodplain (south of Sand Curve) (Figure 3). The darker areas of the photograph along the creek may indicate moist soils or more robust vegetative growth.

Gallaher and Cary (1986), Clark (1974), and EPA (1975) report that untreated mine waters discharged to tributaries of Arroyo del Puerto contained elevated dissolved concentrations of sulfate, uranium, molybdenum, selenium, TDS, radium-226, and lead-210. Major-ion chemistries of mine-water discharges may have evolved, with increasing solute concentrations occurring between initial effluent discharge sites and areas of infiltration along Arroyo del Puerto and San Mateo Creek in a highly energetic hydraulic environment. Chemical evolution of mine-water discharges likely was controlled by surface-water volume and flow rate, residence time, relative concentrations of dissolved and suspended-adsorbed chemicals, mineralogy of suspended sediment, and dissolution and desorption reactions that occurred between surface water and suspended sediment present in the stream channels. A surface water sample collected from Arroyo del Puerto at the NM State Highway 53 (currently NM State Highway 605) bridge, in 1960, during early stages of mine dewatering, contained the following concentrations of dissolved analytes (in mg/L): chloride (44), sodium (154), calcium (57), sulfate (380), magnesium (41), and total alkalinity (as $CaCO_3$) (210 mg/L) (Chavez 1961). EPA (1975) reports a concentration of uranium of 4.7 mg/L in a surface water sample collected from Arroyo del Puerto at the NM State Highway 53 bridge (see Figure 1). Unfortunately, there is a paucity of surface-water quality data, including complete analyses of major ions and trace elements, for mine-water discharges in areas of infiltration along San Mateo Creek downstream of the bridge and in the lower floodplain.

[3] "Sand Curve is a local name for a bend in NM State Highway 605. This bend has also been referred to as "Deadman's Curve."

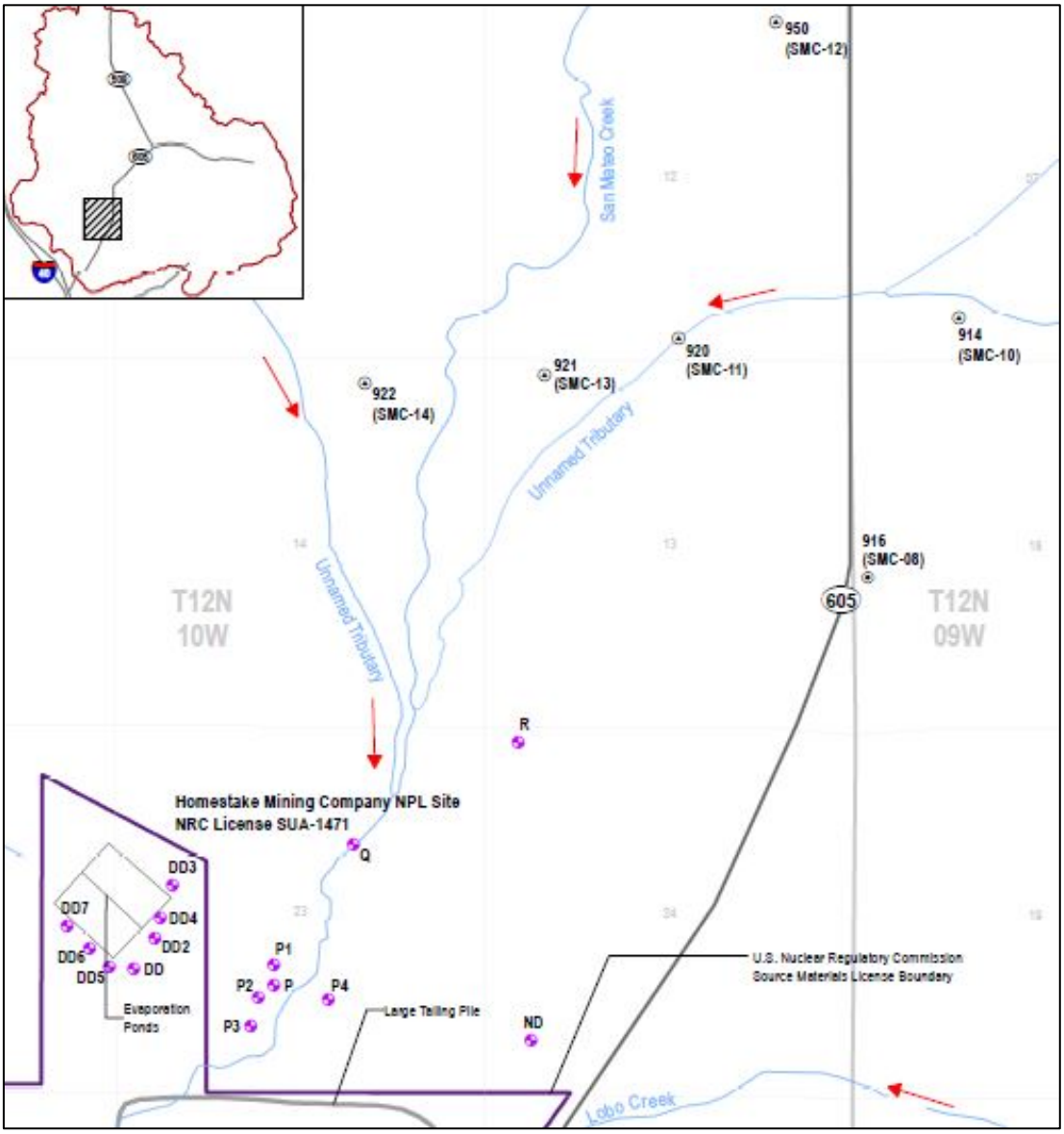

Figure 2. Alluvial monitoring well location map (modified from Figure A4-10, Weston Solutions, Inc. 2018).

In the lower floodplain south of Sand Curve, surface water flowing along San Mateo Creek was observed by local residents to reach as far downstream as the Homestake NPL Site and beyond during the period of mine-water discharge operations. Such flows were observed to occur during storm events that increased the volume of flow in the creek and resulted in widespread flooding. EPA documented this occurrence in the "Findings of an Initial Decision for the Johnny M Mine National Pollution Discharge Elimination System permit (NM 0026573)" (EPA 1980). EPA reported that San Mateo Creek flow had been observed to reach the LTP following heavy rains (Finding No. 10), and periodically (during five-year storm events) to continue past the LTP to the Rio San Jose (Finding No. 11). A rancher who owned property along San Mateo Creek

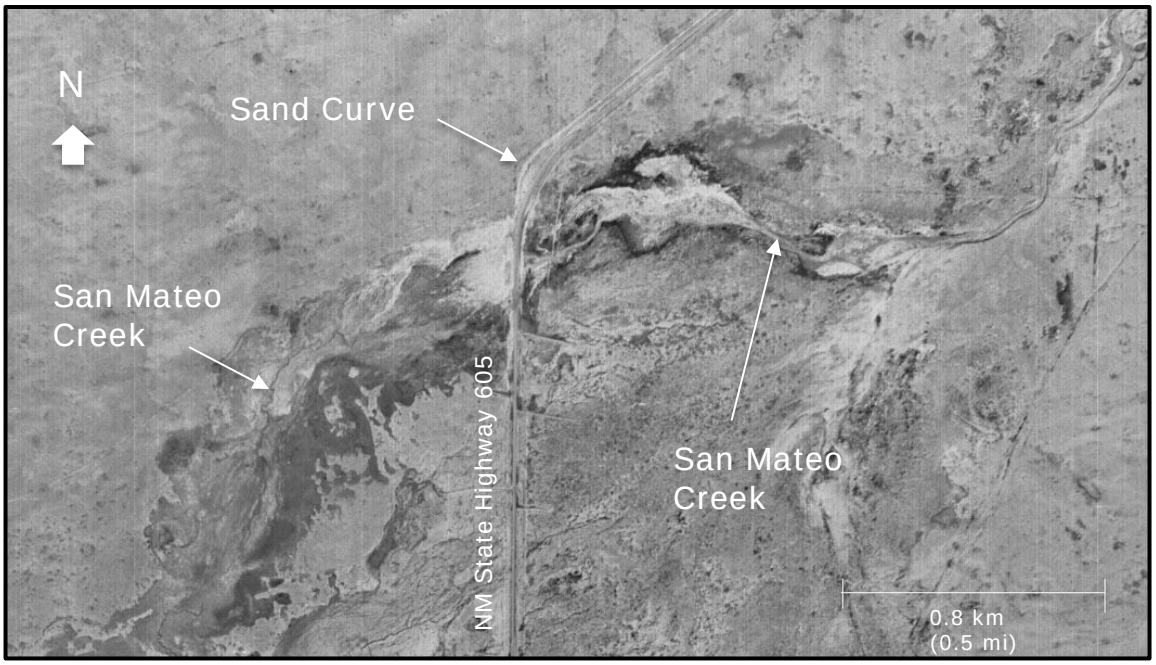

Figure 3. October 1958 aerial photograph of San Mateo Creek at Sand Curve (USGS Earth Explorer).

north of the LTP stated that the large storm events that flooded his property about every five years since the late 1950s sometimes occurred every year for a period of two to three years, with flood waters being as deep as 0.3 to 0.5 m (1 to 1.5 ft.) (K. South, personal communication 2021). An increase in San Mateo Creek surface flow during these storm events likely carried mine-water discharges mixed with storm-water runoff downstream at least as far south as the LTP at the Homestake NPL Site (EPA 1980) that provided recharge to the alluvium.

Earthen spreader dams built along San Mateo Creek in the late 1940s to divert or pond surface-water flow for cattle forage resulted in ponded, standing water after storm events (EPA 1980). Figure 4a shows the remnants of three earthen dams (Google Earth Pro 2021). At least 14 remnant earthen dams can be seen on a 2021 Google aerial image between Sand Curve and the LTP. A northeast-southwest curvilinear feature, which appears to be both a drainage ditch and earthen berm, is observed in a 1958 historical aerial photograph approximately 1.6 km (1 mile) north of the LTP (Figures 4b and 4c). From the photograph, it appears the berm is connected to one of the earlier earthen dams build across the creek. The berm and ditch may have served to divert some surface flow westward and away from San Mateo Creek, possibly toward an agricultural area west of the LTP (Purcell, personal communication 2020). The redirected surface-water flow path is toward well DD (see Figures 4b and 4c). It is assumed this feature was constructed at about the time mine-water discharges started to flow into the lower floodplain, as it is absent from a 1954 aerial photograph of the lower San Mateo Creek floodplain.

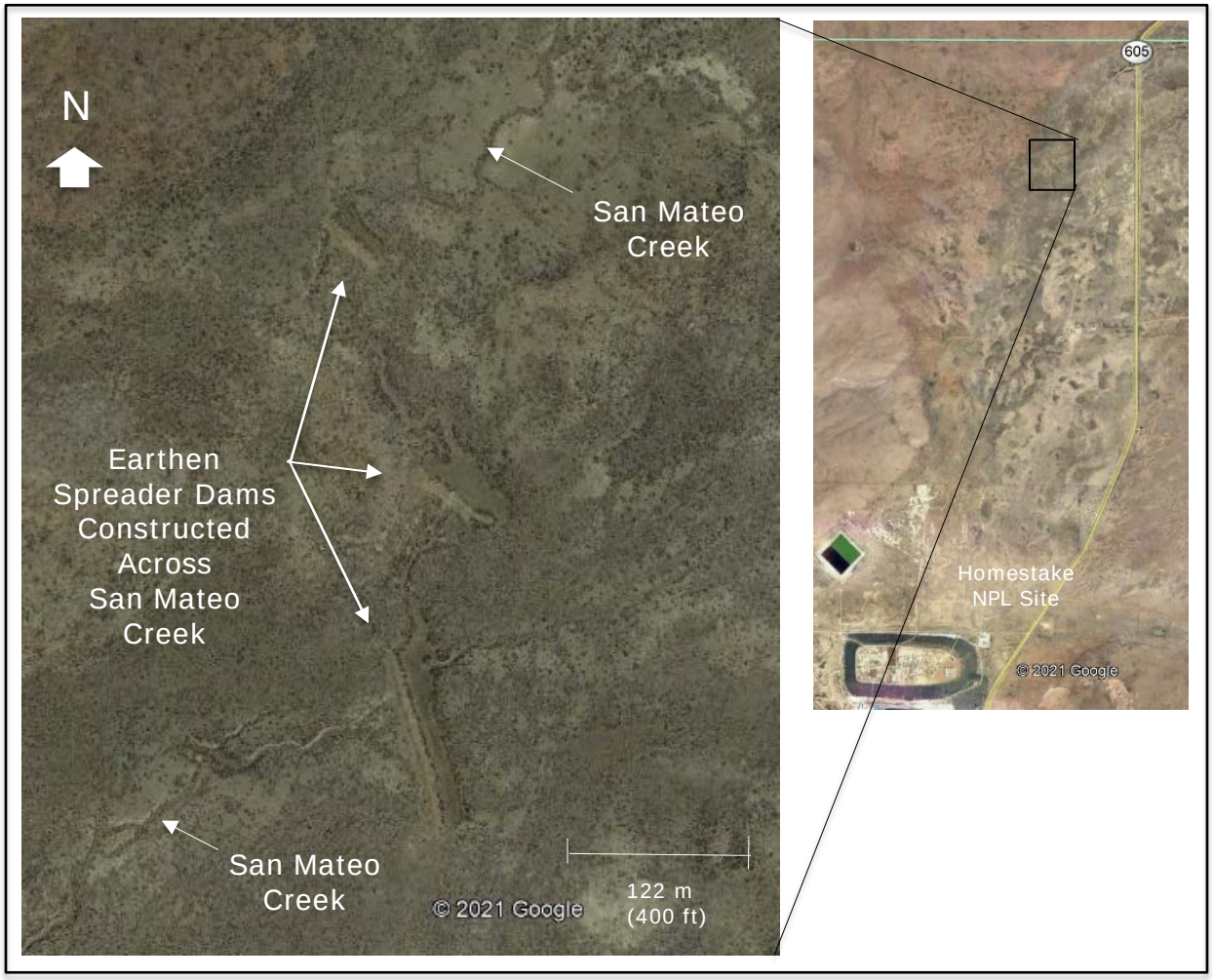

Figure 4a. 2021 Aerial image of remnant earthen spreader dams (Google Earth Pro 2021)

A 1971 historical aerial photograph of the lower San Mateo Creek floodplain north of the Homestake NPL Site shows a darker area that begins at the southwest end of the curvilinear drainage/berm feature and extends to the southwest, possibly indicating moister soil or more robust vegetative growth in response to an increase in the amount of surface water that is channeled to this area. From the photograph, it also appears that the area directly south and downstream of the east end of the curvilinear drainage/berm, along San Mateo Creek, is lighter in color than it was in the 1958 photograph, possibly suggesting less soil moisture or less robust vegetative growth in response to a decrease in the volume of surface water flowing into this area (Figures 5a and 5b).

Perkins and Goad (1980) provide historical hydraulic (flow) and chemical data for treated-mine water discharged to Arroyo del Puerto from 1977 to 1979 at five mine sites that operated in the Ambrosia Lake valley, including the former Kerr-McGee Corporation (Kerr-McGee), United Nuclear Corporation, Ranchers Exploration and Development Corporation (Ranchers), and United Nuclear-Homestake Partners (UN-HP) mines (Table 1). Mine-water discharges have

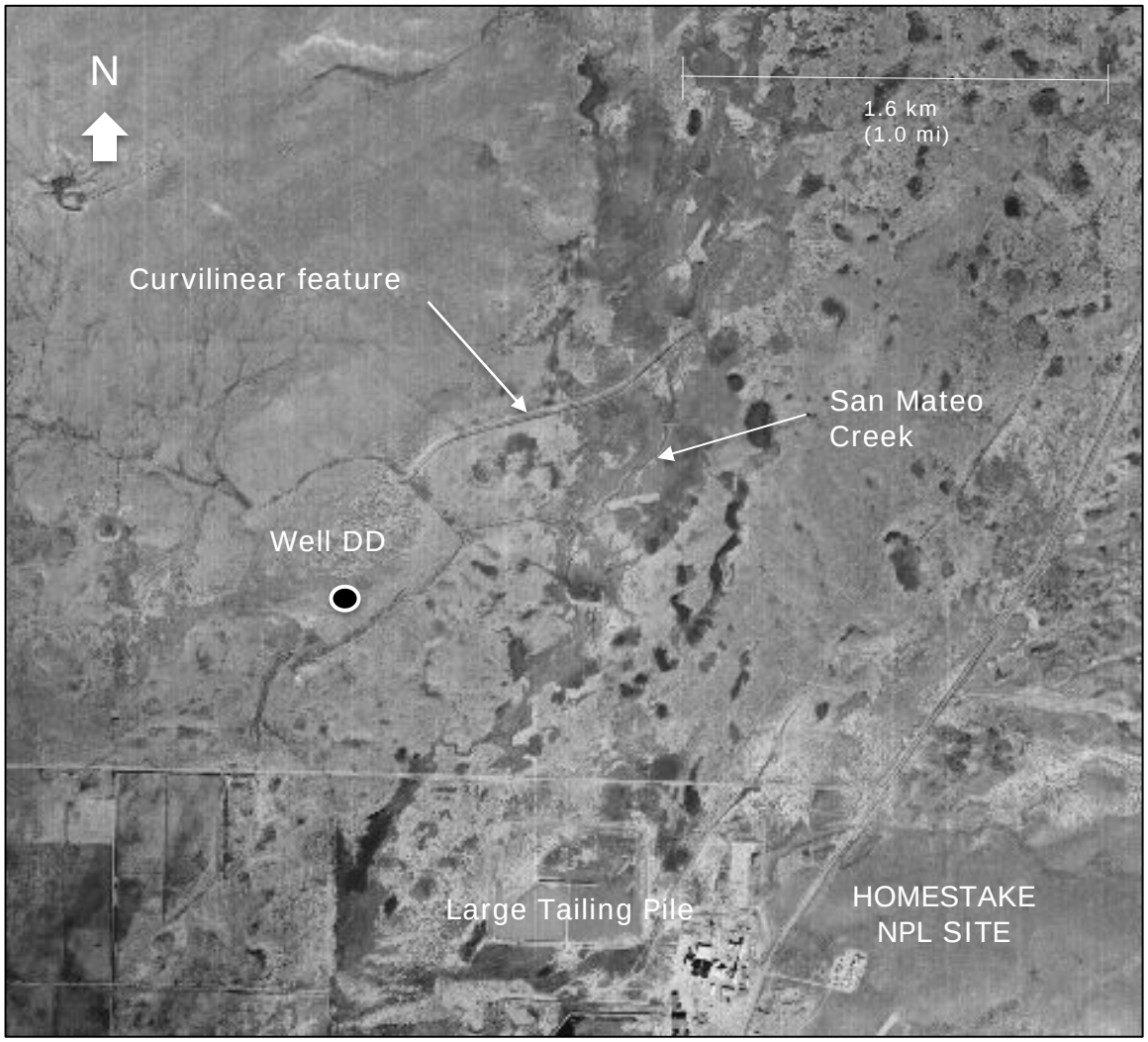

Figure 4b. 1958 Historical aerial photograph of lower San Mateo Creek north of the Homestake NPL Site, Grants, New Mexico (USGS Earth Explorer).

higher concentrations of major ions compared to native alluvial groundwater (e.g., well SMC-08/916); however, they generally have lower concentrations compared to alluvial groundwater at wells DD and DD2. Mine water pumped from the underground mines was collected in settling ponds, and the decant water was either pumped to an ion-exchange plant to remove uranium or discharged directly to surface drainages without removal of solutes (Weston Solutions, Inc. 2018, p. A1-21). Approximately 0.274 MGD of ion-exchange discharge water, originally sourced from the Westwater Canyon Member of the Morrison Formation, were released to Arroyo del Puerto in 1979 from the anion-exchange plant that operated at the former UN-HP facility. During anion exchange, dissolved uranium(VI) adsorbs on the exchange columns as uranyl carbonato complexes ($UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) and displaces chloride, which becomes concentrated in effluent water. The Environmental Improvement Division of the New Mexico Health and Environment Department sampled the outfall from the plant on

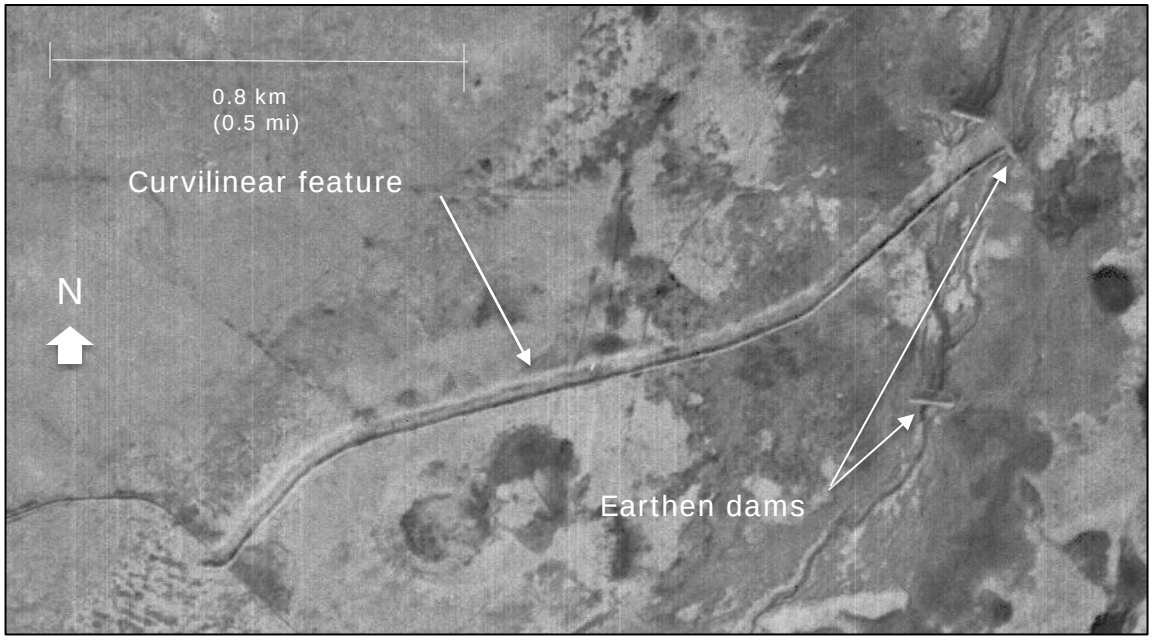

Figure 4c. Enlargement of curvilinear feature north of Homestake NPL Site in the 1958 aerial photograph (USGS Earth Explorer).

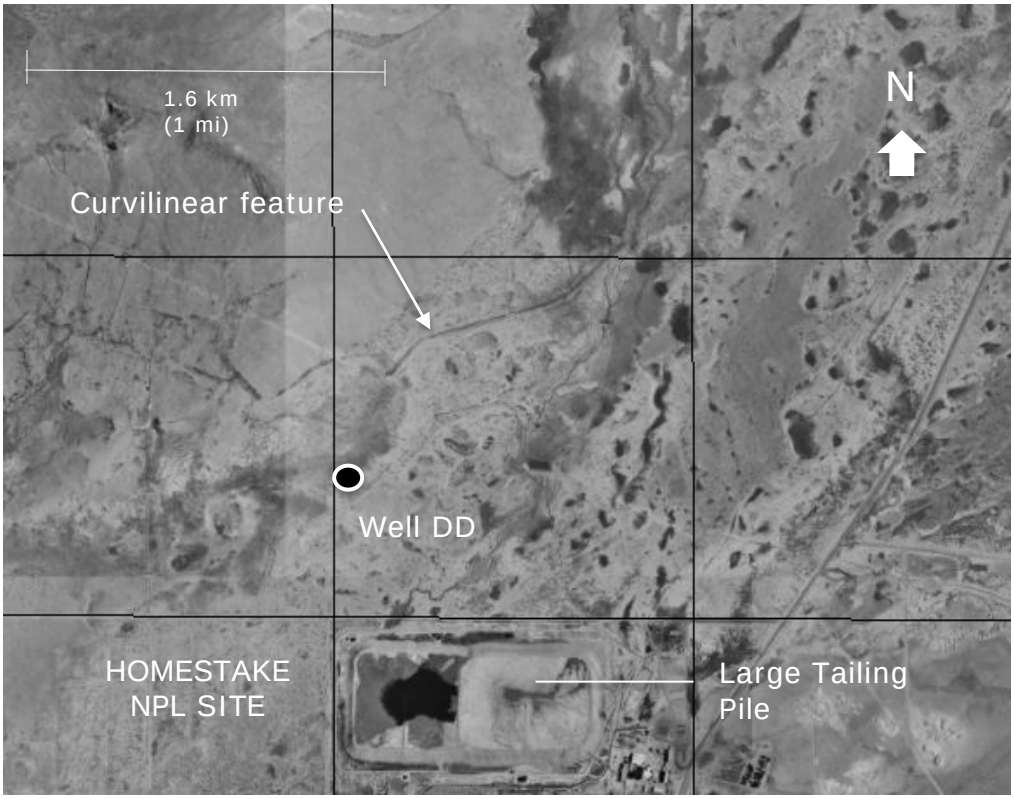

Figure 5a. 1971 Historical aerial photograph of lower San Mateo Creek floodplain north of Homestake NPL Site (USGS Earth Explorer).

November 6, 1979. The sample contained the following concentrations of dissolved analytes (in mg/L) and a pH of 7.25: TDS (1,695), bicarbonate (140), calcium (76.8), chloride (149), magnesium (106), molybdenum (1.331), nitrate plus nitrite(N) (2.09), potassium (12.1), selenium (1.047), sodium (244), sulfate (922), and uranium (2.42) (Perkins and Goad 1980). Mine-discharge waters are typically characterized by mixed cation-sulfate solutions.

The outfall water has a speciated charge balance of -4.67 percent calculated using the computer program PHREEQC. Analytical methods used by State Laboratory Division (SLD) in 1979 included atomic absorption spectrometry (molybdenum, selenium), fluorescence-sodium fusion (uranium), potentiometric titration (bicarbonate/carbonate), colorimetric analysis (chloride, nitrate plus nitrite, and sulfate), EDTA titration (calcium and magnesium), gravimetric analysis (TDS), and flame emission spectrometry (potassium and sodium). Several discharges released to Arroyo del Puerto from the former Kerr-McGee western and central Ambrosia Lake mines in 1977, 1978, and 1979 also had a mixed cation-sulfate composition and an average concentration of dissolve uranium of 2.5 mg/L. Perkins and Goad (1980) present additional water-quality data for several outfalls released to Arroyo del Puerto from the former United Nuclear Corporation (ion exchange), former Kerr-McGee Section 35 (ion exchange discharge), and Section 36 mine.

