Published in final edited form as:

J Hydrol (Amst). 2013 November 11; 504: 207–215. doi:10.1016/j.jhydrol.2013.09.030.

Characterization and quantification of groundwater sulfate sources at a mining site in an arid climate: The Monument Valley site in Arizona, USA

Ziheng Miao^{a,b}, Kenneth C. Carroll^c, and Mark L. Brusseau^{a,b,*}

Mark L. Brusseau: brusseau@email.arizona.edu

^aDepartment of Soil, Water and Environmental Science, University of Arizona, 429 Shantz Building #38, P.O. Box 210038, Tucson, AZ, USA

^bDepartment of Hydrology and Water Resources, University of Arizona, Harshbarger Building #11, Tucson, AZ, USA

^cNew Mexico State University, Las Cruces, NM, USA

Abstract

The Monument Valley site, a former uranium mining site located in the state of Arizona in the Southwest USA, has high concentrations of sulfate in groundwater. Stable isotope analysis of S and O for sulfate, in combination with geochemical and hydrogeological data, was used to characterize the sources and fate of sulfate. The results indicate the existence of two discrete sources of sulfate (in excess of baseline levels): sulfuric acid released during ore processing and sulfate generated via sulfide-mineral oxidation. The contributions of the sources are related to spatial distributions of sulfate in the plume through analysis of groundwater travel times. Quantification of the sources using two isotope-analysis methods yielded similar results. The results indicate that sulfuric acid served as the primary source (mean = 427 mg/L, 74%), with sulfide-mineral oxidation providing a smaller contribution (mean = 147 mg/L, 26%). It appears that the major contribution to the sulfide-mineral oxidation component originates from oxidation of sulfide minerals in exposed bedrock residing in the primary recharge zone of the local aquifer, which provides an elevated sulfate background for groundwater. Conversely, the oxidation of sulfide minerals associated with the mine tailings appears to provide a relatively minor contribution (~8% of the overall total). Interestingly, it appears that sulfuric acid served as a sustained source of sulfate for approximately 40 years. This may be related to the accumulation of sulfate salts (formed after neutralization and disposal of the sulfuric acid) in the source zone due to the arid climate of the site. Contrary to the typical assumption applied at many mining sites that sulfide-mineral oxidation is the primary source of sulfate, these sulfate salts are hypothesized to be the primary source for this site.

Keywords

Groundwater; Sulfate contamination; Stable isotopes; Sulfide oxidation; Sulfuric acid; Mine tailings

1. Introduction

Mines, especially coal mines and metal mines that involve large quantities of sulfide minerals, often serve as sources for sulfate emission into groundwater (e.g., Johnson and Hallberg, 2005; Miao et al., 2012). While this has been recognized for many years, it has recently come under increased scrutiny. Sulfate contamination of groundwater or surface waters is associated with aesthetic problems (bad odor), and may cause diarrhea (e.g., EPA, 1999). It is also associated with other issues such as corrosion of plumbing systems (e.g., Djuric et al., 1996) and enhanced methylation of mercury leading to accumulation of mercury in fish when released into surface water (e.g., Jeremiason et al., 2006).

A common source of sulfate at mining sites is the oxidation of sulfide minerals (e.g., pyrite) in mine tailings and waste rock. At some mining sites, sulfuric acid was or is used during ore processing (e.g., for metal extraction). Although the sulfuric acid is subsequently neutralized by reagents (e.g., lime and ammonia), the sulfate ion is not eliminated and thus constitutes a direct source for groundwater contamination. Other sources of sulfate in groundwater may include dissolution of indigenous sulfate minerals and atmospheric deposition.

It is critical to understand the sources of sulfate at mining sites both qualitatively and quantitatively for better pollution prevention and for improved management and remediation of existing contamination. Such understanding may be enhanced by the use of geochemical and isotopic approaches. Stable isotope analysis (e.g., ^{34}S and ^{18}O) has long been used in characterizing and delineating sulfate sources for a variety of applications (e.g., Krouse and Grinenko, 1991; Krouse and Mayer, 1999), including assessing the provenance and disposition of acid mine drainage (e.g., van Everdingen and Krouse, 1988; Taylor and Wheeler, 1994; Haubrich and Tichomirowa, 2002). However, while the procedure is well established, there are often factors that complicate its use such as mixing (dilution), spatially and/or temporally variable isotopic compositions of the sources, sulfate-mineral dissolution, and bacterial sulfate reduction. Thus, accurate assessment of sulfate sources requires a thorough understanding of the geochemical (including redox) and hydrological aspects of the site.

Extensive sulfate groundwater contamination is present at the Monument Valley site, a former uranium mining site in southwest USA. Two potential sources of sulfate (in excess of baseline levels) were identified based on site history and conditions: the first from the sulfuric acid applied during ore leaching and the other from sulfide-mineral oxidation in the mine tailings. The objective of this study is to evaluate the relative contributions of these and other potential sources and to identify possible processes (e.g., mixing and bacterial sulfate reduction) that affect the fate of the sulfate. This is accomplished using a combination of hydrogeological, geochemical, and isotopic analyses.

2. Site conditions

The Monument Valley site is located in northeastern Arizona, 24 km south of Mexican Hat, Utah. The site is approximately 1460 m above sea level. The climate is arid, with the site receiving approximately 160 mm of precipitation annually (DOE, 2005). Most precipitation usually occurs during July through August and December through February (DOE, 2005). Temperature is high in the summer (daily highs of 32–38 °C), and can be as low as the freezing point in the winter.

Uranium mining at the site occurred from 1943 to 1968 (DOE, 2005). During that time the site was one of the largest producers of uranium in the state of Arizona (with a lifetime production of 767,166 tons of uranium and vanadium ore). From 1955 to 1964, ore was processed by mechanical milling with an upgrader, which crushed the ore and separated by

grain size. Finer-grained material was shipped to other mills for chemical processing while coarser-grained material was stored on site in the “old tailings pile”. The only chemical used during this period of time was minor amounts of flocculent. From 1964 to 1968, batch and heap leaching with sulfuric acid solution was used to process an estimated 1.1 million tons of tailings and low-grade ore at the site. After leaching, ammonia and quicklime (calcium oxide) were added to neutralize the acid and to produce a bulk precipitate (yellowcake) of concentrated uranium and vanadium. The solutions used in ore processing were discharged to the “new tailings pile”, which is believed to have been a primary source of sulfate contamination of groundwater. The new tailings pile contained both sandy tailings and processing solutions. An evaporation pond was on the east side of the new tailings pile. The purpose of the evaporation pond is unknown, but it may have been used to retain seepage from the new tailings pile. The U.S. Department of Energy (DOE) completed surface remediation at this site in 1994, which involved excavation of the tailings piles, heap-leach area, and evaporation pond.

