Geochemical Tracer Based (GTB) Sulfate Balance Models for Active Tailing Basins on Minnesota's Iron Range (III) Well waters, seeps, and downstream surface waters.

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Abstract

As process water seeps from taconite tailing basins in NE Minnesota, its geochemical signature may be affected by factors including (1) dilution by infiltrating precipitation, (2) oxidation and rinsing of sulfide minerals present in the materials used to construct perimeter dikes and dams, and (3) microbial processes that occur when waters contact buried organic matter in the glacial tills and peat on which tailing impoundments are constructed. This is the last of a three-part series of papers that evaluate taconite tailings basin waters. Part I focuses on process waters while Part II focuses on tailings pore fluids. Part III, presented here, uses geochemical tracer based (GTB) methods to quantify the impact of dilution, sulfide oxidation, and microbial sulfate reduction on surrounding surface and ground waters.

Samples collected from wells, seeps, and surface waters outside of five taconite tailings basins were analyzed and compared to process water samples collected from inside the basins. Bromide and chloride concentrations were used to quantify dilution that occurs during seepage. Net changes in sulfate concentration along a flow path were computed by comparing sulfate/chloride and sulfate/bromide ratios to those in the undiluted process waters. Finally, shifts in measured $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values between process waters and surrounding waters were used to help facilitate conversion of net sulfate gains or losses to specific amounts of sulfate added by oxidation of sulfide minerals and/or lost due to sulfate reduction and precipitation as iron sulfide. The result is a full mass balance accounting that could potentially be used to predict the likely outcomes for sulfate treatment options in situations where future sulfate reductions may be necessary.

Results confirm that sulfate behavior downstream of taconite tailings basins is typically nonconservative. Although dilution decreased sulfate concentrations in seeps and wells by ~5 to 80 percent, net sulfate additions following dilution ranged from approximately zero up to 65 percent. Subsequent losses of sulfate due to microbial activity are as large as 80 percent, in some cases. All modeled calculations are subject to uncertainty if the chemical processes taking place in the basin are significantly different from those assumed in the model. Assumptions and associated uncertainties are discussed for each of the five operations studied.

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Introduction

The Biwabik Iron Formation contains minor amounts of iron sulfide minerals. When mine tailings that are generated during taconite processing are placed into taconite tailings basins, these sulfide minerals can oxidize and release sulfate. Some of the sulfate produced by pyrite oxidation is entrained in taconite processing water that cycles through the plant and the basin. Additional sulfate, however, may be generated and added to precipitation infiltrating into taconite tailings basins, potentially contributing to the inventory of sulfate in process waters that leak from tailing basins. Sulfate is also commonly reduced and precipitated as sulfide minerals during the transport of basin waters through the subsurface (Berndt and Bavin, 2011; Kelly et al., 2014). Therefore, to fully address sulfate loading from taconite processing facilities to the surrounding environment, both oxidation and reduction processes must be accounted for somehow.

Geochemical tracer based (GTB) methods were previously developed and applied at U. S. Steel's Minntac taconite facility (Kelly et al., 2014) to help quantify sulfate transport processes. These methods are described again here and used to help quantify the impacts of dilution, sulfide oxidation and sulfate reduction at additional Minntac sites and also at four other taconite tailing basins on Minnesota's Iron Range.

This is the last in a three-part series directed at the modeling of sulfate behavior in taconite tailing basins and associated processing facilities. Part I (Berndt et al., 2016a) quantifies sulfate production and release in taconite process waters and also characterized the water balance and sulfate loading to the environment. Part II (Berndt et al., 2016b) quantifies the in situ rate of sulfate production in waters infiltrating into tailings. The final part discussed here focuses not on processes that take place within the basin, but rather on geochemical processes taking place beneath and outside the basin.

Study Design

This study follows the approach taken by Kelly et al. (2014), which focused specifically on the U. S. Steel Minntac taconite tailings basin. That investigation demonstrated that multiple processes can impact sulfate concentrations in waters downstream of the basin, including (1) dilution as precipitation infiltrates and mixes with mine impacted seepage; (2) oxidation of sulfide minerals in the tailings perimeter dike, adding new sulfate to the balance; and (3) biological reduction of sulfate in the subsurface along the seepage flow path, removing a portion of the sulfate from the balance and trapping it as iron-sulfide minerals. As in the earlier study, geochemical and isotopic information is used here to attempt to separate and quantify the relative impact of each of these three processes in waters surrounding five taconite tailings basins across the Mesabi Iron Range.

Dilution

If a geochemical parameter is nonreactive under environmental conditions, it may be possible to use the parameter as a conservative tracer, providing information on processes such as water movement and dilution. Chloride (Cl^-) and bromide (Br^-) ions are relatively conservative in the environment, and are found at elevated concentrations in taconite mine process waters of northeastern Minnesota relative to nearby background values. The elevated concentrations are likely due to the grinding and addition of fluxstone (marine dolomite, limestone) during pellet production (Engesser, 2006), with potentially other less well known amounts from the ore itself or from the application of chemicals for dust suppression on the basin. Solute concentrations downstream of tailings basin locations generally fall in between those in the tailings basin waters and those measured in nearby background waters/precipitation. Intermediate values suggest that as water flows away from the basin, seepage is diluted by mixing with precipitation and groundwater sources not impacted by mining activity. In this study, the concentration of chloride and bromide in downstream seep, surface, and groundwater samples is compared to basin water to determine the dilution effect of infiltrating precipitation during transport.

Sulfide Oxidation

Sulfate is naturally present in waters of northeastern Minnesota but at relatively low concentrations. The sulfate concentration of local precipitation is typically ~1 mg/L (NADP, 2015), and local surface and groundwater not impacted by mining activity are characteristically <10mg/L (Berndt and Bavin, 2012; Kelly et al., 2015). The oxidation of sulfide minerals exposed as a result of taconite processing, however, can result in elevated sulfate concentrations downstream of mine pits and tailings basin areas (Berndt, 2011; Berndt and Bavin, 2011). Part I of this series (Berndt et al., 2016a) explores the potential source(s) of sulfate as water and rock cycle through a mining operation. Part II of the series (Berndt et al., 2016b) and associated work (Jacobs et al., 2016) focus on the oxidation of sulfide minerals in tailings and the in-situ production of sulfate.

Isotopes of relatively common elements (e.g., hydrogen, oxygen, carbon, nitrogen, sulfur) have a number of applications in environmental studies. Physical, chemical and biological processes can produce predictable changes in the isotopic composition of the involved geochemical species. Through these processes, a mineral or phase can end up being more enriched in either the heavy or light isotopes of a particular element (e.g., ^{34}S vs ^{32}S, respectively) relative to another mineral or phase. The isotopic composition of dissolved sulfate is particularly important to this study, as it may provide information about source materials, mixing, and the bacterial sulfate reduction process. Sulfur and oxygen isotope values (δ^{34}S and δ^{18}O) are typically reported in per mil (‰) units relative to a standard.

Newly formed sulfate has δ^{34}S values similar to those of the sulfide mineral source (Taylor et al., 1984; Toran and Harris, 1989). Measured $\delta^{34}S_{SO4}$ values of dissolved sulfate in taconite mine pit and discharge waters of northeastern Minnesota generally fall between about +4 and +12‰ (Berndt and Bavin, 2012; Kelly et al., 2014). These values overlap the range associated with primary sulfide minerals in the Biwabik iron formation (Carrigan and Cameron, 1991; Johnston et al., 2006; Poulton et al., 2010; Theriault, 2011), suggesting that the origin of dissolved sulfate in mine-impacted waters is the oxidation of primary sulfide minerals present the iron formation, or represents a bulk average of the oxidation of both primary and secondary sulfides. Humidity cell testing of tailings from the U. S. Steel Minntac basin showed that rinsed sulfate from older tailings has sulfur isotopes clustering ~8‰ (Von Korff and Bavin, 2014). Mine pit $\delta^{34}S_{SO4}$ values are variable and slightly more negative towards the western edge of the Mesabi Iron Range, however, falling between -7 and +5‰ (Berndt and Bavin, 2012; Kelly et. al, 2014; unpublished data). This may indicate that in this region, the mineral source for dissolved sulfate source is predominantly secondary sulfides with more negative $\delta^{34}S$ compositions.

Sulfate reduction

Microbial activity within anoxic, reducing sediments beneath and surrounding tailings basins has the potential to greatly impact the geochemistry of seepage water. Sulfate reducing bacteria, for example, convert dissolved sulfate to its reduced form, sulfide (as H_2S or HS^-), while oxidizing available forms of organic carbon. This process is associated with a potentially large sulfur isotope fractionation effect between the reactant (sulfate) and product (sulfide), with the lighter sulfur isotope accumulating in the product sulfide phase causing the residual sulfate to become enriched in the heavier isotope. If the initial composition of source sulfate is known, the measured sulfur isotopic composition of sulfate can be used to identify locations where microbial sulfate reduction process is or has been active. Using this concept, previous studies have demonstrated that sulfate reduction occurs in waters across the Iron Range (Berndt and Bavin; 2011; Kelly et al., 2014; Kelly and Berndt, 2015). Tailings basins in northern Minnesota are often situated on or near wetland rich areas, providing a potential carbon source to support the sulfate reduction process. In cases, the Rayleigh fractionation equation, shown below, may be used to quantify the amount of sulfate reduction that has taken place.

$$R = R_0 f^{(\alpha-1)}$$

In this equation, “R_0” refers to the initial $^{34}S/^{32}S$ ratio of the sulfate, “α” is the isotope fractionation factor for sulfate reduction which characterizes the fractionation process by relating the ratio of $^{34}S/^{32}S$ in the coexisting reactant (SO_4) and product (H_2S) phases, and “f” refers to the fraction of the original sulfate remaining. As reduction proceeds, “f” decreases and the sulfate becomes progressively more enriched in the heavier ^{34}S relative to ^{32}S. To enable the use of measured isotope values, the Rayleigh equation can be converted to delta notation as follows:

$$\delta^{34}S_{SO4} = (\delta^{34}S_{SO4,init} + 1000)\, f^{(\alpha-1)} - 1000$$

A simplified term, Δ, is used in this report to describe the impact of isotope fractionation on reported sulfur isotopic values, and is related to α according to the following equation.

$$\Delta = \delta_{SO4} - \delta_{H2S} \approx 1000\,(\alpha-1)$$

Use of the Rayleigh fractionation equation to quantify sulfate reduction requires that the product sulfide remain isolated from the residual sulfate, as would be the case where sulfide minerals precipitate out of solution. At the U. S. Steel Minntac tailings basin, well waters analyzed in 2012 had sulfide concentrations below detection (MN DNR, unpublished data) despite having sulfate isotope values strongly indicative of sulfate reduction (Kelly et al., 2014). It is presumed that unless evidence exists to the contrary, sulfide produced during sulfate reduction is isolated from the system in the form of iron sulfide minerals. Studies of microbial sulfate reduction using both laboratory cultures and environmental samples show that the isotope fractionation effect associated with sulfate reduction can vary widely, which can also complicate the use of the Rayleigh equation. Laboratory studies typically give a range between ~+2 and +46‰, but under certain conditions a fractionation effect of up to +70‰ is possible (Canfield and Teske, 1996; Detmers et al., 2001; Sim et al., 2011a). The magnitude of the fractionation effect relates to factors such as sulfate reduction rates, make-up of the microbial community, sulfate concentration, temperature, and the type of organic substrate used to fuel the reaction (Bruchert et al., 2001; Canfield, 2001; Detmers et al., 2001; Kleikemper et al., 2004; Sim et al., 2011b; Leavitt et al., 2013).

Geochemical tracer based (GTB) method

The GTB method used in this study takes all of the above processes (dilution, oxidation, reduction) into account, and considers them sequentially. As process water seeps from the basin, infiltrating precipitation dilutes the concentration of chemical constituents. The effect of dilution is determined by comparing measured chloride and bromide concentrations, assuming these constituents are chemically conservative. Infiltrating precipitation may mobilize new sulfate produced as a result of sulfide mineral oxidation within the tailings. An isotope mass balance equation is used to determine the relative amount of preexisting (basin-derived) and new sulfate, using measured basin $\delta^{34}S_{SO4}$ values and an average composition of local mine pit waters, 7.7‰, unless otherwise noted. This value is consistent with the results of Von Korff and Bavin (2014), presuming that, in most cases, the dominant source of sulfate is the oxidation of primary sulfides within the iron formation. Finally, sulfate loss via microbial sulfate reduction may occur along the flow path as waters migrate through sediments beneath and outside the basin, resulting in $\delta^{34}S_{SO4}$ values that are elevated compared to pit source and basin waters. This process is evaluated using the Rayleigh isotope fractionation equation described above. An iterative process is used to simultaneously solve the isotope mass balance and Rayleigh fractionation equations. The solution sets the amount of new sulfate that must be added in order to account for the amount of reduction required by the observed shift in isotope values, thus providing an estimate of the relative impact of oxidation and reduction on downstream waters.

While evidence suggests that both sulfide oxidation and sulfate reduction are prevalent in the mining region of northeastern Minnesota, there are localized areas where downstream sulfate concentrations are minimally impacted by recent sulfide oxidation processes. At these locations, it is possible to evaluate sulfate behavior without the aforementioned isotopic methods. However, the associated geochemical information may still contribute to our understanding of sulfur isotope dynamics by enabling the calculation of the sulfur isotope fractionation factor, given the easily determined fraction of sulfate loss due to reduction. This method was used by Berndt and Bavin (2011) at a site downstream of ArcelorMittal Minorca's Upland Basin site, also visited during this study. The authors arrived at an isotope fractionation value of $\Delta = 17‰$, and this value has been applied by the DNR to estimate the amount of sulfate reduction occurring in various locations across the iron range (Berndt and Bavin; 2011; Kelly et al., 2014; Kelly and Berndt 2015). When it is likely that both sulfide oxidation and sulfate reduction impact measured sulfate concentrations, this 17‰ sulfur isotope fractionation effect is applied despite the uncertainty in using a fixed value for a variable process. While estimates using this assigned value should be used with caution, it appears to be a reasonable approximation based on the body of evidence collected by the DNR in recent years. Additional complications occur, however, when multiple sources of sulfate contribute to the downstream isotopic signal, or additional sulfur cycling takes place along the flow path (Kelly and Berndt, 2015). In these cases, it is not possible to use a simple Rayleigh model to interpret the sulfate isotope signal.