Perkins and Goad (1980) present analytical results for untreated mine water (from Westwater Canyon Member of the Morrison Formation and Dakota Sandstone Formation) sampled in the Section 35 mine formerly operated by Kerr-McGee. The mine water sampled on November 6, 1979, contained the following concentrations of solutes (in mg/L) and a pH of 7.4: TDS (1,323), bicarbonate (259), calcium (92.4), chloride (16.1), magnesium (28.6), molybdenum (2.856), nitrate plus nitrite(N) (0.84), potassium (6.63), selenium (0.238), sodium (274), sulfate (738), and uranium (5.66). The mine-water sample has a speciated charge balance of -0.72 percent and is a sodium and sulfate-dominated solution produced by mining activities, with maximum concentrations of molybdenum, uranium, and selenium in the low mg/L range.

Kelly et al. (1980) and Weston Solutions, Inc. (2018) report that the major-ion chemistry of mine-water discharges released to Arroyo del Puerto and San Mateo Creek evolved over time during mine dewatering that occurred from 1956 to 1982. Early-stage groundwater pumped from the mines consisted of a sodium-bicarbonate-sulfate composition dominantly sourced from the Westwater Canyon Member of the Morrison Formation. More recent mine-water discharges consisted of a sodium-sulfate composition that included a significant volume of groundwater sourced from the overlying Dakota Sandstone Formation. Downward migration of Dakota Sandstone Formation groundwater into the Westwater Canyon Member aquifer was enhanced along flow paths in transmissive faults and by an increasing cone of depression established by extensive mine dewatering (Kelly et al. 1980). Dissolved concentrations of calcium and sulfate are higher in Dakota Sandstone Formation groundwater compared to the Westwater Canyon Member, which is a major contributing source of these two solutes in mine-water discharges and alluvial groundwater in the San Mateo Creek Basin. The TDS of groundwater originally sourced from the Westwater Canyon Member was less than Dakota Sandstone Formation groundwater during mining (Kelly et al. 1980). Dissolved concentrations of either uranium, calcium, nitrate, selenium, sulfate, or TDS have increased in the alluvium aquifer after infiltration of mine water combined with additional leaching of soluble salts in the vadose zone north of the LTP under rising water-table conditions observed at wells DD, Q, and R.

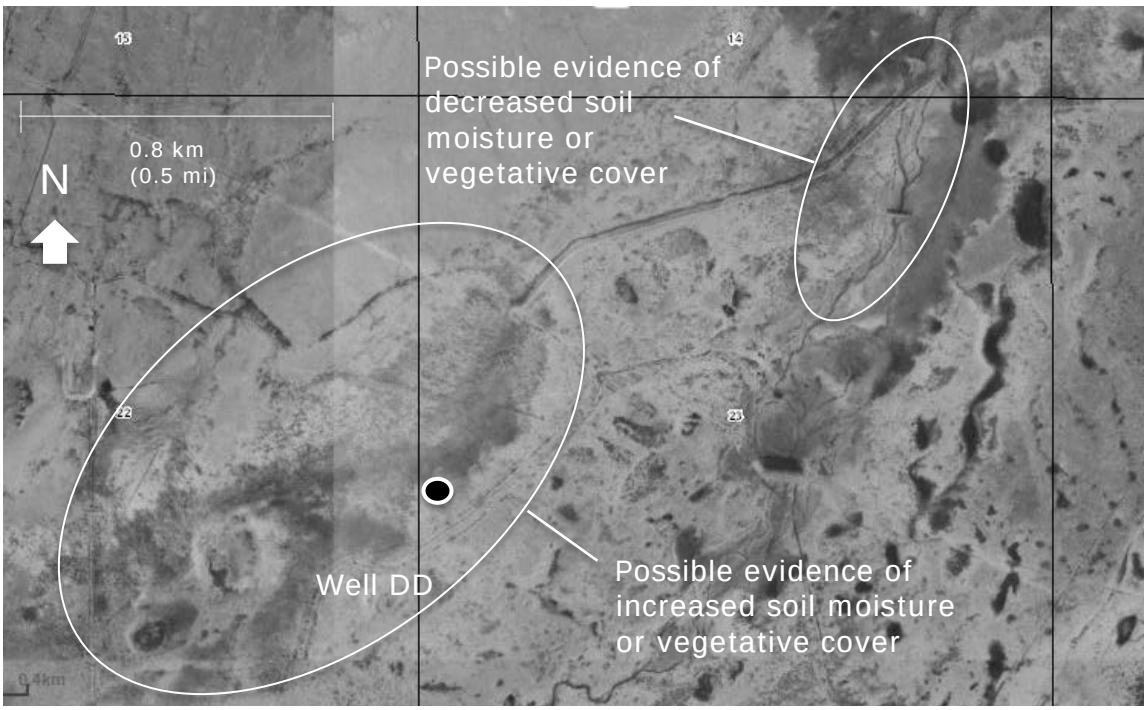

Figure 5b. Enlargement of 1971 historical aerial photograph of lower San Mateo Creek floodplain showing potential effect of curvilinear drainage/berm feature.

Table 1. Major ion and trace element chemistry of ion-exchange discharges released to Arroyo del Puerto in Ambrosia Lake area from 1977 to 1979 (Perkins and Goad 1980). Discharge waters were originally sourced from Westwater Canyon Member of the Morrison Formation and Dakota Sandstone Formation.

Analyte (mg/L)	Mean	Minimum	Maximum	Number of samples
Calcium	100	55.2	178.4	7
Magnesium	48.0	11.5	106	3
Sodium	229	101	428	11
Potassium	7.40	3.51	12.10	7
Bicarbonate	212	140	246	7
Chloride	93.0	8.8	490	11
Sulfate	622	184	1,060	11
Molybdenum	0.876	0.240	1.331	11
Nitrate + Nitrite(N)	0.75	0.12	2.29	8
Selenium	0.239	0.008	2.440	11
Uranium	1.55	0.32	2.95	11
Vanadium	0.133	0.025	0.185	6
Total Dissolved Solids	1,261	511	1,852	11
pH (median)	8.08	7.25	8.35	7

2.2 Hydrology of Alluvial Aquifer

Surface water containing mine-water discharge flowed downstream during episodic storm events (EPA 1980) to near the northern boundary of the Homestake NPL Site and provided local recharge to the alluvial aquifer along losing reaches of San Mateo Creek and adjacent areas of flooding and ponding north of wells DD and DD2. Decades of recharge from infiltrating mine water increased the saturated thickness of the alluvium in the lower San Mateo Creek floodplain on a very large scale (Weston Solutions, Inc. 2018). This long-term recharge and saturation event is evident by comparing water-level data measured at alluvial monitoring wells for different time periods since the mid-1950s.

Weston Solutions, Inc. (2018, Figures A4-8, A4-9, and A4-11) presents measured and estimated water-level data from the late 1950s to 2016 showing very large changes in water levels at several alluvial monitoring wells located between the Crossroads area and the Homestake NPL Site (Figure 6). The changing water levels represent changes in saturation thicknesses of alluvial sediments over time. During this roughly 60-year period, the saturated thickness increased by approximately 15.2 m (50 ft.) at well C-3, north of Sand Curve, 13.5 m (44.3 ft.) at well SMC-12/950, and 7.5 m (24.7 ft.) at well SMC-11/920. At the Homestake near-upgradient monitoring wells, the saturated thickness increased by approximately 5.0 m (16.5 ft.) at well R, 4.2 m (13.9 ft.) at well Q, 4.3 m ((14.0 ft.) at well P, and 3.8 m (12.6 ft.) at well DD. For the monitoring wells located in the farthest upgradient position on Figure 6 (north of Sand Curve (wells C-3 and B0415 O-8 to O-11)), the water-level data also show a subsequent decrease in saturated thickness (declining water level), suggesting a return to natural saturation conditions following cessation of mine-water discharge operations and aquifer recharge by 1982.

The fluctuating water table conditions and saturated thickness of the alluvial aquifer, as estimated by water level measurements taken at monitoring wells from the mid-1950s to 2016, are depicted on Hydrogeologic Cross-section A-A' prepared for this report (Figures 7a and 7b). From the cross section, the large-scale recharge event to the alluvial aquifer is evident, with greater rises in water levels at wells located in the northern portion of the lower floodplain and north of Sand Curve, and a gradual decrease in the magnitude of the water-level rise in wells going southward toward the LTP. The rise in water levels at the near upgradient monitoring wells R, Q, P, and DD is evident when comparing the 1956-60 water table to the 1976-77 water table.[4] The influence of aquifer pumping at well P by Homestake is also evident by the position of the 2000 water table, which is at a lower elevation than the 1976-77 alluvial water table.

Three groundwater elevation maps prepared for this report (Figures 7c, 7d, and 7e) show the groundwater-flow direction and hydraulic gradient of the alluvial aquifer at the Homestake NPL Site. The 1960 map is based on water-level data from Chavez (1961); 1976 and 1983 maps are based on Homestake data. The alluvial aquifer boundary depicted on the maps is based on a map of the base of alluvium structure by Weston Solutions, Inc. (2018) and groundwater elevations of the time period represented by each map. A comparison of Figures 7c and 7d

[4] The water table positions shown on Cross-Section A-A' at well DD do not match exactly with the water-level measurements depicted for well DD as they take into account that well DD is nearly 0.8 km (0.5 mi) west of the plane of the cross section and projected onto the section.

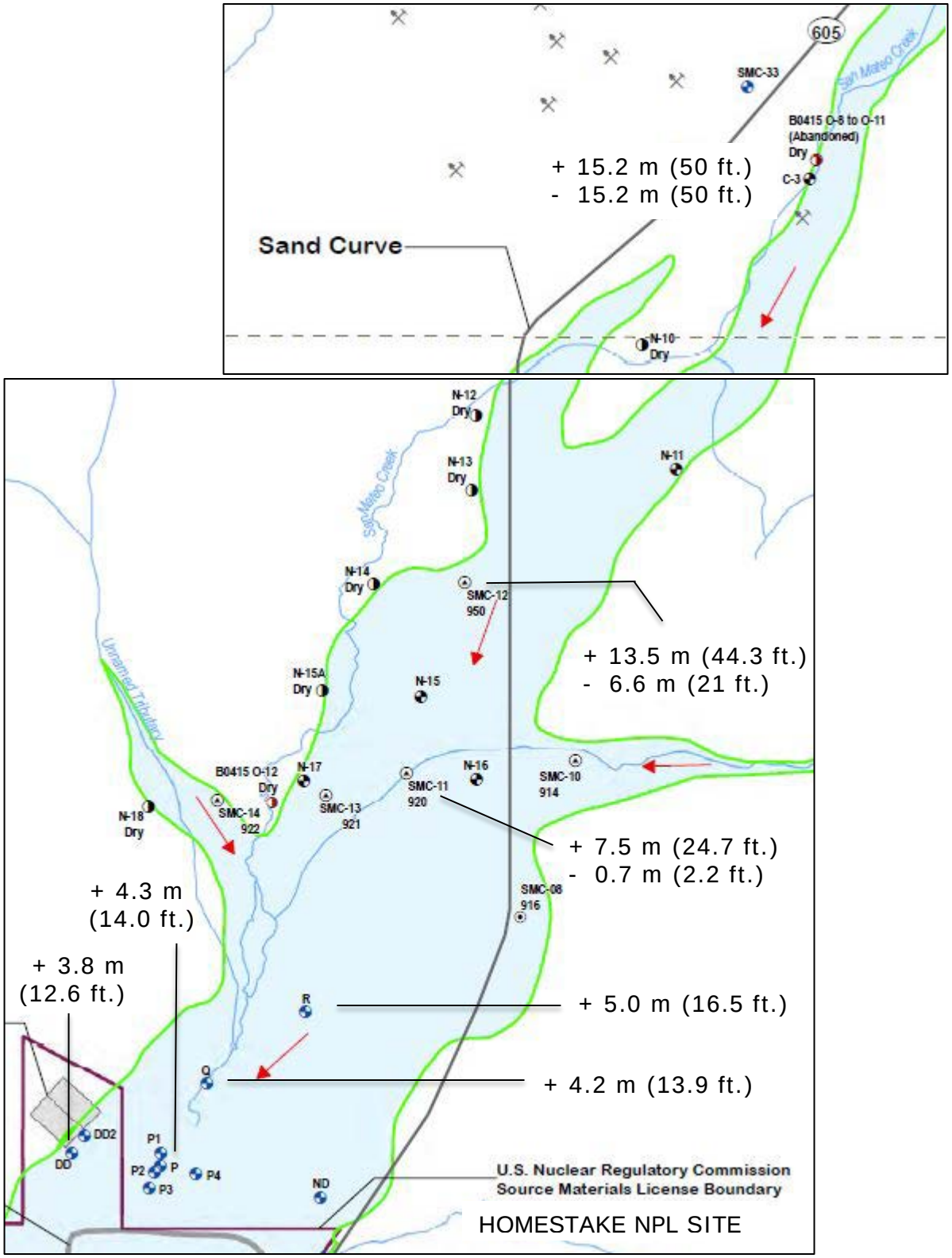

Figure 6. Mid-1950s to 2016 water-level changes in alluvial aquifer, lower San Mateo Creek floodplain (modified from Figure A4-11, Weston Solutions, Inc. 2018).

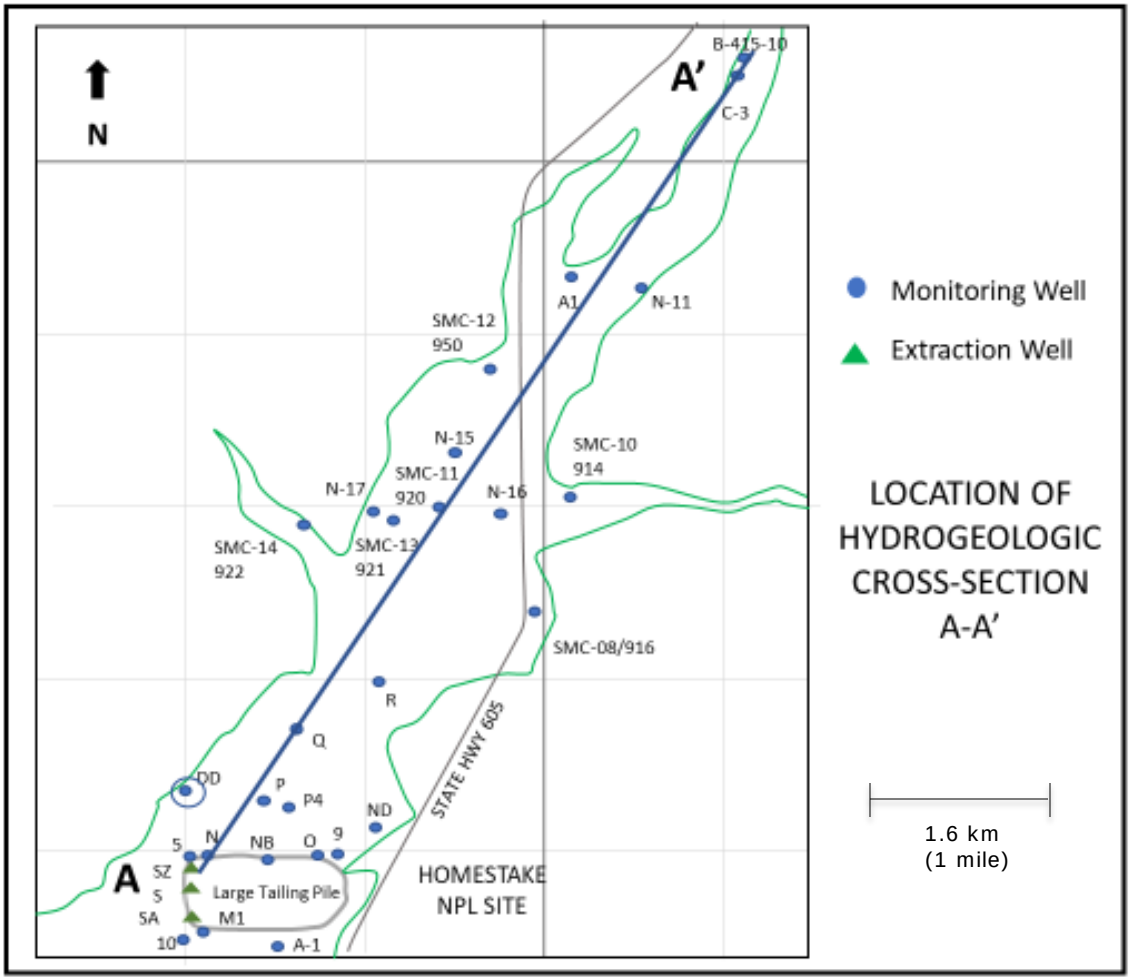

Figure 7a. Hydrogeologic Cross-Section A-A' Location Map

shows the amount of increase in saturated thickness at the near-upgradient monitoring wells between 1960 and 1976. At the well DD location, the saturated thickness increased approximately 1.8 m (5.9 ft.) between 1960 and 1976, as the groundwater elevation increased from approximately 6532.5 ft. above mean sea level (amsl) (map interpretation, Figure 7c) to 6538.4 ft. amsl (water-level measurement at well DD, Figure 7d).[5] This observed increase is likely attributed to a combination of infiltrating mine water recharging the alluvium and groundwater mixing in the area of well DD, plus the effect of the unlined LTP on the hydraulic gradient of the alluvial aquifer (i.e., a flattening of the southwest gradient at and north of the LTP caused by rising water levels at the LTP in response to tailing seepage).[6] In comparison, the increase in saturated thickness at well Q from 1960 to 1976 is approximately 0.7 m (2.3 ft.).

[5] Although wells DD and Q were not constructed until 1976, their locations are depicted on the 1960 map, along with their 1976 groundwater elevations, to aid in the comparison of the two maps. The 1960 groundwater elevation contours and the location of the 1960 Chavez wells are also depicted on the 1976 map for the same purpose.

[6] Annual mean precipitation rates reported for the Grants-Milan Municipal Airport from 1954 to 2016 showed precipitation to be below the cumulative average annual precipitation of 10.10 inches for nearly the entire period from 1960 to 1976 (Weston 2018, Figure A1-9).

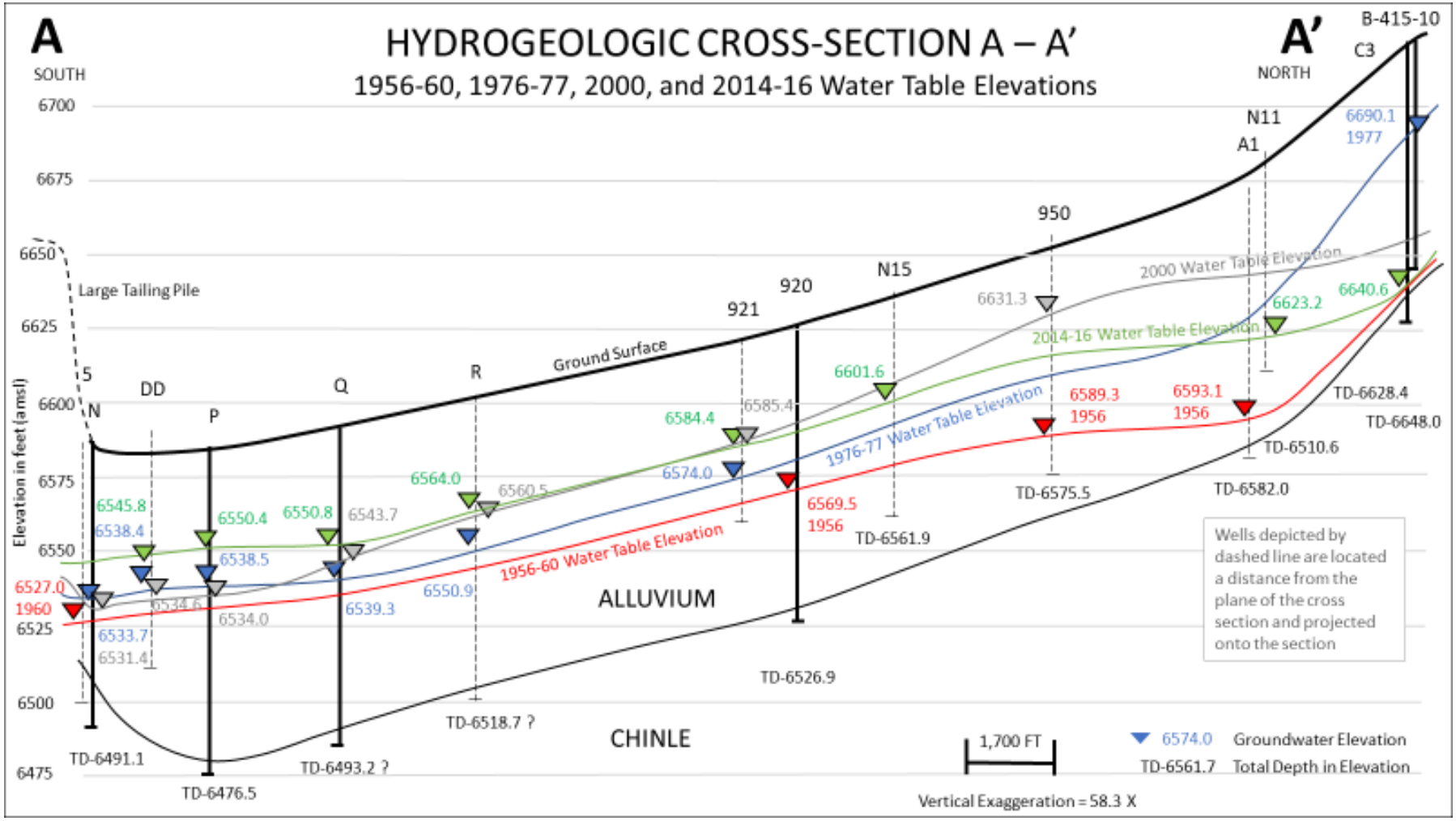

Figure 7b. Hydrogeologic Cross-Section A-A'.

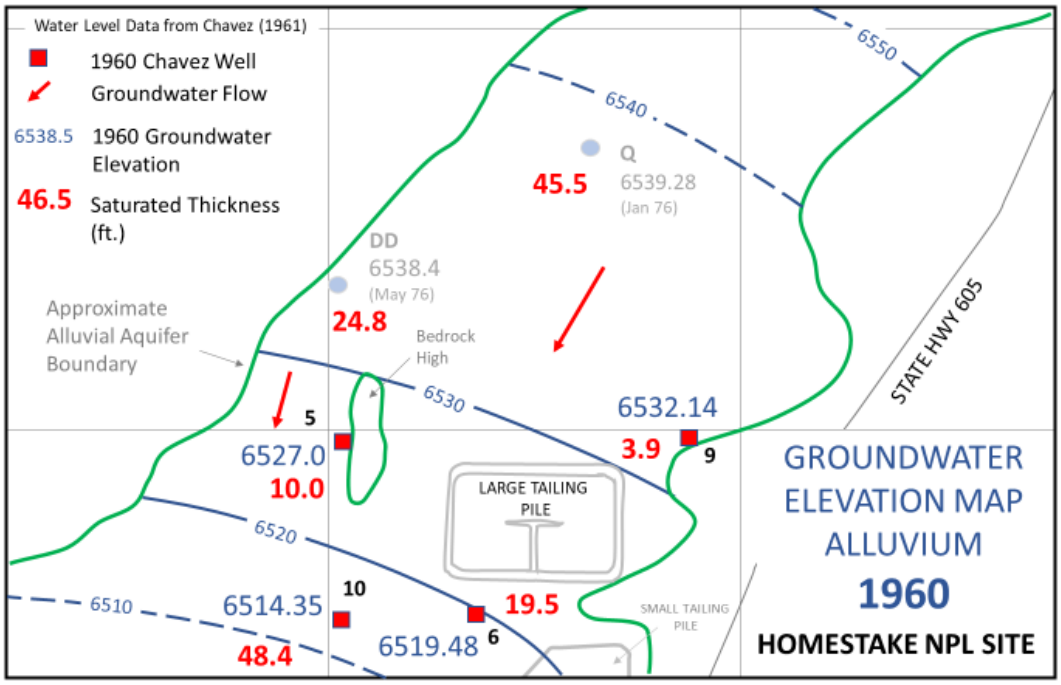

Figure 7c. Groundwater elevation map for the alluvial aquifer in 1960.

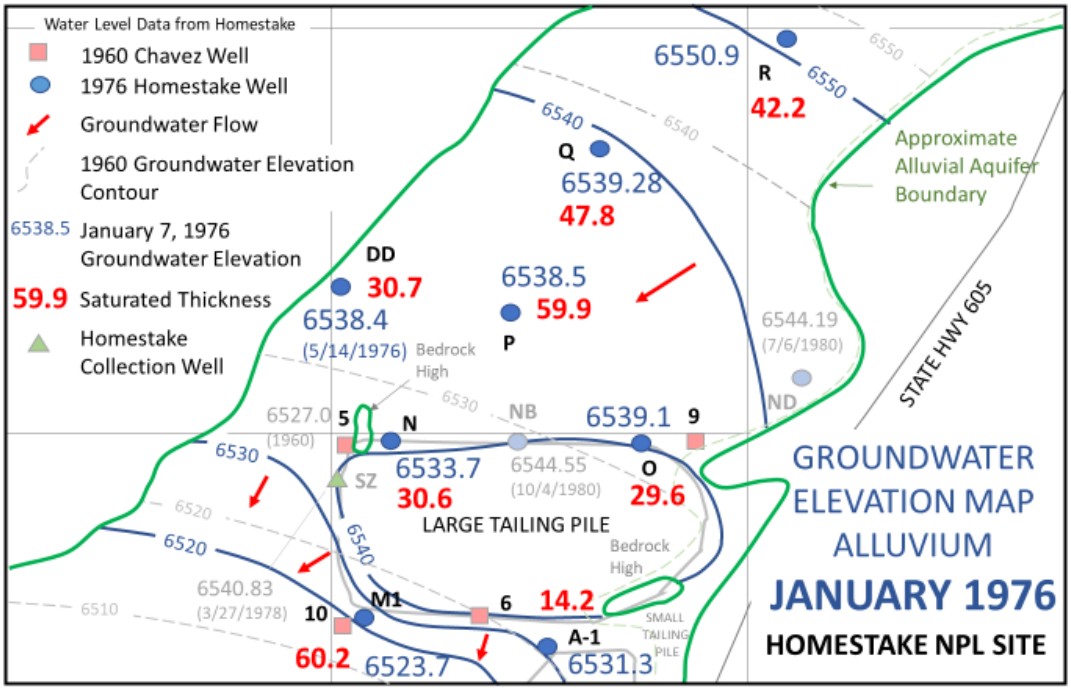

Figure 7d. Groundwater elevation map for the alluvial aquifer in 1976.