The mineralogy of the ore body at the site consists of uranium and vanadium minerals, which occur with copper minerals and cementing minerals consisting of quartz and calcite (Lewis and Trimble, 1959). Sulfide minerals such as copper sulfides, chalcocite, chalcosulfide, and bornite are common in the ore (Lewis and Trimble, 1959). Exposure of these sulfide minerals to the atmosphere due to the disposal of mine tailings containing these minerals can produce sulfate through oxidation processes. This is considered to be another potential primary source of sulfate at this site.

The shallow alluvial aquifer that is the focus of this study resides in a north–south oriented paleovalley that is bounded by bedrock on the south and west sides as well as on the bottom. The aquifer is comprised of well-sorted fine to medium sand deposits interspersed with minor fractions of finer silt and clay sediments. Generally, the alluvial deposits range from 1 to 35 m in thickness, with the greatest depths found in the center of the valley. Bedrock is exposed at the southern and western areas of the source zone, and it has been determined that infiltration at these areas serves as the primary source of recharge to the shallow aquifer (DOE, 1999). It is estimated that only a minor fraction of the low annual precipitation recharges the aquifer in the center of the valley (where the plume resides) due to loss from evaporation and plant uptake (DOE, 1999). Given these conditions, it is anticipated that groundwater flows relatively uniformly northward from the outcrop recharge zone in the south, and that reasonable estimates of advective transport can be obtained using standard travel-time analysis.

Depth to groundwater is approximately 11 m. The screened intervals for most monitoring wells span approximately 15–25 m below ground surface (i.e., 10-m screened interval). The mean hydraulic gradient is approximately 0.01. Hydraulic conductivities range from 0.1 to 5.6 m/day for the entire alluvial aquifer (DOE, 1999). The mean groundwater pore water velocity is calculated to be 44 m/yr with a known porosity of 0.25 and an assumed hydraulic conductivity of 3 m/d. Pore water velocity directly measured from a tracer test on a scale of 10 m is 30 m/yr (Borden et al., 2012). Nitrate, sulfate and uranium are the primary groundwater contaminants.

3. Materials and methods

3.1. Sample collection and analysis

Groundwater samples were collected from 14 selected wells across the entire contaminant plume. In addition, several wells upgradient of the source zone were sampled for background geochemistry. Samples were collected using dedicated bladder pumps and a QED Micropurge controller. Sampling began once field parameters (pH and dissolved

oxygen) stabilized, which typically occurred after the removal of a few borehole-equivalent volumes of groundwater. Measurements of basic field parameters (dissolved oxygen, pH, oxidation-reduction potential, and temperature) were obtained using a flow-through instrument connected to the flow control system. Samples were then collected for cations/anions and for sulfate isotopes. Samples for cations and anions were filtered (0.45 μm) and collected in 250-mL HDPE bottles, separately. Cation analysis samples were preserved with 1 mL of hydrochloric acid (HCl). Both sample sets were stored on ice at 4 $^{\circ}\text{C}$. The isotope samples were filtered (0.45 μm) and collected in separate HDPE bottles of various sizes depending on the concentration. Hydrochloric acid was added to decrease pH to <2 for preservation. All samples were stored on ice in the field then frozen upon returning to the lab.

Major cations were analyzed using a Perkin Elmer ELAN DRC-II ICP-MS (inductively coupled plasma mass spectrometry), following US EPA Method 6020. Major anions (e.g., nitrate and sulfate) were analyzed using a Dionex DX-1000 following EPA standard method 300.0. NH_4^+ analysis was conducted using a Hach colorimetric kit and analyzed on a Hitachi U-2000 Spectrophotometer. The quantifiable detection limits are 0.1 mg/L for NO_3^- and NH_4^+ , 0.5 mg/L for Cl^- and SO_4^{2-} , approximately 10 $\mu\text{g/L}$ for major cations (Na, K, Ca, Mg, Al), and approximately 1 $\mu\text{g/L}$ for Fe and Mn.

The DOE has for many years periodically monitored groundwater at the site for various geochemical parameters using standard sampling and analytical methods. These data were used to supplement the investigation reported herein. For example, their data were used to assess alkalinity.

The sulfur isotopes of sulfate were measured for SO_2 gas with a continuous-flow gas-ratio mass spectrometer (ThermoQuest Finnigan Delta Plus XL) at the Environmental Isotope Laboratory of the University of Arizona. Samples were combusted at 1030 $^{\circ}\text{C}$ with O_2 and V_2O_5 using an elemental analyzer (Costech) coupled to the mass spectrometer. Standardization is based on international standards OGS-1 and NBS123, and several other sulfide and sulfate materials that have been compared between laboratories. Calibration was linear in the range -10 to $+30$ per mil. Precision was estimated to be $\pm 0.15\%$ or better (1 standard deviation), based on repeated internal standards. Oxygen isotopes of sulfate were measured on CO gas in a continuous-flow gas-ratio mass spectrometer (Thermo Electron Delta V). Samples were combusted with excess C at 1350 $^{\circ}\text{C}$ using a thermal combustion elemental analyzer (ThermoQuest) coupled to the mass spectrometer. Standardization is based on international standard OGS-1. Precision is estimated to be $\pm 0.4\%$ or better (1 st.dev.), based on repeated internal standards.

3.2. Data analysis

The dual-isotope approach ($\delta^{18}\text{O}$ vs. $\delta^{34}\text{S}$) was used to identify the sulfate sources and to quantify their relative contributions, based on the concept that sulfate derived from different sources usually has distinct $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values. This approach, which is valid only when the sources have different isotopic compositions, typically provides improved differentiation of potential sources of sulfate compared to using sulfur isotopes alone. It also provides, under certain conditions, patterns that can be used to indicate processes (e.g., mixing or bacterial sulfate reduction) that are affecting the concentrations and/or isotopic compositions of sulfate. Moreover, an end-member mixing analysis can be used to quantify the sources if the dual-isotope plot shows a mixing trend of two or more sources (e.g., Hooper et al., 1990). In the case of two end-members, knowing the original isotopic compositions of the two sources (δ_1 and δ_2) and that of the mixture (δ_{mix}), and the total concentration of the mixture (C_T), allows the calculation of the concentrations of sulfate generated from each

source (C_1 and C_2). The difficulty or uncertainty often lies in determining the original isotopic compositions of the two sources.