Chemical methods

At each basin, grab samples were collected for major cation, anion, and water isotope analysis and filtered either on site using a 0.45 µm cartridge syringe filter, or on rare occasions upon return to the DNR lab in Hibbing, Minnesota with 0.45 µm PES filters. Cation samples were preserved with ultra-pure nitric acid and shipped on ice along with the anion samples for analyses by the University of Minnesota–Geochemistry Laboratory (Minneapolis, Minnesota) for analysis by ICP–AES (Thermo Scientific iCAP 6500) and ion-chromatography (Dionex ICS 2000), respectively. The list of cations analyzed includes aluminum, barium, calcium, iron, potassium, lithium, magnesium, manganese, sodium, phosphorus, silicon, and strontium, while the list of anions includes fluoride, acetate, formate, chloride, nitrite, bromide, nitrate, sulfate, oxalate, thiosulfate, and phosphate. In this document, we report only bromide, chloride, and sulfate. Measured concentrations of other elements are available upon request. Detection limits for bromide, chloride, and sulfate are approximately 0.01, 0.01, and 0.02 mg/L, respectively, on undiluted samples. Samples were diluted by 1 to 10x, depending on the expected and measured concentrations. Any samples that were found to exceed the concentrations measured in the highest standard were diluted to lower concentrations and rerun.

Water isotope samples were stored unpreserved in 30 mL HDPE bottles until shipped to University of Waterloo Environmental Isotope Lab for analysis. Bottles were tightly sealed with limited headspace to minimize evaporative loss. Water isotope samples were analyzed using standard isotope ratio mass spectrometry methods. The $^{18}O/^{16}O$ ratios were determined via gas equilibration and head space injection into an IsoPrime Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS). The $^{2}H/^{1}H$ ratios were determined via chromium reduction on a EuroVector Elemental Analyzer coupled with an IsoPrime CF-IRMS. Internal laboratory standards are calibrated and tested against international standards from the International Atomic Energy Agency (IAEA), including Standard Light Antarctic Precipitation (SLAP), Greenland Ice Sheet Precipitation (GISP), and Vienna Standard Mean Ocean Water (VSMOW). Values for $\delta^{18}O_{H2O}$ and $\delta^{2}H_{H2O}$ are reported in ‰ relative to the international standard Vienna Standard Mean Ocean Water (VSMOW), which approximates the composition of the global ocean. Sample replicates are run approximately every eight samples. Analytical uncertainties are ±0.2‰ and ±0.8‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively.

Depending on the approximate sulfate concentration, between 250 mL and 1 L of water was collected for the isotopic analysis of sulfate. Samples were filtered after collection at the Hibbing laboratory using 0.7 µm glass fiber filter paper. Dissolved sulfate was extracted as solid barium sulfate ($BaSO_4$) at the DNR Hibbing laboratory using procedures modified from Carmody et al. (1998). The $BaSO_4$ precipitate was collected and stored in glass vials until shipment to either Isotope Tracer Technologies (Rounds 1-2) the University of Waterloo Environmental Isotope Laboratory in Ontario, CA (Rounds 3-5) for analysis of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$. Relative ^{34}S and ^{32}S abundances for the precipitates were determined using an Isochrom Continuous Flow Stable Isotope Ratio Mass Spectrometer (GV Instruments, Micromass, UK) coupled to a Costech Elemental Analyzer (CNSO 2010, UK). Relative ^{18}O and ^{16}O abundances for the precipitate were determined using a GVI Isoprime Mass Spectrometer coupled to a Hekatech High Temperature Furnace and a Euro Vector Elemental Analyzer. Values for $\delta^{34}S_{SO4}$ are reported in ‰ units against the primary reference scale of Vienna-Canyon Diablo Troilite meteorite (VCDT), with an analytical precision of 0.3‰. Values for $\delta^{34}S_{SO4}$ are reported relative to VSMOW, with analytical precision of 0.5‰.

Results and Discussion

A selection of plant make-up water, process water, basin water, and downstream seeps, wells and/or stream locations were sampled for each of the five basin areas. Five sampling events took place in 2014 and 2015 (May/June 2014, October 2014, February 2015, May 2015, and September/October 2015). In general, taconite process waters have high concentrations of chloride and bromide relative to pit makeup sources as well as adjacent downstream waters. After dilution is taken into consideration, however, sulfate concentrations in downstream waters are often either relatively high or low compared to the process water sources. The isotopic composition of dissolved sulfate provides key information about sulfur cycling downstream of the tailings basin locations. Figure 2 displays all $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ data collected during this study, and demonstrates that waters downstream of all of the basins tend to trend towards the upper right corner of the graph (higher/more positive isotope values). This trend is indicative of sulfate reduction, which has influenced the isotopic composition of sulfate to varying degrees at each study location.

U. S. Steel - Keetac

United States Steel Corporation's Keewatin Taconite facility is located in Keewatin, Minnesota and is shown as location A in Figure 1. Basin and adjacent sampling locations are shown on the Keewatin Taconite (Keetac) basin area map (Figure 3), and the full data set is presented in Table A1. Ore processing was temporarily halted for scheduled maintenance during the October 2014 sampling round. Sampling proceeded, though process waters were not sampled at that time. In May 2015, operations were temporarily idled for the remainder of the 2015 sampling season.

Makeup water for the operation includes a combination of pit and recycled sources. During the 2014–15 study, water from the Russell Pit, Section 18 Pit, and recycled water from the plant (48-inch pipeline) were combined and piped into Carlz Pit. Carlz Pit water was then pulled into the plant as makeup water, along with return water from the tailings basin. Several tailings basin reservoirs were sampled, including the inner tailings basin, the outer basin 2nd stage pond, and Reservoir 6 (basin return water). During the February 2015 sampling round, Reservoir 2 was also sampled as water was actively pumped from Reservoir 2 into Reservoir 6 at the time. Two groundwater monitoring wells along the south-southeastern corner of the basin were sampled in May 2014 and again in October 2015 to gather some information about processes impacting the chemistry of water that escapes the basin.

Bromide is typically present in the taconite mine waters at concentrations less than 2 mg/L, but concentrations are particularly low at the Keetac basin (<0.2 mg/L) and thus only chloride was considered when making calculations of dilution, oxidation, and reduction. Sulfate/chloride ratios are relatively constant in the process water loop (Berndt et al., 2016a), suggesting little to no sulfate is added or lost within the basin itself. However, well waters have slightly lower sulfate/chloride ratios, plotting below the process water dilution line shown in Figure 4. To better understand the processes responsible for the observed downstream sulfate concentrations, it is necessary to incorporate isotopic information.

The isotopic composition of dissolved sulfate ($\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$) for each sampling location in the Keetac basin area is displayed in Figure 5. The basin perimeter monitoring wells are considerably enriched in the heavy isotopes of both sulfur and oxygen relative to basin water, plotting along a trend characteristic of sulfate reduction, towards the upper right on the graph. Therefore, microbial sulfate reduction is likely responsible for the nonconservative behavior of sulfate in groundwater leaving the Keetac basin.

The GTB method was applied to determine the relative importance of each process impacting sulfate concentrations at the well locations. Well 1 is situated towards the northern extent of the 2nd Stage Pond's western perimeter (Figure 3). Assuming a 17‰ isotope fractionation effect (Δ) and average nearby pit $\delta^{34}S_{SO4}$ (+3.4‰) for the composition of newly oxidized sulfate, the iterative GTB calculation process reveals that new sulfate comprises approximately 59 percent of the total sulfate pool, and about 80 percent of that pool of sulfate is subsequently removed by microbial activity along the flow path (Table 1). We evaluated our results and assumptions with a simple sensitivity analysis. If the assumption is made that no new sulfate was added to seepage waters, we can determine both the fraction of sulfate reduced and the associated value for Δ. In this case, Δ would equal 36.3‰, which is within reason based on the sulfate reduction literature but on the higher end of typically observed fractionation values (see above). On the other hand, a smaller Δ value (10‰) would require a rather unreasonable (approximately 10-fold) increase in sulfate concentration due to oxidation. Unless there is a specific reason for using an alternative value, calculations reported in this study use Δ = 17‰.

Oxidation and reduction were both important at the other two monitoring wells sampled at the Keetac basin as well (Table 1). During the initial sampling round (May 2014), groundwater was sampled at Well 12, located at the southern edge of the 2nd Stage Pond (Figure 3). The oxidation of sulfide minerals in tailings contributes approximately 16 percent of the total sulfate present, and approximately 41 percent of the sulfate pool is reduced along the flow path. During the subsequent round, it was not possible to obtain a water sample from Well 12, and an adjacent well (Well 11) was sampled instead. Sulfate concentration at Well 11 was higher than at Well 12, though it is unclear whether this is related to differences along the flow path or seasonal variability. Approximately 35 percent of the total sulfate was added along the flow path, with a subsequent 45 percent loss due to bacterial sulfate reduction. It is evident that both sulfide oxidation and sulfate reduction influence measured sulfate concentrations in groundwater near the Keetac basin perimeter. How and where this water daylights further downstream is not addressed here, since there were not any downstream surface water samples collected as part of this study.

Hibbing Taconite

The Hibbing Taconite facility is located in Hibbing, Minnesota and is shown as location B in Figure 1. Twelve sites were sampled during each of the five 2014–15 rounds, with the exception of two locations (tailings basin return water, SD002) that were not accessible in February due to ice and snow conditions. Relevant sampling locations for this study are shown on the Hibbing Taconite (Hibtac) basin area map (Figure 6), and the full data set for the Hibbing Taconite sampling locations is available in Table A2.

The main source of makeup water for Hibbing Taconite operations is the Scranton Pit, with the Morton Pit used as a backup when Scranton Pit water is unavailable. Both pits were sampled in 2014–15, as well as a pipeline from the Group 5 Pits that is pumped directly to the tailings basin. Additional process water and basin sampling locations included fine tailings discharge to the basin, agglomerator/floor wash discharge to the basin, an internal basin weir, and return water from the tailings basin.

Several locations downstream of the tailings basin were also sampled. Three of these sites are culvert outfalls close to the basin's western perimeter (SD002, SD003, and SD004) that also collect some discharge water from relief wells within the basin. An additional two surface water stream sites were sampled (Day Lake Road, SD001). The Day Lake Road surface water site is located downstream of the three surface discharge locations on the west side of the tailings basin, while the SD001 site is located north of the tailings basin along Highway 5.

Solute concentrations and water isotope values in tailings discharge and basin water vary seasonally. Chloride, for example, ranges between ~45 and 70 mg/L over an annual cycle. Locations downstream of the basin also exhibit seasonal fluctuations, reflecting that seen in the basin, but with varying degrees of dilution relative to the more concentrated basin water.

The two stream locations, SD001 and Day Lake Road, are distinct from the seeps in that they have consistently higher chloride/bromide ratios relative to the dilution trend shown in Figure 7. It is possible that runoff of road salt applied during the winter months provides an additional source of chloride, as these two sampling locations are each situated along road or highway. The SD001 stream also receives water from a drainage ditch coming from the processing plant area, potentially impacting the measured chloride concentrations as well. Calculated dilution amounts based on chloride are therefore likely to be underestimates at those locations, and the amount of freshwater mixing at downstream sites is estimated using bromide concentrations rather than chloride. A comparison of dilution percentages based on both chloride and bromide are listed in Table 2b.

Figure 8 shows that all of the downstream seeps and river locations plot below the process water bromide dilution trend, indicating a net loss of sulfate beyond what would be expected if fresh water mixing alone caused the changes in concentration. Sulfate isotope results for all Hibtac sampling sites are shown in Figure 9. The downstream seep and river waters plot to the upper right relative to basin and pit waters, trending towards more positive isotope values. Again, this trend suggests that sulfate reduction is responsible for the net loss of sulfate in waters downstream of the basin.

As before, the isotope mass balance and Rayleigh fractionation equations were solved simultaneously to estimate the relative impact of sulfide oxidation and sulfate reduction along each flow path. However, using the calculated dilution estimates, it was not possible to converge on logical solutions assuming impacts from both oxidation and reduction, and applying $\Delta = 17‰$ and average pit $\delta^{34}S_{SO4}$ for the composition of newly oxidized sulfate (4.3‰). Instead, the assumption was made that no new sulfate is added as water escapes from the Hibtac basin and moves downstream. Tailings pore water analysis suggests that some degree of in-situ sulfate release does occur at certain locations within the Hibtac basin (Part II of this three part series, Berndt et al., 2016b). However, there is no evidence that this additional sulfate returns to the process water loop (Berndt et al., 2016a), and any impact on water exiting the basin is not yet understood.

If we assume that changes in sulfate concentration are caused by dilution and reduction alone, we can easily determine how much sulfate loss is due to reduction without the use of sulfate isotopes. It is also possible to use measured values to back-calculate the fractionation effect (Δ) associated with sulfate reduction. Results of these calculations are listed in Table 2. The seep located near the southwest corner of the basin, SD004, had an average sulfate concentration of 25 mg/L over the five 2014–15 sampling rounds. If no sulfate is added along the flow path, approximately 75 percent of the original sulfate is reduced (beyond the impact of dilution) by the time the basin–derived seepage water arrives at the sampling location. At SD002, about 30 percent of the sulfate pool is reduced along the flow path. For both sites, the calculated isotope fractionation effect associated with sulfate reduction is between 10-12‰. Provided the assumptions made are valid, this is the first instance on the Iron Range where geochemical evidence suggests a fractionation value less than 17‰. As mentioned previously, estimates were made under the assumption that oxidation of sulfide minerals within the basin does not contribute to reported downstream sulfate concentrations. Greater sulfate addition generally necessitates use of a smaller fractionation effect to produce the measured downstream isotopic values. Alternatively, if the initial sulfate/chloride ratio was lower than expected based on measured basin concentrations, the higher fractionation effect would produce acceptable results. This underlines the fact that there is some uncertainty involved in the use of isotopic methods to calculation individual amounts of oxidation and reduction along a flow path.

The remaining seepage monitoring location along the western edge of the basin, SD003, has consistently low sulfate concentrations (on average, <1 mg/L) which prohibited the analysis of sulfate isotopes. Based on bromide and sulfate concentrations, however, it appears that most of the sulfate remaining after dilution is lost to sulfate reduction. Calculations were also made for the surface water location downstream of the western seepage outfalls (Day Lake Road), and results indicate that approximately 60 percent of the total sulfate load is lost due to reduction. The $\delta^{34}S_{SO4}$ values at Day Lake Road are intermediate relative to SD002 and SD004, and it appears as though source mixing and dilution are the main processes responsible for changes in the sulfate signature between the seepage locations and downstream at Day Lake Road. Calculated values for the surface water location north of the basin, SD001 at HW 5, are much more variable than those at the other downstream sites (Table 2). Sulfate loss due to reduction ranges from 23 to 80 percent, and is negatively correlated with calculated Δ values ($r^2 = 0.81$), which fall between 51‰ and 13‰. Sulfur isotope fractionation can be related to the sulfate reduction rate (Leavitt et al., 2013), and the observed pattern may relate to seasonally variable reduction rates along this flow path. However, a ditch feeding into this stream also carries storm water and drainage from the plant area, so it is perhaps more likely that the variability is a reflection of undefined sulfate inputs that vary over the course of a typical year.