Well Q is located farther upgradient of the LTP than well DD and has about one third of the increase in saturated thickness estimated at well DD, suggesting that the LTP tailing seepage has less of an hydraulic effect on well Q due to its greater distance from the LTP. The increasing saturated thickness, shown at the Homestake near-upgradient monitoring wells from 1960 to 1976, is consistent with groundwater modeling performed by Homestake (2016). The saturated thickness of the alluvium, which is depicted for each well on Figures 7c and 7d, ranges from 1.2 m (3.9 ft.) to 18.3 m (60.2 ft.). The paleotopography of the base of the alluvium controls the variable saturated thickness of the aquifer, from the central axis of the San Mateo Creek paleochannel to its eastern and western boundaries. This may be a contributing factor controlling the extent of mixing of native alluvial groundwater with infiltrated mine water, especially at wells P, Q, R, DD, and DD2.

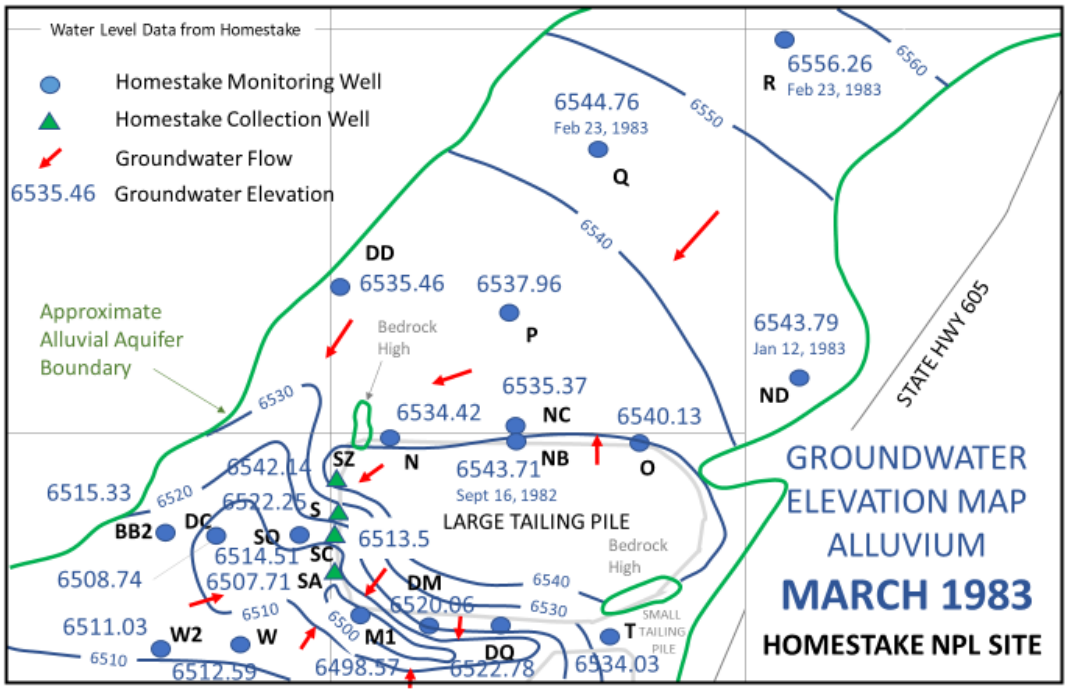

Figure 7e. Groundwater elevation map for the alluvial aquifer in 1983.

Alluvium saturated thickness has continued to increase in wells R and Q to present day, while at well DD and other wells, a decrease in saturated thickness was observed for a number of years beginning in the early 1980s. The decrease is attributable to aquifer pumping that commenced in the late 1970s/early 1980s as part of the Homestake NPL Site groundwater remediation. The 1983 groundwater elevation map (see Figure 7e) shows the influence of pumping on the hydraulic flow regime along the western and southern perimeters of the LTP. A chart of hydrographs for wells R, Q, P, DD, and SC (an alluvial pumping well) depicts the fluctuating water levels from 1976 to 1984 (Figure 8a). The drawdown of the water level at pumping well SC corresponds to water-level declines in wells DD and P. A chart of hydrographs for a larger set of upgradient monitoring wells depicts the fluctuating water levels from the late 1950s through 2020 (Figure 8b). The water level changes for Homestake pumping well SZ is also depicted on this chart to show the influence aquifer pumping had on other wells.

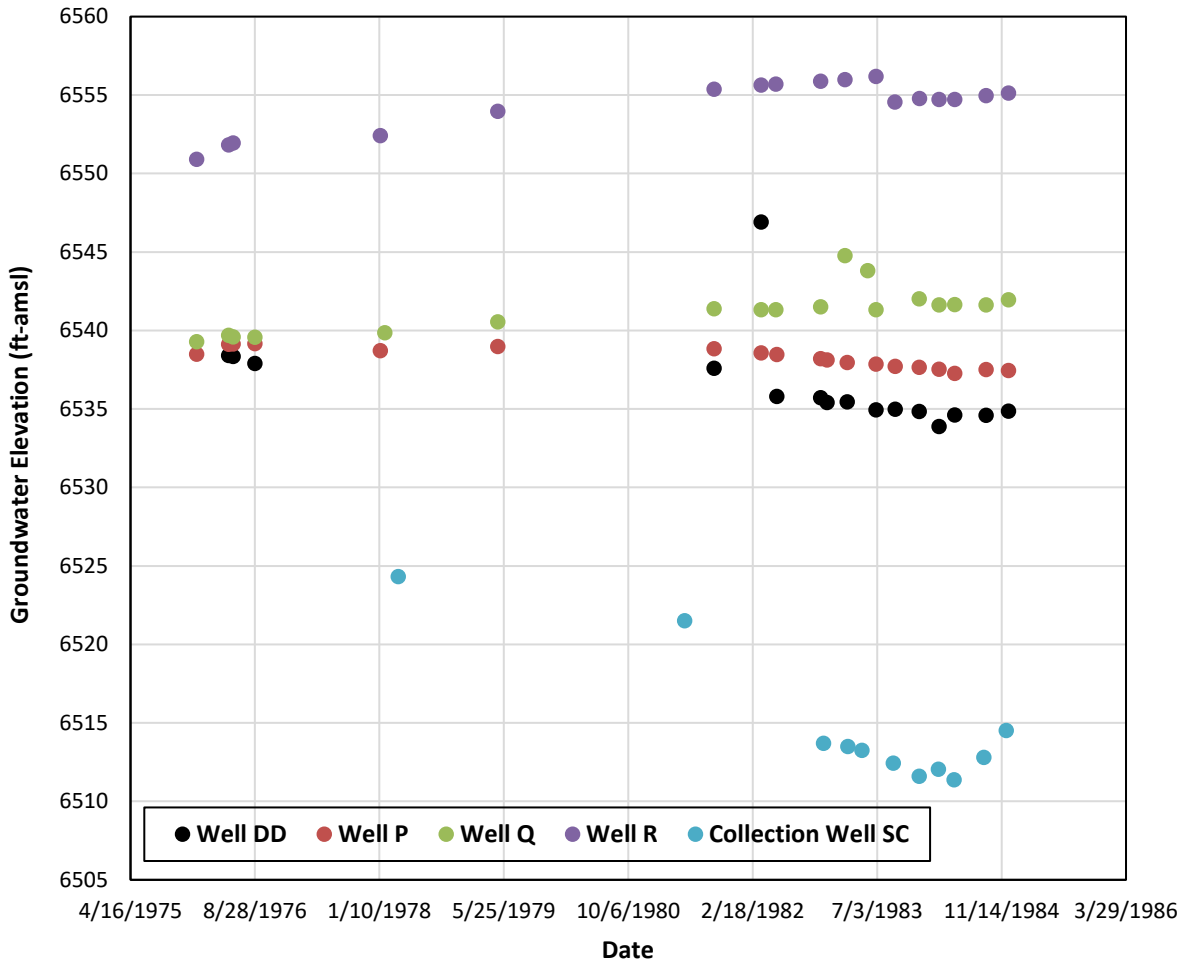

Figure 8a. Hydrographs of alluvial monitoring wells DD, P, Q, and R, and alluvial collection well SC from 1976 to 1984.

The hydrographs depicted on Figure 8b show rising water levels for the far upgradient monitoring wells (SMC-10/914, SMC-11/920, SMC-12/950, SMC-13/921, and SMC-08/916) with the exception of well SMC-14/922, which is located in a tributary drainage west of the San Mateo Creek paleochannel (Weston Solutions, Inc. 2018). The water levels begin to rise at these wells sometime after the mid-1950s. For wells SMC-13/921 and SMC-10/914, a subsequent lowering of water levels is also observed beginning in the early 2000s. For the other far upgradient alluvial monitoring wells, it is likely that water levels may be dropping, however, there are an insufficient number of water-level measurements at those wells to show a downward trend on the hydrographs.

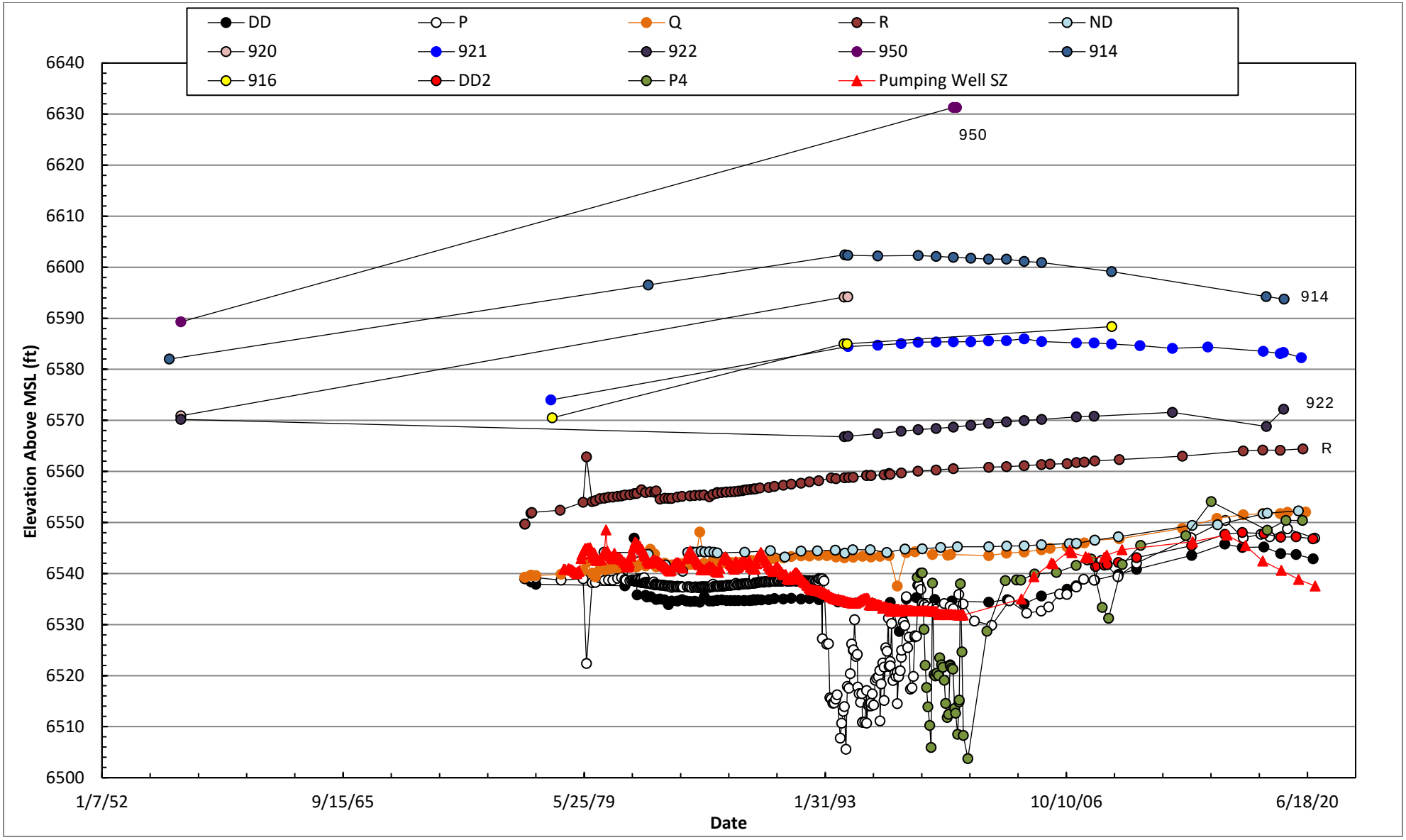

Figure 8b. Hydrographs of alluvial monitoring wells upgradient of Homestake NPL Site from early 1950s to 2020.

The hydrographs depicted on Figure 8b for the near upgradient alluvial monitoring wells R and Q show rising water levels from the time they were constructed in 1976. The hydrographs for the other near upgradient alluvial monitoring wells located closer to the LTP (DD, DD2, P, P4 and ND) indicate that Homestake's groundwater pumping operations caused fluctuation of the water table in the area of these wells. The fluctuating water levels correspond with water-level changes at pumping well SZ. The large water-level drawdowns observed at wells P and P4 from about 1993 to 2001 also reflect the effect of pumping operations at those wells. The water levels at well DD show a fairly constant to gradually lowering trend over many years while Homestake pumped the alluvial aquifer. However, beginning in about 2004, a rise in the water level at well DD and then a subsequent lowering in about 2015 correspond with a rise and lowering of the water levels in pumping well SZ. Similar fluctuations to water levels are observed at wells DD2, and P. Although well Q shows a continual upward trend in water levels from 1976 to 2020, pumping operations appear to have some effect on the water table at well Q. This is evident by a gradual steepening of the upward trend that corresponds with the cessation of pumping of well P4 in 2003. Well Q is located approximately 1.2 km (0.7 miles) north of the LTP.

3.0 Historical Groundwater Geochemical Data for the Alluvial Aquifer

Recharge of historical mine-water discharges to the alluvial aquifer in San Mateo Creek Basin that increased the saturated thickness of the aquifer also changed the chemistry of the groundwater from a sodium-sulfate-bicarbonate solution to a calcium-sodium-sulfate solution (Homestake database). The aqueous chemistry of alluvial groundwater in San Mateo Creek Basin prior to the recharge by mine-water discharges beginning in 1956 is not known with absolute certainty, based on paucity of published results for major ions, nutrients, and trace elements. Brod and Stone (1981) and Homestake (2019) provide groundwater geochemical data for numerous alluvial and bedrock wells located within the San Mateo Creek Basin. On August 24, 1977, Brod and Stone (1981) sampled an alluvial well (well no. A5), located 2.4 km (1.5 miles) northeast of the Homestake NPL Site near the eastern boundary of the alluvial aquifer (Figure 2). Weston Solutions, Inc. (2018) lists this well as SMC-08 and Homestake (2019) designates it as 916. The total depth of well SMC-08/916 is 30.5 m (100 ft.). The depth to the alluvial water table was 16.6 m (54.5 ft.) below ground surface at the time of sampling in August 1977 (Brod and Stone 1981). Analytical results for well SMC-08/916 are provided in Table 2. Groundwater samples collected from well SMC-08/916 have relatively low concentrations of major cations and anions compared to sample data from other numerous alluvial monitoring wells sampled by Homestake on a regular basis. Well SMC-08/916 samples are characterized by a sodium-bicarbonate composition compared to well DD having a calcium-sodium-sulfate composition. Concentrations of nitrate(as N) measured in groundwater samples collected from well SMC-08/916 average 4.54 mg/L between 1997 and 2005, and its origin is unknown. Mean dissolved concentrations of selenium and uranium are 0.017 mg/L and 0.0086 mg/L, respectively. It is likely that alluvial groundwater at this location is not impacted by historical mine-water discharges and possibly represents a component of native (non-mining influenced) groundwater in this area of the alluvium. Drilling of additional alluvial wells north of well SMC-08/916 along the eastern boundary of the alluvial aquifer should provide more data for assessing natural background groundwater quality.

Table 2. Analytical results of groundwater sampling conducted by Homestake (1997 – 2005) and Brod and Stone (1981) at alluvial well SMC-08/916, located hydraulically upgradient (northeast) of the Homestake NPL Site, Cibola County, New Mexico.

Parameter	Brod and Stone (1981) (08-24-77)	Homestake Mean Concentrations (1997 – 2005) (n = 8, except where noted)
Bicarbonate (mg/L)	293	252
Bicarbonate Alkalinity (mg $CaCO_3$/L)	240	207
Chloride (mg/L)	24	26.3
Sulfate (mg/L)	49	46.5
Nitrate-N (mg/L)	3.6	4.54 (n = 7)
Calcium (mg/L)	14	5.5
Magnesium (mg/L)	3.9	1.3
Sodium (mg/L)	134	127.4
Potassium (mg/L)	0.5	1.4 (n = 2)
Selenium (mg/L)	Not Reported	0.017
Uranium (mg/L)	Not Reported	0.0086
Total Dissolved Solids (mg/L)	445	371
Speciated Cation-Anion Charge Balance (%, 25°C)[1]	+7.8	+4.41
pH	Not Reported	8.19 (median)

[1.] Speciated charged calculated balance performed by P. Longmire, using PHREEQC, on May 11 and 12, 2020.

Figure 9 shows dissolved concentrations of uranium versus time at wells DD, DD2, ND, P, P1, P2, P3, P4, Q, and R (Myers 2020). Lower concentrations of dissolved uranium, typically less than 0.060 mg/L, are observed at wells P, P1, P2, P4, and ND since 2000, while higher concentrations of this actinide are observed at wells DD and DD2 (Myers 2020). The trend of uranium concentrations at well DD is characterized by a concave-downward curve, with maximum uranium concentrations occurring from approximately 1997 to 2009 and decreasing since about 2008. Infiltration of mine-water discharges to the alluvial aquifer north of well DD may have produced the strong transient chemical conditions observed through 1990, as illustrated by several spikes in uranium concentrations.

Similar concentration spikes in dissolved chloride, nitrate-N, selenium, sulfate, or TDS are also observed at wells DD, Q, P, and R (Homestake database) (Figure 9). This observation supports the concept that episodic infiltration of mine-water discharges and mixing with native alluvial groundwater produced transient geochemical conditions in the alluvial aquifer north of the LTP. Distributions of dissolved concentrations of uranium observed over time at well DD suggest that there is higher variability in uranium mass along a specific groundwater-flow path in alluvial groundwater compared to other background monitoring wells north of the LTP. The increasing slope of the concave-downward curve, with variable concentrations, suggests that an advancing uranium plume migrated along one or more preferred groundwater-flow paths leading to well DD. The decreasing trend of uranium concentrations at wells DD and DD2 since about 2008 also suggests that the centroid of a uranium plume has migrated past these wells.

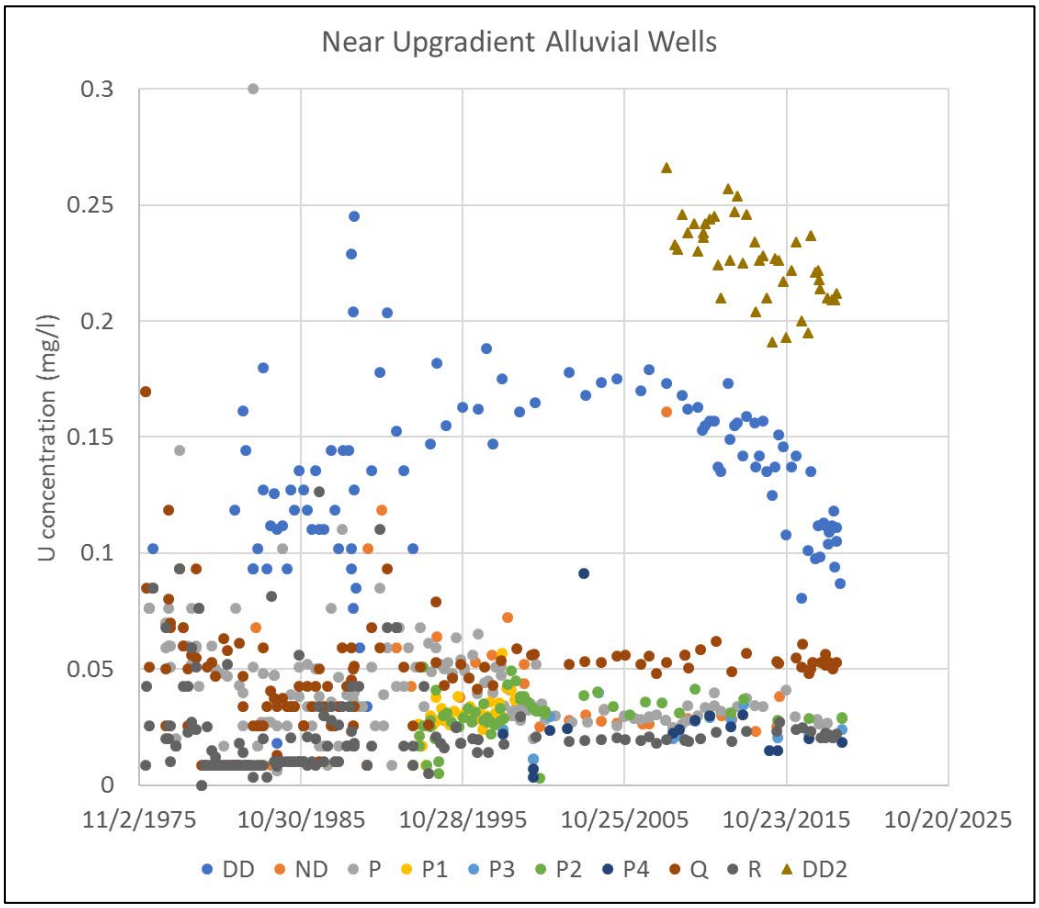

Figure 9. Dissolved concentrations of uranium versus time at background monitoring wells DD, DD2, ND, P, P1, P2, P3, P4, Q, and R north of the large tailing pile (LTP), Homestake NPL Site, Cibola County, New Mexico (Myers 2020). (Data source: Homestake database).

Dissolved concentrations of bicarbonate, calcium, chloride, sodium, sulfate, and uranium versus time at well DD are shown in Figure 10. Dissolved concentrations of bicarbonate, chloride, and sodium are fairly constant from 1997 to 2019 and possibly represent steady-state chemical conditions. Concentrations of calcium and sulfate, however, gradually increase over time beginning in about 2008, suggesting that these two solutes are being leached from the vadose zone during rising (and subsequent lowering) water-table conditions observed at well DD since 2005 (see Figure 8b). Concentrations of dissolved uranium gradually decrease during this same time period, which is opposite to the dissolved calcium and sulfate trends. This decreasing uranium trend occurs independent of the rise and lowering of the water table at well DD.

The geochemical information presented on Figure 10, together with the hydrological information presented on Figures 8a and 8b, support an alternate hypothesis that the transient chemical conditions observed at wells DD and DD2 are a result of vadose leaching caused by water table fluctuations associated with Homestake's groundwater pumping operations near the LTP. However, this hypothesis is only supported for some chemicals such as dissolved calcium and sulfate, not dissolved uranium. Homestake's groundwater pumping operations, the infiltration and recharge by mine-water discharges, and the hydraulic influence of tailing

seepage on the alluvial aquifer are likely the most significant factors contributing to alluvial water table fluctuations upgradient of the LTP that caused vadose zone leaching and chemical transience since the 1950s (see Figures 7b, 7c, 7d, 8a, and 8b). Hence, the three end members influencing groundwater chemistry at well DD consist of (1) native groundwater residing in the alluvium for centuries or longer; (2) infiltration of mine-water discharges since 1956; and (3) hydrological and chemical impacts associated with a fluctuating alluvial water table and vadose zone leaching.

Surface-water flow containing mine-water discharges represents the early stage of non-point recharge in San Mateo Creek Basin eventually impacting wells DD and DD2. Groundwater mixing occurs at a slower rate controlled by groundwater-flow velocities when compared to surface-water transport, which acts as a non-point source of recharge. Lower dissolved concentrations of uranium measured at wells P, Q, and R may result from a mixture of a larger fraction of native alluvial groundwater and a smaller fraction of uranium-enriched mine water compared to wells DD and DD2, which have higher fractions of infiltrated mine water.