A second approach was used for source quantification, based on a technique of plotting the isotopic composition relative to the inverse of concentration (e.g., Krouse, 1980; Krouse and Mayer, 1999; Miller and Tans, 2003). The basis for this method is that, due to mass conservation, $C_T\delta_{mix} = C_1\delta_1 + C_2\delta_2$, and $C_T = C_1 + C_2$, where δ and C designate isotopic composition and concentration, respectively, and subscripts 1, 2, mix, and T designate source 1, source 2, the mixture, and total concentration, respectively. Rearranging these two

equations in terms of δ_{mix} : $\delta_{mix} = \frac{1}{C_T} C_1(\delta_1 - \delta_2) + \delta_2$. Therefore, if a linear relationship is yielded by plotting the isotopic composition of the mixture against the inverse of the total concentration, the slope equals $C_1(\delta_1 - \delta_2)$ and the y-intercept equals the isotopic composition of the second source. Note that this method is valid only when C_1 (the concentration of the first source) is constant. Thus, it is often used when a source with a constant background concentration is mixed with another source with a highly variable concentration (e.g., Krouse and Mayer, 1999; Miller and Tans, 2003).

The concentration of the constituent of interest can be normalized by a presumably conservative constituent to attempt to eliminate the effects of dilution or evapotranspiration (e.g., Krouse and Mayer, 1999). In such a case, the equation above becomes

$$\delta_{mix} = \frac{1}{\left(\frac{C_T}{C'}\right)} \left(\frac{C_1}{C'}\right) (\delta_1 - \delta_2) + \delta_2, \text{ where } C' \text{ is the concentration of the conservative tracer.}$$

The slope thus equals $\frac{C_1}{C'}(\delta_1 - \delta_2)$. Quantification of each source concentration is also

possible using this method. C_1 is calculated using the equation $\text{slope} = \frac{C_1}{C'}(\delta_1 - \delta_2)$ by obtaining the slope and knowing δ_1 , δ_2 , and C' (if C' is used). C_2 simply equals $C_T - C_1$. The results obtained from this mass-conservation mixing analysis were compared to those obtained with the dual-isotope method.

4. Results and discussion

4.1. Geochemistry

The groundwater geochemistry is summarized in Table 1. The background groundwater geochemistry, inferred from several upgradient uncontaminated wells, shows a transition from calcium-magnesium-bicarbonate type to sodium-sulfate type (DOE, 2005). The sodium-sulfate composition is suspected to be a result of local evapotranspiration effects (DOE, 2005). Review of the historic DOE database indicates stable geochemical conditions exist at the site based on assessment of many chemical parameters and constituents. This long-term database provides a reference to which the results of our analyses can be compared. Consistency between our results (Table 1) and those reported by DOE indicates robustness of the study methods and results. Charge balances were calculated using the data reported in Table 1, with errors generally less than 5%.

Generally, groundwater samples collected from within the contaminant plume have much higher concentrations of calcium, magnesium, sulfate, nitrate, and ammonium compared to the background groundwater. Similar water chemistry (sulfate, calcium, and bicarbonate rich) has been observed at other mining sites (e.g., Toran, 1987; Armienta et al., 1997). Groundwater samples collected from within the contaminant plume also have much higher values of total dissolved solids compared to samples collected from the background wells.

As previously noted, the high sulfate concentrations (in excess of baseline levels) were hypothesized to originate from past mining-associated activities at the site (sulfuric acid released during ore processing and sulfate generated via sulfide-mineral oxidation in the tailing piles). This hypothesis will be evaluated in detail in forthcoming sections. However, it is informative to evaluate sulfate distributions and associated sources for the background conditions to understand their relative contributions to the contaminant plume. Inspection of Table 1 shows that groundwater collected from the background wells has very low concentrations of nitrate, ammonium, and TDS compared to the contaminant plume, indicating that these wells are not influenced by the contaminant source.

Sulfate concentrations of ~ 100 mg/L are observed for groundwater samples collected from wells 400, 601, 602, and 603 (Table 1), which are background wells located upgradient of the contaminant source zone in the primary aquifer recharge area (where bedrock is exposed). Conversely, significantly lower sulfate concentrations (~ 27 mg/L) are obtained for background wells 402 and 403, which are located to the east of the source zone and not in the outcrop/recharge area. It is hypothesized that the higher concentrations observed for the wells in the outcrop/recharge area reflect the impact of sulfate generation from oxidation of sulfide minerals in the exposed bedrock. This process may serve as the major background source of sulfate to the local site groundwater. The lower concentrations observed for wells 402 and 403 may represent the regional baseline condition, reflecting the impact of sources such as precipitation (perhaps concentrated through evapotranspiration) and sulfate-bearing minerals. The measured baseline sulfate concentrations are very low compared to the concentrations observed for the plume. Conversely, the elevated local background concentrations (~ 100 mg/L) are sufficiently high to warrant consideration in the analysis of the plume sources.

The Ca and Mg were likely introduced by the quicklime that was applied at the end of ore processing for neutralization. The ammonium is from ammonia application during ore processing, and the nitrate is most likely from nitrification of ammonium (Carroll et al., 2009; Miao et al., 2013). The contaminated groundwater has a lower pH (7.4 ± 0.2) than the background groundwater (8.0 ± 0.3). This is likely a result of acid use during ore processing and/or acid release during subsequent sulfide-mineral oxidation.

The mean sulfate to chloride ratio is 29.3 for contaminated groundwater compared to a value of 4.4 for background groundwater (Table 1). However, the chloride concentration of contaminated groundwater (mean = 19.6 mg/L) is comparable to the background chloride concentration (mean = 17.8 mg/L). This indicates that chloride originates from natural rather than anthropogenic sources. Chloride input from ore processing or other mining activities is expected to be negligible because no chloride species were used in the ore processing, and the minerals associated with the mine tailings lack chloride. With minimal input of chloride associated with mining activities at the site, it is reasonable to assume that chloride can serve as a conservative tracer in this study.

The redox condition of the background groundwater is oxidizing (ORP ~ 299 mV) (DOE, 1999). The contaminated groundwater is generally under oxidizing conditions as well, reflected in DO values ranging from 0.9 to 12.7 mg/L. Nitrate concentrations (10.9–223.8 mg/L as N) are elevated in all contaminated wells. Iron and manganese concentrations are generally below 100 μ g/L and vary significantly for both contaminated and background groundwater. No H_2S was detected in a subset of wells located in the middle (near well 765) of the plume. These properties are consistent with oxic conditions. Such redox conditions are not suitable for bacterial sulfate reduction (e.g., Christensen et al., 2000).