U. S. Steel - Minntac

The United States Steel Corporation's Minntac facility is located near Mountain Iron, Minnesota and is shown as location C in Figure 1. The Minntac basin was also studied by the DNR in 2011–12, and some results from that study were presented in Kelly et al. (2014). A similar but larger set of sampling sites were visited during the 2014–15 study, with basin area sampling locations shown on Figure 10. Data is reported in Table A3(a-c).

Initially, the makeup water source at Minntac was the Mountain Iron Pit, but was switched to a source with a lower sulfate concentration (Transfer Sump) in 2015. Various process waters were also sampled: scrubber makeup, agglomerator, concentrator sewage, tailings; basin water (Cell 2, Cell 1/Basin Return); and an extensive suite of sites downstream of the basin. Sampling locations outside of the basin include two seepage collection points along the eastern toe of the basin (P1 CB5, P2 CB10), one seep along the western toe (SD001), and a number of monitoring wells located around the basin (see basin area map, Figure 10). Two surface water stream locations were also sampled; the Sand River (Sand River at Hwy 53, and Dark River at CR 668).

The Minntac tailings basin is situated on top of the hydrologic divide between the Dark River Watershed on the west and Sand River Watershed on the east. The Dark River originates beneath the tailings basin and flows towards the northwest. The Sand River emerges from the east side of the tailings basin. The concentration of chemical parameters are elevated in the Minntac tailings basin relative to surrounding waters, and efforts to understand the quality and quantity of water escaping from the basin have been ongoing for many years (Lapakko and Jagunich, 1991). In an attempt to reduce surface seepage from the basin, a seepage pumpback system was installed on the eastern side of the basin and became operational in June 2011. Surface seepage is collected and returned to the basin at two locations (P1 CB5, P2 CB10). A seepage collection system is also planned for the west side of the basin, but is not yet in place. Surface seepage on the west side of the basin is represented by sampling location SD001, near the current headwaters of the Dark River.

Results are generally consistent with the previous study of the Minntac basin (Kelly et al., 2014). Chloride and bromide are tightly correlated, suggesting the two ions behave conservatively as process waters mix with infiltrating precipitation and escape from the basin (Figure 11). Sulfate/chloride ratios vary in downstream waters, but typically increase relative to tailings discharge and basin water (Figure 12). Background conditions are represented by MW-9 on the western side of the basin, MW-10 near the southeastern corner of the basin, and MW-14 to the north. Of these, MW-10 is the only well with high enough sulfate concentrations to analyze for sulfate isotopes, and measured values indicate that sulfate reduction has little to no impact on groundwater there. However, sulfate isotope data from the remaining perimeter wells indicates that sulfate reduction is prevalent around the basin (Figure 13). There is evidence for both sulfate addition and sulfate loss in surrounding waters, and thus it is necessary to solve both the isotope mass balance equation and the Rayleigh fractionation equation to determine the relative impact of oxidation and reduction. Calculations for the seeps and wells are made using average anion and isotope values compared to either Cell 1 Basin Return water or Fine Tailings Discharge, depending on which side of the basin the well is located. Reported values assume that new sulfate has a δ^{34}S of 7.7‰, and Δ = 17‰, though a range of solutions may be possible using alternate fractionation factors or assumptions. Results for each seep and well location are listed in Table 3a and 3b.

The GTB method approximations for dilution, oxidation, and reduction in seep and well waters around the basin are variable, but clear patterns emerge. A trend is observed on both sides of the basin where $\delta^{34}S_{SO4}$ values progressively increase from the basin to seeps to wells to downstream surface water locations, suggesting that sulfate reduction cumulatively impacts waters moving further away from the basin (Figure 13). On the Dark River side, MW-8 is the exception, with relatively high $\delta^{34}S_{SO4}$ values representing an approximate modeled 42 percent loss of sulfate to reduction (Table 3b). Downstream Dark River water may represent an average of the more reduced sulfate pool from this area and contributions of less reduced ground and surface waters (SD001, MW-6, MW-7) as they move downstream, though the relative contributions from the various seepage areas are not known. Another exception is MW-1, located along the eastern perimeter dike towards the southern extent of Cell 1. Groundwater at this location looks essentially like process water in terms of both anion concentrations and isotopic composition, with little to no oxidation or reduction along presumably short, direct flow paths.

Wells located near the northeastern corner of the basin (PZ-5 and 12 well nests, PZ-PT-06d) demonstrate a general decrease in sulfate concentrations as well depth increases. With the exception of PZ-5s, sulfate reduction estimates are consistently about 30 percent in these wells and their $\delta^{34}S_{SO4}$ values cluster fairly tightly (Figure 13). Similar reduction percentages are associated with MW-3, located on the side flank of a bedrock valley emerging from the eastern perimeter dike. Interestingly, shallow groundwater at PZ-5s is diluted by about 40 percent, but has the highest net sulfate concentration of all of the groundwater wells, suggesting a large amount of new sulfate is present. During the first two sampling rounds, the PZ-5s $\delta^{34}S_{SO4}$ values (2.6‰ average) were lower than basin water and the assumed composition of newly oxidized primary sulfide minerals (7.7‰). This may be an indication that the oxidation of recently precipitated secondary sulfide minerals, a product of previous sulfate reduction and trapping of iron sulfide in the area, contributed at least a portion of the new sulfate. The secondary sulfide minerals are expected to have more negative (lower) $\delta^{34}S$ values than the original sulfate. Because PZ-5s is a shallow well, screened between 5-10 ft. below the ground surface, this also suggest that at least some of the sulfate reduction occurs near the ground surface. Efforts to understand where sulfate is added and where sulfate is reduced along each flow path continue, as results from Parts I, II, and III of this series will be incorporated into ongoing Permit to Mine related basin modeling efforts.

As part of the expanded basin modeling effort, Sand and Dark River sampling (see Appendix, Table A3-c) was supplemented with approximately monthly visits by U.S. Steel personnel (monthly data available upon request). Flow was measured by a Pygmy meter using the USGS Midsection Method, with the exception of the February 2015 sampling round (flow measured March 5, 2015) when a cooperative state agency stream gaging crew assisted with measurements using a SonTek Flow Tracker Acoustic Doppler Velocimeter system. Chloride concentrations were used as a conservative tracer to determine the proportion of undiluted process water from the basin present at the downstream locations during each monthly sampling event. An approximate annual average (October 2014 to September 2015) indicates roughly 3000 gallons per minute (gpm) of total process water flow from the basin, with an average downstream sulfate loading from the basin of approximately 16 metric tons per day. Because it is difficult to capture a complete picture of sulfate loading using only spot measurements of flow and concentration, this is likely a low estimate. Significant portions of stored sulfate load may be flushed out during high flow events such as spring runoff or heavy precipitation events throughout the year, which don't necessarily line up with the sampling schedule. This may partially explain why average sulfate loading from the Minntac basin calculated using methods described in Part I of this series (Berndt et al., 2016a) is higher, 23.6 metric tons per day. Additionally, the Berndt et al. (2016) method reports the sulfate load that leaves the basin, and does not consider oxidation of sulfide minerals within the dike or sulfate reduction outside of the basin. The total process water loss rate for the basin estimated by the Berndt et al. (2016a) method is also higher (4126 gpm) than the estimate based on downstream measurements, and may include an additional loss to groundwater beneath the basin. Monthly flow and chemistry sampling by U. S. Steel at the downstream locations is ongoing to further refine some of these calculations.

United Taconite

Cliffs Natural Resources' United Taconite tailings basin and processing facilities are located near Forbes, Minnesota, shown as location D in Figure 1. Site specific sampling locations are shown on the United Taconite (Utac) basin area map (Figure 14), and the full data set is reported in Table A4. The tailings basin complex consists of two basins, Basin 1 and Basin 2. Basin 1 was deactivated in 2000, after which fine tailings were discharged into Basin 2. Operations at Utac were temporarily idled beginning in summer 2015, so the basin was not included in the final October 2015 sampling round.

Makeup water at the United Taconite operation is pulled in from the nearby St. Louis River. The St. Louis River (SLR on Figure 14) was sampled near the intake location, along with tailings discharge to Basin 2 and return water from Basin 2. Two locations just outside of the basin were regularly sampled during 2014–15, an unnamed wetland (W-1) on the west side of Basin 2, and Little Tony Lake (LT-1) to the north of Basin 2/east of Basin 1 (see Figure 14). Additional sites surrounding the basin were sampled periodically. Three nearby lakes are sampled for United Taconite by a contracted party on an annual basis: Twin Lakes (SW003), Perch Lake (SW004), and Round Lake (SW005). The annual sampling took place in July 2014, and sample splits were provided to the DNR for processing. Two additional downstream locations were added during the February 2015 and May 2015 sampling rounds: one downstream of the unnamed wetland (W-2) and the other downstream of Little Tony Lake (LT-2).

The chemistry of water samples from the unnamed wetland (W-1) near the western toe of Basin 2 suggests that the site is essentially comprised of process water, representing an approximate average composition with relatively little seasonal variability (Figure 15). However, there is a slight increase in the sulfate/chloride ratio, indicating that some new sulfate is present in the wetland waters (Figure 16). There is no evidence for sulfate addition within the basin itself, as discussed in Berndt et al. (2016a). Therefore, the additional sulfate present downstream must be added along the flow path as water from the basin escapes into the environment. At W-1, up to approximately 20 percent of the total sulfate is added, given the assumptions that Δ = 17‰ and new sulfate $\delta^{34}S_{SO4}$ = 7.7‰ (Table 4). The isotopic composition of dissolved sulfate brackets the range in values observed in basin waters, suggesting that sulfate reduction has little impact on sulfate concentrations at this location (Figure 17, Table 4).

Little Tony Lake (LT-1), located along the eastern perimeter of Basin 1, is variably diluted relative to process water based on lower relative chloride and bromide concentrations (Figure 15), but the sulfate versus chloride plot demonstrate that a large amount of sulfate is added along this flow path (Figure 16). As indicated in Table 4, this new sulfate accounts for approximately 80 percent of the total (basin-derived plus new) concentration. The outlet of Little Tony Lake (LT-2) has slightly higher bromide and chloride concentrations than the LT-1 site, along with slightly more positive $\delta^{18}O_{H2O}$ and $\delta^{2}H_{H2O}$. This information might suggest that evaporation within the lake impacts the isotopic composition near the outlet. However, sulfate concentrations measured at the lake outlet are considerably lower than those at LT-1, and it does not appear that sulfate reduction is responsible for the lower sulfate/chloride ratio as $\delta^{34}S_{SO4}$ values are similar at the lake's inlet and outlet. Alternatively, an additional source of water may be daylighting within or near the lake outlet, located slightly north and further away from the perimeter dike. This additional seepage source would likely have a composition similar to Basin 2 water (elevated bromide and chloride), but unlike at the LT-1 location closer to the basin, a much smaller amount of new sulfate is added along this alternative flow path. If this interpretation is correct, shallow seepage through the dike is contributing a majority of the additional sulfate load found in downstream waters for this site.

At both Little Tony Lake sampling locations, $\delta^{34}S_{SO4}$ values are >2‰ heavier than basin water (Figure 17). At LT-1, however, $\delta^{18}O_{SO4}$ values are more negative than basin water, potentially due to the large amount of additional sulfate present at this location. The new source of sulfate likely derives its oxygen molecules from meteoric water during the oxidation process (Von Korff and Bavin, 2013), which has an average oxygen isotopic composition of ~-10-11‰. Water escaping the basin is first diluted, followed by the addition of newly oxidized sulfate which shifts $\delta^{18}O_{SO4}$ downward (Path 2A on Figure 17). Subsequent sulfate reduction will then cause the isotopic composition of sulfate to proceed along a new trajectory towards the upper left of the plot (Path 2B on Figure 17), with the net result being the measured isotopic composition at LT-1. This model indicates that about 20 percent of the sulfate pool is reduced (Table 4b). A similar process may be impacting sulfate in the downstream Little Tony Lake sampling location, LT-2. However, a larger proportion of the sulfate present is process water and thus the impact of newly oxidized sulfate and subsequent sulfate reduction on the isotopic composition of sulfate is less evident.

ArcelorMittal Minorca

ArcelorMittal's Minorca mining operation is located in Virginia, Minnesota and is shown as location E in Figure 1. Site specific sampling locations are shown on the ArcelorMittal basin area map (Figure 18) and data results are presented in Table A5. Plant makeup water comes from the Enterprise Pit, which is combined with input from the plant site settling basin (PSSB) and return water from the Upland Basin. Drainage from the Upland Basin flows towards a wetland to the north, which was sampled at two locations, one relatively close to the basin perimeter (W-1, ATV Trail) and another at the wetland outlet located approximately a mile to the north (W-2, Fireweed Rd). The two wetland locations were part of a 2010 DNR study which also attempted to utilize chloride concentration, sulfate concentration, and sulfate isotopes to determine sulfate behavior in seepage waters, albeit without detailed information from the basin itself (Berndt and Bavin, 2011). On one or two occasions, samples were also taken from several monitoring wells located around the north/northeastern side of the Upland Basin. An additional flow downstream of the PSSB was sampled during the first two rounds to see how the PSSB impacts downstream waters.

Chloride and bromide concentrations for this basin exhibit a well-defined dilution trend, with process waters consistently more concentrated than for waters collected from the surrounding locations (Figure 19). Sulfate to chloride ratios are generally lower in the well, wetland, and stream locations, suggesting a net loss of sulfate downstream of the Upland Basin and the PSSB (Figure 20). Due to wet conditions and high water levels during the spring 2014 sampling round, water from the Upland Basin was discharged directly towards the northern wetland locations in May and June of that year. Therefore, the chemistry of downstream waters was overwhelmingly dominated by basin water during the May 2014 sampling event. Subsequent sampling rounds, however, show distinct differences developing in chemistry for process and downstream waters, similar to those observed during the 2010 study (Berndt and Bavin, 2011). Most notably, wetland sulfate concentrations drop considerably relative to chloride (Figure 20). The drop in sulfate corresponds with a large shift in $\delta^{34}S_{SO4}$ at the near-basin wetland location (Figure 21, Figure 22).