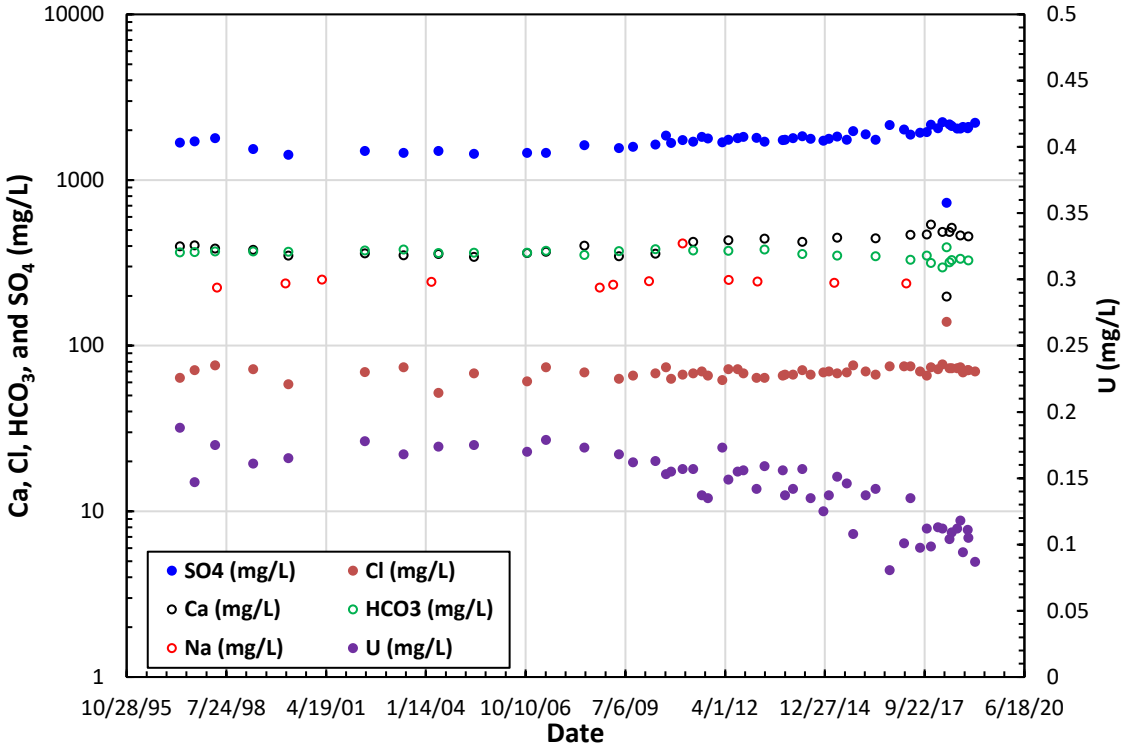

Figure 10. Dissolved concentrations of bicarbonate, calcium, chloride, sodium, sulfate, and uranium versus time at background monitoring well DD northwest of the large tailing pile (LTP) Homestake NPL Site, Cibola County, New Mexico (Data source: Homestake database; note the log scale for the left y-axis).

Inverse relationships occur between dissolved concentrations of sulfate and uranium (Figure 11) and calcium and uranium (Figure 12) since 2006 at well DD. The increases in dissolved concentrations of sulfate and calcium, starting in 2008, may result from groundwater mixing of native alluvial groundwater with infiltrated mine water and vadose zone leaching that produce geochemical transients. Dissolved concentrations of uranium gradually decrease at well DD

since May 2008, possibly in response to either geochemical interactions or dilution by groundwater with lower concentrations of uranium. Dissolved concentrations of calcium, sulfate, and uranium at well DD are not representative of natural groundwater background as evident by changing dissolved concentrations.

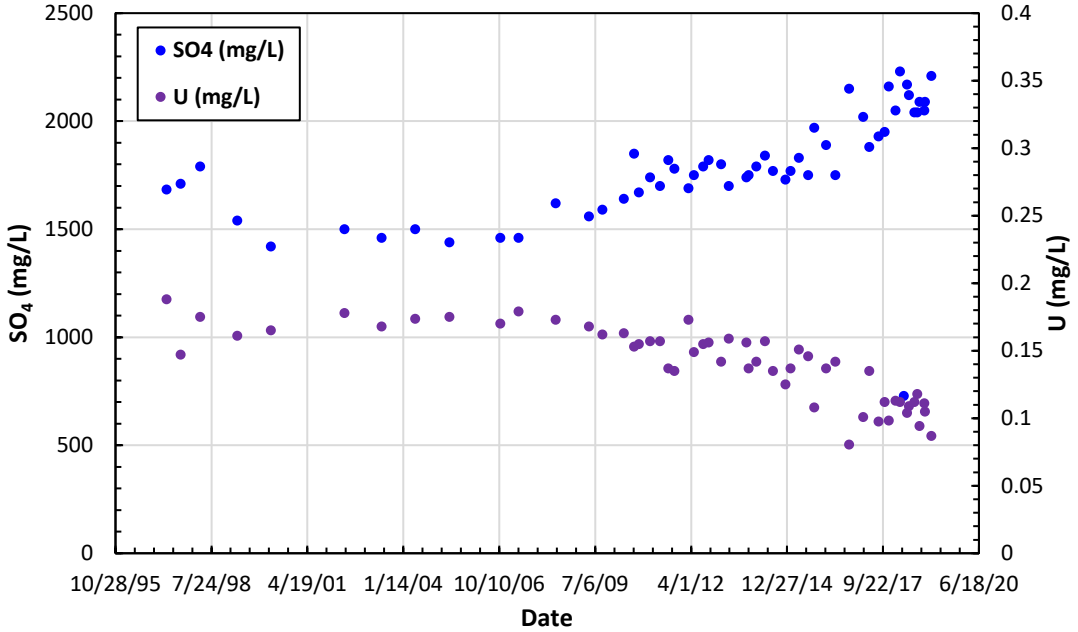

Figure 11. Dissolved concentrations of sulfate and uranium versus time at background monitoring well DD north of the large tailing pile (LTP), Homestake NPL Site, Cibola County, New Mexico (Data source: Homestake database).

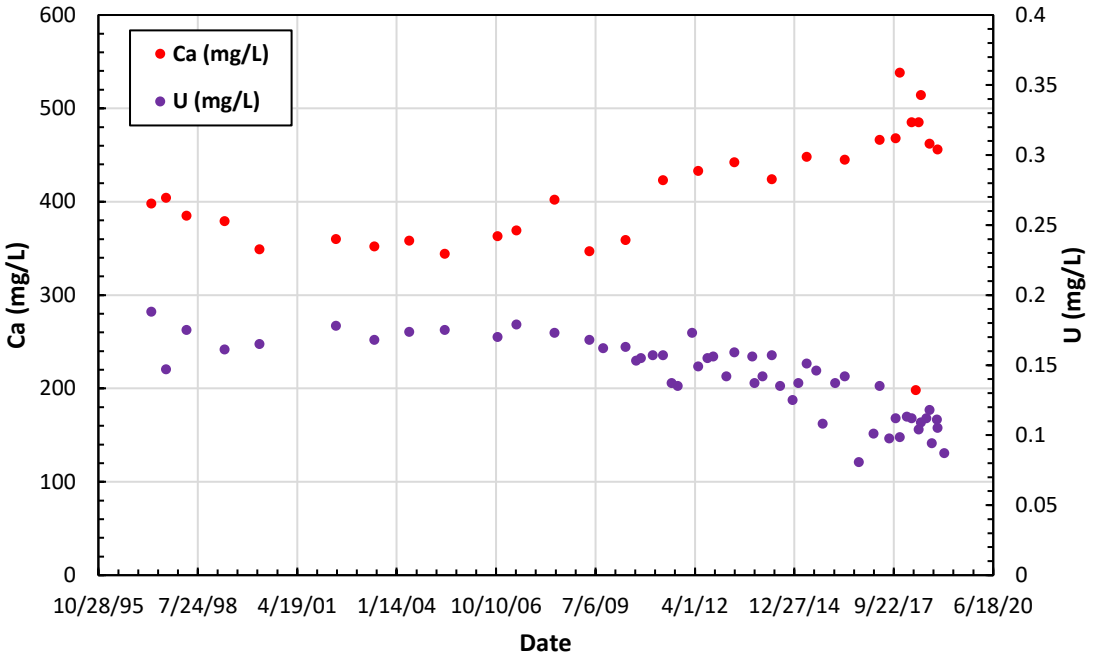

Figure 12. Dissolved concentrations of calcium and uranium versus time at background monitoring well DD north of the large tailing pile (LTP), Homestake NPL Site, Cibola County, New Mexico (Data source: Homestake database).

It can be reasonably assumed that prior to recharge from industrial surface water and vadose zone leaching of chemicals in San Mateo Creek Basin, native groundwater in the alluvium reacted with the aquifer matrix for hundreds to thousands of years producing steady-state concentrations of major ions and trace elements, such as that observed at well SMC-08/916. Reactive minerals, such as calcite, gypsum, ferric (oxy)hydroxide, and smectite, reach or approach equilibrium and typically control aqueous chemistry of major ions and trace elements in most aquifer systems (Langmuir 1997). Small variations in background solute concentrations typically are commonly observed in aquifers at other locations around the U.S. (for example, groundwater background at Los Alamos National Laboratory (LANL 2016)), but not to the extent observed in the alluvium within several hundred meters north of the Homestake NPL Site.

Figures 13 and 14 show a strong inverse relationship between dissolved concentrations of uranium and nitrate-N occurring at well DD, possibly resulting from a combination of vadose zone leaching of nitrate and geochemical interactions and groundwater mixing diluting dissolved concentrations of uranium. Groundwater elevations at well DD start to increase in 2005, corresponding to increasing concentrations of dissolved calcium, nitrate, and sulfate in alluvial groundwater. Dissolved concentrations of nitrate substantially increase from 2013 to present at well DD (Figure 13). Dissolved concentrations of uranium start to decrease in 2008 at well DD (Figure 13). This suggests that uranium(VI) is either (1) being diluted through groundwater mixing with a component containing lower dissolved concentrations of uranium or (2) leaching from the vadose zone does not contribute additional dissolved concentrations of uranium to groundwater near wells DD and DD2. Calcite present in the alluvial sediments may potentially adsorb small amounts of anionic uranyl species based on its pH point of zero charge (pH_{pzc}, 8.5, 10.8, Langmuir 1997). Adsorption of uranium(VI) onto ferrihydrite is not likely to be substantial in the bicarbonate-rich and oxic alluvial aquifer at well DD and other well locations.

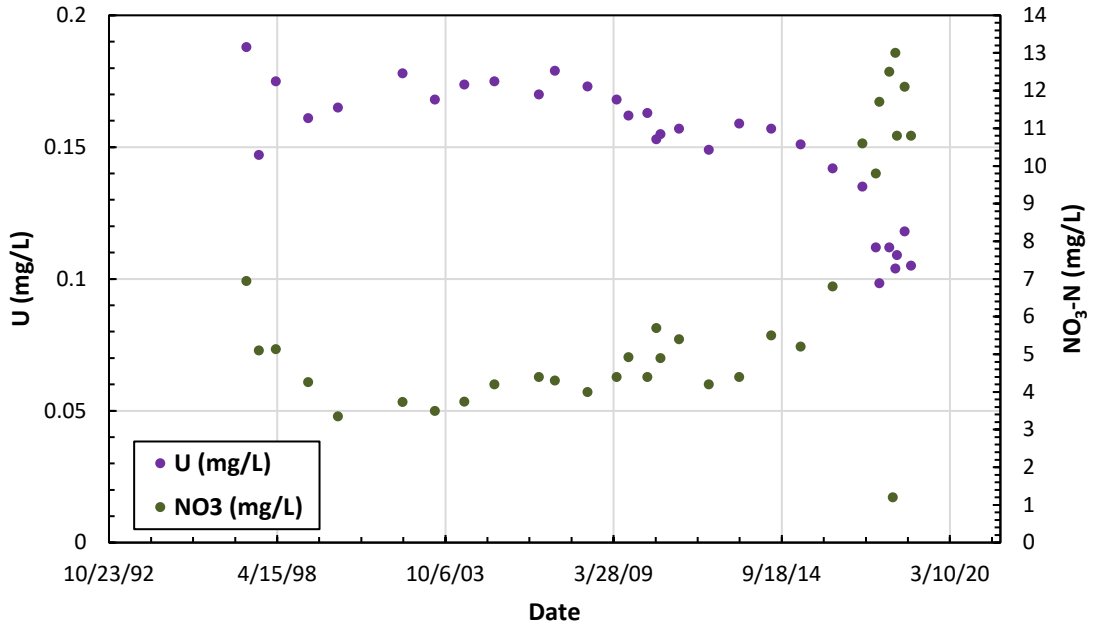

Figure 13. Dissolved concentrations of uranium and nitrate versus time at background monitoring well DD north of the large tailing pile (LTP), Homestake NPL Site, Cibola County, New Mexico (Data source: Homestake database).

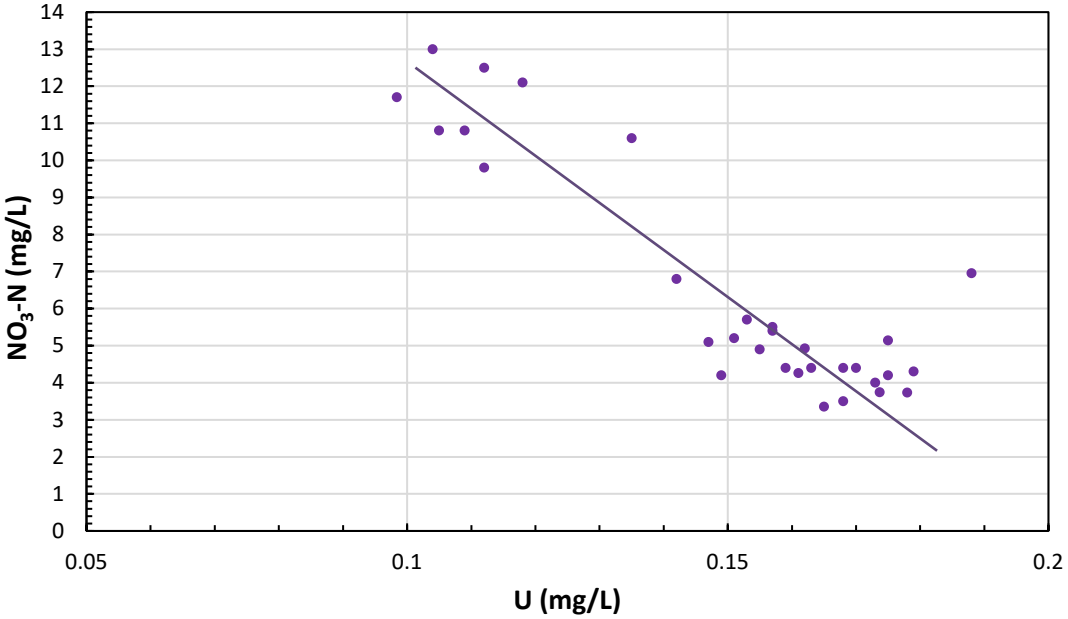

Figure 14. Dissolved concentrations of nitrate versus uranium at background monitoring well DD, from 1997 to 2018, north of the large tailing pile (LTP), Homestake NPL Site, Cibola County, New Mexico (Data source: Homestake database).

Distributions of uranium and nitrate shown in Figure 14 fall into two separate groupings: pre-2016 data with higher uranium and lower nitrate-N concentrations and post-2016 data with lower uranium and higher nitrate-N concentrations. Identifying sources of nitrate should be conducted in future investigations. Appendix A provides a thermochemical discussion on redox chemistry of nitrate and uranium(IV) with nitrate serving as an electron acceptor.

From selective extraction tests, uranium is associated with carbonate minerals present in alluvial sediments near wells DD and DD2 (Arcadis 2018) and Ulrich et al. 2019), suggesting that calcite is a sink for natural and anthropogenic uranium. Several experimental studies using radioisotopes of uranium (Chen et al. 2016) and extended X-ray absorption fine structure (EXAFS) and luminescence spectroscopies (Kelly et al. 2003, Kelly et al. 2006, Reeder et al. 2000, Reeder et al. 2001, Heberling et al. 2008, and Curti 1999) have provided quantitative data and information on the local structure and coordination of uranium(VI) species (UO_2^{2+}) on calcite. Kelly et al. (2006) report that UO_2^{2+} substitutes for Ca^{2+} in the calcite structure, consisting of the crystal class hexagonal scalenohedral (3m, H-M symbol 3 2/m). Reeder et al. (2000) report that calcite coprecipitates up to 1900 ppm uranium(VI) from aqueous solution under circumneutral pH conditions. Reeder et al. (2001) examined the incorporation of uranyl carbonate species into calcite at pH values of 7.6 and 8.2, and confirm that the dominant mechanism of crystal growth during coprecipitation of calcite with UO_2^{2+} is spiral growth on the (104) face of calcite.

Arcadis (2019) reports results of selective extractions for calcium, iron, molybdenum, selenium, uranium, and vanadium using borehole samples collected from BK1, BK2, and BK3, which quantify leaching of trace elements from metal (oxy)hydroxide, carbonate (calcite), and solid organic matter/sulfide phases. Figure 15 shows locations of the Arcadis boreholes. Uranium leached from carbonate phases in samples collected below the alluvial water table range from

32 percent (0.1 mg/kg U) to 55 percent (0.5 mg/kg U) of total uranium released from the soluble fraction, not including the residual or resistate fraction (e.g. smectite and other clay minerals).

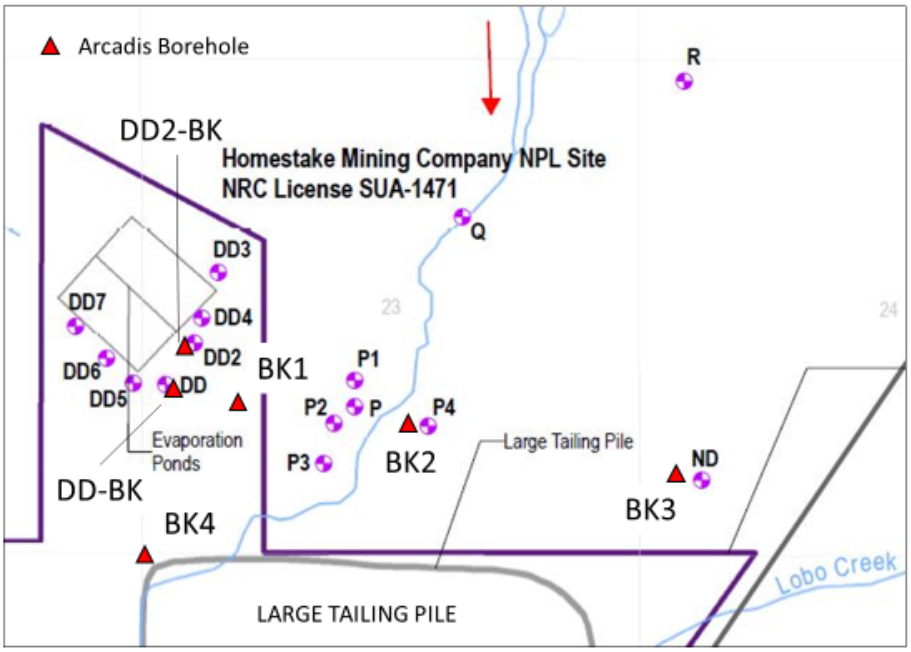

Figure 15. Arcadis alluvial borehole location map.

The alluvial aquifer in San Mateo Creek Basin likely consists of a mixture of pre-mining influenced native groundwater and infiltrated mine water previously released to Arroyo del Puerto and San Mateo Creek from underground uranium mines within the Ambrosia Lake valley from 1956 to 1982 (Gallaher and Cary 1986, Weston Solutions, Inc. 2018). Figure 16 represents a trilinear diagram for numerous alluvial and bedrock wells and the general composition of historical mine-water discharges. Wells DD, DD2, and P3 fall in the domain of the Arroyo del Puerto mine waters shown in yellow and light orange on Figure 16 (Weston Solutions, Inc. 2018). There are close similarities in major-ion chemistry and TDS between wells DD, DD2, and P3 and Arroyo del Puerto historical mine waters (1977 – 1979), based on groundwater sampling conducted from 2014 to 2016 (Weston Solutions, Inc. 2018).

Geochemical evidence suggests that mixing of mine-water discharges and native groundwater occurred in the alluvium north of the Homestake NPL Site at least as early as the mid- to late-1970s. Gallaher and Cary (1986) present chemical data for alluvial well Roundy-1 (well SMC-13/921) (see Figures 2 and 6), which has an average concentration of dissolved uranium of 0.129 ± 0.011 mg/L, in 12 groundwater samples collected from 1977 to 1982. The recent major ion chemistry of well SMC-13/921 is similar to the historical Arroyo del Puerto mine waters (see Figure 16). This well is located near the western edge of the alluvial aquifer and San Mateo Creek, approximately 3.2 km (2.0 miles) northeast and upgradient of well DD and 3.5 km (2.2 miles) southwest of Sand Curve on NM State Highway 605. The chemical data for well SMC-13/921 suggest that uranium, calcium, sulfate, and other solutes are similar in composition to mine-water discharges, have experienced groundwater mixing, and migrated along groundwater-flow paths in the alluvium since the mid- to late-1970s.

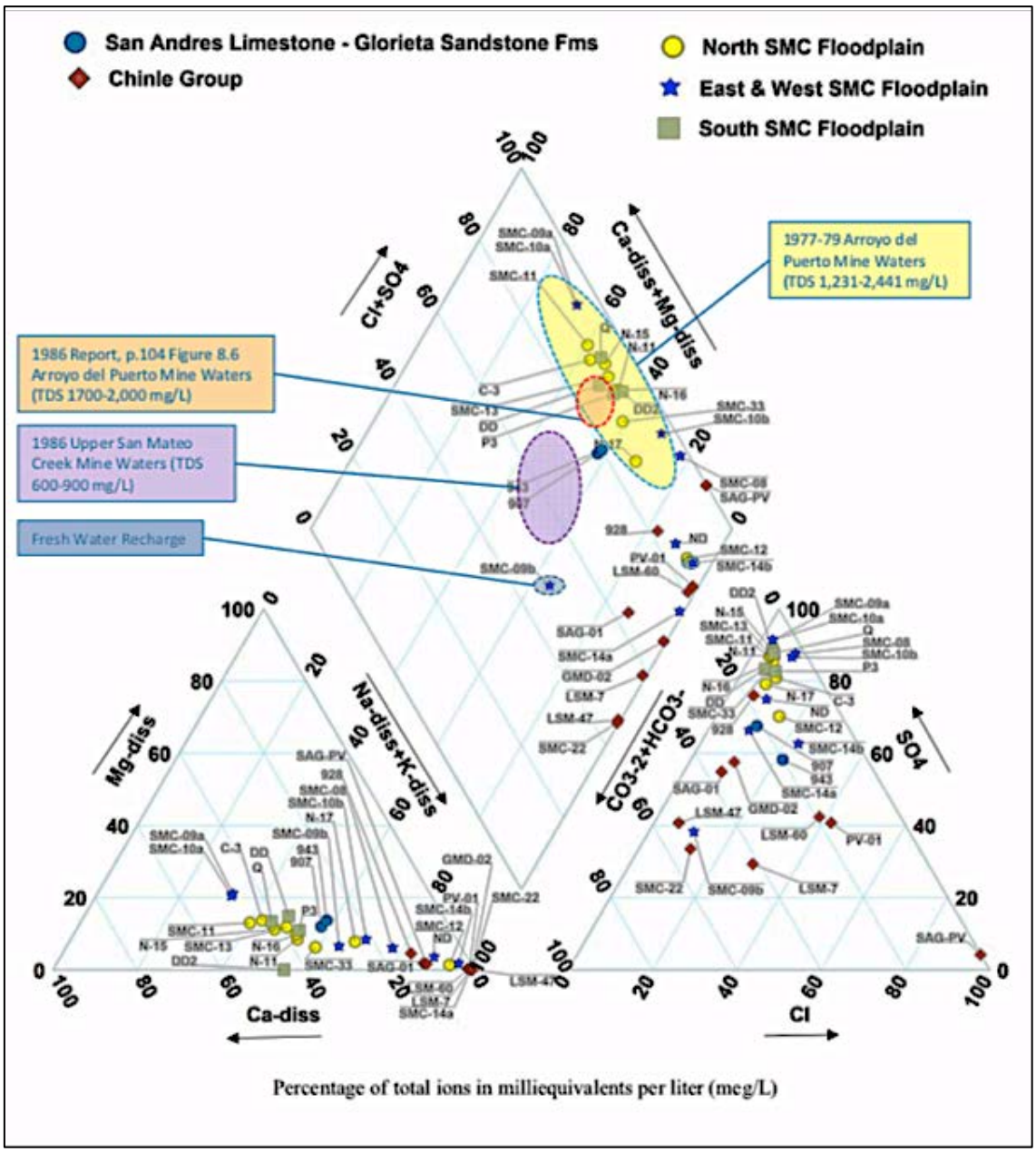

Figure 16. Trilinear diagram for Lower San Mateo Creek Basin alluvium and bedrock groundwater samples collected from 2014 to 2016, including monitoring wells at the Homestake NPL Site, and historical mine-water discharges from the Upper San Mateo Creek Basin (Weston Solutions, Inc. 2018).

3.1 Groundwater Chemistry at Well DD Sampled on October 6, 2016

Analytical results for filtered and non-filtered groundwater samples collected at well DD by Arcadis (2018) and Homestake on October 6, 2016, are provided in Table 3. This sampling round was selected for discussion based on complete measurements of field parameters, including oxidation-reduction potential (ORP), and analytes consisting of major ions, trace elements,

speciated dissolved iron(II, III), total organic carbon, isotopic uranium, and stable isotopes of sulfur, nitrogen, oxygen, and hydrogen. The results serve as input for geochemical simulations using the computer program PHREEQC. The speciated cation-anion charge balance is -4.83 percent using PHREEQC, indicating that analytical errors associated with inorganic analyses are within ±10 percent using ion chromatography (IC), alkalinity titration, inductively coupled plasma-mass spectrometry (ICP-MS), and optical emission spectroscopy (OES). Groundwater at well DD is oxic with a concentration of dissolved oxygen (DO) of 3.37 mg/L. Arcadis (2018) and Ulrich et al. (2019) report a field Eh value of +256 millivolts (mV) (ORP = +76.2 mV) that is consistent with an oxidizing solution, assuming electrochemical equilibrium with various redox-active species, such as iron and manganese. The solution has a circumneutral pH (7.15) and a calcium-sodium-sulfate composition with an ionic strength of 0.06794 molal.

Concentrations of total dissolved iron and ferrous iron are less than analytical detection (Arcadis 2018, Ulrich et al. 2019; see Table 3 of this paper). The dissolved concentration of manganese is 0.383 mg/L (Table 3), confirming that this redox-sensitive metal is stable as soluble manganese(II) at pH 7.15 (see Section 4.1). Groundwater at well DD is oxidizing with respect to dissolved iron (<30 µg/L) and is reducing with respect to manganese, which is a common redox condition in groundwater (Drever 1988). Concentrations of dissolved selenium and uranium are 0.114 mg/L and 0.0944 mg/L, respectively. The redox species distribution for dissolved selenium is not known at well DD; however, selenate (Se(VI)) is expected to dominate over selenite (Se(IV)) based on a field-measured Eh (+256 mV) (Arcadis 2018, Ulrich et al. 2019) and non-detect concentrations of total dissolved iron (< 30 µg/L) and detected dissolved manganese concentrations. Thermochemical stability fields of ferric iron and manganese(II) overlap with selenium(VI) between pH 7.0 and 8.0 (Brookins 1988). Dissolved concentrations of uranium and selenium are higher at well DD compared to other wells, including well SMC-08/916 (Table 2).