The sulfate plume emanating from the source zone extends for 2 km to the northeast. Concentrations including those in background wells range from 17 to 1500 mg/L (Fig. 1). Within the plume, concentrations are generally >100 mg/L. Unlike many contaminated sites where the highest concentrations occur in the source zone, concentrations within the source zone are low (generally <100 mg/L), which is likely due to the remediation of the surface area of the source zone during 1992 to 1994. The highest sulfate concentrations at this site are observed at two hot spots, 450 m (well 771) and 1400 m (well 762) downgradient of the source zone, respectively.

The source of extensive sulfate input was presumably terminated after the surface remediation efforts. This termination of the source would result in development of a zone of higher concentration (hot spot) that would migrate downgradient at the effective groundwater velocity. Given a groundwater pore velocity of 30 m/yr (Borden et al., 2012) and a travel time of 14 years (1994–2008), it is estimated that the hot spot should currently be located approximately 420 m from the source area. This coincides well with the location of the closer observed hot spot (450 m).

The more distant hot spot is probably caused by the sulfuric acid application during 1964 to 1968. Given the approximate travel time of 42 years (1966–2008) and groundwater velocity of 30 m/yr, a travel distance of 1260 m is estimated, which is in reasonable agreement with the distance of the distal hot spot (1400 m) from the source area. Therefore, conceptually, it appears that the distal hot spot is caused by direct input of sulfate from sulfuric acid used during the mill operation, while the remainder of the plume is caused by long-term release of sulfate from the source area prior to its remediation.

4.2. Stable isotopes of sulfate

The sulfur and oxygen isotope compositions of sulfate exhibit a strongly linear relationship ($R^2 = 0.89$) on a dual-isotope ($\delta^{18}\text{O}$ vs. $\delta^{34}\text{S}$) plot, with a slope approximately equal to 1:4 (Fig. 2). Fig. 2 also shows the ranges of isotopic compositions of sulfate from different sources. The top end of the linear regression line resides in the region associated with evaporites, while the bottom end can be extrapolated into the region associated with sulfide-mineral oxidation.

A linear relationship between $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ is consistent with mixing of two sulfate sources with differing isotopic compositions. However, bacterial sulfate reduction also results in simultaneous enrichment of ^{18}O and ^{34}S . In fact, results reported in the literature suggest a slope of 1:4 for $\delta^{18}\text{O}$ vs. $\delta^{34}\text{S}$ during bacterial sulfate reduction (e.g., Mizutani and Rafter, 1973), which coincides with the slope in Fig. 2. To delineate the potential contribution of bacterial sulfate reduction, $\delta^{34}\text{S}$ is plotted relative to sulfate concentration in Fig. 3. It is observed that $\delta^{34}\text{S}$ increases with increasing sulfate concentration, which is the opposite of the behavior observed for bacterial sulfate reduction wherein $\delta^{34}\text{S}$ increases with decreasing sulfate concentration (the residual sulfate becomes enriched in the heavier isotope during the biotransformation process). This result combined with the redox conditions present at the site indicate that the linear relationship is not caused by bacterial sulfate reduction. Concomitantly, this suggests that a two-source mixing process is responsible.

If the observed isotopic behavior is a result of mixing, the two sources should be sulfuric acid and sulfide-mineral oxidation as identified above. The original isotopic composition of the sulfate generated from sulfide-mineral oxidation should be associated with the region of sulfide-mineral oxidation in Fig. 2 (bottom end of the regression line). Therefore, the other end of the regression line (within the range of evaporites in Fig. 2) must be associated with the isotopic composition of the sulfuric acid. The isotopic composition of industrial sulfuric acid depends on the isotopic composition of the raw materials. Therefore, it is possible to

have an isotopic composition in the range of evaporites if the sulfuric acid used at the site was produced from evaporites. Prior researchers have reported $\delta^{18}\text{O}$ -sulfate values ranging between 6‰ and 24‰ and $\delta^{34}\text{S}$ -sulfate values ranging between 7‰ and 40‰ for sulfate evaporites such as gypsum (Parafiniuk et al., 1994; Krouse and Mayer, 1999; Knoller et al., 2005; Samborska et al., 2013). Despite the fact that presently most sulfuric acids have a $\delta^{34}\text{S}$ value close to 0 due to their production from oxidation of elemental sulfur, values of $\delta^{34}\text{S}$ as high as 18‰ have been reported for sulfuric acid (Hesslein et al., 1988).

To further assess the mixing process, the sulfur isotope composition of sulfate is plotted relative to the inverse of sulfate concentration. The results show a linear negative relationship (slope = -1727.4 , intercept = 17.9‰ , $R^2 = 0.663$) (Fig. 4, top). This inverse relationship is significantly improved when sulfate concentration is normalized by chloride concentration (slope = -268.1 , intercept = 24.3‰ , $R^2 = 0.866$) (Fig. 4, bottom). This result, in combination with the observed linear relationship between $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of sulfate and the absence of bacterial sulfate reduction, indicates the presence of a two-source mixing process.

4.3. Quantification of sulfate sources

The robust linear relationship between $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ (Fig. 2) provides an opportunity to quantify the contribution of each sulfate source with a relatively high degree of confidence using the dual-isotope end-member mixing analysis presented in Section 3.2. In this study, the two identified sources contributing to the excess levels of sulfate (above regional baseline) at the site are (1) sulfuric acid applied during ore processing and (2) sulfate generated from sulfide-mineral oxidation in the outcrop/recharge area and in the tailings piles. The sulfuric acid is no longer obtainable and, hence, direct measurement of the isotopic composition of this source is not possible. However, it is possible to determine a reasonable estimate for the source associated with sulfide-mineral oxidation.