As in the 2010 study, sulfur isotope values at the W-1 wetland location are elevated by more than 30‰ when the basin wasn't being discharged (Table 5). To draw a comparison with the previous study, the isotope fractionation effect was estimated for each sampling round assuming no new sulfate was added between the basin and the W-1 site. The calculated average Δ-value was 17‰, upholding the value derived using the 2010 data (Table 5b). Accordingly, about 75 percent (50 mg/L) of the sulfate that escapes the basin is lost to reduction along the flow path, again consistent with the 2010 study. Two rounds of isotope data (June 2014, September 2014) are available to make similar calculations for the surface water site downstream of the PSSB. Here, it is a particularly safe assumption that no additional sulfate was added along the flow path, as the PSSB is not surrounded by a large scale coarse tailings dike where oxidation is likely to take place. On average, approximately 41 percent of the total sulfate is reduced along this flow path, and the corresponding Δ-value is calculated to be 12.8‰. If this value is applied for the W-1 site just north of the Upland Basin, there is an increase in both the estimated fraction of total sulfate attributed to oxidation along the flow path (new sulfate, 42.2 percent) and fraction of total sulfate lost to reduction (85.3 percent).

Further north of the Upland Basin at the W-2 site, sulfate isotope values remained only slightly elevated compared to basin waters up to a full year after the spring 2014 basin discharge occurred, though $\delta^{34}S_{SO4}$ did increase by ~10‰ during the final October 2015 sampling round. After the basin discharge event, sulfate/chloride ratios become higher at the W-2 site than the W-1 site, suggesting that a new source of sulfate is present in downstream waters. It is possible that the additional sulfate source is from the relatively slow draining of sulfate that is temporarily stored within the wetland complex after high volumes of basin water were discharged downstream. At the nearby Long Lake Creek wetland, which is periodically impacted by similar seasonal mine discharge events, additional sulfur cycling within the wetland downstream was also found to impact the downstream isotopic composition (Kelly and Berndt, 2015). The GW006 well is located south of the W-1 site, and has sulfate concentrations slightly higher than background values indicating some impact from the basin, but $\delta^{34}S_{SO4}$ values are negative (average = -0.8‰). Similar to the shallow PZ-5s well at Minntac, this may result from the oxidation of recently precipitated secondary sulfides, in support of the above interpretation that sulfate is stored and possibly reduced within the downstream wetland. Accordingly, the Rayleigh fractionation model should probably not be used here to quantify sulfate reduction at the W-2 location. Combined results from this and the 2010 study, however, suggest that the downstream wetland locations respond in a relatively consistent and predictable way, both after basin discharge events and due to seasonal changes.

Modeling Uncertainties and application

As with any modeling application, the reported results are only accurate if the assumptions used in the construction of the model are accurate. Here, the net change in sulfate concentration at any location is determined using sulfate/chloride or sulfate/bromide ratios, and the dilution of basin water is accounted for using measured chloride or bromide concentrations. These calculations are least likely prone to inaccuracy, except, perhaps, where longer flow paths result in long travel times. In these cases, long term changes in the initial chloride or bromide concentrations (i.e., basin water) may impact the results. Similar problems could arise when there are multiple contributing water sources along the flow path, each with different concentration ratios. This complication was observed at the United Taconite tailings basin, where it is likely that some water draining to Little Tony Lake is coming from Basin 1 rather than from Basin 2.

Uncertainties associated with the isotopic assumptions made in the GTB model (described here and in Kelly et al., 2014) may also impact the accuracy of calculations. The assumed isotopic value of “new” sulfate is derived from the average of many regional mine pit lakes, which overlaps the range in composition of primary sulfide minerals from the iron formation and is further corroborated by humidity cell testing of oxidized coarse tailings from the Minntac basin (Von Korff and Bavin, 2014). Alternative values were used at Hibtac and Keetac, where on-site pit lake sulfur isotope averages were slightly lower than the average value for locations to the east. Furthermore, the $\delta^{34}S_{SO4}$ of new sulfate is typically fairly similar to measured basin pond values, and thus has a relatively minor impact on calculations compared to the impact of fractionation during sulfate reduction. The model uses a 17‰ fractionation effect to describe the isotopic shift associated with sulfate reduction, based on empirical evidence where alternative means exist to calculate the amount of sulfate lost to reduction (Berndt and Bavin, 2011). However, at several locations downstream of the Hibtac tailings basin, the 17‰ value failed to accurately reproduce the observed trends in sulfate concentration and isotopic composition. Instead, a value between ~10 to 12‰ looks more appropriate at those locations. It is not unexpected that the fractionation of sulfur during sulfate reduction can be variable due to population dynamics and localized environmental conditions, as suggested by this finding, and caution should be used where additional information is not available to refine the value used in calculations. Additional comparisons are currently underway between the GTB isotope model results and those from a concurrent reactive transport modeling effort at the U. S. Steel Minntac tailings basin. Comparisons with the calibrated model results may shed light on representation, patterns, and variability of the geochemical and biogeochemical processes impacting downstream sulfate concentrations.

Despite the aforementioned uncertainties, the methods developed and tested in the paper provide a systematic method for quickly quantifying the relative impacts of dilution, sulfide oxidation, and sulfate reduction at taconite operations across the Iron Range. As taconite operations approach closure, it will become more important to have a better understanding of site-specific sulfate reduction processes and how these processes can be reasonably accounted for to make future predictions. At the Minntac basin, where the largest downstream dataset is available, a loose correlation is observed between percent dilution and percent reduction, suggesting that slower or longer flow paths are associated with a greater loss of sulfate due to reduction. Further exploration of this relationship may ultimately help guide closure plans, and whether certain aspects of closure could be modified to slow down the flow of water to enhance sulfate reduction along the flow path. Potential also exists to improve overall understanding through direct examination of the subsurface peat and sediments. It is assumed that the majority of sulfide produced during reduction is precipitated out of solution in the form of secondary iron sulfide minerals, thereby removing a portion of the sulfur load from the system. This assumption should be tested through identification and analysis of secondary iron sulfide minerals found in the subsurface. If these secondary sulfide minerals are precipitating within the near surface sediments, there may be consequences in terms of downstream sulfate concentrations if the water table falls in the area after closure. Newly exposed secondary sulfide minerals may oxidize and release sulfate, which may be flushed out during subsequent precipitation and flooding events. This isotopic study identified two locations (Minntac and ArcelorMittal) where similar processes have likely occurred. These are several areas that will likely require future research in Minnesota's mining region in order to refine assumptions, inputs, and calibration targets for the GTB method and any other reactive transport modeling efforts.

Summary

The geochemical tracer based (GTB) method was initially described in Kelly et al. (2014), and is applied here at five taconite tailings basins across the Mesabi Iron Range of northeastern Minnesota. Tailings basin water and a variety of adjacent surface and/or groundwater locations were analyzed for geochemical parameters including major cations and anions, and water and sulfate isotopes. A geochemical and isotope mass balance approach, combined with the Rayleigh isotope fractionation equation, was utilized to determine the approximate amounts of dilution, sulfate addition through the oxidation of sulfide minerals in mine tailings, and sulfate loss due to microbial sulfate reduction.

This study unequivocally demonstrates that sulfate behavior is nonconservative in waters downstream of all five tailings basins, though the relative impact of sulfide oxidation and sulfate reduction varies considerably from site to site. While sulfide oxidation within the tailings dike does not appear to have a sizeable impact on downstream sulfate loading at the Hibtac and ArcelorMittal basins, it does contribute considerable amounts of additional sulfate to seepage waters at the Minntac and Utac basins. Based on geochemical mass balance and isotopic information, it is clear that sulfate reduction influences waters downstream of each operation, counterbalancing a portion of the new sulfate produced at several of the basins.

The GTB method relies on several assumptions and assigned values, namely the isotopic composition of new sulfate and the sulfur isotope fractionation effect associated with the reduction process. Based on previous DNR studies, an isotope fractionation value of 17‰ was assigned for associated calculations. However, results from the current study suggest that at a few specific locations, such as downstream of the Hibtac basin and ArcelorMittal's plant site settling basin, slightly smaller values in the range of 10 to

12‰ may be more appropriate. The method can also become complicated in situations where additional downstream sulfate sources are present or temporary water storage occurs. These and other chemical and flow uncertainties need to be considered when applying modeled results. However, the geochemical and isotopic tracer method described here has shown that simply considering the net gain or loss of sulfate does not accurately reflect the sulfur cycling processes occurring along any particular flow path. When operational changes (e.g., expansion, closure) are proposed, mining companies face environmental questions and possible concerns from the public. The GTB method provides a way to account for both sulfide oxidation and sulfate reduction in seepage waters, and can potentially help estimate the impact of various sulfate treatment options if and where downstream sulfate loading from taconite processing facilities is deemed necessary.

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Tables

Table 1: Geochemical tracer based (GTB) estimates for the Keetac basin perimeter wells. See basin map (Figure 3) for sampling locations. Average basin values were used for all calculations.

		5/21/15	10/7/15	Avg
Inner/Outer Basin Average	***Cl (measured, mg/L)***			25.4
	Br (measured, mg/L)			0.15
	SO_4 (measured, mg/L)			120.7
	$\delta^{34}S_{SO4}$ (‰)			5.8
Basin Monitoring Well 1	***Cl (measured, mg/L)***	23.3	23.8	23.6
	Br (measured, mg/L)	0.11	0.12	0.12
	SO_4 (measured, mg/L)	43.8	65.9	54.8
	$\delta^{34}S_{SO4}$ (‰)	35.7	28.7	32.2
	% dilution (Cl-based	8.3	6.3	7.3
	% oxidation ("new" sulfate)	58.3	58.0	59.1
	% reduction (sulfate lost)	83.5	75.5	79.9
	ΔS (‰)	17	17	17
Basin Monitoring Well 12	***Cl (measured, mg/L)***	17.2	–	–
	Br (measured, mg/L)	0.08	–	–
	SO_4 (measured, mg/L)	57.4	–	–
	$\delta^{34}S_{SO4}$ (‰)	14.6	–	–
	% dilution (Cl-based	32.2	–	–
	% oxidation ("new" sulfate)	16.3	–	–
	% reduction (sulfate lost)	41.3	–	–
	ΔS (‰)	17	–	–
Basin Monitoring Well 11	***Cl (measured, mg/L)***	–	23.3	–
	Br (measured, mg/L)	–	0.14	–
	SO_4 (measured, mg/L)	–	93.1	–
	$\delta^{34}S_{SO4}$ (‰)	–	15.3	–
	% dilution (Cl-based	–	8.3	–
	% oxidation ("new" sulfate)	–	35.0	–
	% reduction (sulfate lost)	–	45.3	–
	ΔS (‰)	–	17	–

Table 2: Geochemical tracer based (GTB) estimates for the available Hibtac downstream locations. See map (Figure 6) for sampling locations.

		6/25/15	10/2/15	2/19/15	5/7/15	9/29/15	Avg
Tailings Basin Return	***Cl (measured, mg/L)***	45.6	53.9	–	52.5	52.8	51.2
	Br (measured, mg/L)	0.27	0.32	–	0.29	0.29	0.29
	SO_4 (measured, mg/L)	144.5	169.9	–	174.1	176.1	166.1
	$\delta^{34}S_{SO4}$ (measured, ‰)	7.4	7.3	–	7.5	6.9	7.3
Culvert outfall 220; SD002	***Cl (measured, mg/L)***	38.8	49.7	–	45.3	45.6	44.8
	Br (measured, mg/L)	0.24	0.27	–	0.24	0.27	0.25
	SO_4 (measured, mg/L)	79.8	105.7	–	96.5	87.7	92.4
	$\delta^{34}S_{SO4}$ (measured, ‰)	12.3	12.0	–	12.0	13.7	12.1
	% dilution (Br-based)	14.9	16.4	–	18.0	6.5	21.6
	% oxidation ("new" sulfate)	0	0	–	0	0	0
	% reduction (sulfate lost)	34.3	32.6	–	32.4	42.3	36.5
	ΔS (‰)	11.6	12.2	–	11.6	12.2	10.8
Culvert outfall 240; SD004	***Cl (measured, mg/L)***	15.7	39.0	38.2	32.4	33.0	35.6
	Br (measured, mg/L)	0.14	0.26	0.30	0.21	0.23	0.25
	SO_4 (measured, mg/L)	0.2	26.5	25.0	21.5	50.3	30.8
	$\delta^{34}S_{SO4}$ (measured, ‰)	–	22.9	27.0	28.3	22.9	25.3
	% dilution (Br-based)	50.4	17.7	30.0	26.0	21.8	22.7
	% oxidation ("new" sulfate)	–	0	0	0	0	0
	% reduction (sulfate lost)	–	78.5	84.0	83.3	54.4	73.4
	ΔS (‰)	–	10.0	10.7	11.4	20.1	13.0
Surface water; Day Lake Rd	***Cl (measured, mg/L)***	9.8	38.7	52.3	22.8	14.6	37.5
	Br (measured, mg/L)	0.04	0.10	0.19	0.05	0.04	0.12
	SO_4 (measured, mg/L)	1.3	3.1	32.3	12.2	2.3	22.3
	$\delta^{34}S_{SO4}$ (measured, ‰)	–	–	22.4	19.2	–	20.8
	% dilution (Br-based)	85.1	67.4	55.6	82.2	85.2	62.9
	% oxidation ("new" sulfate)	–	–	0	0	–	0
	% reduction (sulfate lost)	–	–	67.5	60.1	–	66.4
	ΔS (‰)	–	–	13.5	12.6	–	12.3
Culvert outfall 100; SD001	***Cl (measured, mg/L)***	37.2	52.3	63.0	42.1	50.2	49.0
	Br (measured, mg/L)	0.13	0.21	0.32	0.14	0.20	0.20
	SO_4 (measured, mg/L)	14.0	37.3	103.5	64.8	33.1	50.5
	$\delta^{34}S_{SO4}$ (measured, ‰)	28.9	34.7	20.0	21.2	27.4	26.2
	% dilution (Br-based)	52.6	33.7	23.9	51.6	31.7	31.5
	% oxidation ("new" sulfate)	0	0	0	0	0	0
	% reduction (sulfate lost)	79.6	66.9	39.2	23.2	72.5	55.6
	ΔS (‰)	13.2	24.4	25.7	51.4	15.6	23.0

*Averages were calculated using only the sampling rounds where sulfate isotope results were available.