Results of stable isotope analysis of nitrogen and oxygen in nitrate suggest that fractionation or enrichment of ^{15}N and ^{18}O in residual nitrate is occurring in groundwater at well DD with a $\delta^{15}N$-NO_3 ratio of +23.7 permil (‰) and a $\delta^{18}O$-NO_3 ratio of +6.23‰ (Table 3) (Arcadis 2018, Ulrich et al. 2019). The concentration of nitrate plus nitrite is measured at 16 mg/L (Table 3) using automated colorimetry (EPA Method 353.2). The nitrogen isotope value provided in Table 3, along with results reported by Blake et al. 2019, imply that nitrate in alluvial groundwater is likely derived from a combination of primary anthropogenic sources that include historical ranching and mining (mine-water discharges), and secondary natural sources, such as deposition of atmospheric nitrogen. Ammonium nitrate used during expansion of wet underground mine adits at uranium mines in the Ambrosia Lake area is one of the viable sources of nitrate measured in mine-water discharges and alluvial groundwater, which needs to be further investigated. Concentrations of nitrate-N greater than 2 mg/L are measured in alluvial groundwater north of the Homestake NPL Site, which are higher than expected for natural soil source (Clark and Fritz 1997). Significant isotope fractionation of nitrogen and oxygen in nitrate suggest that denitrification has occurred (Clark and Fritz 1997) and that total organic carbon (2.6 mgC/L, Arcadis 2018, Ulrich et al. 2019) is a likely electron donor or reductant.

Stable isotopes of sulfur and oxygen in sulfate suggest that fractionation or enrichment of ^{32}S and ^{18}O is occurring at well DD, which produce a $\delta^{34}S$-SO_4 ratio of -25.34‰ and a $\delta^{18}O$-SO_4 ratio of +3.42‰ (Table 3). The light or negative $\delta^{34}S$-SO_4 ratio suggests that dissolved sulfate at well DD is derived from a biogenic source through oxidative dissolution of pyrite associated with uranium ore mined from Ambrosia Lake (Weston Solutions, Inc. 2018 (pages A5-43 – 50), Jensen

1963). The light isotopic signature for $\delta^{34}S\text{-}SO_4$ ratio suggests that dissolved sulfate at well DD and other alluvial wells (DD2 and P3) are primarily sourced from voluminous historical mine-water discharges and secondarily from oxidation of trace pyrite present in the alluvium. Oxidation of biogenic pyrite produces light $\delta^{34}S\text{-}SO_4$ ratios at wells DD and DD2 (-25.52‰ and -27.05‰, permil, respectively). Light $\delta^{34}S\text{-}SO_4$ ratios typically less than -20 permil measured in alluvial groundwater along the central axis of the San Mateo Creek alluvial paleochannel and near the western boundary of the paleochannel are the same as those for pyrite examined from uranium ore samples collected from the Westwater Canyon Member of the Morrison Formation of Jurassic age. These areas possibly represent deeper portions of the paleochannel that provide the greatest groundwater flux for transporting infiltrated mine water in the alluvial aquifer. Heavier or less negative $\delta^{34}S\text{-}SO_4$ ratios occur along the eastern boundary of the alluvial aquifer at wells SMC-10/914 and ND. Variable and light $\delta^{34}S\text{-}SO_4$ ratios (‰) are measured at wells C-3 (-22.95), N-11 (-7.8), N-15 (-21.9), N-16 (-11.6), SMC-08/916 (-6.12), SMC-10/914 (-3.96), SMC-11/920 (-24.97), SMC-12/950 (-11.11), SMC-13/921 (-21.2), SMC-33 (-8.21), ND (-5.43), P3 (-25.74), and Q (-31.0) (Weston Solutions, Inc. 2018, Figure A5-28). Heavier $\delta^{34}S\text{-}SO_4$ ratios at wells ND and SMC-10/914 may represent a baseline sulfur isotope signature for the alluvial aquifer. Additional stable isotope analyses of sulfur should refine sulfate sources.

Table 3. Analytical results for dissolved major ions, metals, and stable isotopes at alluvial well DD on October 6, 2016, Homestake NPL Site, Cibola County, New Mexico, reported by Arcadis 2018 (all parameters except isotopes) and U. S. Geological Survey (isotopes) (Blake et al. 2019, Harte et al. 2019).

Parameter	Result	Parameter	Result	Parameter	Result	Parameter	Result
pH	7.15	**Mg (mg/L)**	109	**Cu (µg/L**	3.2, J	**V (µg/L)**	0.25, J
T (°C)	13.6	**Na (mg/L)**	392	**F (mg/L)**	0.5	**Zn (µg/L)**	30
DO (mg/L)	3.37	**K (mg/L)**	6.2	**Fe(II) (µg/L)**	10, U	**NH_4-N (mg/L)**	0.05, U
Spec. Cond. (µS/cm)	4,057	**Cl (mg/L)**	79	**Fe (µg/L)**	30, U	**$\delta^{15}N\text{-}NO_3$[1] (‰)**	+23.7
Turbidity (NTU)	2.66	**SO_4 (mg/L)**	2,330	**Mo (µg/L)**	2	**$\delta^{18}O\text{-}NO_3$[1] (‰)**	+6.23
Eh (mV)	+256	**Ba (µg/L)**	8.7, J	**Mn (µg/L)**	383	**$\delta^{18}O\text{-}H_2O$[1] (‰)**	-9.11
Ionic Charge Balance (%)	-4.83	**Co (µg/L)**	3.7, J	**$NO_3 + NO_2$ (N) (mg/L)**	16	**$\delta^{2}H\text{-}H_2O$[1] (‰)**	-70.36
Alk. (mg $CaCO_3$/L)	238	**Pb (µg/L)**	0.07	**Se (µg/L)**	114	**$\delta^{34}S\text{-}SO_4$[1] (‰)**	-25.34
Ca (mg/L)	509	**Si (mg/L)**	7.9	**U (µg/L)**	94.4	**$\delta^{18}O\text{-}SO_4$[1] (‰)**	+3.42
Al (µg/L)	5.5, J	**TOC (mgC/L)**	2.6	**Br (mg/L)**	0.5	**$^{234}U/^{238}U$[2]**	1.4505

Notes:
J result was above the method detection limit but below the quantitation limit.
U result was below the method detection limit.
[1]Analytical results for stable isotopes reported by U.S. Geological Survey on October 6, 2016.
[2]Units are pCi/L.
Total organic carbon (TOC) is from an unfiltered sample.
Energy Laboratories performed inorganic and radiochemical analyses (Arcadis 2018, Ulrich et al. 2019).

Weston Solutions, Inc. (2018) present $\delta^{18}O$ and $\delta^{2}H$ ratios for alluvial wells drilled in the San Mateo Creek Basin (Figure A5-15), including well DD. Stable isotope data for hydrogen and oxygen suggest that there is an evaporative component to alluvial groundwater. Evaporation of mine-water influenced surface water that infiltrated through the vadose zone to alluvial groundwater is one physical process capable of producing such $\delta^{18}O$ and $\delta^{2}H$ ratios (Weston

Solutions, Inc. 2018). Surface water infiltrating through the vadose zone to the alluvial water table will retain its enriched isotope signature for hydrogen and oxygen prior to mixing with native alluvial groundwater.

The activity ratio of $^{234}U/^{238}U$ is slightly above unity (1.45) in groundwater sampled at well DD (Table 3) (Arcadis 2018, Ulrich et al. 2019), suggesting that secular equilibrium between these two isotopes is not established. Total activities of ^{234}U and ^{238}U in groundwater are 39.6 pCi/L and 27.3 pCi/L, respectively. ^{238}U has a half-life of 4.47E+09 years (Parrington et al. 1996) and decays at a constant rate to ^{234}U, which has a much shorter half-life of 2.46E+05 years (intermediate radiogenic isotopes include short-lived ^{234}Th and ^{234}Pa). Activity ratios of $^{234}U/^{238}U$ provide quantitative information on leaching of ^{234}U and ^{238}U from aquifer solids, sediments, and soils (Clark and Fritz 1997). Secular equilibrium is achieved when activity ratios of $^{234}U/^{238}U$ and other decay chain isotopes equal unity (Clark and Fritz 1997). Groundwaters typically have activity ratios of $^{234}U/^{238}U$ greater than unity (Paces et al. 2002, Cizdzeil et al. 2005, Finkel 1981) resulting from the higher aqueous solubility of ^{234}U, which is located in crystal lattices damaged by alpha decay of ^{238}U, and due to recoil of ^{234}Th ($^{1/2}T$ equals 24.10 days) from fracture surfaces into solution following alpha decay of ^{238}U (Andrews et al. 1982). The isotope ^{234}Th, releases 198 kiloelectron volts (keV) of energy during beta decay to ^{234}Pa, which has a $^{1/2}T$ of 1.17 minutes (Parrington 1996) and ^{234}Pa undergoes beta decay to ^{234}U.

4.0 PHREEQC

Geochemical-thermodynamic computer programs are used as one of several quantitative tools, along with groundwater analytical results and hydrogeological, mineralogical, and geophysical data and information, for conducting site characterization and remediation investigations. Analytical results from groundwater samples collected by Homestake and Arcadis (2018) at well DD in October 2016 serve as input to the model simulations. Batch equilibrium-geochemical modeling was performed using the computer program PHREEQC (**pH**-**RE**dox-**EQ**uilibria-**C**++ computer language)-Version 3 (Parkhurst and Appelo 2013). Reactive transport modeling was not performed at this stage of the investigation because several geochemical and hydraulic parameters, including mineral surface area, kinetic rate constants, and solute and groundwater residence times, required for more elaborate simulations are not known for the alluvial aquifer. Batch equilibrium modeling is an appropriate initial approach to evaluate mineral equilibrium and adsorption processes occurring at well DD in the absence of key kinetic parameters required for reactive transport modeling for the alluvial aquifer. Geochemical and hydraulic transient conditions occur at several monitoring wells, including DD and DD2 that place constraints on applicability of batch-equilibrium modeling. Mass transfer of reactive minerals, such as gypsum, and surface complexation of uranium(VI), selenium(IV, VI), and other trace elements onto hydrous ferric oxide (HFO), represented as $Fe(OH)_3$, in groundwater systems at circumneutral pH conditions (Langmuir 1997) are typically independent of reaction kinetics. Reactive minerals reaching equilibrium over short periods of time in groundwater systems are evaluated as part of the PHREEQC simulations. Minteq.v4.dat is the chemical thermodynamic database used in the geochemical simulations because it contains compiled and critically reviewed speciation and solubility data for aqueous and solid phases of uranium(IV, VI) (Grenthe et al. 1992).

Thermodynamic databases may contain systematic errors associated with experimental studies that hinder accuracy and internal consistency. Critical evaluation of thermodynamic data for major ions, radionuclides, and metals/trace elements, including arsenic, chromium, and uranium, however, have been conducted by the U. S. Geological Survey, universities, and

research institutions over the past three decades. Such efforts improve the meaningfulness and relevance of geochemical models and their application to environmental investigations. Solute speciation, mineral saturation indices, and adsorption calculations for calcium, sulfate, and uranium were carried out using PHREEQC. Transport of uranium(VI) in groundwater is controlled by redox and pH conditions, solution composition, especially total carbonate alkalinity and dissolved calcium, and the presence of adsorbents, including ferric (oxy)hydroxide, solid organic matter, and clay minerals with large surface areas (smectite) (Langmuir 1997).

4.1 Solute Speciation Calculations

Results of solute speciation calculations for the groundwater samples collected at well DD on October 6, 2016, are provided in Table 4. Oxidation-reduction potential (ORP, Eh) was measured during sampling (Arcadis 2018, Ulrich et al. 2019) and a pe (-$\log_{10}$ activity of electron) value of 4.4989 (Eh = +256 mV at 13.6°C) was calculated based on the calculated Eh, which represents moderately oxidizing conditions. Groundwater at well DD is oxidizing with respect to sulfur, with sulfate concentrations of 2,330 mg/L, and iron having non-detection of total dissolved iron (<30 µg/L) and Fe(II) (<10 µg/L) (Table 3). A concentration of total dissolved iron of 15 µg/L, which is one-half of the analytical detection limits using either ICP-OES or ICP-MS, is selected for PHREEQC simulations. Based on PHREEQC simulations, dissolved uranium is dominantly stable as soluble ternary complexes of uranium(VI) carbonate (neutral charge) and carbonato (anion) species. Such anionic aqueous complexes are weak adsorbates that do not significantly accumulate on solid surfaces under circumneutral pH conditions (Langmuir 1997). Formation constants for dissolved ternary calcium-uranyl carbonate complexes provided by Dong and Brooks (2006) were added to the Minteq.v4.dat database because of the calcium-rich alluvial groundwater containing uranium at concentrations exceeding 0.100 mg/L at well DD. Specifically, these ternary complexes greatly decrease uranyl adsorption onto HFO and other solids because of steric hindrance and net-negative surface charge on adsorbents under circumneutral pH conditions. Calculated dissolved concentrations of iron(II) and selenium(IV) are 2.854E-17 molal and 6.942E-19 molal, respectively, and are not included for discussion.

Table 4. Results of PHREEQC speciation calculations using groundwater samples collected on October 6, 2016, at well DD, Homestake NPL Site, Cibola County, New Mexico (Source of data for calculations: Arcadis 2018 and Ulrich et al. 2019).

Solute	Molality	Speciated Form	Molality	Percentage
Ca(II)	1.275E-02	Ca^{2+}	7.670E-03	60.16
		$CaSO_4^0$	4.870E-03	38.20
		$CaHCO_3^+$	1.943E-04	1.52
Fe(III)	2.696E-07	$Fe(OH)_2^+$	2.629E-07	97.51
		$Fe(OH)_3^0$	6.180E-09	2.29
Mn(II)	6.997E-06	Mn^{2+}	5.117E-06	73.13
		$MnSO_4$	1.745E-06	24.94
		$MnHCO3^-$	1.290E-07	1.84
Se(VI)	1.449E-06	SeO_4^{2-}	1.449E-06	100.00
U(VI)	3.981E-07	$Ca_2UO_2(CO_3)_3^0$	3.203E-07	80.46
		$CaUO_2(CO_3)_3^{2-}$	7.143E-08	17.94
		$UO_2(CO_3)_3^{4-}$	5.694E-09	1.43

4.2 Mineral Saturation Index Calculations

Results of saturation index calculations of several reactive minerals identified by Arcadis (2018) and Ulrich et al. (2019) are provided in Table 5. Reactive minerals and amorphous solids

precipitate from solution when the reaction half-time of a given phase is shorter than groundwater residence time, allowing equilibrium to be reached within minutes, hours, days, or months (Langmuir 1997). Several classes of reactive minerals and amorphous solids include alkaline earth carbonates and sulfates, metal oxides-hydroxides, amorphous silicates, and metal (oxy)hydroxides. Non-reactive minerals (feldspars, amphiboles, and pyroxenes) may take thousands of years to precipitate, require elevated temperatures, and generally do not control solution compositions or influence contaminant migration in most aquifer systems. Non-reactive minerals include most high temperature and pressure silicates. The saturation index (SI) is defined as (Langmuir 1997):

$SI = \log_{10}[(\text{ion activity product})/(\text{solubility product})]$.

Equilibrium between a given amorphous solid and mineral and aqueous solution is reached when SI equals 0 ± 0.05 and forward (precipitation) and reverse (dissolution) reaction rates are equal; oversaturation occurs when SI is greater than zero and precipitation of a solid takes place; and undersaturation occurs when SI is negative and dissolution of a solid is expected (Langmuir 1997). Groundwater at well DD is oversaturated with barite, calcite, ferrihydrite, gibbsite, and pyrolusite and is undersaturated with carnotite, $CaMoO_4$, chalcedony, dolomite (ordered, disordered), K-jarosite, rhodochrosite, tyuyamunite, and uraninite according to PHREEQC simulations (Table 5).

Table 5. Results of gas and mineral-solid phase saturation indices calculated by PHREEQC for groundwater samples collected at well DD, Homestake NPL Site, Cibola County, New Mexico (Source of data for calculations: Arcadis 2018 and Ulrich et al. 2019).

Phase	Saturation Index
Barite ($BaSO_4$)	+0.43
Calcite ($CaCO_3$)	+0.22
$CaMoO_4$	-2.61
Carnotite (KUO_2VO_4)	-6.32
Chalcedony	-0.19
CO_2 gas	-1.85
Dolomite ($CaMg(CO_3)_2$) (disordered)	-0.62
Dolomite ($CaMg(CO_3)_2$) (ordered)	-0.02
Ferrihydrite ($Fe(OH)_3$)	+1.37
Gibbsite ($Al(OH)_3$)	+0.69
Gypsum ($CaSO_4 \cdot 2H_2O$)	-0.01
K-Jarosite ($KFe_3SO_4(OH)_6$)	-0.52
Pyrolusite (MnO_2)	+7.90
Rhodochrosite ($MnCO_3$)	-0.97
Tyuyamunite ($Ca(UO_2)_2(VO_4)_2$)	-11.48
Uraninite (UO_2)	-29.09

Groundwater at well DD is effectively in equilibrium with gypsum (SI = -0.01), maintained by 509 mg/L of dissolved calcium and 2,330 mg/L of dissolved sulfate. Arcadis (2018) and Ulrich et al. (2019) report that gypsum was occasionally detected, using X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS), in alluvial sediments collected from boreholes DD-BK and DD2-BK. This solution is slightly oversaturated with calcite (SI = +0.22) ($K_{\text{solubility product}}$ (K_{sp}) = $10^{-8.42}$

M), which is 6,310 times less soluble than gypsum ($K_{sp} = 10^{-4.62}$ M) and requires lower dissolved concentrations of Ca^{2+} to precipitate. Authigenic or *in situ* precipitation of gypsum (1 wt. percent) and calcite (1 and 3 wt. percent) occur below the alluvial water table at boreholes DD-BK and DD2-BK (Arcadis 2018, Ulrich et al. 2019). Precipitation of carnotite and tyuyamunite in groundwater requires much higher concentrations of uranium(VI) and vanadium(V) that typically are achieved through evapoconcentration occurring within the vadose zone. It is very unlikely that these two uranyl minerals will precipitate in alluvial groundwater hydraulically upgradient from the LTP due to insufficient dissolved concentrations of uranium and vanadium.

Groundwater at well DD is significantly undersaturated with uraninite and oxidation or corrosion of this mineral, if present, is expected in oxidizing groundwater. Undersaturated chemical conditions also occur for iron sulfides, such as pyrite, amorphous FeS, and mackinawite in oxidizing groundwater at well DD. Arcadis (2018) and Ulrich et al. (2019) demonstrate that sulfide dissolution is taking place in borehole samples collected from DD-BK and DD2-BK using scanning electron microscopy. Iron sulfides oxidize to form K-jarosite, under acidic pH conditions, which, in turn, dissolves to form ferrihydrite and amorphous ferric hydroxide under increasing pH conditions. Presence of calcite in alluvial sediments at boreholes DD-BK and DD2-BK and other locations prevent sulfuric acid production during sulfide oxidation while maintaining circumneutral pH conditions in alluvial groundwater in San Mateo Creek Basin.

An additional PHREEQC simulation consisting of mass transfer of solid phases, assuming an initial concentration of 10 moles of gypsum, calcite, and ferrihydrite, was conducted by fixing well DD groundwater in equilibrium with gypsum (SI = -0.01) and oversaturated with calcite (SI = +0.22) and ferrihydrite (SI = +1.37) (Table 5). Approximately 0.08628 millimoles of gypsum precipitate and 7.456 micromoles of calcite dissolve, which slightly decreases dissolved concentrations of calcium and sulfate. Calcite and gypsum are observed in sediment samples collected at boreholes DD-BK and DD2-BK (Arcadis 2018, Ulrich et al. 2018). The simulation calculates that 4.624 nanomoles of ferrihydrite precipitate from alluvial groundwater at well DD.

4.3 Adsorption (Surface Complexation) Calculations

Adsorption is considered to be the only viable geochemical process that potentially decreases uranium(VI) and selenium(VI) concentrations in oxic groundwater at well DD. Coprecipitation of the uranyl cation (UO_2^{2+}) with calcite, which may remove a stoichiometric fraction of uranium from groundwater at the Site, is not included in the PHREEQC simulations. PHREEQC is used to quantify adsorption processes, including surface complexation with HFO (as $Fe(OH)_3$), based on the diffuse double layer model discussed in detail by Langmuir (1997). This phase commonly occurs in soils, sediments, and aquifer systems worldwide and is an important adsorbent for numerous cations and anions. One millimole concentration of HFO (0.089 g HFO) is assumed for the PHREEQC simulations discussed below. This adsorbent provides active negative- and positive-charged binding sites for cations and anions, respectively, under varying pH conditions, temperature, and solution composition. Ulrich et al. (2019) suggest that three weight percent (30 g/kg) of amorphous iron hydroxide, which is not detected by X-ray diffraction analysis, is present in sediment samples collected at DD2-BK. Therefore, 0.089 g of HFO is a reasonable assumption and may actually underestimate the adsorption capacity of alluvial sediments at boreholes DD-BK and DD2-BK. This amount of adsorbent, however, can still provide a substantial concentration of binding sites for metal adsorption, especially for cations under circumneutral pH conditions characteristic of well DD. Adsorption calculations using PHREEQC

do not include adsorption or partitioning of aqueous uranyl species onto solid organic matter and clay minerals such as gibbsite, kaolinite, and smectite.

The specific surface area of HFO is 600 meters^2/gram solid (Langmuir 1997). Hydrous ferric oxide has 0.005 mol/mol iron of high energy or strong sites (Hfo_sOH) and 0.2 mol/mol iron of low energy or weak sites (Hfo_wOH) (Langmuir 1997). Surface charge on HFO changes from a net-positive charge to a net-negative charge with increasing pH, which enhances adsorption of cations at higher or more basic pH values. Intrinsic adsorption constants (K^{int}) for bicarbonate and carbonate (llnl database) and uranium(VI) (Mahoney et al. 2009, NRC 2006b) were added to the minteq.v4.dat database to quantify adsorption of these species onto HFO by making the PHREEQC simulations more realistic and applicable to site conditions at well DD. Intrinsic adsorption constants for bicarbonate, carbonate, and uranium(VI) with HFO are provided below.

Hfo_wOH + CO_3^{2-} + H^+ = Hfo_wOCO_2^- + H_2O	log K^{int} = 12.56 (llnl.dat)
Hfo_wOH + CO_3^{2-} + $2H^+$ = Hfo_wOCO_2H^0 + H_2O	log K^{int} = 20.62 (llnl.dat)
Hfo_sOH + UO_2^{2+} = Hfo_sOUO_2^+ + H^+	log K^{int} = 3.735 (Mahoney et al. 2009)
Hfo_wOH + UO_2^{2+} = Hfo_wOUO_2^+ + H^+	log K^{int} = 2.534 (Mahoney et al. 2009)
Hfo_wOH + UO_2^{2+} + CO_3^{2-} = Hfo_w$OUO_2CO_3^-$ + H^+	log K^{int} = 9.034 (Mahoney et al. 2009)
Hfo_wOH + UO_2^{2+} + $2CO_3^{2-}$ = Hfo_w$OUO_2(CO_3)_2^{3-}$ + H^+	log K^{int} = 15.28 (Mahoney et al. 2009)
Hfo_wOH + $Ca_2UO_2(CO_3)_3^0$ + $2H^+$ = Hfo_wOUO_2^+ + $3HCO_3^-$ + $2Ca^{2+}$	log K^{int} = 3.01 (NRC 2006b)
Hfo_wOH + $Ca_2UO_2(CO_3)_3^0$ + H^+ + H_2O = Hfo_wOUO_2OH^0 + $3HCO_3^-$ + $2Ca^{2+}$	log K^{int} = -4.88 (NRC 2006b)
Hfo_sOH + $Ca_2UO_2(CO_3)_3^0$ + $2H^+$ = Hfo_sOUO_2^+ + $3HCO_3^-$ + $2Ca^{2+}$	log K^{int} = 6.25 (NRC 2006b)
Hfo_sOH + $Ca_2UO_2(CO_3)_3^0$ + H^+ + H_2O = Hfo_sOUO_2OH^0 + $3HCO_3^-$ + $2Ca^{2+}$	log K^{int} = -1.65 (NRC 2006b).

Table 6 provides results of the surface complexation calculations, at pH 7.15, using PHREEQC and analytical results shown in Table 3. One millimole of HFO (0.089 g), which is equilibrated with well DD groundwater, contains 5.0E-06 moles of strong sites and 2.0E-04 moles of weak sites with the concentration of weak adsorption sites exceeding the number of strong sites. Results of the PHREEQC simulation show that Ca^{2+} dominates adsorption onto strong sites that significantly limits other cations from adsorbing onto HFO, including the uranyl cation (UO_2^{2+}). Bicarbonate dominates adsorption onto weak sites present on HFO and limits adsorption of sulfate (SO_4^{2-}) and selenate (SeO_4^{2-}). Concentrations of dissolved calcium (509 mg/L, Table 3) greatly exceed uranium (0.0944 mg/L), which enhances Ca^{2+} adsorption onto strong sites present on HFO resulting in less adsorption of UO_2^{2+} with a positive net log K^{int} for calcium and uranyl cation. Displacement of uranyl cation from strong sites by calcium is shown by:

Hfo_sOH + Ca^{2+} = Hfo_s$OHCa^{2+}$	log K^{int} = 4.97 (Langmuir 1997)
Hfo_s$OHUO_2^{2+}$ = Hfo_sOH + UO_2^{2+}	log K^{int} = -3.735 (Mahoney et al. 2009)
Hfo_s$OHUO_2^{2+}$ + Ca^{2+} = Hfo_s$OHCa^{2+}$ + UO_2^{2+}	net log K^{int} = 1.23.