As noted above, background wells 601 and 602 are located upgradient of the source zone where the bedrock is exposed and, hence, they likely received sulfate generated from oxidation of sulfide minerals in the bedrock. This is reflected in their sulfate concentrations (~ 100 mg/L), which are greater than the regional baseline concentrations as discussed. Isotopic composition values for groundwater from wells 601 and 602 ($\delta^{18}\text{O} = 4.4\text{‰}$, $\delta^{34}\text{S} = -11.5\text{‰}$) are used to represent the isotopic composition of the source associated with oxidation of sulfide minerals in the bedrock in the outcrop/recharge area. It is noted that these values are within the range of sulfate isotope values reported for sulfide-mineral oxidation (e.g., Krouse and Mayer, 1999). It is assumed that the values obtained for sulfide-mineral oxidation for the bedrock source are also representative for oxidation of sulfide minerals present in the mine tailings. Absent a means to obtain an independent estimate, the source term for the sulfuric acid was determined from regression analysis. Specifically, a $\delta^{34}\text{S}$ value of 24.3‰ was determined from the y-intercept of the $\delta^{34}\text{S}$ vs. Cl/SO_4 plot (Fig. 4, bottom), and a $\delta^{18}\text{O}$ value of 12‰ was determined from the $\delta^{18}\text{O}$ vs. Cl/SO_4 regression (data not shown). These values are within the range of values reported in the literature for sulfate associated with gypsum and other sulfate evaporites, as noted above. The baseline sulfate concentration is ignored in the analysis since it is much lower compared to concentrations associated with the contaminant plume.

There are uncertainties associated with the estimation of the isotopic values of these two sources. The value used for the sulfide-mineral oxidation source was determined by analyzing groundwater samples collected from background wells located in an outcrop area that serves as the primary source of recharge for the aquifer. This approach was considered to provide the best available option for characterizing this source term. The fact that only very low levels of nitrate and ammonium are present in groundwater collected from these

wells (Table 1), compared to the high values present within the plume, indicates that the sulfate present in the groundwater samples is not from anthropogenic sources. However, uncertainty exists in the representativeness of the measured value. For example, there may be spatial and temporal variability in oxidation processes at the site such that the measured value is not reflective of prior conditions. It is noted, however, from inspection of Fig. 2 that the measured value obtained from the background wells matches well with the best-fit regression of the data measured for the plume. This convergence provides some degree of confidence in the source value. The uncertainty associated with the isotopic value for the sulfuric acid is related to the absence of a measured value for the source, and its determination by linear regression. However, the results of calculations indicate that the analysis has only moderate sensitivity to the end-member values. For example, if the $\delta^{34}\text{S}$ of the sulfuric acid source is reduced by two units to 22.3‰, the calculated source concentration of sulfate originating from sulfide oxidation changes from approximately 147 to 122 mg/L. Such relatively small changes will not significantly influence the overall conclusions regarding the relative contributions of the two sources.

The resultant concentrations and proportions of each source for each well are listed in Table 2 and visualized in Fig. 5. Sulfate concentrations associated with sulfuric acid (mean = 427 mg/L) are significantly higher in general compared to concentrations generated from sulfide-mineral oxidation (mean = 147 mg/L). The mean relative contribution for the sulfuric acid source is 74%, compared to 26% for sulfide-mineral oxidation.

Finally, quantification of the sulfate sources is performed using the method based on plotting isotopic composition relative to the inverse of concentration (the mass-conservation mixing method presented in Section 3.2). This method is further extended by the key

equation $\text{slope} = \frac{C_1}{C'}(\delta_1 - \delta_2)$. Using the slope of -268.1 (Fig. 4 bottom), estimates of δ_1 (-11.5‰) and δ_2 (24.3‰), and the average chloride concentration of 19.6 (Table 1), the representative sulfate concentration for the first source is estimated to be 146.8 mg/L. This value is in good agreement with the 147.4 mg/L calculated using the dual-isotope end-

member mixing approach (Fig. 2). In fact, using the same equation $\text{slope} = \frac{C_1}{C'}(\delta_1 - \delta_2)$ and the individual chloride concentrations for groundwater for each well, it is possible to quantify each sulfate source. The results are listed in Table 2. The two methods yielded very comparable results (Fig. 6).

5. Discussion

The results presented above indicate that sulfuric acid appears to be the primary source of sulfate in the groundwater contaminant plume, comprising approximately three-fourths of the total, with a smaller contribution from sulfide-mineral oxidation. It appears that the major contribution to the sulfide-mineral oxidation component originates from oxidation of minerals in the exposed bedrock residing within the primary recharge zone of the local aquifer, with a smaller contribution from oxidation of sulfide minerals associated with the mine tailings. The relatively minor contribution ($\sim 8\%$ of the overall total) from the mine tailings is consistent with the arid conditions of the site.

The results also indicate that the sulfuric acid source persisted at the site for at least approximately 40 years. However, sulfuric acid was used and disposed of at the site for only a few years. It is hypothesized that, given the climatic conditions at the site, sulfate salts (formed from neutralization of sulfuric acid) accumulated in and beneath the tailings pile during the mill operation. The formation of sulfate-salts (i.e., evaporation of solutions rich in SO_4) has been widely observed in arid regions at large (geologic) scales (e.g., Farpour et al.,

2004). The formation of sulfate salts, so-called efflorescent salts, has also been reported for mining sites, with sulfide-mineral oxidation serving as the typical source (Nordstrom, 1999; Jambor et al., 2000). Infiltrating rainwater would likely dissolve some of the salts, providing a long term source of sulfate. The rainfall in this area is not only sparse but also unevenly distributed (mostly in the summer monsoon and winter period), meaning that the leaching would likely be periodic rather than continuous (e.g., Nordstrom, 2009).

Results of prior studies conducted at the site support the hypothesis of sulfate-salt formation. Before the removal of the tailings, tailing solutions were collected using lysimeters implemented up to 6 m below the tailings pile (DOE, 1999). Sulfate concentrations as high as 4510 mg/L were observed. After the removal of the tailings, subpile sediments were collected (at locations where tailing piles were previously located) and leached with DI water. Leachable sulfate concentrations as high as 9190 mg/kg of sediment were reported, compared to ~200 mg/kg for background samples (DOE, 1999). Both data sets indicate the accumulation of large quantities of leachable sulfate salts in the tailing piles and subpile sediments. Based on the analyses reported herein, these sulfate salts appear to have originated primarily from the sulfuric acid that was used during mill operation. The formation of sulfate salts from evaporation and precipitation of the neutralized sulfuric acid solution would be expected to exhibit negligible isotope fractionation for $\delta^{34}\text{S}$ (e.g., Thode and Monster, 1965; Holser and Kaplan, 1966; Raab and Spiro, 1991) and minor fractionation for $\delta^{18}\text{O}$ (Lloyd, 1968). Thus, the isotopic composition of the sulfate salts is expected to be similar to that of the original sulfuric acid.