** GTB results are in grey text and italics because at this location, it is likely that an additional sources complicates the use of a simple Rayleigh fractionation model

Table 3a: Geochemical tracer based (GTB) estimates for the Minntac seep and well locations on the east and north sides of the basin (wells listed counterclockwise from SE corner, see Figure 10). Calculations are based on average chemical concentrations and isotopic values for wells/seeps relative to average tailings basin return values.

Avg Basin Return	Cl (measured, mg/L)	146.4			
	Br (measured, mg/L)	1.17			
	SO_4 (measured, mg/L)	897.1			
	$\delta^{34}S_{SO4}$ (measured, ‰)	8.4			
P1 CB5	Cl (measured, mg/L)	132.7	**PZ-12S**	Cl (measured, mg/L)	131.5
	Br (measured, mg/L)	1.07		Br (measured, mg/L)	1.04
	SO_4 (measured, mg/L)	933.1		SO_4 (measured, mg/L)	588.4
	$\delta^{34}S_{SO4}$ (‰)	10.8		$\delta^{34}S_{SO4}$ (‰)	15.1
	% dilution (Cl-based)	9.4		% dilution (Cl-based)	10.2
	% oxidation ("new" sulfate)	54.7		% oxidation ("new" sulfate)	7.3
	% reduction (sulfate lost)	21.1		% reduction (sulfate lost)	32.3
	ΔS (‰)	17		ΔS (‰)	17
P2 CB10	Cl (measured, mg/L)	93.1	**MW-12**	Cl (measured, mg/L)	100.1
	Br (measured, mg/L)	0.74		Br (measured, mg/L)	0.81
	SO_4 (measured, mg/L)	995.5		SO_4 (measured, mg/L)	436.7
	$\delta^{34}S_{SO4}$ (‰)	12.1		$\delta^{34}S_{SO4}$ (‰)	15.3
	% dilution (Cl-based)	36.4		% dilution (Cl-based)	31.6
	% oxidation ("new" sulfate)	22.2		% oxidation ("new" sulfate)	6.0
	% reduction (sulfate lost)	-35.7		% reduction (sulfate lost)	33.1
	ΔS (‰)	17		ΔS (‰)	17
MW 1	Cl (measured, mg/L)	150.7	**PZ PT 6D**	Cl (measured, mg/L)	29.6
	Br (measured, mg/L)	1.20		Br (measured, mg/L)	0.24
	SO_4 (measured, mg/L)	936.2		SO_4 (measured, mg/L)	218.9
	$\delta^{34}S_{SO4}$ (‰)	8.5		$\delta^{34}S_{SO4}$ (‰)	14.5
	% dilution (Cl-based)	0.3		% dilution (Cl-based)	79.8
	% oxidation ("new" sulfate)	2.1		% oxidation ("new" sulfate)	43.0
	% reduction (sulfate lost)	0.8		% reduction (sulfate lost)	31.1
	ΔS (‰)	17		ΔS (‰)	17
MW 3	Cl (measured, mg/L)	132.3	**MW 4**	Cl (measured, mg/L)	90.2
	Br (measured, mg/L)	0.97		Br (measured, mg/L)	0.73
	SO_4 (measured, mg/L)	743.5		SO_4 (measured, mg/L)	513.5
	$\delta^{34}S_{SO4}$ (‰)	14.7		$\delta^{34}S_{SO4}$ (‰)	14.3
	% dilution (Cl-based)	12.5		% dilution (Cl-based)	38.4
	% oxidation ("new" sulfate)	25.1		% oxidation ("new" sulfate)	24.5
	% reduction (sulfate lost)	31.3		% reduction (sulfate lost)	29.8
	ΔS (‰)	17		ΔS (‰)	17
PZ-5D	Cl (measured, mg/L)	130.4	**MW 13**	Cl (measured, mg/L)	37.6
	Br (measured, mg/L)	1.00		Br (measured, mg/L)	0.28
	SO_4 (measured, mg/L)	810.9		SO_4 (measured, mg/L)	309.0
	$\delta^{34}S_{SO4}$ (‰)	13.9		$\delta^{34}S_{SO4}$ (‰)	21.3
	% dilution (Cl-based)	13.8		% dilution (Cl-based)	74.3
	% oxidation ("new" sulfate)	29.4		% oxidation ("new" sulfate)	65.6
	% reduction (sulfate lost)	28.4		% reduction (sulfate lost)	53.9
	ΔS (‰)	17		ΔS (‰)	17

Table 3b: Geochemical tracer based (GTB) estimates for the Minntac seep and well locations on the west side of the basin (see Figure 10). Calculations are based on average chemical concentrations and isotopic values for wells/seeps relative to average tailings discharge values.

Avg Tailings Discharge	*Cl (measured, mg/L)*	151.2			
	Br (measured, mg/L)	1.23			
	SO_4 (measured, mg/L)	838.8			
	$\delta^{34}S_{SO4}$ *(measured, ‰)*	8.2			
SD002	*Cl (measured, mg/L)*	130.3	**MW 7**	*Cl (measured, mg/L)*	103.4
	Br (measured, mg/L)	1.05		*Br (measured, mg/L)*	0.80
	SO_4 (measured, mg/L)	1019.5		*SO_4 (measured, mg/L)*	878.4
	$\delta^{34}S_{SO4}$ (‰)	8.8		$\delta^{34}S_{SO4}$ (‰)	11.0
	% dilution (Cl-based)	13.8		*% dilution (Cl-based)*	31.6
	% oxidation ("new" sulfate)	32.1		*% oxidation ("new" sulfate)*	45.1
	% reduction (sulfate lost)	4.2		*% reduction (sulfate lost)*	16.0
	ΔS (‰)	17		*ΔS (‰)*	17
MW 6	*Cl (measured, mg/L)*	106.3	**MW 8**	*Cl (measured, mg/L)*	91.7
	Br (measured, mg/L)	0.80		*Br (measured, mg/L)*	0.71
	SO_4 (measured, mg/L)	874.6		*SO_4 (measured, mg/L)*	606.0
	$\delta^{34}S_{SO4}$ (‰)	10.9		$\delta^{34}S_{SO4}$ (‰)	17.3
	% dilution (Cl-based)	29.7		*% dilution (Cl-based)*	39.4
	% oxidation ("new" sulfate)	43.1		*% oxidation ("new" sulfate)*	51.4
	% reduction (sulfate lost)	15.7		*% reduction (sulfate lost)*	42.1
	ΔS (‰)	17		*ΔS (‰)*	17

Table 4: Geochemical tracer based (GTB) estimates for the Utac downstream wetland and lake locations. See basin map (Figure 14) for sampling locations.

		6/11/14	10/1/14	2/17/15	5/12/15	Avg
Tailings basin return to plant	***Cl (measured, mg/L)***	45.8	55.2	80.0	57.0	59.5
	Br (measured, mg/L)	0.33	0.37	0.60	0.38	0.42
	SO_4 (measured, mg/L)	139.9	188.3	302.3	228.0	214.6
	$\delta^{34}S_{SO4}$ (measured, ‰)	7.8	8.5	7.6	7.9	8.0
Wetland near Twin Lakes* (W-1)	***Cl (measured, mg/L)***	51.0	54.4	52.8	54.2	53.1
	Br (measured, mg/L)	0.40	0.44	0.43	0.38	0.41
	SO_4 (measured, mg/L)	250.3	289.0	217.0	209.5	241.4
	$\delta^{34}S_{SO4}$ (measured, ‰)	7.9	7.1	8.3	9.3	8.1
	% dilution (Cl-based)	14.3	8.6	11.2	8.9	10.8
	% oxidation ("new" sulfate)	26.5	28.8	14.1	13.9	21.8
	% reduction (sulfate lost)	0.0	-4.9	2.2	7.7	1.4
	ΔS (‰)	17	17	17	17	17
Wetland, downstream (W-2)	***Cl (measured, mg/L)***	–	–	66.6	42.5	54.5
	Br (measured, mg/L)	–	–	0.57	0.25	0.41
	SO_4 (measured, mg/L)	–	–	333.6	189.4	261.5
	$\delta^{34}S_{SO4}$ (measured, ‰)	–	–	8.7	9.4	9.1
	% dilution (Cl-based)	–	–	16.7	25.6	20.4
	% oxidation ("new" sulfate)	–	–	29.1	18.1	25.2
	% reduction (sulfate lost)	–	–	6.0	8.6	7.4
	ΔS (‰)	–	–	17	17	17
Little Tony Lake near SD001 (LT-1)	***Cl (measured, mg/L)***	30.3	39.1	37.9	35.2	35.6
	Br (measured, mg/L)	0.13	0.23	0.24	0.14	0.19
	SO_4 (measured, mg/L)	295.8	531.1	599.1	435.6	465.4
	$\delta^{34}S_{SO4}$ (measured, ‰)	12.1	11.1	11.6	14.5	12.3
	% dilution (Cl-based)	33.9	29.2	52.6	38.3	40.1
	% oxidation ("new" sulfate)	75.8	79.2	81.0	78.2	78.9
	% reduction (sulfate lost)	22.6	17.1	20.4	32.5	23.4
	ΔS (‰)	17	17	17	17	17
Little Tony Lake, outlet (LT-2)	***Cl (measured, mg/L)***	–	–	45.2	39.0	42.1
	Br (measured, mg/L)	–	–	0.29	0.20	0.25
	SO_4 (measured, mg/L)	–	–	336.8	302.8	–
	$\delta^{34}S_{SO4}$ (measured, ‰)	–	–	11.2	–	–
	% dilution (Cl-based)	–	–	43.5	29.3	–
	% oxidation ("new" sulfate)	–	–	58.7	–	–
	% reduction (sulfate lost)	–	–	18.6	–	–
	ΔS (‰)	–	–	17	–	–

*Averages were calculated using only the sampling rounds where sulfate isotope results were available.**At the W-1 wetland site, dilution, oxidation, and reduction percentages were calculated relative to average basin return water for each round. This approach was taken because the site lacks seasonal variability and appears to reflect average basin conditions.

Table 5: Geochemical tracer based (GTB) estimates for the ArcelorMittal downstream wetland and stream locations. See basin map (Figure 18) for sampling locations.

		6/10/14	9/30/14	2/18/15	5/15/15	10/13/15	Avg*
Upland basin return to plant	***Cl (measured, mg/L)***	56.8	64.0	73.5	68.8	74.3	67.5
	Br (measured, mg/L)	0.58	0.66	0.77	0.67	0.69	0.67
	SO_4 (measured, mg/L)	57.3	63.7	78.8	76.5	77.2	70.7
	$\delta^{34}S_{SO4}$ (measured, ‰)	10.8	11.5	10.5	10.3	10.5	10.7
Wetland, N of Upland Basin (W-1)	***Cl (measured, mg/L)***	55.0	65.6	65.8	53.2	64.5	60.8
	Br (measured, mg/L)	0.56	0.64	0.70	0.51	0.58	0.60
	SO_4 (measured, mg/L)	53.4	10.4	19.4	19.4	11.2	22.8
	$\delta^{34}S_{SO4}$ (measured, ‰)	11.4	–	32.5	32.6	38.0	28.6
	% dilution (Cl-based)	3.2	–	10.4	22.6	13.2	15.7
	% oxidation ("new" sulfate)	0	–	0	0	0	0
	% reduction (sulfate lost)	3.8	–	72.5	67.2	83.3	65.2
	ΔS (‰)	16.0	–	16.7	19.6	15.0	17.1
	Cl (measured, mg/L)	52.2	64.1	–	36.8	49.2	50.6
	Br (measured, mg/L)	0.54	0.59	–	0.29	0.41	0.46
	SO_4 (measured, mg/L)	49.4	14.2	–	27.8	15.6	–
	$\delta^{34}S_{SO4}$ (measured, ‰)	13.0	–	–	13.8	23.6	–
	% dilution (Cl-based)	8.1	–	–	46.4	33.8	–
	% oxidation ("new" sulfate)	0	–	–	0	0	–
	% reduction (sulfate lost)	*6.1*	–	–	*32.2*	*69.5*	–
	ΔS (‰)	*35.1*	–	–	*8.9*	*10.9*	–
	Cl (measured, mg/L)	58.0	92.6	–	–	–	75.3
	Br (measured, mg/L)	0.48	0.83	–	–	–	0.66
	SO_4 (measured, mg/L)	49.5	76.1	–	–	–	62.8
	$\delta^{34}S_{SO4}$ (measured, ‰)	9.2	9.6	–	–	–	9.4
Downstream of PSSB, at HW 53	***Cl (measured, mg/L)***	49.6	38.7	–	–	–	44.1
	Br (measured, mg/L)	0.37	0.25	–	–	–	0.31
	SO_4 (measured, mg/L)	28.2	15.4	–	–	–	21.8
	$\delta^{34}S_{SO4}$ (‰)	14.8	17.5	–	–	–	16.2
	% dilution (Cl-based)	14.5	58.2	–	–	–	41.4
	% oxidation ("new" sulfate)	0.0	0.0	–	–	–	0.0
	% reduction (sulfate lost)	33.4	51.6	–	–	–	40.8
	ΔS (‰)	13.7	10.8	–	–	–	12.8

*The average for the W-1 site excludes data from the first two rounds.** GTB results are in grey text and italics because at this location, it is likely that an additional sulfate source complicates the use of a simple Rayleigh fractionation model

Figures

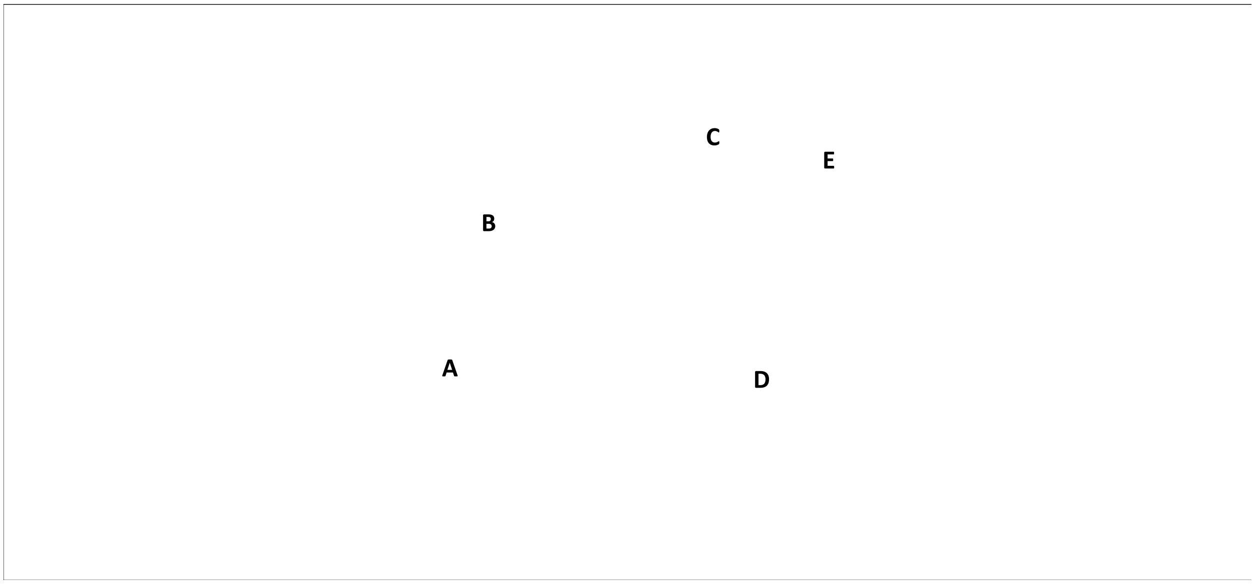

Figure 1: Map of the Mesabi Iron Range in northeastern Minnesota, highlighting the location of taconite tailings basins (green), pits (brown), and other mining features (grey). Taconite tailings basins discussed in this report are labeled from west to east **(A)** U.S. Steel – Keetac, **(B)** Hibbing Taconite, **(C)** U.S. Steel – Minntac, **(D)** Cliffs Natural Resources United Taconite, and **(E)** ArcelorMittal Minorca.