Moles of selenate (5.198E-13 and 3.511E-10) and uranyl cation (1.272E-10 and 4.945E-11) present on strong and weak adsorption sites, respectively, are orders of magnitude lower than those for calcium (3.795E-06 and 1.003E-06) (Table 6). Approximately 0.152 mg of Ca^{2+} adsorbs onto strong sites with 1 millimole HFO corresponding to a mole fraction equal to 0.759. Bicarbonate dominates adsorption on weak sites at 1.093E-04 moles (6.667 mg) with a mole fraction of 0.547. Competition of adsorption sites between dissolved calcium and uranyl cation

(UO_2^{2+}) and uranyl carbonate complexes results in poor adsorption of uranyl species on alluvial sediments at well DD. A total of 1.59E-08 moles (3.78E-03 mg) of uranium are removed from solution by adsorbing onto HFO, which enhances mobility of uranium(VI) in alluvial groundwater at well DD. Only 1.435E-08 moles of the surface complex, Hfo_w$OUO_2(CO_3)_2^{3-}$ dominates weak adsorption sites present on ferrihydrite according to the PHREEQC simulation.

A PHREEQC simulation was performed with equilibrating the surface of HFO (0.089 g) with well SMCO-8/916 groundwater (Table 2) and mixing this groundwater with mine-water discharge (Table 1). The mixed solution contains an average dissolved concentration of uranium of 0.165 mg/L measured at well DD from 1997 to 2019 and has fractions of well SMC-08/916 groundwater and mine-water discharges of 0.8985 and 0.1015, respectively. An insignificant amount of uranium (Σ = 9.181E-08 moles, 2.185E-02 mg), represented as surface complexes Hfo_sOUO_2^+, Hfo_sOUO_2OH^0, Hfo_w$OUO_2(CO_3)_2^{3-}$, Hfo_w$OUO_2CO_3^-$, Hfo_wOUO_2OH^0, and Hfo_wOUO_2^+, poorly adsorb onto strong and weak sites of the HFO surface equilibrated with the mixed solution containing 0.165 mg/L of dissolved uranium at pH 8.16. This simulation supports the high mobility of dissolved uranium(VI) in the oxic alluvial aquifer at the Homestake NPL Site.

Table 6. Results of PHREEQC surface complexation calculations for groundwater samples collected at well DD on October 6, 2016, Homestake NPL Site, Cibola County, New Mexico. Concentration of HFO equals one millimole (0.089 g HFO) equilibrated with well DD groundwater, pH = 7.15. Source of data for calculations: Arcadis (2018) and Ulrich et al. (2019).

Surface Species-Strong Sites	Moles or Molality	Mole Fraction	Percentage
Hfo_s$OHCa^{2+}$	3.795E-06	0.759	75.9
Hfo_sOCu^+	7.921E-07	0.158	15.8
Hfo_sOZn^+	3.295E-07	0.066	6.6
Hfo_sOH	4.109E-08	0.008	0.8
Hfo_sOH_2^+	3.098E-08	0.006	0.6
Hfo_sOUO_2^+	1.272E-10	2.544E-05	2.5E-03
Hfo_sOUO_2OH	4.138E-11	8.276E-06	8.3E-04
Hfo_s$OHSeO_4^{2-}$	5.198E-13	1.040E-07	1.0E-05
Hfo_s$OHUO_2^{2+}$	5.874E-20	1.175E-14	1.2E-12
Surface Species-Weak Sites	**Moles or Molality**	**Mole Fraction**	**Percentage**
Hfo_wOCO_2H	1.093E-04	0.547	54.7
Hfo_wOH	2.775E-05	0.139	13.9
Hfo_wOCO_2^-	2.462E-05	0.123	12.3
Hfo_wOH_2^+	2.092E-05	0.105	10.5
Hfo_wOMg^+	6.864E-06	0.034	3.4
Hfo_w$OHSO_4^{2-}$	4.090E-06	0.020	2.0
Hfo_WOCu^+	2.744E-06	0.014	1.4
Hfo_w$OUO_2(CO_3)_2^{3-}$	1.435E-08	7.175E-05	7.2E-03
Hfo_w$OUO_2CO_3^-$	1.290E-09	6.450E-06	6.4E-04
Hfo_w$OHSeO_4^{2-}$	3.511E-10	1.759E-06	1.8E-04
Hfo_wOUO_2^+	4.945E-11	2.472E-07	2.5E-05
Hfo_wOUO_2OH	1.646E-11	8.230E-08	8.2E-06

5.0 Volumetric Mixing of Mine-water Discharges with Native Alluvial Groundwater

This section presents a preliminary or first-order calculation that quantifies mixing of mine-water discharges with alluvial groundwater from 1956 to 1982. Groundwater mixing between native alluvial groundwater and historical mine-water discharges probably continues today in the alluvium north of the Homestake NPL Site. This first-order calculation is conservative using low volumes of mine-water discharges with an overestimated volume of groundwater present in the alluvium extending from the Crossroads area south to the northern boundary of the Homestake NPL Site. This first-order calculation does not consider (1) fluctuating water table in the alluvium, (2) leaching or desorption of chemicals from the vadose zone, (3) dissolution of soluble salts in the vadose zone, (4) increasing saturated thickness resulting from infiltration of mine-water discharges, and (5) decreasing saturated thickness resulting from seepage of alluvial groundwater to underlying bedrock aquifers (for example, Dakota Sandstone Formation and Chinle Group). Uniform groundwater mixing in a homogeneous and isotopic aquifer matrix is implicit with this first-order calculation. Hydraulic conductivity, hydraulic gradient, recharge rates, and permeability are not considered in this calculation. Sustained surface-water flow in the San Mateo Creek south of the Crossroads area (Gallaher and Cary 1986) provided an historical non-point source of recharge to the alluvial aquifer for several kilometers. This source of recharge was transported into the lower San Mateo Creek floodplain, likely as far downstream as the Homestake NPL Site, during storm events (EPA 1980). Such conditions shortened the amount of time and increased the distance for recharge by mine water to take place from 1956 to 1982, as compared to groundwater mixing between native alluvial groundwater and mine water in the lower floodplain.

The alluvial aquifer has the following assumed dimensions from the Crossroads area to Homestake NPL Site:

Length: 8.75 miles (4.620E+04 ft.)
Width: 1.0 mile (5.280E+03 ft.)
Thickness: 90 ft.
Porosity: 0.40 (Freeze and Cherry 1979, page 37)
Average saturated thickness: 60 ft.

Volume of alluvium = (4.620E+04 ft.)(5.280E+03 ft.)(90 ft.) = 2.195E+10 ^{3}ft.
Volume of saturated zone = (2.195E+10 ^{3}ft.)(60 ft./90 ft.)(0.40) = 5.854E+09 ^{3}ft.

Converting ^{3}ft of water to gallons:

1 gallon of water = 1.336806E-01 ^{3}ft.

Gallons of native alluvial groundwater = (5.854E+09 ^{3}ft)(1.336806E-01 gal/^{3}ft) = 782628260.198 gals. = 782.628 million gallons (MG) (7.82628E+02 MG) of native alluvial groundwater.

Gallaher and Cary (1986) report that 2.16 MGD of surface water, dominated by mine-water discharges, flowed in San Mateo Creek a distance of 4.8 km (3 miles) south of the Crossroads area (see Figure 1) from 1979 to 1981. Using this surface-water discharge rate provided by Gallaher and Cary (1986), a calculated volume of 2.05124E+04 MG of mine water were potentially discharged and flowed in San Mateo Creek from 1956 to 1982, which is a lower bounding volume. This volume is approximately 16 percent of the estimated 125 billion gallons

of groundwater pumped from the Westwater Canyon Member of the Morrison Formation (Gallaher and Cary 1986). The average pumping rate was 13.46 MGD for the Ambrosia Lake area for 26 years of mine-water discharge, calculated from data presented by Gallaher and Cary (1986). Greater volumes of groundwater were pumped from the Westwater Canyon Member of the Morrison Formation during early stages of mine development (from 1959 to 1965), with the dewatering and discharge of mine water to Arroyo del Puerto (Gallaher and Cary 1986). Kelly et al. (1980) report between 0.15 and 3.77 MGD of mine-water discharges took place between 1962 and 1978 in the Ambrosia Lake valley from different operating mines.

For one preliminary or first-order calculation, it is assumed that one percent of the surface water infiltrated and recharged the alluvial aquifer, resulting in 2.05124E+02 MG of surface water mixing with 7.82628E+02 MG of native alluvial groundwater. Volumetric mixing fractions are 0.2622 (26.22 percent) of mine-water discharges and 0.7378 (73.78 percent) of native alluvial groundwater. For a second preliminary or first-order calculation, three percent of surface water infiltrated and recharged the alluvial aquifer, 6.1537E+02 MG of surface water mixes with 7.82628E+02 MG of native alluvial groundwater. This results in volumetric mixing fractions equal to 0.7867 (78.67 percent) of mine-water discharge and 0.2133 (21.33 percent) of native alluvial groundwater. For a third preliminary or first-order calculation, alluvial groundwater completely mixes with mine-water discharges, from the Crossroads area south to the north boundary of the Site, if four percent of the calculated mine-water discharges (8.20496E+02 MG) potentially recharged the alluvium from 1956 to 1982.

These first-order volumetric mixing calculations most likely underestimate actual groundwater mixing that occurred between mine-water discharges and native alluvial groundwater because higher volumes of mine water were discharged to Arroyo del Puerto and to San Mateo Creek during the early- to mid-years of the total 26-year period of mine outfall discharges. The actual percentage of recharge of surface water to alluvial groundwater in San Mateo Creek Basin is uncertain in the absence of a detailed and well calibrated-water balance; however, recharge to the alluvial aquifer probably is greater than three percent based on the permeable nature of the coarser-grained alluvial sediments along San Mateo Creek that allowed greater infiltration and percolation to the water table (Gallaher and Cary 1986), little native vegetation, the hydrogeological setting, climatic conditions, and the many earthen spreader dams built along the creek by the local rancher to pond water along the creek for cattle forage. Surface-water flow allowed a large volume of mine water to recharge the alluvial aquifer over a large area of the lower San Mateo Creek floodplain very early in the uranium mining industry's period of discharge operations (1956-1982). This surface-water flow most likely provided localized recharge to the alluvial aquifer in the vicinity of wells DD and DD2 prior to 1976, resulting in higher concentrations of dissolved uranium and other solutes in alluvial groundwater. The curvilinear drainage/berm feature built in the late 1950s from the creek toward the area of wells DD and DD2 may have enhanced the localized recharge at those wells (see Figures 5a and 5b).

6.0 Binary Mixing of Native Alluvial Groundwater with Mine-water Discharges: Uranium

This section presents results of a simplistic binary mixing calculation for uranium to quantify mixing of native groundwater at well SMC-08/916, which represents potential background, with mine-water discharges. Dissolved uranium(VI) is assumed to be conservative in alluvial groundwater under site conditions, however, some attenuation may occur through adsorption on solid organic matter and clay minerals and coprecipitation with calcite. Groundwater mixing is a complex process actively occurring in the alluvial aquifer in the San Mateo Creek Basin, and

the initial mixing calculations presented in this report assume that native alluvial groundwater and mine-water discharges are the only types of water present. Mixing of those two end members was evaluated to assess relative percentages of uranium at well DD, without considering potential leaching of uranium from the vadose zone during rising water table conditions observed in the alluvial aquifer. Additional leaching of uranium from the vadose zone at well DD is unlikely because dissolved concentrations of uranium significantly decrease as the water table fluctuated since 2005 (see Figure 8b). Groundwater analytical results provided by Homestake from 1997 to 2019 were used in the mixing calculation. The average concentration of dissolved uranium at well SMC-08/916 (1997 to 2005) is 0.0086 mg/L (Table 2, n = 8 samples) (Homestake database). The average dissolved concentration of uranium measured in mine outfall waters is 1.55 mg/L (Table 1) (Perkins and Goad 1980, n = 11 samples). The average dissolved concentration of uranium measured at well DD is 0.165 mg/L from 1997 to 2019 (Homestake database, n = 57 samples).

Binary mixing of native alluvial groundwater (well SMC-08/916) with outfall waters to produce an intermediate value for uranium (well DD) is represented by the following equation:

$C = A(x) + B(1-x)$,

where,

A = component A (average uranium background, well SMC-08/916, 0.0086 mg/L)
x = fraction of A (well SMC-08/916)
B = component B (average uranium in mine-water outfalls, 1.55 mg/L)
1-x = fraction B (mine-water discharge)
C = component C (average uranium at well DD, 0.165 mg/L).

Solving for x,

$0.165 = 0.0086x + 1.55(1 - x)$
$0.165 = 0.0086x + 1.55 - 1.55x$
$1.385 = 1.5414x$
$x = 1.385/1.5414$
$x = 0.8985$ and $1 - x = 0.1015$.

Results of this calculation suggest that 89.85 percent of native alluvial groundwater (well SMC-08/916) mixes with 10.15 percent mine-water discharge (outfalls) to produce an average of 0.165 mg/L of dissolved uranium measured at well DD. This calculation assumes that (1) uranium is mobile with minimal or no adsorption; (2) no mineral precipitation that would remove uranium from groundwater is occurring under the oxidizing conditions prevailing in the alluvial aquifer in San Mateo Creek Basin; and (3) no uranium is mobilized from the vadose zone.

These first-order calculations support the concept of groundwater mixing of historical mine-water discharges with native alluvial groundwater. Additional mixing calculations should refine fractions of components involved in binary mixing occurring in the alluvial aquifer north of the Homestake NPL Site. Dissolved concentrations of uranium in mine-water discharges ranged between 0.32 and 2.95 mg/L and solutions are characterized by a sodium-calcium-sulfate composition (Perkins and Goad 1980, Weston Solutions, Inc. 2018). Water-level increases in

alluvial wells, including DD (see Figures 7b and 8b), support a model of recharge from mine-water discharges present in San Mateo Creek and the adjacent floodplain episodically at least since 1976, and probably earlier. With surface-water transport, mine-water discharges infiltrating and mixing with native alluvial groundwater is a viable physical process occurring downgradient of the mines and upgradient of the Homestake NPL Site.

Additional geochemical analyses using PHREEQC were conducted to evaluate potential groundwater mixing in the alluvial aquifer with three end members, consisting of mine-water discharges, slightly impacted groundwater (well P), and native alluvial groundwater (well SMC-08/916). The PHREEQC simulations included mass transfer of gypsum and calcite, set at an initial concentration of 10 moles for each mineral, reacting with the mixed solutions. The motivation for this analysis is based on (1) hydrological factors, including historical surface-water flow in San Mateo Creek and increasing saturated thickness in the alluvial aquifer measured by increasing groundwater elevations at wells P, Q, R, DD, and other monitoring wells (Weston Solutions, Inc. 2018) and (2) variable or transient (non-steady state) concentrations of dissolved calcium, sulfate, uranium, selenium and other solutes measured at several alluvial wells. Increasing saturated thickness of the alluvium at wells DD, DD2, P, Q, and R has occurred since the mid-1950s (see Figure 7b).[7] Some of this increase is attributed to infiltration of mine water along San Mateo Creek and the adjacent floodplain north of the LTP that recharges the alluvial aquifer. During 1976, the saturated thickness of the alluvium measured at well P (18.3 m, 59.9 ft.) was greater than the saturated thickness recorded at well DD (9.4 m, 30.7 ft.) (see Figure 7d). This suggests that there probably was a greater fraction of native alluvial groundwater (with lower solute concentrations) and a smaller fraction of mine-water discharge at well P compared to well DD. Since 1976, dissolved concentrations of uranium are higher at well DD compared to well P (Homestake database), which may result from a higher fraction of mine-water discharge.

PHREEQC simulations were conducted to evaluate mixing of alluvial groundwater (well P) with mine-water discharges, including mass transfer of gypsum and calcite, to constrain major-ion chemistry observed at well DD in 1976 and 2016. Well P is located near and cross-gradient from well DD, and is selected for this geochemical simulation because the well is completed in a deep portion of the alluvial channel, contains substantial saturated thickness, and is considered representative of less-impacted alluvial groundwater. Input is provided in Table 7a that includes an average chemical composition of groundwater at well P from 1979 and 1980 (Homestake database) and an average chemical composition of mine-water discharge from 1977 through 1979 (Perkins and Goad 1980). The simulated mixture, with emphasis on dissolved calcium and sulfate concentrations, is compared to well DD sampled on August 27, 1976, and October 6, 2016 (Arcadis 2018, Ulrich et al. 2019). Alluvial groundwater at well P has lower concentrations of calcium, sulfate, uranium, and other solutes compared to well DD. The PHREEQC simulations quantify mass transfer gypsum and calcite, which controls dissolved concentrations of calcium and sulfate in alluvial groundwater at well DD. Calcite and gypsum contain calcium; however, gypsum is much more soluble than calcite, which preferentially dissolves through the common-ion effect. This chemical interaction refers to the decrease in aqueous solubility of a less soluble

[7] Saturated thickness of the alluvium decreases in wells DD and P in response to aquifer pumping at the Homestake NPL Site from the late 1970s until the mid-2000s (see Figure 8b). Wells P and P4 were pumped from approximately 1993 to 2001.

precipitate (calcite) by the addition of a common ion (calcium) from a more soluble precipitate (gypsum), which is shown by the following reaction:

$CaSO_4 \cdot 2H_2O + 2HCO_3^- \rightarrow CaCO_3 + SO_4^{2-} + 3H_2O + CO_2(g)$.

Results of the PHREEQC simulations provided in Table 7a show that volumetric mixing between less-impacted alluvial groundwater at well P and mine-water discharge, followed by mass transfer of gypsum and calcite, produce a solution that is very similar to well DD that is enriched with calcium and sulfate. Fractions of well P groundwater and mine-water discharge are 0.9711 and 0.0289, respectively, which are determined from dissolved concentrations of detectable uranium measured at well DD (0.0944 mg/L) on October 6, 2016 (Arcadis 2018, Ulrich et al. 2019), and at well P (0.0511 mg/L) during 1979 and 1980 (average of 8 samples) (Homestake database). Groundwater samples collected from well P with dissolved concentrations of uranium below analytical detection limits (<0.00848 mg/L) were not included as part of the mixing calculations using PHREEQC. The simulated pH 6.97 of the mixed solution reacting with gypsum and calcite and not allowing PCO_2 gas to be fixed is slightly more acidic compared to pH 7.15 measured at well DD on October 6, 2016 (Arcadis 2018, Ulrich et al. 2019).

A groundwater sample collected at well DD on August 27, 1976 had a pH of 7.3 and dissolved concentrations (in mg/L) of bicarbonate, calcium, chloride, sodium, and sulfate of 345, 579, 64, 450, and 1,938, respectively (Table 7a, Homestake database). This historical water chemistry is characterized by a calcium-sodium-sulfate ionic composition that is very similar to the more recent sampling results provided by Arcadis (2018) and Ulrich et al. (2019). Dissolved concentrations of sulfate have increased to 2,330 mg/L during a sampling event conducted on October 6, 2016 by Arcadis. Major-ion chemistry for well DD plots within the field for the 1977 – 1979 Arroyo del Puerto mine waters shown on the trilinear diagram presented on Figure 16, which suggests that the infiltrated mine water has impacting well DD.

Results of the PHREEQC simulations quantifying gypsum and calcite solubility are consistent with results of X-ray diffraction analyses provided by Arcadis (2018). Gypsum equilibrium controls dissolved concentrations of calcium and sulfate at well DD. Calcite is present between one wt. percent (10,000 mg/kg) and seven (70,000 mg/kg) wt. percent, with an average concentration of four wt. percent, in six sediment samples collected from boreholes DD-BK and DD2-BK. Gypsum was detected in only one sediment sample at one wt. percent, using XRD, collected at DD2-BK below the alluvial water table (Arcadis 2018, Ulrich et al. 2019). Gypsum was observed in the sediment samples analyzed by scanning electron microscopy-energy dispersive spectroscopy at concentrations below one wt. percent in boreholes DD-BK and DD2-BK.

PHREEQC simulations for well DD (Table 7a), using alluvial groundwater represented by well P, over-calculate the dissolved concentration of calcium by 106 percent (1976 data) and 120 percent (2016 data) in absence of Ca-smectite precipitation. The simulations for well DD under-calculate the dissolved concentration of sulfate by 7.4 percent (1976 data) and 20.9 percent (2016 data) in comparison to analytical results for groundwater samples collected on August 27, 1976 (Homestake database), and October 6, 2016 (Arcadis 2018, Ulrich et al. 2019). The simulations under-calculate dissolved concentrations of magnesium, sodium, potassium, bicarbonate, and chloride ranging from 15.2 percent (chloride) to 63.3 percent (magnesium) for wells DD and P. Partial dissolution of illite, montmorillonite, plagioclase, biotite, and chlorite and one or more unidentified metal carbonate/sulfate phases containing potassium, sodium,

and magnesium potentially contributes additional divalent cations to alluvial groundwater. In addition, cation exchange with smectite (Ca^{2+} exchanging with Na^{+}) observed in sediment samples collected at boreholes DD-BK and DD2-BK (Arcadis 2018, Ulrich et al. 2019) is another viable geochemical process influencing solution composition at well DD. Dissolved concentrations of sodium at well DD possibly are, in part, sourced from the LTP. Approximately 5.97E-04 moles of calcite precipitate and 1.11E-02 moles of gypsum dissolve after mixing of well P groundwater and mine-water discharge, which is set in equilibrium with gypsum and is oversaturated with calcite at well DD (Table 5). PHREEQC mixing and mass transfer simulations using well P and mine-water discharge produce a solution that is enriched in dissolved calcium and sulfate similar to groundwater sampled at well DD.

Table 7a. Results of PHREEQC mixing calculations using mean analytical results for mine-water discharges and groundwater samples collected at well P during 1979 and 1980, Homestake NPL Site, Cibola County, New Mexico.

Well P (1979 – 1980, Homestake database) (mean, mg/L), [number of samples]	**Mine-water Discharges (1977 – 1979, Perkins and Goad 1980) (mean, mg/L), [number of samples]**	**PHREEQC, Mixed Composition (mg/L) (0.9711 of well P and 0.0289 of mine-water discharge) in equilibrium with gypsum (SI = -0.01) and oversaturated with calcite (SI = +0.22) at well DD**	**Well DD (August 27, 1976, first result, and October 6, 2016, second result, Homestake database, Arcadis 2018) (mg/L)**
Ca, 180, [5]	Ca, 100, [7]	**Ca, 613**	**Ca, 579, 509**
Mg, 40, [5]	Mg, 48, [3]	Mg, 40	Mg, –, 109
K, 4.8, [5]	K, 7.40, [7]	K, 4.9	K, –, 6.2
Na, 256, [10]	Na, 229, [11]	Na, 260	Na, 450, 392
HCO_3, 329, [10]	HCO_3, 212 [7]	HCO_3, 292	HCO_3, 345, 290
Cl, 65, [5]	Cl, 93 [11]	Cl, 67	Cl, 64, 79
SO_4, 754, [10]	SO_4, 622, [11]	**SO_4, 1,843**	**SO_4, 1,938, 2,330**
Se, 0.125, [10]	Se, 0.239, [11]	Se, 0.130	Se, 0.11, 0.114
U, 0.0511, [8]	U, 1.55, [11]	U, 0.0945	U, 0.1018, 0.0994
V, 0.005, [2]	V, 0.133, [6]	V, 0.004	V, –, 0.25
pH (median), 7.7, [3]	pH (median), 8.08, [7]	pH, 6.97	pH, 7.3, 7.15
pe, 4.0, Eh (+235.9 mV)	pe, 4.0, Eh (+236.7 mV)	pe, 5.161, Eh (+303 mV)	pe, 4.499, Eh (+256 mV)
Temp. (°C), 24	Temp. (°C), 25 (assumed)	Temp. (°C), 24	Temp. (°C), 13.6
Calcite precipitated (moles)	Not applicable	5.966E-04	Not applicable
Gypsum dissolved (moles)	Not applicable	1.111E-02	Not applicable

Notes:

Fractions of mine-water discharge (0.0298) and groundwater at well P (0.9711) are oversaturated with calcite (saturation index, SI = +0.22) and in equilibrium with gypsum (SI = -0.01) at well DD. $PCO_2(g)$ is not fixed for the PHREEQC simulation. The parameter, pe (4.0) is assumed for mine-water discharge and well P. Source of data for calculations: Homestake database, Perkins and Goad (1980), Arcadis (2018), and Ulrich et al. (2019). Hyphen (–) means analytical results for Mg, K, and V are not available for the sampling round conducted on August 27, 1976 at well DD).

Bolded values for Ca and SO_4 reflect over-prediction (for Ca) and under-prediction (for SO_4) of values measured in well DD.

An additional set of PHREEQC simulations was conducted to evaluate mixing of native alluvial groundwater (well SMC-08/916) with mine-water discharge and reacting with gypsum and calcite (initial concentration set at 10 moles) to constrain major-ion chemistry observed at well DD in 1976 and 2016. Well SMC-08/916 is located northeast and upgradient from well DD and is selected for this geochemical simulation because the well is considered representative of native alluvial groundwater. Input is provided in Table 7b that includes an average chemical composition of groundwater at well SMC-08/916 from 1997 and 2005 (Homestake database) and an average chemical composition of mine-water discharge from 1977 through 1979 (Perkins and Goad 1980). The simulated mixture is compared to well DD sampled on August 27, 1976, and October 6, 2016 (Arcadis 2018, Ulrich et al. 2019).

Table 7b. Results of PHREEQC mixing calculations using mean analytical results for mine-water discharges and groundwater samples collected at well SMC-08/916 during 1979 and 1980, Homestake NPL Site, Cibola County, New Mexico.