Chloride was used to normalize sulfate concentrations in an attempt to account for dilution and other effects for the analysis presented in Fig. 4, bottom. Comparison of Fig. 4 top and bottom shows that such normalization improved the correlation. It is noted that the data points for wells 762 and 669 (circled in Fig. 4) are influenced the most by applying concentration normalization. In fact, they are the two wells with the highest and lowest sulfate concentrations, 1450 and 101 mg/L, respectively, compared to an average of 575 mg/L (Table 1). They also have the highest and lowest chloride concentrations, 63.6 and 6.4 mg/L, respectively, compared to an average of 19.6 mg/L. Comparing the measured chloride concentrations for the specific plume wells to the mean background chloride concentration, the solutions were apparently concentrated by approximately $63.6/17.8 = 3.6$ times for well 762 and were diluted by approximately $17.8/6.4 = 2.8$ times for well 669.

The successful use of chloride as a conservative tracer herein indicates that chloride and sulfate experience coincident concentration or dilution effects during evaporation or recharge, respectively. The low sulfate and chloride concentrations observed for well 669, which is located just to the east of the western outcrop area (groundwater recharge area), are most likely caused by a dilution effect associated with the greater volumes of recharge experienced at that location. The highest sulfate and chloride concentrations are observed for well 762. This corresponds to the distal hotspot (Fig. 1), which as discussed above, is hypothesized to be associated with the disposal of sulfuric acid solution during the time it was used at the site in the mid-1960s. This time frame so happens to coincide with a severe drought that occurred during the 1950s and 1960s in Arizona (Nace and Pluhowski, 1965; McPhee et al., 2004). It is hypothesized that higher rates of evaporation in the recharge/source area during that time may have resulted in a concentration effect, increasing sulfate concentrations. Further evaluation of this hypothesis would require detailed mathematical modeling that is beyond the scope of this effort.

6. Conclusions

A combined hydrogeochemical and isotopic approach was used to characterize the sources contributing to the sulfate plume at a former uranium mill tailing site. The regional baseline concentration of sulfate in groundwater is relatively low. The local background sulfate concentration for the site groundwater is elevated, most likely due to sulfide-mineral oxidation occurring in bedrock outcrops that reside in the primary recharge zone of the local aquifer. The contributions of two anthropogenic sources typically considered to be primary sources at mining sites, sulfuric acid and sulfide-mineral oxidation of mine tailings, were quantified using two isotopic-analysis methods, which yielded similar results. The results indicated that sulfuric acid provided the major contribution, with a smaller contribution from sulfide-mineral oxidation. It appears that the major contribution to the sulfide-mineral oxidation component originates from the local background associated with the outcrop/recharge zone, with a relatively minor contribution from oxidation of sulfide minerals associated with the mine tailings. These results illustrate the benefits associated with the use of combined hydrogeochemical/isotopic methods for source characterization at mining sites. Such information would assist risk assessments and evaluation of remediation alternatives.

It is hypothesized that sulfate salts accumulated in the source zone after neutralization and disposal of sulfuric acid solutions. These salts appear to have served as a persistent and significant source for sulfate contamination of groundwater. Such accumulation is likely made possible by the arid climate. The methods used in the study allowed identification and quantification of the contribution of this process, which may be significant but not delineated for other sites.

The results of these and related characterization efforts at the site indicate that contaminant discharge from the source appears to have been reduced due to the surface remediation efforts. In addition, the groundwater contaminant plume appears to be experiencing minimal natural attenuation through processes such as bacterial sulfate reduction. It is therefore anticipated that the sulfate plume will continue to persist at the site for many decades while it slowly migrates away from the source.

Acknowledgments

This research was supported by the University of Arizona TRIF Water Sustainability Program through the Center for Environmentally Sustainable Mining, and the NIEHS Superfund Research Program (P42 ES04940). We thank members of the contaminant transport lab of the University of Arizona for assisting the field work. We thank Dr. Christopher Eastoe of the Environmental Isotope Laboratory at the University of Arizona for sulfur isotope analysis. We also thank the reviewers for their constructive comments.

References

- Armienta M, Rodriguez R, Aguayo A, Cenicerros N, Villaseñor G, Cruz O. Arsenic contamination of groundwater at Zimapán, Mexico. *Hydrogeology Journal*. 1997; 5(2):39–46.
- Borden AK, Brusseau ML, Carroll KC, McMillan A, Akyol NH, Berkompas J, Miao ZH, Jordan F, Tick G, Waugh WJ, Glenn EP. Ethanol addition for enhancing denitrification at the uranium mill tailing site in Monument Valley, AZ. *Water, Air, and Soil pollution*. 2012; 223(2):755–763.
- Carroll KC, Jordan FL, Glenn EP, Waugh WJ, Brusseau ML. Comparison of nitrate attenuation characterization methods at the Uranium mill tailing site in Monument Valley, Arizona. *Journal of Hydrology*. 2009; 378(1–2):72–81.
- Christensen TH, Bjerg PL, Banwart SA, Jakobsen R, Heron G, Albrechtsen HJ. Characterization of redox conditions in groundwater contaminant plumes. *Journal of Contaminant Hydrology*. 2000; 45(3–4):165–241.
- Djuric M, Ranogajec J, Omorjan R, Miletic S. Sulfate corrosion of portland cement-pure and blended with 30% of fly ash. *Cement and Concrete Research*. 1996; 26(9):1295–1300.