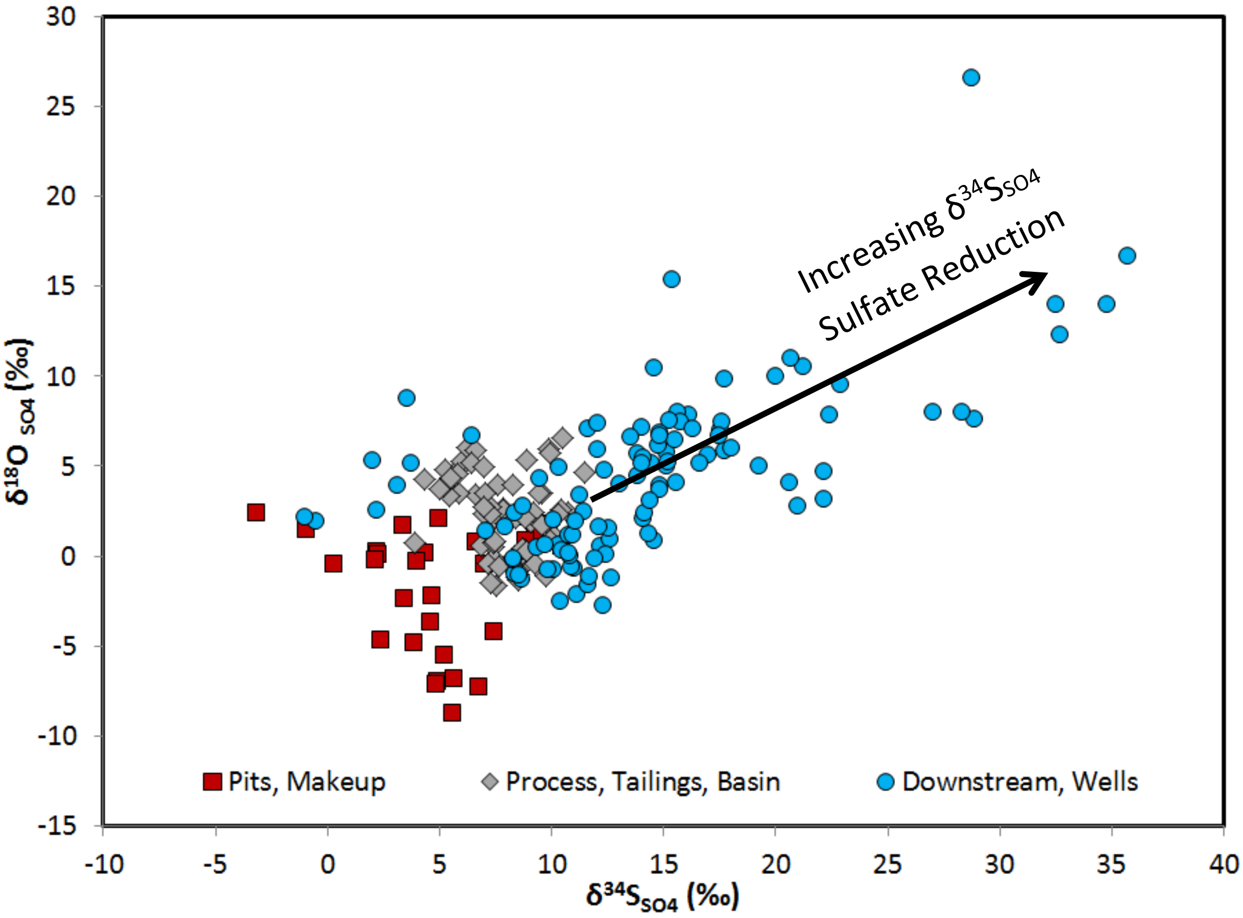

Figure 2: Sulfate isotope data ($\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$) for all sampling locations and dates. Downstream sampling locations tend to plot towards the upper right of mine pits and process water sites. Microbial sulfate reduction is the main process that causes sulfur isotope values of sulfate to increase. Therefore, the observed trend likely indicates the widespread prevalence of sulfate reduction downstream of taconite mining areas in northeastern Minnesota.

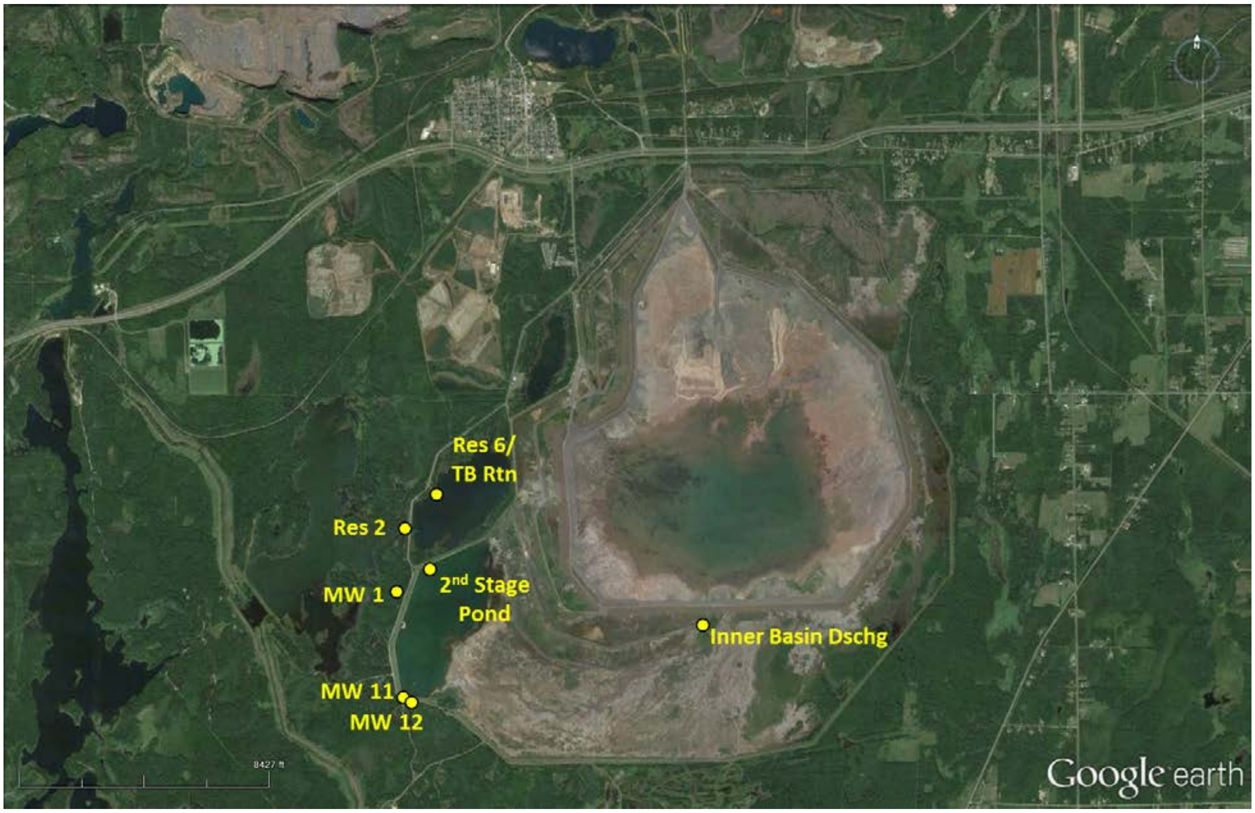

Figure 3. The U. S. Steel Keetac basin area map. Select sampling locations are labeled.

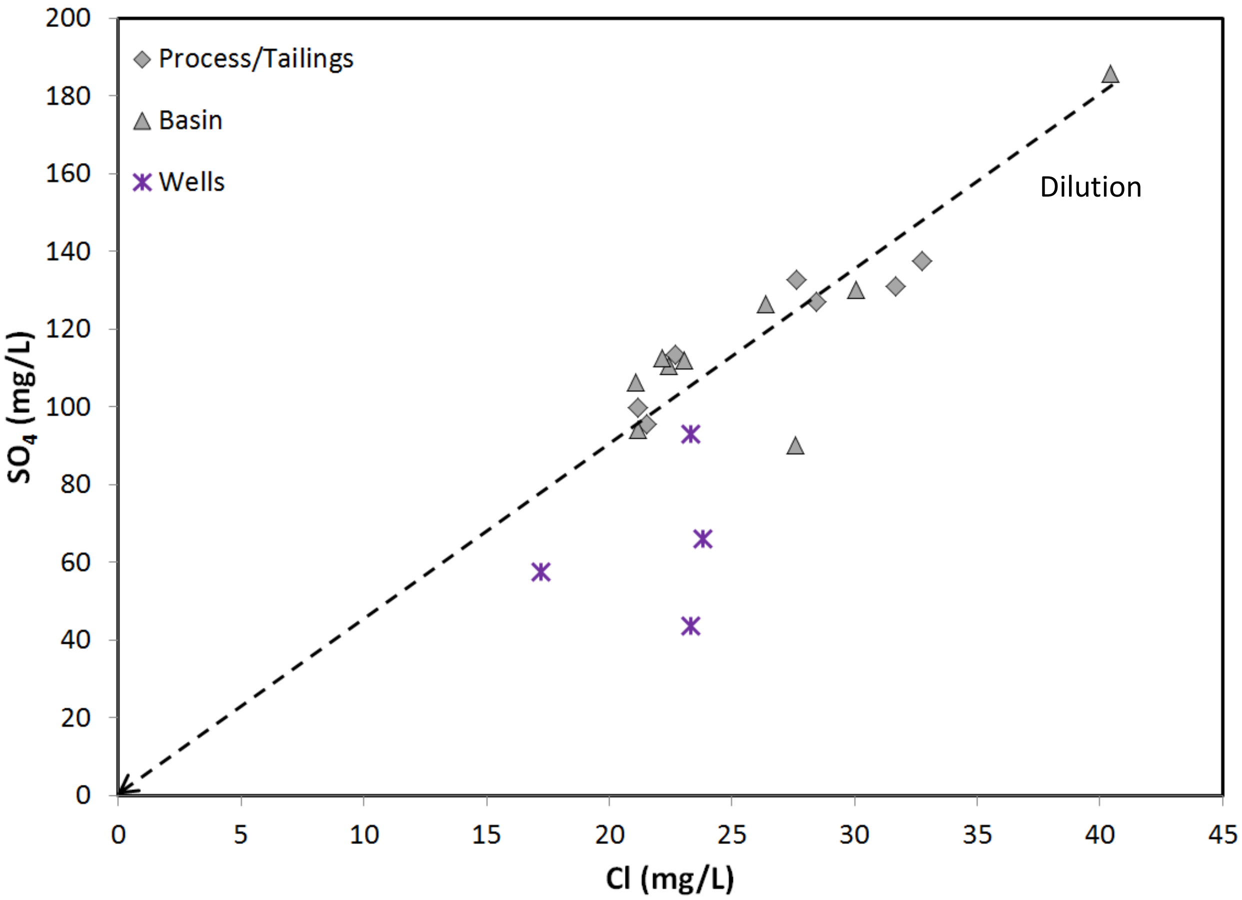

Figure 4. Chloride concentration plotted relative to sulfate concentration for all Keetac sampling locations. A dilution regression line was drawn through the basin and process waters towards the origin. Basin perimeter wells fall below the dilution line (lower SO_4/Cl ratios), suggesting that a net loss of sulfate occurs along the flow path.