Well SMC-08/916 (1997 – 2005, Homestake database) (mean, mg/L), [number of samples]	**Mine-water Discharges (1977 – 1979, Perkins and Goad 1980) (mean, mg/L), [number of samples]**	**PHREEQC, Mixed Composition (mg/L) (0.8985 of SMC-08/916 and 0.1015 of mine-water discharge) in equilibrium with gypsum (SI = -0.01) and oversaturated with calcite (SI = +0.22) at well DD**	**Well DD (August 27, 1976, first result, and October 6, 2016, second result, Homestake database, Arcadis 2018) (mg/L)**
Ca, 5.5, [8]	Ca, 100, [7]	**Ca, 635**	**Ca, 579, 509**
Mg, 1.3, [8]	Mg, 48, [3]	Mg, 6.0	Mg, –, 109
K, 1.4, [2]	K, 7.40, [7]	K, 2.0	K, –, 6.2
Na, 127.4, [8]	Na, 229, [11]	Na, 138	Na, 450, 392
HCO_3, 255, [8]	HCO_3, 212 [7]	HCO_3, 221	HCO_3, 345, 290
Cl, 26.3, [8]	Cl, 93 [11]	Cl, 33	Cl, 64, 79
SO_4, 46.5, [8]	SO_4, 622, [11]	**SO_4, 1,637**	**SO_4, 1,938, 2,330**
Se, 0.017, [8]	Se, 0.239, [11]	Se, 0.0395	Se, 0.11, 0.114
U, 0.0086, [8]	U, 1.55, [11]	U, 0.165	U, 0.1018, 0.0994
V, –	V, 0.133, [6]	V, –	V, –, 0.25
pH (median), 8.19, [8]	pH (median), 8.08, [7]	pH, 7.03	pH, 7.3, 7.15
pe, 4.0, Eh (+235.9 mV)	pe, 4.0, Eh (+236.7 mV)	pe, 8.641, Eh (+512 mV)	pe, 4.499, Eh (+256 mV)
Temp. (°C), 25	Temp. (°C), 25 (assumed)	Temp. (°C), 25	Temp. (°C), 13.6
Calcite precipitated (moles)	Not applicable	4.839E-04	Not applicable
Gypsum dissolved (moles)	Not applicable	1.596E-02	Not applicable

Notes:

Fractions of mine-water discharge (0.1015) and groundwater at SMC-08/916 (0.8985) are oversaturated with calcite (saturation index, SI = +0.22) and in equilibrium with gypsum (SI = -0.01) at well DD. PCO_2(g) is not fixed for the PHREEQC simulation. The parameter, pe (4.0) is assumed for mine-water discharge and well SMC-08/916. Source of data for calculations: Homestake database, Perkins and Goad (1980), Arcadis (2018), and Ulrich et al. (2019).

Hyphen (–) means analytical results for Mg, K, and V are not available for the sampling round conducted on August 27, 1976 at well DD).

Bolded values for Ca and SO_4 reflect over-prediction (for Ca) and under-prediction (for SO_4) of values measured in well DD.

Alluvial groundwater at well SMC-08/916 has much lower dissolved concentrations of calcium, sulfate, uranium, and other solutes compared to wells DD and DD2. The simulated pH 7.03 of the mixed solution reacting with gypsum and calcite is slightly more acidic compared to pH 7.15 measured at well DD on October 6, 2016 (Arcadis 2018). Results of the PHREEQC simulations provided in Table 7b show that volumetric mixing between native alluvial groundwater at well SMC-08/916 and mine-water discharge, followed by reacting with calcite and gypsum, produces a major-ion chemistry that is similar to that at well DD, but the modeling of well P produced a closer similarity to well DD groundwater chemistry. The mixed solution after reacting with calcite and gypsum becomes enriched with calcium and sulfate. Fractions of well SMC-08/916 groundwater and mine-water discharge are 0.8985 and 0.1015, respectively, which are determined from dissolved concentrations of detectable uranium measured at well DD (0.0944 mg/L) on October 6, 2016 (Arcadis 2018, Ulrich et al. 2019), and at well SMC-08/916 (0.0086 mg/L) during 1997 and 2005 (8 samples).

PHREEQC simulations for well DD (Table 7b), using native alluvial groundwater represented by well SMC-08/916, over-calculate the dissolved concentration of calcium by 110 percent (1976 data) and 125 percent (2016 data) in absence of Ca-smectite precipitation. The simulations under-calculate the dissolved concentration of sulfate by 16 percent (1976 data) and 30 percent (2016 data) with well SMC-08/916. The simulations under-calculate dissolved concentrations of magnesium, sodium, potassium, bicarbonate, and chloride ranging from 36.5 percent (bicarbonate) to 94.5 percent (magnesium) for 2016 data. Dissolution of illite, chlorite, biotite, and plagioclase and one or more unidentified metal carbonate/sulfate phases containing potassium, sodium, and magnesium potentially contributes additional divalent cations to alluvial groundwater. Approximately 4.84E-04 moles of calcite precipitate and 1.60E-02 moles of gypsum dissolve after mixing native alluvial groundwater with mine-water discharge (Table 7b), which is in equilibrium with gypsum (SI = -0.01) and oversaturated with calcite (SI = +0.22) at well DD (Table 5). PHREEQC mixing and mass transfer simulations using well SMC-08/916 and mine-water discharge produce a solution that is enriched in dissolved calcium and sulfate similar to groundwater sampled at well DD.

Mixing of mine-water discharges with native alluvial groundwater (well SMC-08/916), without including mass transfer of gypsum and calcite does not accurately reproduce groundwater chemistry measured at well DD. For example, calculated dissolved concentrations of calcium and sulfate are 15.1 mg/L and 105 mg/L, respectively, based on PHREEQC simulations. Additional sources of dissolved calcium and sulfate measured at well DD may include: (1) contaminated alluvial groundwater consisting of infiltrated mine water mixed with native alluvial groundwater; (2) dissolution of gypsum leached from the vadose zone under rising water table conditions; and (3) sulfate-rich groundwater sourced from the LTP that has become mobilized during injection of treated water and extraction of contaminated groundwater.

6.1 Inverse Geochemical Modeling

Additional PHREEQC simulations consisting of inverse modeling were conducted to quantify general water-rock interactions under equilibrium conditions, including precipitation and dissolution reactions, that produces or controls the major ion chemistry along one or more groundwater-flow paths leading to well DD. The inverse modeling calculations presented in this report are a first-order evaluation of observed changes in groundwater geochemistry of major ions along one or more groundwater flow paths extending from north-northeast to south-southwest in the alluvial aquifer north of the Homestake NPL site. Reactive transport modeling,

including kinetic parameters for mineral precipitation/dissolution, should be conducted as more site-specific hydrological, geological, mineralogical, and geochemical data and information become available in future investigations conducted in the San Mateo Creek Basin.

PHREEQC calculates concentrations of solutes and specified minerals that either dissolve or precipitate to produce a final groundwater composition during inverse modeling. A minimum of two water compositions measured at different locations along a groundwater-flow path are required, in addition to a suite of minerals that react with a less chemically-evolved groundwater to produce a chemical composition of a more evolved groundwater. Model input consists of mean chemical compositions of mine-water discharges (Table 1) and well SMC-08/916 (Table 2) and a suite of known and hypothesized reactive minerals present in the alluvium in San Mateo Creek Basin. Inverse modeling is conducted to determine geochemical reactions that account for the change in chemical concentration of groundwater along a specific or known groundwater-flow path (Parkhurst and Appelo 2013). Dissolved gases and amorphous solids, such as chalcedony, silica glass, and ferric hydroxide, can be included in a mineral suite based on results of site-specific characterization of soils and sediments. Groundwater and reactive minerals are included in inverse modeling to provide cations, neutral species, and anions as either a sink (precipitation) or source (dissolution) to achieve mole balances to accurately quantify a change in chemical concentration along a specific flow path. The WATEQ4F chemical thermodynamic database was used for the PHREEQC inverse modeling of well DD, which contains smectite (calcium-rich montmorillonite), chlorite, and illite that occur in the alluvial sediments at the Homestake NPL Site (Arcadis 2018, Ulrich et al. 2019).

Chemical kinetics and surface complexation-adsorption reactions are not included as part of the inverse modeling presented in this report, with the main focus being on major ion chemistry. The PHREEQC simulations has shown that adsorption of uranium(VI) species, including UO_2^{2+}, uranyl carbonate-carbonato, and oxo-hydroxo complexes, onto HFO does not provide a significant attenuation process for removing this actinide from alluvial groundwater in San Mateo Creek Basin. Gypsum and calcite are reactive minerals that precipitate/dissolve at rates that are conducive for controlling dissolved calcium, sulfate, and total carbonate alkalinity measured at numerous wells, including well DD, completed in the alluvium in the San Mateo Creek Basin. Precipitation and dissolution of non-reactive silicate minerals present in the alluvial aquifer require much longer periods of time to control concentrations of solutes, such as sodium, aluminum, potassium, and magnesium. Alluvial groundwater has a mixed age with measurable tritium (Arcadis 2018, Blake et al. 2019) representing a modern component of recharge (post 1950s) and much older infiltrated mine water sourced from the Westwater Canyon Member of the Morrison Formation (Gallaher and Cary 1986, Weston Solutions, Inc. 2018). Pore-water chemistry from the vadose zone is not available and is not included in the inverse modeling simulations to represent additional leaching of solutes.

During inverse modeling, PHREEQC produces, with each output file, two or more possible mole-balance models calculated from input data that generate a final groundwater composition (Parkhurst and Appelo 2013). Mole-balance models consist of a set of mole transfers of one or more solid phases and solutes or reactants that account for the change in composition along a known groundwater-flow path. Some of the minerals selected may not be included in all of the mole-balance models generated by PHREEQC during inverse modeling.

The PHREEQC input files consist of mean concentrations of solutes present in mine-water discharges and SMC-08/916 groundwater and a suite of site-specific minerals to produce groundwater chemistry measured at well DD. Arcadis (2018, 2019) and Ulrich et al. (2019) report that smectite, gypsum, calcite, halite, plagioclase, chalcedony, or illite typically occur in alluvial sediment samples collected at boreholes DD-BK, DD2-BK, BK1, BK2, and BK3. Chlorite7A, biotite, and uranophane are hypothesized to potentially occur in the alluvium north of the LTP for modeling purposes. Uranophane was added to the mineral suite because this mineral has been identified in oxidizing zones of uranium deposits within the Westwater Canyon Member of the Morrison Formation (Brookins 1980) and provides an additional source of dissolved uranium(VI), calcium, and silica for mole-balance models generated by PHREEQC. Dissolution of uranophane and other known uranium(IV and VI) minerals, including coffinite, uraninite, carnotite, and tyuyamunite, during mining most likely contributed dissolved uranium concentrated in oxic mine-water discharges. Other secondary sources of natural uranium present in the alluvium include uranium adsorbed on solid organic matter and clay minerals, such as smectite and kaolinite (Arcadis 2018, Ulrich et al. 2019).

Adsorption processes involving the uranyl cation, other uranyl complexes, and HFO are not included in the PHREEQC inverse modeling because attenuation of this actinide via surface complexation with HFO is not significant in the alluvial aquifer characterized by a circumneutral pH, bicarbonate-rich groundwater, and oxic conditions. Carbon dioxide gas is also included in the site-specific mineral suite to adjust pH and control the solubility of carbonate minerals, such as calcite. A total of twelve plausible mole-balance models were generated as part of the output file consisting either of well SMC-08/916 groundwater, mine-mine-water discharge, and a specified suite of minerals. Uranophane was only included in six of the twelve mole-balance models with well SMC-08/916 groundwater and a suite of minerals, and did not include mine-water discharges. The mineral suite used as input during inverse modeling includes biotite, calcite, chalcedony, chlorite7A, carbon dioxide gas, gypsum, halite, illite, kaolinite, montmorillonite-Ca, plagioclase, and uranophane. Partial dissolution of the above minerals occurs under oxidizing and circumneutral pH conditions. The above mineral suite, excluding chlorite7A and uranophane, has been identified at boreholes DD-BK and DD2-BK (Arcadis 2018, Ulrich et al. 2019).

Results of inverse modeling simulations, consisting of six of the twelve mole-balance models, using mine-water discharges, well SMC-08/916 groundwater, and site-specific minerals identified in the alluvium near well DD suggests:

(1) Dissolved uranium concentrated in mine-water discharges is the dominant source of uranium measured at well DD, with mixing fractions of well SMC-08/916 and mine-water discharges equal to 0.94 and 0.06, respectively, in six of twelve mole-balance models. These mixing fractions compare closely with mixing fractions of well SMC-08/916 and mine-water discharges of 0.90 and 0.10, respectively, previously discussed herein. The fraction of well DD groundwater equals unity when mine-water discharges and well SMC-08/916 are included in all twelve inverse modeling simulations.

(2) Uranophane was not a component of six of the twelve mole-balance models of well DD using mine-water discharges and well SMC-08/916. Uranyl minerals are not required for inverse modeling for well DD to achieve a mole balance for uranium in the presence of mine-water discharges with a mean dissolved concentration of 1.55 mg/L (Perkins and

Goad 1980). Uranyl minerals have not been identified in sediment samples collected at boreholes DD-BK and DD2-BK (Arcadis 2018, Ulrich et al. 2019).

(3) In all twelve mole-balance models generated by the PHREEQC simulation, calcite and chalcedony always precipitate and gypsum, halite, carbon dioxide gas, biotite, and plagioclase always dissolve. Kaolinite and calcium-rich montmorillonite always precipitate when they are included in individual mole-balance models (kaolinite: four of twelve mole-balance models and montmorillonite: six of twelve mole-balance models). Chlorite7A and illite either precipitate or dissolve when they are included in individual mole-balance models (chlorite7A: eight of twelve mole-balance models and illite: ten of twelve mole-balance models).

(4) Specified minerals either dissolve or precipitate ranging from 0.0001 to 23 millimoles. Dissolution of gypsum is the primary source of dissolved calcium and sulfate, in addition to dissolved calcium and sulfate present in mine-water discharges and well SMC-08/916 groundwater. Gypsum is in equilibrium with mixed alluvial groundwater at well DD, even though 22.31 milimoles dissolve, in the absence of uranophane, calculated by PHREEQC.

Results of inverse modeling simulations for well DD, consisting of six of the twelve mole-balance models, using mean analytical results for well SMC-08 and specified minerals, including uranophane in the absence of mine-water discharges suggest:

(1) Dissolution of uranophane, which is hypothesized to occur in the alluvial aquifer as part of the PHREEQC inverse modeling simulations, is the major source of dissolved uranium in six of twelve mole-balance models that do not include mine-water discharges. Alluvial groundwater at wells SMC-08/916 and DD is undersaturated with uranophane with SI values of -12.60 and -10.64, respectively. It is highly unlikely that this mineral is stable or present in the alluvium, suggesting that mine-water discharges are the dominant source of dissolved uranium. In the absence of infiltrated mine water mixing with native alluvial groundwater, dissolution of one or more uranyl minerals, such as uranophane, carnotite, and tyuyamunite could hypothetically produce elevated concentrations of dissolved uranium(VI), if they are present in alluvial sediments. This scenario is not probable because uranium(VI) minerals have not been identified in the alluvium near wells DD and DD2. Migration of uranium-rich infiltrated mine water in the alluvial aquifer north of the Homestake NPL Site is supported by rising water table conditions at several wells (DD, P, Q, and R), vadose zone leaching of solutes, transient solute concentrations, and stable isotopes of sulfate reflective of oxidative dissolution of biogenic pyrite originally sourced from uranium ore bodies in the Westwater Canyon Member of the Morrison Formation (Jensen 1963, Weston Solutions, Inc. 2018). Mixing fractions of wells SMC-08/916 and DD are 0.999 and 1.0, respectively, in the six mole-balanced models used to generate groundwater chemistry of well DD in the absence of mine-water discharge.

(2) In all six mole-balance models using well SMC-08/916 groundwater and the site-specific minerals, calcite and chalcedony always precipitate and gypsum, halite, carbon dioxide gas, biotite, uranophane, and plagioclase always dissolve. Kaolinite and calcium-rich montmorillonite always precipitate when included in individual mole-balance models.

Chlorite7A and illite either precipitate or dissolve when they are included in individual mole-balance models of well DD.

(3) Specified minerals either dissolve or precipitate that range from 0.1 to 23 millimoles, excluding dissolution of uranophane of approximately 0.0002 millimoles. Dissolution of gypsum is the primary source of dissolved calcium and sulfate, in addition to dissolved calcium and sulfate present at well SMC-08/916. Gypsum is in equilibrium with mixed alluvial groundwater at well DD, even though 22.64 milimoles dissolve, in the presence of uranophane, calculated by PHREEQC. Dissolution of uranophane produces 0.0994 mg/L of dissolved uranium measured at well DD.

Results of inverse modeling using PHREEQC to quantify water-rock reactions controlling groundwater chemistry along one or more groundwater-flow paths leading to well DD are considered relevant and meaningful for the purpose of evaluating infiltration and migration of mine water contributing to groundwater chemistry measured at alluvial well DD. The PHREEQC simulations include mean chemical compositions of mine-water discharges, well SMC-08/916 groundwater, and site-specific minerals occurring in the alluvium (Arcadis 2018, Ulrich et al. 2019). Results of inverse modeling of well DD using mine-water discharges and well SMC-08/916 groundwater are compatible with results of the PHREEQC mixing and mass-transfer simulations previously presented in this report. The rationale for including mine-water discharges to the inverse modeling simulations is based on the 125 billion gallons of groundwater pumped from the Westwater Canyon Member of the Morrison Formation and discharged to Arroyo del Puerto and San Mateo Creek from 1956 to 1982 (Perkins and Goad 1980, Gallaher and Cary 1986). Results of inverse modeling of well DD using well SMC-08/916 groundwater and site-specific minerals, in the absence of mine-water discharges, are not relevant to San Mateo Creek Basin, because it requires dissolution of one or more uranyl minerals, for example uranophane, that have not been identified in the oxic alluvial aquifer. Dissolution of uranium(IV and VI) minerals likely occurred during mining operations in Ambrosia Lake area resulting in low-mg/L concentrations of residual dissolved uranium in mine-water discharges released to Arroyo del Puerto and San Mateo Creek from 1956 to 1982. Gypsum equilibrium and calcite oversaturation in alluvial groundwater controls dissolved concentrations of calcium and sulfate measured at several alluvial wells located north of the Homestake NPL Site based on results of the PHREEQC simulations.

7.0 Redox Processes and Mass-transfer Reactions Between Solutes and Solid Phases

The alluvial aquifer at wells DD and DD2 most likely consists of a mixture of native groundwater (represented by well SMC-08/916) and mine-water discharges. This mixed groundwater contains dissolved concentrations of sodium, calcium, sulfate, uranium, TDS, and other solutes above those measured at well SMC-08/916 (Homestake database, Perkins and Goad 1980, Gallaher and Cary 1986, and Weston Solutions, Inc. 2018). Oxidizing alluvial groundwater sampled at wells DD and DD2 is characterized by a calcium-sodium-sulfate composition and likely contain dissolved concentrations of uranium dominantly sourced from historical mine-water discharges. Dissolved concentrations of calcium, nitrate, selenium, sulfate, and uranium vary over time at well DD and likely result from a combination of this groundwater mixing and vadose zone leaching. Leaching of solutes from the vadose zone results from alluvial water table fluctuations attributable primarily to mine-water discharge recharge, hydraulic influence by tailing seepage from the LTP and STP, and aquifer pumping by Homestake. It is unlikely that

solute transients occurring at wells DD and DD2 represent natural background because of such anthropogenic influences on the groundwater chemistry.

Arcadis (2018) and Ulrich et al. (2019) demonstrate that sediment-bound uranium ranging from one to ten mg/kg is present in the alluvium at boreholes DD-BK and DD2-BK, located near wells DD and DD2, respectively (see Figure 15). Uranium is heterogeneously associated with clay minerals, carbonate minerals, solid organic matter, and iron sulfide (pyrite) in the borehole samples. Localized reducing zones associated with fine-grained sediments occur at these two borehole locations. Oxidative dissolution of pyrite and precipitation of ferric (oxy)hydroxide and iron oxide are observed in borehole sediments (Arcadis 2018, Ulrich et al. 2019).

Arcadis (2019) presents mineralogical and geochemical data for additional sediment samples collected and analyzed from three other new boreholes (BK1, BK2, and BK3) drilled in 2019, which are located east-southeast of boreholes DD-BK and DD2-BK (see Figure 15). One additional borehole, BK4 is located south of DD-BK and immediately north of the LTP that did not have sediment samples collected for geochemical and mineralogical analyses. Lower concentrations of total (acid-extractable) uranium were solubilized from sediments collected and analyzed from boreholes BK1, BK2, and BK3 compared to DD-BK and DD2-BK (Arcadis 2018, Arcadis 2019). Less than one mg/kg of uranium (non-detect) was extracted from 29 sediment samples collected from boreholes BK1, BK2, and BK3, and three samples had detectable uranium at concentrations (in mg/kg) of 1, 2, and 2 (Arcadis 2019). Arcadis (2019) reports results of selective extractions of soluble uranium and other analytes, using deionized water and a mixed solution of 0.0144 M sodium bicarbonate and 0.0028 M sodium carbonate, showing that most of the uranium is associated with solid carbonate and clay minerals (resistates). Concentrations of soluble uranium leached from BK1, BK2, and BK3 sediments are less than 0.005 mg/L, which are much lower than dissolved concentrations of uranium measured at wells BK1f, BK1c, BK2f, and BK2c and P, Q, R, and ND (Arcadis 2019 and Homestake database). The BK series wells were completed in coarse-grained sediments (e.g., BK1c) and fine-grained sediments (e.g., BK1f) at the location of the Arcadis BK1 and BK2 boreholes.

Arcadis (2018) and Ulrich et al. (2019) report that uranium was not detected (<1,000 mg/kg, or <0.10 wt. percent) in sediment samples collected at boreholes DD-BK and DD2-BK using X-ray diffraction and scanning electron microscopy-energy dispersive spectroscopy. Non-detection of sediment-bound uranium is consistent with either (1) weak partitioning or adsorption of uranium(VI) (as UO_2^{2+}) onto HFO, clay minerals, solid organic matter, and other adsorbents present in the borehole samples or (2) absence of uranium(IV) minerals in alluvial sediments. Arcadis (2018) and Ulrich et al. (2019) suggest that uranium is either segregated into individual minerals, such as uraninite, or finely disseminated in sediment samples at concentrations below analytical detection limits. The DD-BK and DD2-BK sediments, however, are overall oxidizing based on high abundance of amorphous iron (oxy)hydroxides and crystalline iron oxides. It is not known if trace concentrations of potential and assessable uranium(IV) solids have partly or completely oxidized and dissolved to form low concentrations of uranium(IV) aqueous species. These include $Ca_2UO_2(CO_3)_3^0$, $CaUO_2(CO_3)_3^{2-}$, and $UO_2(CO_3)_3^{4-}$, which are mobile in the oxidizing alluvial aquifer system in San Mateo Creek Basin.

Arcadis (2018) and Ulrich et al. (2019) present results of detailed acid-extraction and carbonate alkalinity batch-leach tests for molybdenum, selenium, uranium, vanadium, and other elements conducted on 19 sediment samples collected at boreholes DD-BK and DD2-BK. Ten sediment

samples were collected from borehole DD-BK and nine sediment samples were collected from borehole DD2-BK. Arcadis (2018) and Ulrich et al. (2019) followed EPA Method 3050B, consisting of nitric acid digestion with hydrogen peroxide oxidation at pH 1-2, to quantify total or acid-extractable metal concentrations in units of mg chemical/kg dry sediment mass, and EPA Method 1312, a synthetic precipitation leaching procedure modified with an alkaline (basic) extractant, with leachate concentrations reported in units of mg/L. The modified EPA Method 1312 consisted of 18 hours extraction using a 0.0144 M $NaHCO_3$ and 0.0028 M Na_2CO_3 solution (pH 9.4), with a solution to solid ratio of 20:1, to represent total carbonate alkalinity in basic alluvial groundwater north of the LTP. More uranium, however, is likely to be leached from alluvial sediments at pH 9.4 compared to ambient sediment pH values ranging from 7.9 to 8.6 (Arcadis 2019). Field-measured pH values varied between 7.01 and 7.94 at well DD from April 1997 to May 2018, which are less basic than solutions used during batch-least tests. Uranium(VI) complexes will leach or desorb from HFO under basic pH conditions in the presence of total carbonate alkalinity (Langmuir 1997), resulting in the formation of uranyl carbonato ($UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) and ternary calcium uranyl carbonate-carbonato complexes ($CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3^0$). The solution to solid ratio most likely diluted dissolved concentrations of uranium resulting in an underestimation of true concentrations of uranium leached from solids. Batch-leach tests do not provide sufficient or reliable data to determine that dissolved uranium measured at well DD is entirely sourced from alluvial sediments at this location. Column tests would have provided more meaningful and relevant results for accurately quantifying the release of uranium from alluvial sediments collected from the boreholes. Properly designed column tests using site-specific sediments, actual alluvial groundwater, and a more realistic solution to solid ratio, for example 0.25:1, 0.30:1, or 0.35:1 that is based on the effective porosity of the alluvial aquifer should be conducted in future experimental investigations.

Typical natural concentrations of uranium in the Earth's crust (average continental), granite (average), and shale, in units of µg/g or mg/kg, are 2.7, 4.4, and 3.8, respectively (Wanty and Nordstrom 1995). Gera (1975) reports that sandstones, limestones (USA), and bentonites-montmorillonites (USA) have 0.5 to 1 mg/kg, 2.2 mg/kg, and 5 mg/kg, respectively, of total uranium. Concentrations of total uranium using EPA Method 3050B dominantly were 2 mg/kg or less, excluding two samples that contain 5 mg/kg and 10 mg/kg of extractable uranium, in sediment samples collected for borehole DD2-BK. The majority of the sediment samples have extractable uranium that fall in the range of geologic materials with natural concentrations of this actinide. Concentrations of total uranium were less than analytical detection (< 1 mg/kg dry mass) in 8 of 19 (42%) sediment samples collected from both boreholes. Arcadis (2018) and Ulrich et al. (2019) report that three clay samples collected from borehole DD-BK contain 1 mg/kg of detectable uranium, with two of the samples collected from the vadose zone and the other from the saturated zone. Three clay samples collected from borehole DD2-BK contained total uranium concentrations of 10 mg/kg in one vadose-zone sample and 1 mg/kg and 2 mg/kg in two saturated zone samples. Other coarser-grained sediment samples collected from borehole DD2-BK contained concentrations of total uranium of 1 mg/kg in one vadose zone sample and three samples collected from the saturated zone contained 1 mg/kg, 2 mg/kg, and 5 mg/kg of total uranium.