- DOE. Final site observational work plan for the UMTRA project site at the Monument Valley, Arizona. US Department of Energy, Office of Legacy Management; 1999. Document: U0018101
- DOE. Environmental Assessment of Ground Water Compliance at the Monument Valley, Arizona, Uranium Mill Tailings Site. 2005 DOE/EA-1313.
- EPA. Health effects from exposure to high levels of sulfate in drinking water study. USA: US Environmental Protection Agency; 1999. EPA 815-R-99-001, Washington, DC
- Farpoor MH, Khademi H, Eghbal MK, Krouse HR. Mode of gypsum deposition in southeastern Iranian soils as revealed by isotopic composition of crystallization water. *Geoderma*. 2004; 121(3–4):233–242.
- Haubrich F, Tichomirowa M. Sulfur and oxygen isotope geochemistry of acid mine drainage – the polymetallic sulfide deposit Himmelfahrt Fundgrube in Freiberg (Germany). *Isotopes Environment Health Studies*. 2002; 38:121–138.
- Hesslein RH, Capel MJ, Fox DE. Sulfur isotopes in sulfate in the inputs and outputs of a canadian shield watershed. *Biogeochemistry*. 1988; 5(3):263–273.
- Holser WT, Kaplan IR. Isotope geochemistry of sedimentary sulfates. *Chemical Geology*. 1966; 1:93–135.
- Hooper RP, Christophersen N, Peters NE. Modelling streamwater chemistry as a mixture of soilwater end-members — An application to the Panola Mountain catchment, Georgia, USA. *Journal of Hydrology*. 1990; 116(1–4):321–343.
- Jambor JI, Nordstrom DK, Alpers CN. Metal-sulfate salts from sulfide mineral oxidation. *Sulfate Minerals – Crystallography, Geochemistry and Environmental Significance*. 2000; 40:303–350.
- Jeremiason JD, Engstrom DR, Swain EB, Nater EA, Johnson BM, Almendinger JE, Monson BA, Kolka RK. Sulfate addition increases methylmercury production in an experimental wetland. *Environmental Science & Technology*. 2006; 40(12):3800–3806. [PubMed: 16830545]
- Johnson DB, Hallberg KB. Acid mine drainage remediation options: a review. *Science of the Total Environment*. 2005; 338(1–2):3–14. [PubMed: 15680622]
- Knoller K, Trettin R, Strauch G. Sulphur cycling in the drinking water catchment area of Torgau–Mockritz (Germany): insights from hydrochemical and stable isotope investigations. *Hydrological Processes*. 2005; 19:3445–3465.
- Krouse, HR. Sulphur isotopes in our environment. In: Fritz, P.; Fontes, JCh, editors. *Isotope Geochemistry The Terrestrial Environment*. Vol. 1. Elsevier; Amsterdam: 1980. p. 435–471.
- Krouse, HR.; Grinenko, VA. *Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment*. John Wiley and Sons Ltd; 1991.
- Krouse, HR.; Mayer, B. Sulfur and oxygen isotopes in sulphate. In: Cook, PG.; Herczeg, AL., editors. *Environmental Tracers in Subsurface Hydrology*. Kluwer; Boston: 1999. p. 195–231.
- Lewis, RQ.; Trimble, DE. Contributions to the geology of uranium, US Geological Survey Bulletin 1087-D. United States Government Printing Office; Washington, DC: 1959. *Geology and Uranium Deposits of Monument Valley San Juan County, Utah*.
- Lloyd RM. Oxygen isotope behavior in the sulfate-water system. *Journal of Geophysical Research*. 1968; 73(18):6010–6099.
- McPhee J, Comrie A, Garfin G. *Drought and Climate in Arizona: Top Ten Questions & Answers*. 2004
- Miao Z, Brusseau ML, Carroll KC, Carreon-Diazconti C, Johnson B. Sulfate reduction in groundwater: characterization and applications for remediation. *Environmental Geochemistry and Health*. 2012; 34(4):539–550. [PubMed: 21947714]
- Miao Z, Akyol NH, McMillan AL, Brusseau ML. Transport and fate of ammonium and its impact on uranium and other trace elements at a former uranium mill tailing site. *Applied Geochemistry*. 2013; 38:24–32.
- Miller JB, Tans PP. Calculating isotopic fractionation from atmospheric measurements at various scales. *Tellus B*. 2003; 55(2):207–214.
- Mizutani Y, Rafter TA. Isotopic behaviour of sulphate oxygen in the bacterial reduction of sulphate. *Geochemical Journal*. 1973; 6:183–191.

- Nace, RL.; Pluhowski, EJ. Drought of the 1950s with Special Reference to the Midcontinent. US Government Printing Office; 1965.
- Nordstrom, D. Fernández Rubio, R. Mine, Water & Environment II. Sevilla: International Mine Water Association; 1999. Efflorescent Salts and their Effects on Water Quality and Mine Plugging; p. 543-546.1 tab.
- Nordstrom DK. Acid rock drainage and climate change. *Journal of Geochemical Exploration*. 2009; 100(2–3):97–104.
- Parafiniuk J, Kowalski W, Halas H. Stable isotope geochemistry and the genesis of the Polish native sulphur deposits –s a review. *Geological Quarterly*. 1994; 38(3):473–496.
- Raab M, Spiro B. Sulfur isotopic variations during seawater evaporation with fractional crystallization. *Chemical Geology*. 1991; 86(4):323–333.
- Samborska L, Halas S, Bottrell SH. Sources and impact of sulphate on groundwaters of Triassic carbonate aquifers, Upper Silesia, Poland. *Journal of Hydrology*. 2013; 486:136–150.
- Taylor, B.; Wheeler, M. Sulfur- and oxygen-isotope geochemistry of acid mine drainage in the western United States. In: Alpers, CN.; Blowes, DW., editors. *Environmental Geochemistry of Sulfide Oxidation Am Chem Soc Symp Series*. Vol. 550. 1994. p. 481-514.
- Thode HG, Monster J. Sulfur isotope geochemistry of petroleum, evaporites and ancient seas. In: *Fluids in Subsurface Environments*. Am Assoc Pet Geol. 1965:367–377. Mere No. 4.
- Toran L. Sulfate contamination in groundwater from a carbonate-hosted mine. *Journal of Contaminant Hydrology*. 1987; 2(1):1–29.
- van Everdingen RO, Krouse R. Interpretation of isotopic compositions of dissolved sulfates in acid mine drainage. US Bureau Mines Information Circulations. 1988; 9183:147–156.

Fig. 2. $\delta^{18}\text{O}$ vs. $\delta^{34}\text{S}$ for all plume wells (circles). Also shown are ranges of isotopic composition of sulfate from different sources (Krouse and Mayer, 1999). The diamond represents the isotopic composition of the sulfuric acid source and the square represents the sulfide-mineral oxidation source. The presumed sulfuric acid value was determined based on a regression analysis (Fig. 4). The value representing sulfide-mineral oxidation was obtained from measurement of samples collected from background wells (see text).

Fig. 3.
 $\delta^{34}\text{S}$ of sulfate relative to sulfate concentrations.

Fig. 4. $\delta^{34}\text{S}$ of sulfate relative to the inverse of sulfate concentration (top) and relative to the inverse of normalized (by Cl) sulfate concentration (bottom).

Fig. 5. Concentrations of sulfate derived from sulfuric acid and sulfide-mineral oxidation relative to the distance from the source. The dashed line at 147 mg/L delineates the average concentration for sulfate generated from sulfide-mineral oxidation.

Fig. 6.

Correlation between the results calculated by the two methods. C_{sulfuric} is the sulfate concentration derived from sulfuric acid calculated by the dual isotope method. C'_{sulfuric} is the sulfate concentration derived from sulfuric acid calculated by the isotope vs. inverse concentration method.