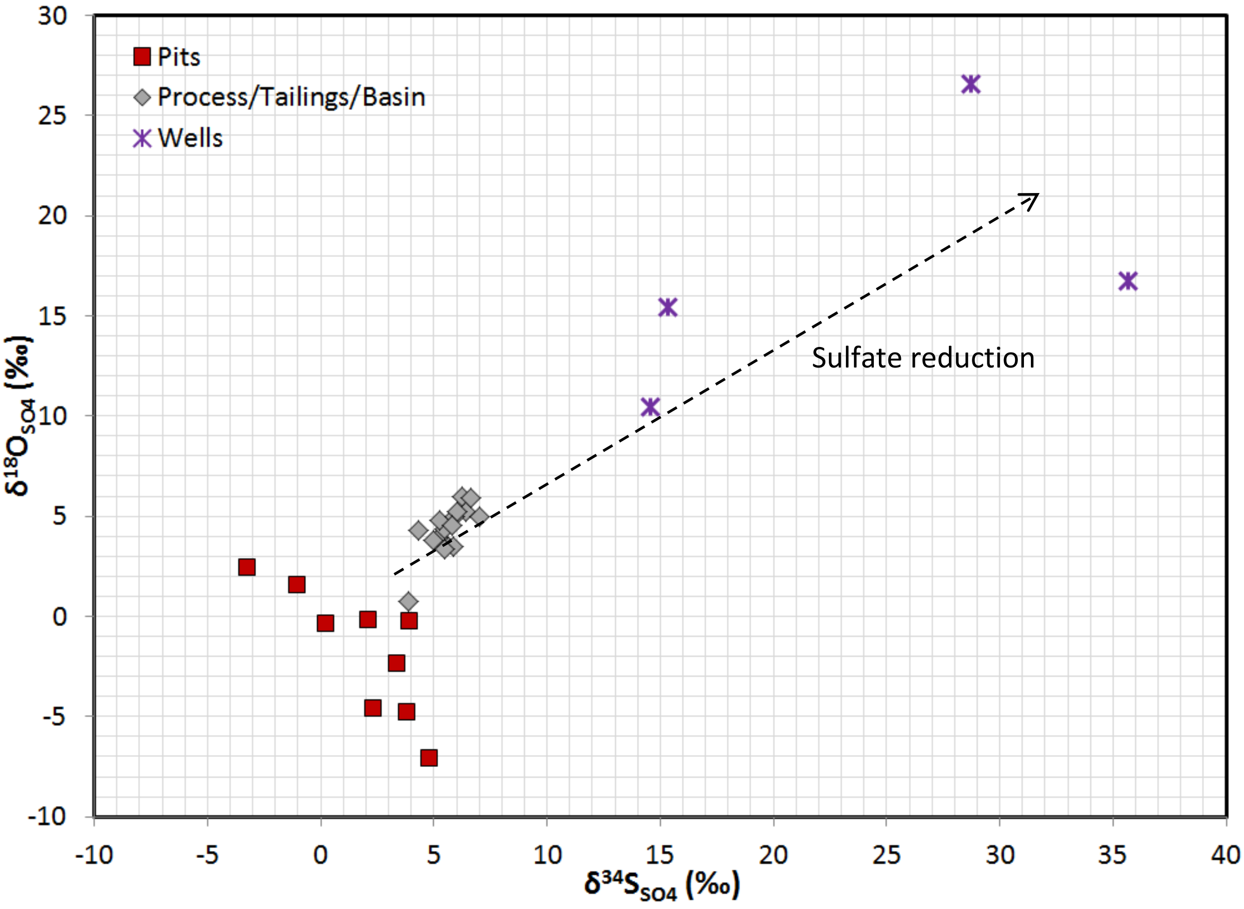

Figure 5. Plot of $\delta^{18}O_{SO4}$ versus $\delta^{34}S_{SO4}$ for the Keetac pits, tailings basin, and surrounding wells. The arrow depicts an increasing isotopic trend associated with bacterial sulfate reduction.

Figure 6. Hibbing Taconite (Hibtac) basin area map. Select sampling locations are labeled.

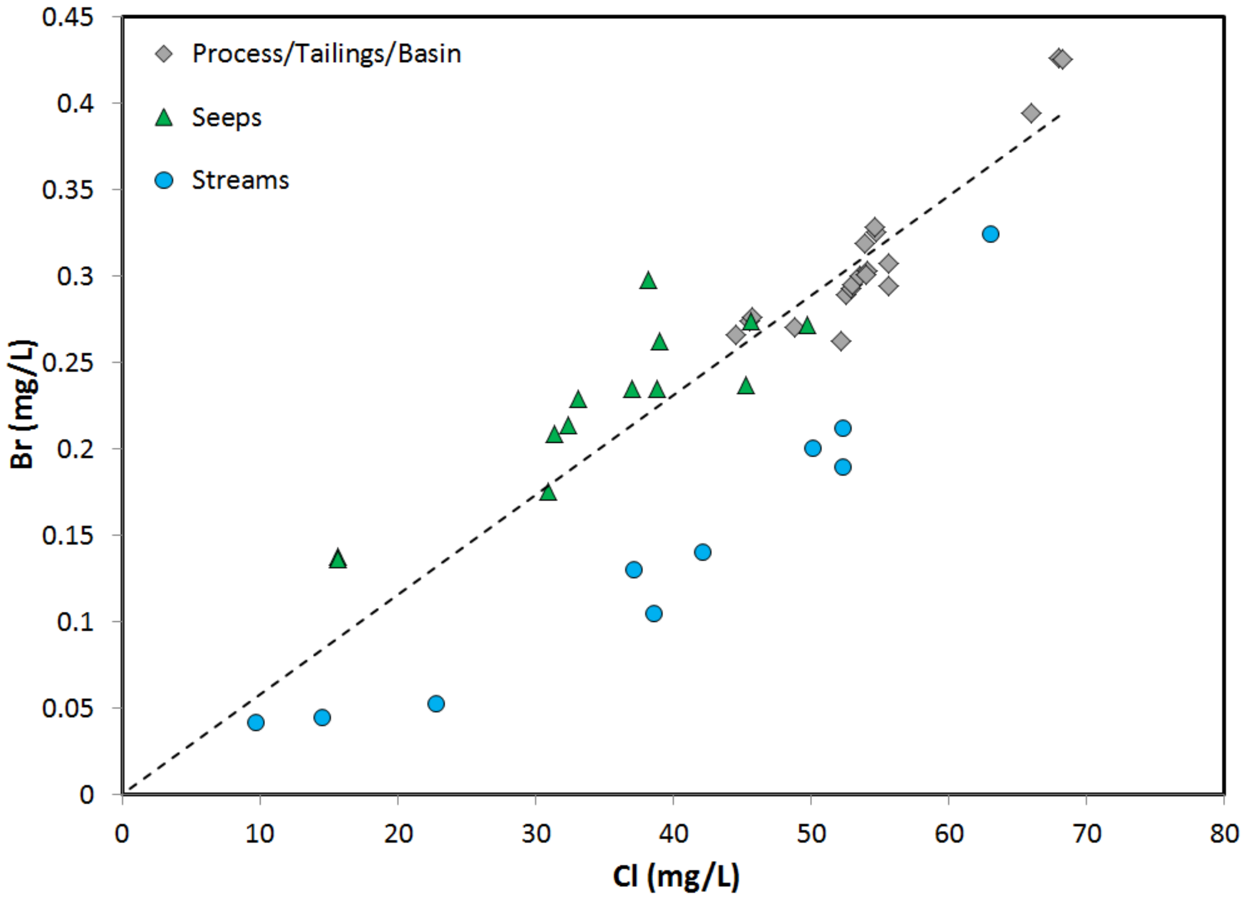

Figure 7. Chloride versus bromide concentrations measured in Hibtac process and basin waters (grey diamonds) and surrounding downstream locations, including seepage outfalls (green triangles) and streams (blue circles). The stream locations are offset from the dilution trend towards higher chloride concentrations, likely due to additional runoff from nearby roads and/or plant area drainage.

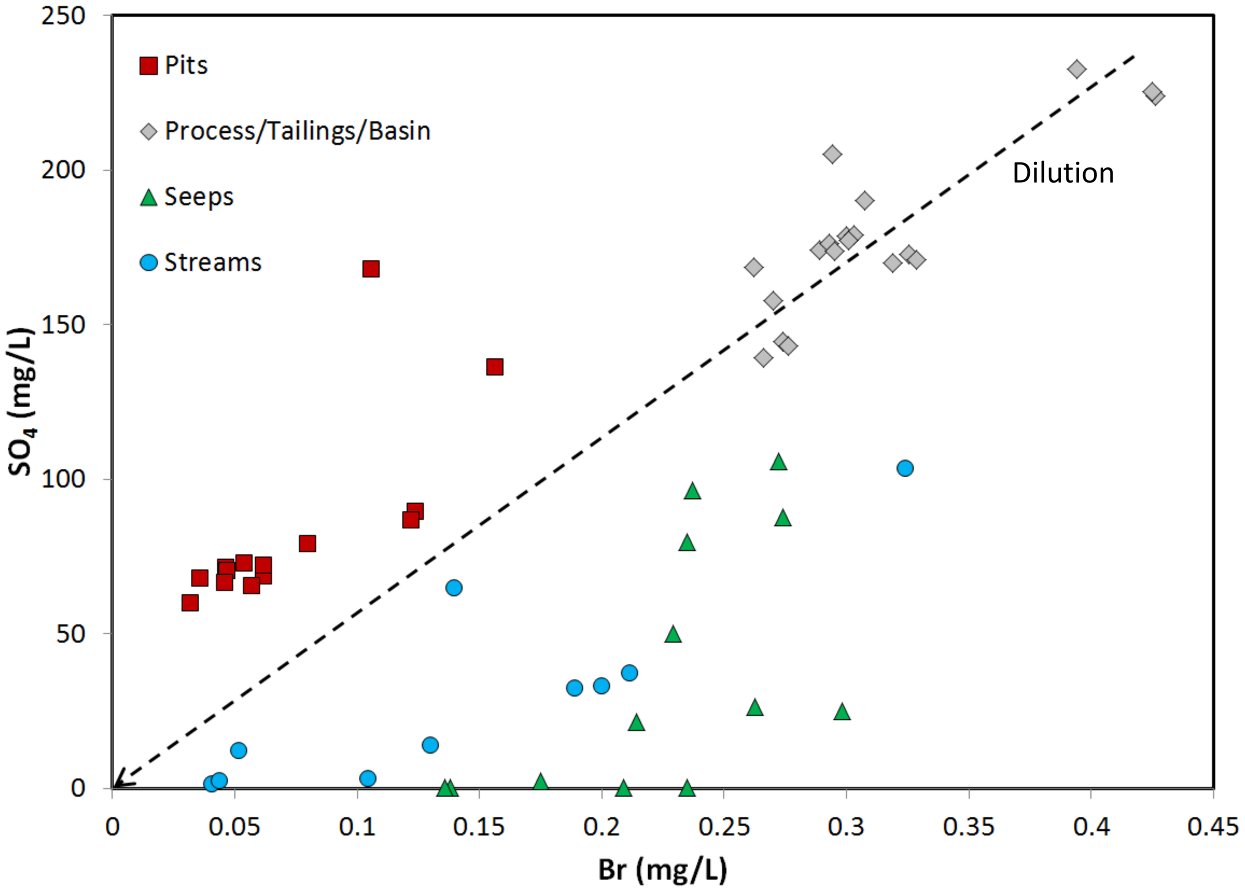

Figure 8. Bromide (Br) concentration plotted relative to sulfate (SO_4) concentration for all Hibtac basin area sampling locations. Downstream locations consistently plot below the process water dilution trend, indicating a net sulfate loss as water moves from the basin into the surrounding environment. At some locations, sulfate concentrations are near zero despite having bromide concentrations well above typical background concentrations.

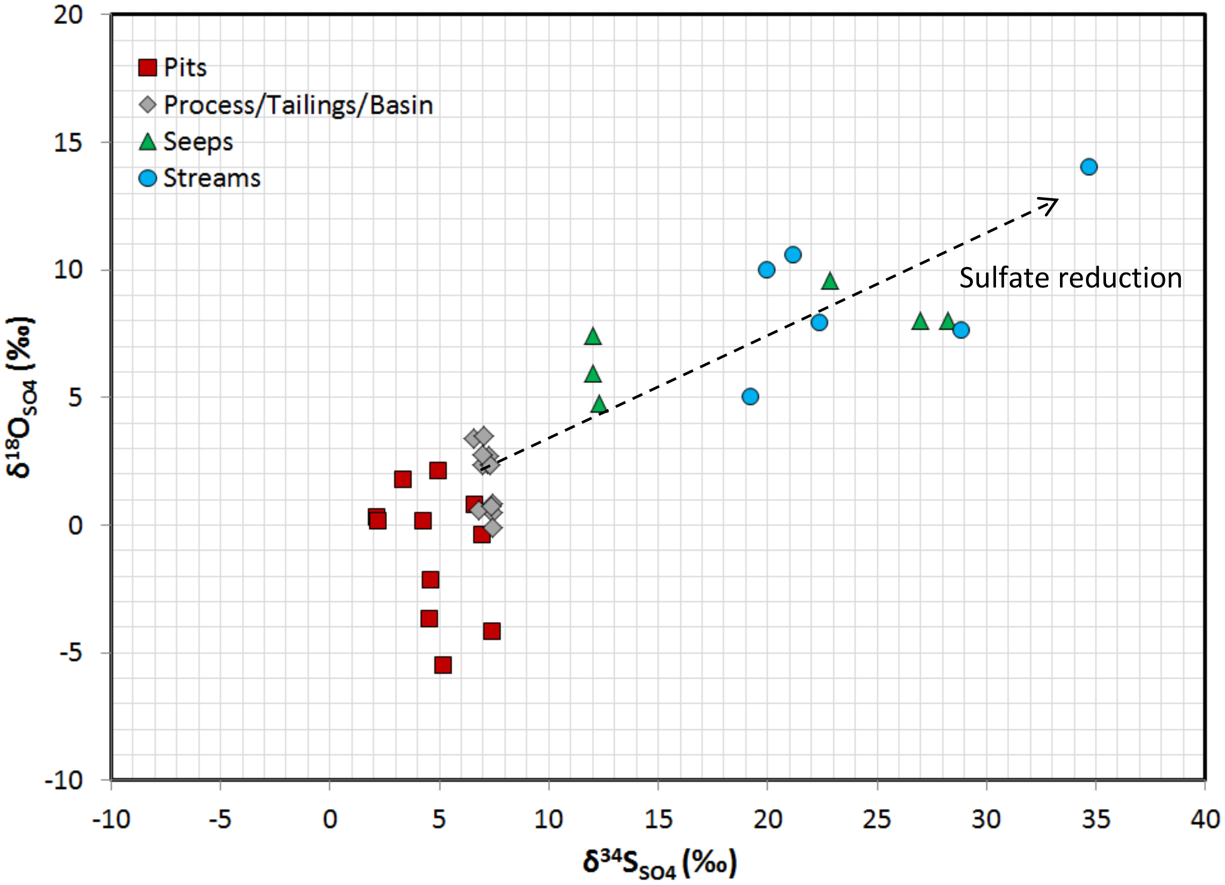

Figure 9. Plot of $\delta^{18}O_{SO4}$ versus $\delta^{34}S_{SO4}$ for the Hibtac pits, tailings basin, and surrounding waters. The arrow depicts an increasing isotopic trend associated with bacterial sulfate reduction.