Between 0.0012 mg/L and 0.0127 mg/L of dissolved uranium were leached from ten DD-BK sediment samples, with a mean concentration of 0.0075 mg/L, using a modified synthetic precipitation leaching procedure consisting of an alkaline rather than a slightly acidic solution

(EPA Method 1312) (Arcadis 2018, Ulrich et al. 2019). Four of the ten DD-BK sediment samples were collected below the alluvial water table. Leachate concentrations of dissolved uranium varied from 0.0079 mg/L to 0.179 mg/L, with a mean concentration of 0.0353 mg/L, for the nine DD2-BK sediment samples. Six of the nine DD2-BK sediment samples were collected below the alluvial water table. Leachate concentrations of dissolved uranium were less than 0.009 mg/L in 12 of the 19 sediment samples collected from the two boreholes. The anomalously high leachate concentration of sediment-bound uranium of 0.179 mg/L is associated with a clay sample, consisting of 23 wt. percent smectite and 11 wt. percent kaolinite, collected from borehole DD2-BK at a depth interval of 3.4 to 3.7 m (11 to 12 ft.) bgs in the vadose zone (Arcadis 2018, Ulrich et al. 2019). Higher dissolved concentrations of uranium were solubilized using a modified alkaline synthetic precipitation leaching procedure from the DD2-BK sediment samples compared to the DD-BK sediment samples, especially for samples collected from the vadose zone.

Concentrations of dissolved uranium measured at well DD2, with a mean of 0.226 mg/L measured in 43 groundwater samples from 2008 to 2018 (Homestake database), greatly exceed leachable uranium extracted from the six saturated DD2-BK sediment samples (mean of 0.0136 mg/L) using the modified alkaline synthetic precipitation procedure during batch-leach test (Arcadis 2018, Ulrich et al. 2019). The ratio of dissolved uranium measured in groundwater at well DD2 from 2008 to 2018 to leachable uranium from saturated DD2-BK sediments is 16.62.

Three clay samples collected from borehole DD-BK have alkaline-leachate concentrations of dissolved uranium ranging from 0.0022 mg/L to 0.0127 mg/L (Arcadis 2018, Ulrich et al. 2019). Three clay samples collected from borehole DD2-BK contain alkaline-leachate concentrations of dissolved uranium ranging from 0.0079 mg/L to 0.179 mg/L. Ratios of total uranium (EPA Method 3050B) to carbonate alkalinity-leachable uranium (EPA Method 1312) range from 21 to 164 in 11 sediment samples, having detectable concentrations of uranium, collected from boreholes DD-BK and DD2-BK (Arcadis 2018 , Ulrich et al. 2019). This suggests that most of the sediment-bound uranium at boreholes DD-BK and DD2-BK is not soluble or leachable under the prevailing oxidizing and circumneutral pH conditions occurring in alluvial groundwater at wells DD and DD2. The sediment-bound uranium quantified by the modified synthetic precipitation leaching procedure most likely occurs as uranyl carbonato and oxo-hydroxo complexes that are weakly adsorbed onto calcite, smectite, kaolinite, and ferric (oxy)hydroxide present in the DD-BK and DD2-BK sediment samples (Arcadis 2018, Ulrich et al. 2019).

The mean concentration of uranium leached from nine DD2-BK sediment samples is 0.0353 mg/L using an alkaline synthetic precipitation leaching procedure. This value is calculated from nine analytical results presented in Arcadis (2018) and Ulrich et al. (2019). Approximately 14 percent of accessible uranium is weakly bound to DD2-BK sediments, based on the ratio of mean concentration of leachable uranium (0.0353 mg/L), using modified EPA Method 1312, to the mean concentration of dissolved uranium (0.226 mg/L) at well DD2 plus leachable uranium (0.0353 mg/L). The ratio quantifies total uranium present in groundwater at well DD2 and sediment at borehole DD2-BK. The majority of uranium is dissolved in alluvial groundwater at well DD2, confirming that either desorption of uranium(VI) or oxidative dissolution of trace uranium(IV) minerals is a minor or secondary process contributing soluble uranium to groundwater. This suggests that the majority of dissolved uranium present at well DD2 is originally sourced from historical mine-water discharges released to Arroyo del Puerto and San Mateo Creek. This is consistent with surface-water chemistry of the mine outfalls and Arroyo

del Puerto water that contained much higher dissolved concentrations of uranium (Table 1) (Perkins and Goad 1980, Gallaher and Cary 1986, Weston Solutions, Inc. 2018, and EPA 1975).

The mean dissolved concentration of uranium measured in 55 alluvial groundwater samples collected at well DD, from 1997 to 2019, is 0.165 mg/L (Homestake database). The mean concentration of uranium leached from ten DD-BK sediment samples is 0.0057 mg/L using modified EPA Method 1312 (Arcadis 2019, Ulrich et al. 2019). Approximately three percent of accessible uranium is bound to DD-BK sediments, based on the ratio of concentration of alkaline-leachable uranium (0.0057 mg/L), using modified EPA Method 1312, to the mean concentration of dissolved uranium at well DD (0.165 mg/L) plus alkaline-leachable uranium (0.0057 mg/L). Similar to well DD2, the majority of uranium is dissolved in alluvial groundwater at well DD, confirming that either desorption of uranium(VI) complexes or oxidative dissolution of uranium(IV) minerals is a minor or secondary process contributing soluble uranium to groundwater. This also suggests that the majority of dissolved uranium present at well DD is from historical mine-water discharges to Arroyo del Puerto and San Mateo Creek.

The mean dissolved concentration of sulfate measured in 56 alluvial groundwater samples collected at well DD, from 1997 to 2019, is 1,785 mg/L (Homestake database). Sulfate present in the alluvial aquifer is associated with gypsum, which is originally derived from two processes: (1) oxidation of abundant biogenic pyrite occurring in primary (reducing) uranium ore zones in groundwater pumped from the Westwater Canyon Member of the Morrison Formation, treated, and discharged to Arroyo del Puerto and San Mateo Creek from 1956 to 1982 and (2) oxidation of trace amounts of native pyrite present in alluvial sediments filling San Mateo Creek Basin over geologic time. The following generalized reaction shows acid production and irreversible oxidative dissolution of pyrite forming amorphous (am) ferric hydroxide and dissolved sulfate:

$$3.5H_2O + FeS_2 + 3.75O_2^0 \rightarrow 2SO_4^{2-} + Fe(OH)_3(am) + 4H^+.$$

Oxidation of one mole of pyrite produces two moles of dissolved sulfate according to the above reaction. The molecular weights of sulfate and pyrite are 96.06 g/mol and 119.98 g/mol, respectively. Assuming that dissolved sulfate is entirely produced from oxidative dissolution of pyrite at well DD, 1,115 mg of pyrite (0.1115 wt. percent) is required to produce a mean dissolved concentration of sulfate equal to 1,785 mg/L. It is likely that this relatively high amount of pyrite would have been detected in sediment samples analyzed by Arcadis (2018) and Ulrich et al. (2019) if present. Because pyrite was not detected in such amounts, this suggests that the majority of the dissolved sulfate measured at well DD is primarily derived from mine-water discharge, as surface-water recharge, infiltrating and mixing with native alluvial groundwater that enhances precipitation of gypsum. Using the same approach for well SMC-08/916, representing native alluvial groundwater with an average dissolved concentration of sulfate of 46.5 mg/L (Table 2), 29.0 mg of pyrite (0.0029 wt. percent) would potentially oxidize and dissolve producing sulfate at this monitoring well. Alluvial groundwater at well SMC-08/916 is undersaturated with gypsum, and sulfate behaves as a conservative solute at this well.

8.0 Summary and Conclusions

8.1 Sources and Transport of Solutes in the Alluvial Aquifer

Geochemical and hydrological processes described in detail in this updated report form the basis of a dynamic and complex conceptual-site model for groundwater background in the alluvial aquifer system in San Mateo Creek Basin north of the Homestake Mining Company of California (Homestake) National Priorities List (NPL) Site (Homestake NPL Site). Approximately 125 billion gallons of mine water (12.672 million gallons per day (GPD) averaged over 26 years, 0.383 million acre-feet) were pumped from the Westwater Canyon Member of the Morrison Formation and Dakota Sandstone Formation (Perkins and Goad 1980, Gallaher and Cary 1986) in the Ambrosia Lake area and released to Arroyo del Puerto and San Mateo Creek north of the Homestake NPL Site from 1956 to 1982. Historical (pre-1983) surface-water flow in San Mateo Creek, consisting of mine-water discharges and treated effluents, acts as a non-point source of recharge to the alluvial aquifer in San Mateo Creek Basin. Uranium and other inorganic solutes are concentrated in mine-water discharges compared to native alluvial groundwater. Leaching of natural and anthropogenic chemicals from the vadose zone is occurring under rising water table conditions during migration of contaminated groundwater through the alluvium. Groundwater mixing is supported by increasing saturated thickness in the alluvium, solute transients, and a close similarity of major-ion chemistry between historical mine-water discharges and alluvial groundwater north of the Homestake NPL Site.

Surface-water flow likely allowed a large volume of mine water to recharge the alluvial aquifer over a substantial area of the lower San Mateo Creek floodplain very early in the uranium mining industry's period of discharge operations (1956-1982). As a result, surface water infiltrated and provided localized recharge to the alluvial aquifer for several kilometers or miles along San Mateo Creek north of alluvial monitoring well DD possibly as early as the late 1950s. Well DD is located near the western edge of the alluvial paleochannel approximately 0.6 km (0.4 miles) north of the large tailing pile (LTP), and consistently exhibits higher dissolved concentrations of calcium, nitrate, sulfate, uranium, and total dissolved solids (TDS) compared to other monitoring wells located near the LTP.

Alluvial well SMC-08/916 is located along the eastern edge of the San Mateo Creek paleochannel approximately 2.4 kilometers (km) (1.5 miles) northeast of the LTP. Well SMC-08/916 exhibits lower dissolved concentrations of calcium, nitrate, sulfate, uranium and TDS, and likely represents a component of native alluvial groundwater that is not impacted from mine-water discharges originally released to Arroyo del Puerto and San Mateo Creek. Solute concentrations at this well have been consistent since 1997. Drilling of one or two additional alluvial monitoring wells north of well SMC-08/916 should refine groundwater background.

Infiltration and mixing of mine-water discharges with native alluvial groundwater likely changed the major-ion chemistry from a sodium-calcium-bicarbonate solution to a calcium-sodium-sulfate solution in equilibrium with gypsum. Infiltration of mine-water discharges, groundwater mixing, and leaching of solutes from the vadose zone likely produced transient conditions in concentrations of calcium, sulfate, nitrate, uranium, selenium, and TDS at several monitoring wells (DD, DD2, P, Q, and R) located north of the LTP. Dissolution of gypsum in the vadose zone produces increasing dissolved concentrations of calcium and sulfate in alluvial groundwater at well DD. Leaching of solutes occurs in the vadose zone under rising water table conditions at wells DD, DD2, Q, and R. Aquifer pumping of alluvial groundwater at and near the LTP by

Homestake is contributing to the geochemical and hydraulic transients observed at well DD. Based on transient geochemical conditions observed at upgradient monitoring wells as early as 1976, such as well DD and nearby well DD2, dissolved concentrations of uranium, selenium, nitrate, sulfate, TDS, and calcium are not representative of natural groundwater background in the alluvium at the Homestake NPL Site.

The majority of the sediment samples collected from boreholes DD-BK and DD2-BK have total extractable uranium that is within the range of natural geologic materials (0.5 mg/kg to 4.4 mg/kg). The original source of sediment-bound uranium, ranging from one to 10 mg/kg, present at these two boreholes is dominantly from naturally mineralized sediments transported and deposited over geologic time (>10,000 years) and heterogeneously distributed in San Mateo Creek Basin. Geochemical and mineralogical characterization studies conducted by Arcadis (2018, 2019) and Ulrich et al. (2019) confirm that natural sources of low concentrations of sediment-bound uranium occur with carbonate and oxide phases. Uranium(IV and VI) minerals, if present in alluvial sediments, are at concentrations less than analytical detection limits.

It is recognized that groundwater flow in the alluvium, from north-northeast to south-southwest, is complex in the fluvial sediments characterized by variable, non-isotropic and heterogeneous hydraulic properties and preferred flow paths along one or more buried paleochannels. Dissolved uranium(VI) is an excellent groundwater tracer to assess groundwater mixing in the alluvial aquifer in San Mateo Creek Basin characterized by circumneutral pH and oxic conditions. Based on simple, first-order binary mixing of dissolved uranium, approximately 97.11 percent of alluvial groundwater at monitoring well P (1979 - 1980) mixes with 2.89 percent of infiltrated mine water to produce an average dissolved concentration of uranium of 0.165 mg/L measured at well DD from 1997 to 2019. Using the same approach, approximately 89.85 percent of native alluvial groundwater at well SMC-08/916 (1997 - 2005) mixes with 10.15 percent of infiltrated mine water to produce average dissolved concentrations of uranium measured at well DD. These mixing ratios provide plausible percentages of native alluvial groundwater that are impacted from infiltrating mine water, which possibly occurred at least since 1976 near well DD.

Most of the dissolved uranium present in alluvial groundwater at wells DD and DD2 is likely derived from historical mine-water discharges based on documented long-term (26 years) discharges that produced substantial transients in water table elevations and solute chemistry. The inconclusive results of batch-leach tests conducted by Arcadis (2018, 2019) do not demonstrate predominance of naturally occurring uranium leached from alluvial sediment. Approximately 14 percent of environmentally accessible uranium is weakly bound to DD2-BK sediments and 86 percent of uranium is dissolved in groundwater at well DD2. Approximately 3 percent of environmentally accessible uranium is bound to DD-BK sediments and 97 percent of uranium is dissolved in groundwater at well DD. Either desorption of uranium(VI) complexes or oxidative dissolution of trace uranium(IV) minerals is a minor or secondary process contributing a fraction of soluble uranium to alluvial groundwater at wells DD and DD2.

Partial evaporation of surface water, consisting of mine-water discharges and storm water, occurred prior to infiltrating through the vadose zone to alluvial groundwater, based on enriched isotopic ratios of δ^2H-H_2O and $\delta^{18}O$-H_2O (Weston Solutions, Inc. 2018). Enriched isotopic ratios of hydrogen and oxygen likely result from infiltrated stagnant surface water held

in the earthen spreader dams built along San Mateo Creek that resulted in ponded, standing water after storm events (EPA 1980).

Light or negative $\delta^{34}S\text{-}SO_4$ ratios measured in alluvial groundwater in San Mateo Creek Basin are the same as those for pyrite examined from uranium ore samples collected from the Westwater Canyon Member of the Morrison Formation of Jurassic age (Weston Solutions, Inc. 2018). Light $\delta^{34}S\text{-}SO_4$ ratios typically less than -20 permil measured in alluvial groundwater flowing along the San Mateo Creek paleochannel are the same as those for pyrite examined from uranium ore samples collected from the Westwater Canyon Member. This corresponds to the location of the paleochannel that provides the greatest groundwater flux for transporting infiltrated mine water in the alluvial aquifer. Heavier or less negative $\delta^{34}S\text{-}SO_4$ ratios occur along the eastern boundary of the alluvial aquifer at wells SMC-10/914 and ND, which may represent a baseline sulfur isotope signature for the alluvial aquifer. Depleted sulfur isotope signatures in sulfate in alluvial groundwater are consistent with most of the dissolved sulfate originally and dominantly sourced from uranium ore zones. Oxidative dissolution of trace amounts of pyrite in alluvial sediments may have also contributed to depleted $\delta^{34}S\text{-}SO_4$ ratios measured in alluvial groundwater north of the Homestake NPL Site. Additional stable isotope analyses of sulfur should refine sulfate sources in alluvial groundwater.

8.2 Geochemical Modeling and Other Calculations

Geochemical-thermodynamic computer programs, such as PHREEQC, are used as one of several quantitative tools, along with groundwater analytical results and hydrogeological, mineralogical, and geophysical data and information, as part of conducting site characterization and remediation investigations. Reactive transport modeling was not performed at this stage of the investigation because several hydraulic and geochemical information and parameters, including groundwater and solute residence times, groundwater-flow rates, complete delineation of groundwater-flow paths, geometry of one or more paleochannels, mineral reaction rates, and mineral surface areas, are not known for the alluvial aquifer north of the LTP. In addition, detailed geochemical and mineralogical characterization and column testing has not been conducted using sediment samples collected at other locations in the San Mateo Creek Basin to provide relevant and meaningful data and information that is essential for reactive transport modeling. Batch equilibrium modeling is an appropriate initial approach to evaluate mineral stability and adsorption processes occurring at well DD, in the absence of key hydraulic and surface chemistry parameters required for kinetic and reactive transport modeling.

Based on PHREEQC speciation simulations, dissolved uranium in alluvial groundwater at well DD is stable as soluble ternary complexes of uranium(VI) carbonate ($Ca_2UO_2(CO_3)_3^0$) and carbonato ($CaUO_2(CO_3)_3^{2-}$) species. Such anionic aqueous complexes are weak adsorbates that do not significantly accumulate on solid surfaces, including ferric (oxy)hydroxide, under circumneutral pH conditions (Langmuir 1997) characteristic of alluvial groundwater at well DD.

Based on results of batch-equilibrium simulations using the computer program PHREEQC (Parkhurst and Appelo 2013), alluvial groundwater at well DD is in equilibrium with gypsum and dolomite (ordered); is oversaturated with barite, calcite, ferrihydrite (represented as amorphous $Fe(OH)_3$), gibbsite, and pyrolusite; and is undersaturated with $CaMoO_4$, carnotite, chalcedony, dolomite (disordered), K-jarosite, rhodocrosite, tyuyamunite, and uraninite. Quartz, smectite, kaolinite, orthoclase, plagioclase, kaolinite, biotite, calcite, illite, gypsum, and halite occur in

alluvial sediments near wells DD and DD2 (Arcadis 2018, Ulrich et al. 2019). Uranium(IV, VI) phases are not observed in the alluvial sediments collected near the two monitoring wells. Surface complexation of metals binding to hydrous ferric oxide (HFO) (represented by amorphous $Fe(OH)_3$) and other adsorbents is important for influencing the fate and transport of oxyanions, such as selenium(IV, VI), uranium(VI), arsenic(III, V), and chromium(VI). Surface adsorption sites present on HFO having a negative charge are not strong binding sites for ternary uranyl complexes, including $Ca_2UO_2(CO_3)_3^0$ and $CaUO_2(CO_3)_3^{2-}$, that are predicted to occur in alluvial groundwater at well DD. In addition, surface complexation of UO_2^{2+} and other uranyl carbonate-carbonato-oxy-hydroxo adsorbates onto HFO is minimal based on PHREEQC simulations using DD groundwater, which is equilibrated with the HFO surface. A total of 1.59E-08 moles (3.78E-03 mg) of uranium are removed from solution by adsorbing onto HFO, which is consistent with the mobility of uranium(VI) in alluvial groundwater at well DD. Only 1.435E-08 moles of the surface complex, $Hfo\_wOUO_2(CO_3)_2^{3-}$ dominates weak adsorption sites present on 0.089 g of HFO according to the PHREEQC simulation.

The PHREEQC modeling results are consistent with variable and high dissolved concentrations of uranium commonly exceeding 0.100 mg/L measured at well DD since 1976. Based on results of PHREEQC simulations, non-complexed or free calcium (Ca^{2+}) concentrated in alluvial groundwater effectively competes for adsorption sites on HFO in the presence of other adsorbates, including poorly adsorbed uranyl cation-carbonate-carbonato-oxo-hydroxo complexes that are both associated with strong-and weak-binding sites.

A PHREEQC simulation was performed with equilibrating the surface of HFO (0.089 g) with well SMC-08/916 groundwater and mixing with mine-water discharge. The mixed solution contains an average dissolved concentration of uranium of 0.165 mg/L measured at well DD from 1997 to 2019, and has fractions of well SMC-08/916 groundwater and mine-water discharges of 0.8985 and 0.1015, respectively. An insignificant amount of uranium (Σ = 9.181E-08 moles, 2.185E-02 mg), represented as surface complexes $Hfo\_sOUO_2^+$, $Hfo\_sOUO_2OH^0$, $Hfo\_wOUO_2(CO_3)_2^{3-}$, $Hfo\_wOUO_2CO_3^-$, $Hfo\_wOUO_2OH^0$, and $Hfo\_wOUO_2^+$, poorly adsorb onto strong and weak sites of the HFO surface equilibrated with the mixed solution at pH 8.16. This simulation supports the high mobility of dissolved uranium(VI) in the oxic alluvial aquifer at the Homestake NPL Site.

PHREEQC mixing and mass transfer simulations using well P and mine-water discharge produce a solution that is enriched in dissolved calcium and sulfate similar to groundwater sampled at well DD. PHREEQC simulations for well DD, however, over-calculate the dissolved concentration of calcium in absence of Ca-smectite precipitation. The simulations for well DD under-calculate the dissolved concentration of sulfate in comparison to analytical results for groundwater samples reported by Arcadis (2018) and Ulrich et al. (2019). The simulations under-calculate dissolved concentrations of magnesium, sodium, potassium, bicarbonate, and chloride by not including partial dissolution of illite, montmorillonite, plagioclase, biotite, and chlorite and one or more unidentified metal carbonate/sulfate phases. In addition, cation exchange with smectite (Ca^{2+} exchanging with Na^+) observed in sediment samples collected at boreholes DD-BK and DD2-BK (Arcadis 2018, Ulrich et al. 2019) is another viable geochemical process influencing solution composition at well DD. Approximately 5.97E-04 moles of calcite precipitate and 1.11E-02 moles of gypsum dissolve after mixing of well P groundwater and mine-water discharge, which is set in equilibrium with gypsum and is oversaturated with calcite at well DD.

Results of PHREEQC simulations show that volumetric mixing between native alluvial groundwater sampled at wells P and SMC-08/916 and mine-water discharge reacting with calcite and gypsum produces a major-ion chemistry with respect to calcium and sulfate that is similar to that measured at well DD. The modeling of well P produced a closer similarity to well DD groundwater chemistry compared to well SMC-08/916. Dissolution and precipitation of known minerals, such as calcite, gypsum, plagioclase, illite, and smectite, occurring in alluvial sediments and cation exchange likely control dissolved concentrations of sodium, magnesium, potassium, sulfate, and bicarbonate at wells DD and DD2.

Inverse geochemical modeling using PHREEQC was conducted to quantify water-rock reactions controlling groundwater chemistry along one or more groundwater-flow paths leading to alluvial well DD. The PHREEQC inverse simulations include mean chemical compositions of mine-water discharges and well SMC-08/916 groundwater and site-specific minerals (calcite, gypsum, montmorillonite-Ca, kaolinite, illite, plagioclase, biotite, halite, and chalcedony) occurring in the alluvium (Arcadis 2018, Ulrich et al. 2019), in addition to chloriteA7 and uranophane that have not been identified in the alluvium. Results of inverse modeling of well DD using mine-water discharges and well SMC-08/916 groundwater are compatible with results of the PHREEQC mixing and mass-transfer simulations presented in this report. Modeling results show that gypsum dissolves, while maintaining equilibrium, and calcite is oversaturated and precipitates from alluvial groundwater. Gypsum provides the major source of dissolved calcium and sulfate measured at well DD, which is likely influenced by (1) mixed contaminated groundwater containing infiltrated mine water and native alluvial groundwater; (2) vadose zone leaching of calcium, sulfate, and other solutes occurring with rising water table conditions caused primarily by mine water recharge; and (3) hydraulic influence from tailing seepage, and aquifer pumping at and near the LTP by Homestake for the past several decades.

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Appendix A: Thermochemical Evaluation of Nitrate and Uranium

Nitrate has the thermodynamic capability to oxidize uranium(IV) minerals to soluble aqueous uranium(VI) species through oxidative dissolution. This electrochemically active redox couple between nitrate and uranium(IV) is of considerable interest to the alluvial aquifer system present in the San Mateo Creek Basin, New Mexico where both chemicals are concentrated above groundwater background. Nitrate and uranium(IV) solids serve as an electron acceptor (oxidizing agent) and electron donor (reducing agent), respectively.

Nitrate sourced from agricultural and industrial sites abiotically oxidizes U(IV) minerals, such as uraninite and coffinite, to uranyl carbonate-carbonato complexes under oxic and anoxic groundwater conditions (Asta et al. 2020, Berk and Fu 2017, Nolan and Weber 2015, Tesoriero et al. 2019, Weber et al. 2011, Ginder-Vogel et al. 2006, Senko et al. 2002, and Senko et al. 2005). Nolan and Weber (2015) present a detailed statistical analysis on oxidative dissolution of uranium(IV) phases by nitrate for hundreds of groundwater samples collected from the High Plains and Central Valley aquifers across 22,375 km^2 where 1.9 million people live. Senko et al. (2005) and Senko et al. (2002) report that abiotic and biotic nitrate reduction reactions will also produce reactive intermediate chemicals, including nitrite and nitrous oxide, which will abiotically oxidize uranium(VI) solids to soluble aqueous uranyl species.

Examples of two redox reactions combining denitrification with oxidative dissolution of uraninite (UO_2) are given by:

$$2NO_3^- + CH_2O + 3UO_2 + 6Ca^{2+} + 8HCO_3^- \rightarrow N_2(g) + 4H_2O + 2H^+ + 3Ca_2UO_2(CO_3)_3^0 \text{ and}$$

$$2NO_3^- + 5UO_2 + 10Ca^{2+} + 15HCO_3^- \rightarrow N_2(g) + 6H_2O + 3H^+ + 5Ca_2UO_2(CO_3)_3^0.$$

In the upper reaction, 16 mg/L of nitrate-N (1.143E-03 M) measured at well DD on October 6, 2016, potentially can oxidize a maximum of 0.463 g (1.714E-03 moles) of uraninite, forming 408 mg/L of $Ca_2UO_2(CO_3)_3^0$ (expressed as uranium). Solid organic matter is represented by a generic form of carbohydrate (CH_2O) and potentially serves as an additional electron donor in the upper reaction. A maximum of 0.771 g (2.857E-03 moles) of uraninite is oxidized, forming 680 mg/L of $Ca_2UO_2(CO_3)_3^0$ (expressed as uranium), according to the lower reaction. The maximum dissolved concentration of uranium measured at well DD on February 15, 1989 is 0.245 mg/L (Homestake database), which suggests that these two redox reactions are not in complete electrochemical equilibrium. The above two redox reactions are controlled by kinetics and that complete nitrate reduction to dissolved nitrogen gas has not taken place at well DD. Incomplete reduction of nitrate is verified by measurable and residual nitrate concentrations and enriched or positive stable isotope signatures of $\delta^{15}N$ and $\delta^{18}O$ in nitrate in alluvial groundwater at well DD. The dominant source of dissolved uranium measured at well DD is contaminated alluvial groundwater that is most likely impacted by infiltration of mine water possibly occurring for several decades prior to 1976.