Groundwater geochemistry from 14 contaminated wells and 6 background wells. “-” means no measurement. Concentrations are in mg/L except for Al, Mn, and Fe (ug/L).

Table 1

	Well ID	DO	PH	Ca	Mg	Na	K	Al (ug/L)	Mn(ug/L)	Fe (ug/L)	Alkalinity (as CaCO ₃)	Cl	SO ₄	NO ₃ as N	NH ₄ as N	TOC	TDS	SO ₄ /Cl
Contaminated	606	1.0	7.1	138.8	93.2	71.0	6.4	11.6	61.9	10.4	209	19.5	361.3	223.8	116.1	1.2	1760	18.6
	648	0.9	7.5	115.9	115.9	125.6	6.8	10.4	1.0	2.2	215	20.5	811.7	53.0	6.3	1.3	-	39.6
	656	2.3	7.8	25.7	20.8	67.8	6.4	13.4	1.8	8.3	253	14.1	161.4	56.9	40.8	6.5	737	11.4
	662	7.5	7.4	108.8	59.0	27.0	1.7	14.2	0.2	0.9	205	14.0	273.5	22.5	0.0	0.7	1220	19.5
	669	2.0	7.6	51.7	36.1	30.8	3.4	11.5	2.4	1.3	190	6.4	101.4	10.9	2.6	0.2	568	15.9
	728	12.7	7.7	98.2	94.4	85.2	16.5	14.3	67.1	1.5	-	23.7	574.6	130.5	105.8	9.1	-	24.2
	729	3.6	7.4	111.2	90.9	81.9	15.9	16.2	8.0	53.7	-	19.6	581.3	143.1	127.2	6.7	-	29.6
	730	3.3	7.4	104.0	92.8	84.0	16.3	16.7	17.8	9.3	-	16.4	525.7	112.7	134.9	6.5	-	32.1
	731	2.2	7.2	110.3	91.8	83.2	16.0	14.6	74.2	144.1	-	15.8	572.6	122.7	127.0	6.5	-	36.2
	761	5.4	7.4	100.7	89.2	52.5	0.6	7.6	0.2	1.0	182	15.1	478.7	31.6	0.3	0.6	1050	31.8
	762	3.2	7.6	157.4	151.6	366.3	3.6	12.5	2.3	1.4	225	63.6	1450.2	107.2	0.1	1.7	2240	22.8
	764	6.4	7.7	101.3	78.7	41.2	1.1	13.5	0.2	0.0	188	11.9	280.0	42.2	0.4	0.3	988	23.5
	765	2.3	7.4	69.0	45.6	44.8	6.3	6.0	3.8	1.0	253	16.7	586.2	170.6	107.8	2.7	1800	35.1
	771	1.8	7.2	177.4	137.5	85.2	47.8	6.9	1.8	33.3	287	17.3	1287.8	198.2	276.2	11.6	4800	74.6
Background	Avg ± Stdv	3.9 ± 3.2	7.4 ± 0.2	105 ± 39.1	85.5 ± 36.4	89.0 ± 84.1	10.6 ± 12.2	12.1 ± 3.3	17.3 ± 27.8	19.2 ± 39.1	220.7 ± 34.0	19.6 ± 13.3	574.7 ± 388.4	101.9 ± 67.6	74.7 ± 81.7	4.0 ± 3.7	1685 ± 1289	29.3 ± 29.2
	400	-	7.8	26.7	43.4	102.0	3.1	-	70.0	0.0	355	36.4	90.2	-	-	-	523	2.5
	402	-	8.4	10.7	36.9	54.6	3.1	-	0.0	0.0	150	13.3	17.0	0.1	0.0	-	255	1.3
	403	-	7.7	23.5	30.8	54.5	3.2	-	60.0	0.0	301	13.9	37.4	-	-	-	325	2.7
	601	0.7	7.8	28.3	18.3	100.0	1.9	-	270.0	30.0	229	14.6	112.1	1.2	0.0	-	398.0	7.7
	602	3.8	7.9	27.3	18.9	106.0	2.0	-	0.0	150.0	205	15.4	100.0	0.8	0.0	-	447	6.5
	603	0.6	8.0	18.0	14.0	85.0	2.7	-	2.0	0.0	198	13.0	110.0	0.4	0.1	-	385	8.5
	Avg ± Stdv	1.7 ± 1.8	7.9 ± 0.3	22.4 ± 6.9	27.1 ± 11.8	83.7 ± 23.7	2.7 ± 0.6	-	67 ± 104	30.0 ± 60	239.7 ± 75.0	17.8 ± 9.2	77.8 ± 40.5	0.6 ± 0.5	0.0 ± 0.1	-	388.8 ± 93.2	4.4 ± 4.4

Table 2

Sulfate isotope results for groundwater samples collected from each well and estimated fraction and sulfate concentrations from each sulfate source. Subscripts T , sulfuric, and sulfide designate total, sulfuric acid, and sulfide-mineral oxidation, respectively. C_{sulfuric} and C_{sulfide} are calculated using the dual isotope approach and C'_{sulfuric} and C'_{sulfide} are calculated using the isotope composition vs. inverse concentration approach.

Well ID	C_T (mg/L)	$\delta^{34}\text{S}$ (‰)	$\delta^{18}\text{O}$ (‰)	% C_{sulfuric}	% C_{sulfide}	C_{sulfuric} (mg/L)	C_{sulfide} (mg/L)	C'_{sulfuric} (mg/L)	C'_{sulfide} (mg/L)
606	361	13.7	7.1	70	30	254	107	215.5	145.8
648	812	17.3	9.9	80	20	652	160	658.2	153.6
656	161	1.8	5.7	37	63	60	101	55.7	105.7
662	274	7.8	7.3	54	46	147	126	168.7	104.9
669	101	4.0	6.0	43	57	44	58	53.6	47.8
728	575	15.8	9.0	76	24	438	136	397.0	177.6
729	581	16.2	9.1	77	23	450	131	434.3	146.9
730	526	16.4	8.9	78	22	409	116	403.1	122.5
731	573	16.5	9.2	78	22	447	125	454.0	118.6
761	479	16.4	9.3	78	22	373	106	365.8	112.9
762	1450	10.9	8.1	63	37	908	542	974.1	476.1
764	280	13.5	9.1	70	30	195	85	190.7	89.3
765	586	16.1	9.2	77	23	452	134	461.3	124.9
771	1288	20.5	10.6	89	11	1152	136	1158.5	129.3
Average	575	-	-	74	26	427	147.4	427.9	146.8
STDV	388	-	-	-	-	311	116	321.0	99.7