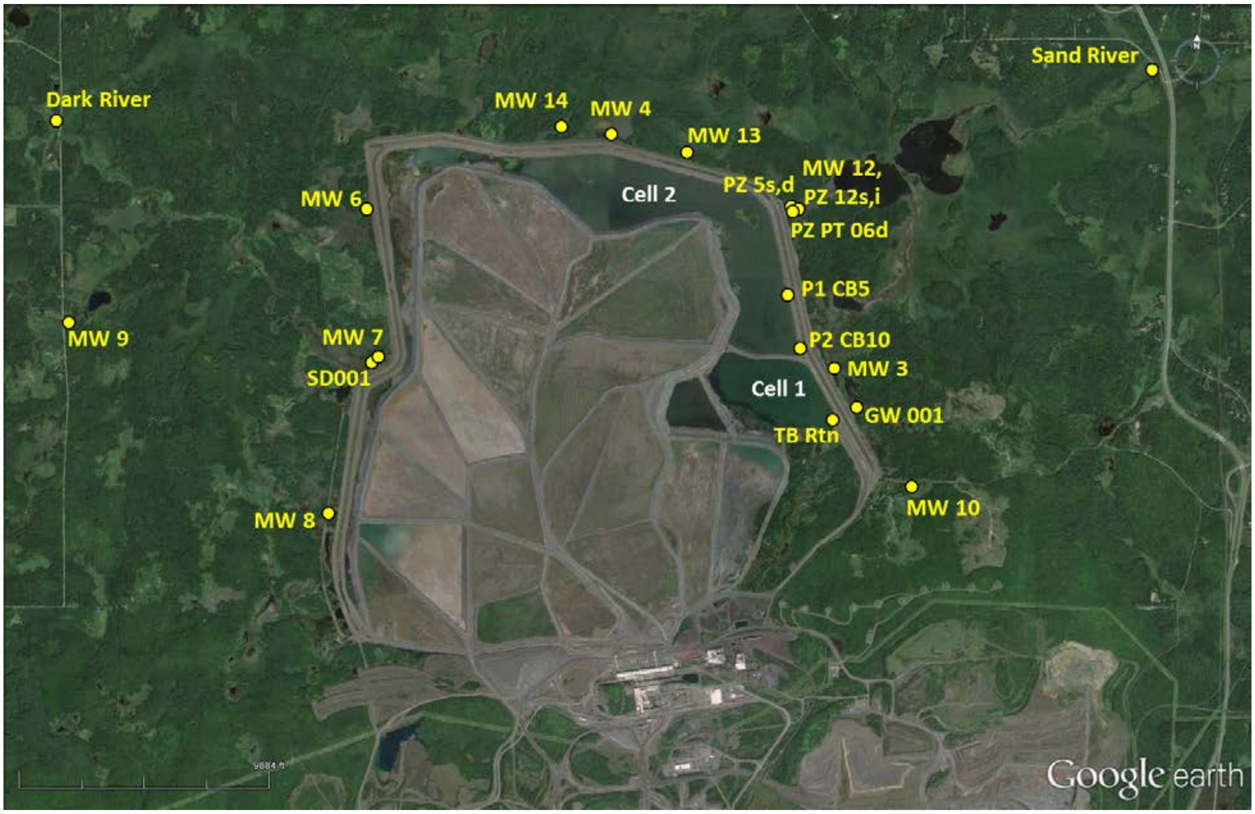

Figure 10. U.S. Steel's Minntac basin area map. The basin sampling locations, seepage pumps, numbered wells, and stream sites are labeled.

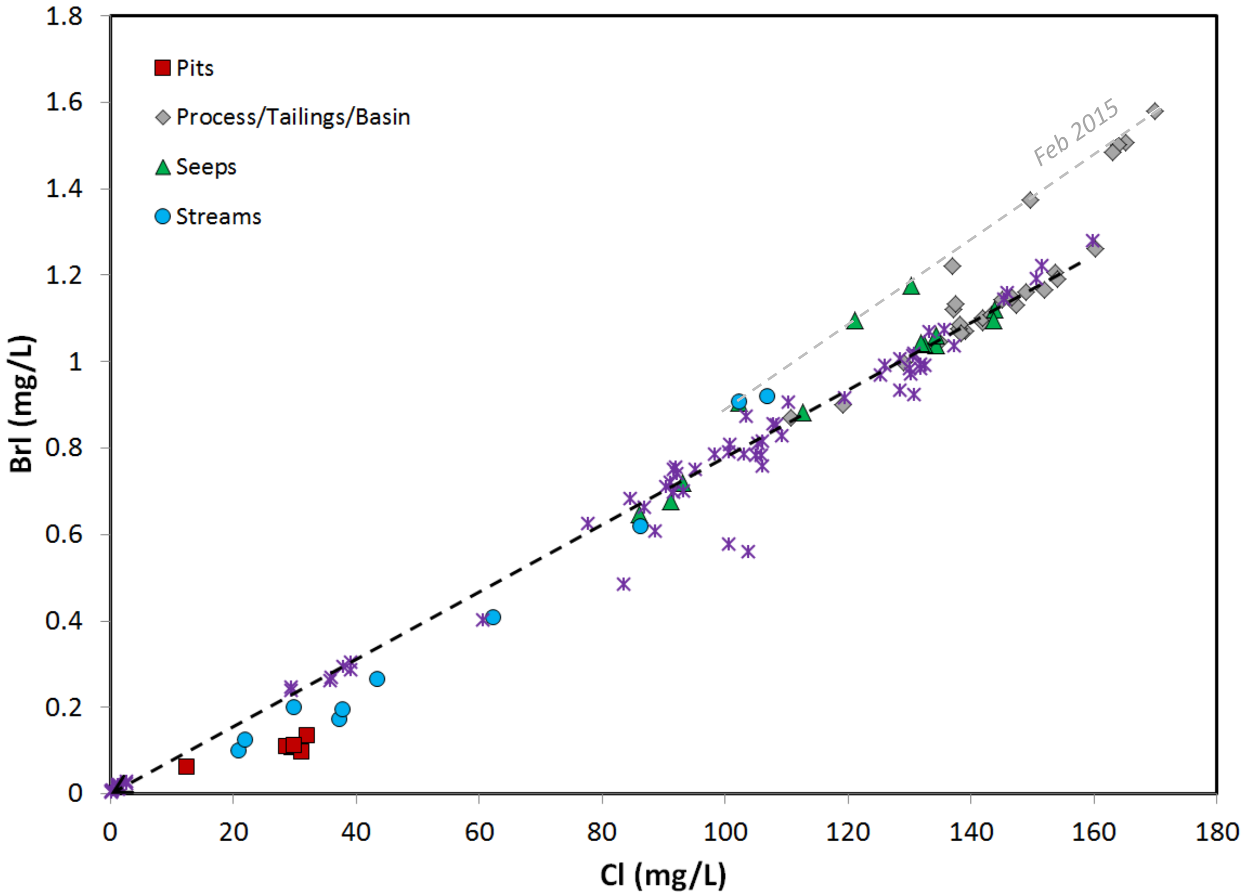

Figure 11. Chloride (Cl) versus bromide (Br) concentrations measured in Minntac process and basin waters (grey diamonds) and all downstream locations, including seeps (green triangles), monitoring wells (purple Xs), and streams (blue circles). Results from the February 2015 sampling round plotted along a different slope. The reason for this difference is unknown, and these results were not included when developing the process water dilution line presented here.

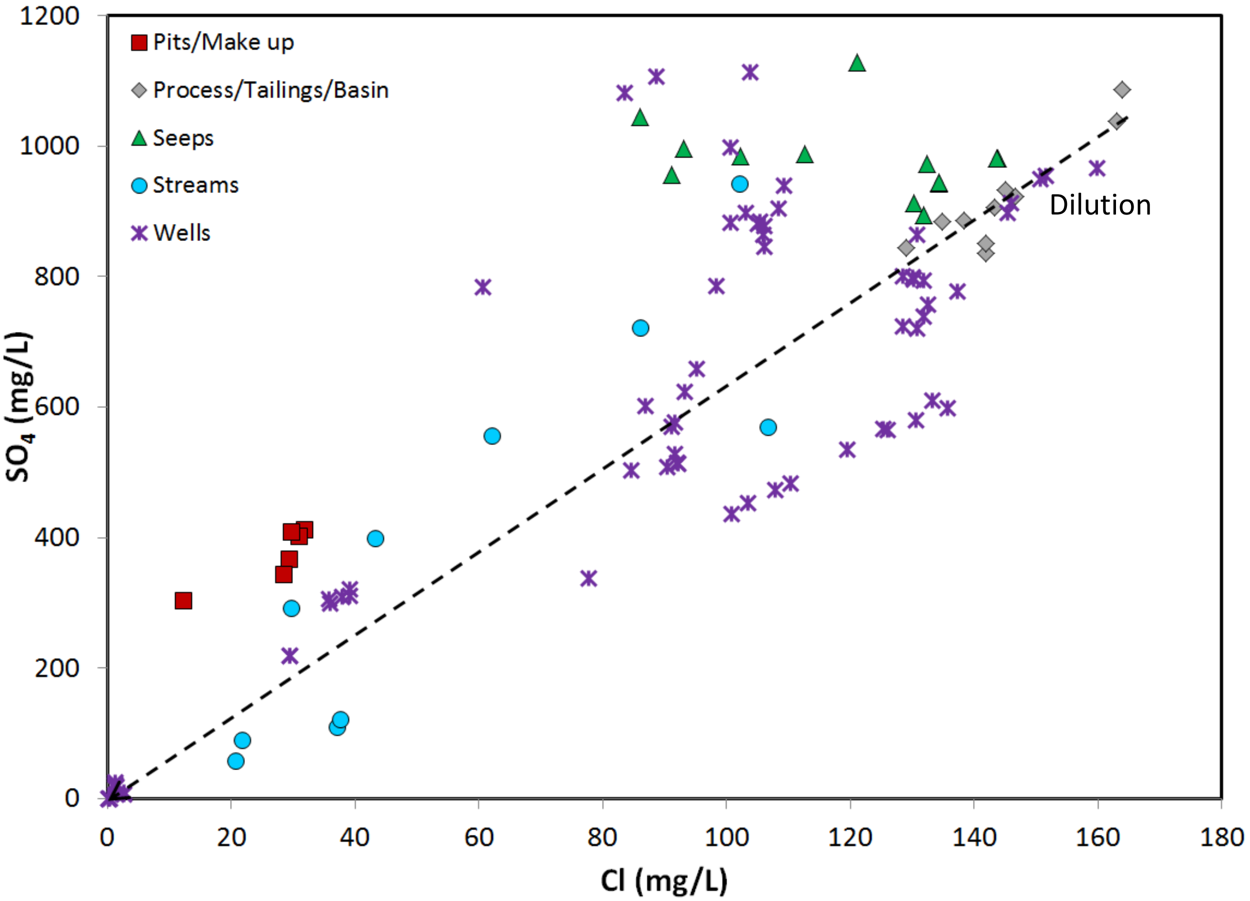

Figure 12. Chloride (Cl) concentration plotted relative to sulfate (SO_4) concentration for all Minntac basin area sampling locations. Downstream locations plot on either side of the process water dilution trend. This suggests that some combination of sulfide oxidation and sulfate reduction is likely contributing the measured sulfate concentrations downstream of the basin.

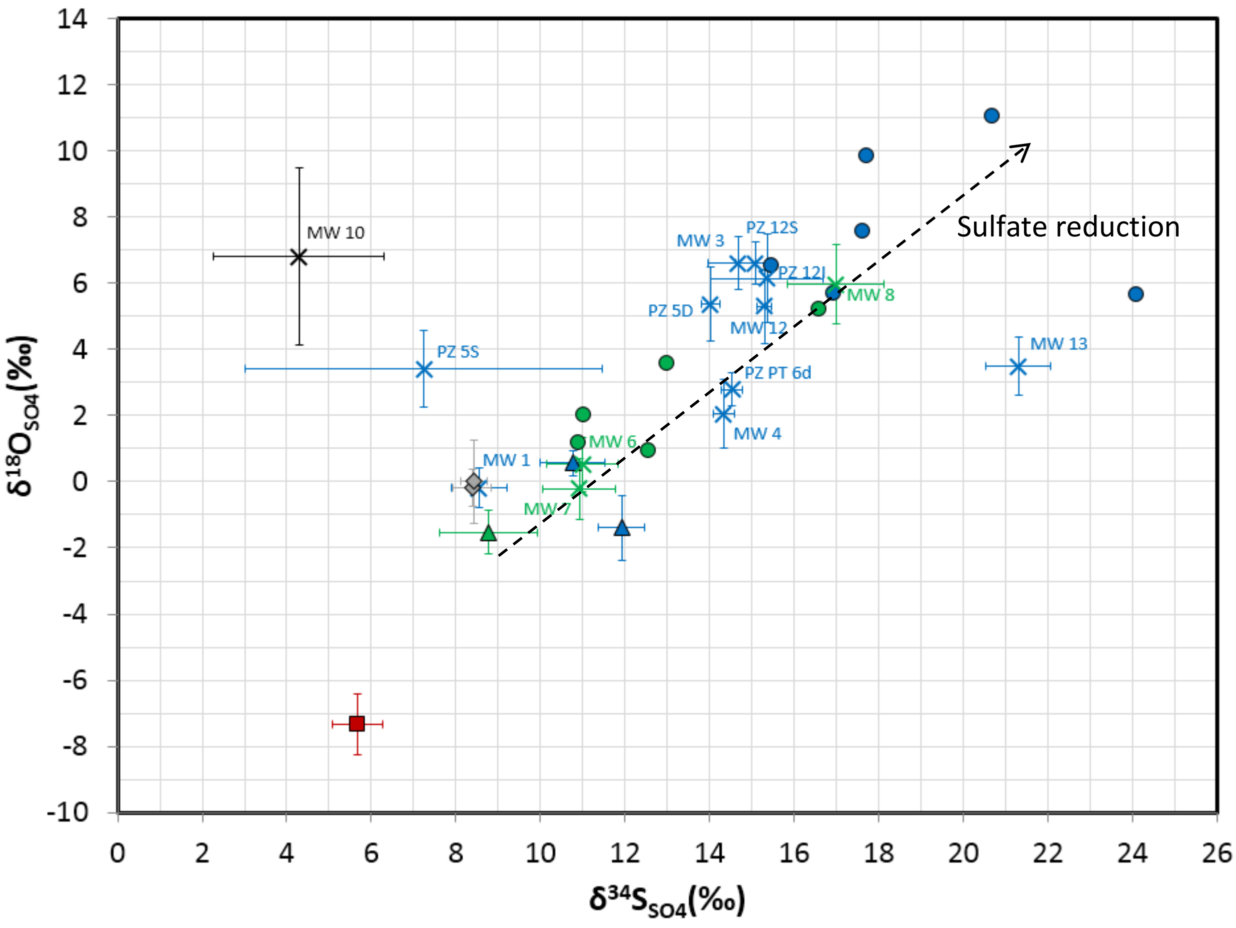

Figure 13. Plot of $\delta^{18}O_{SO4}$ versus $\delta^{34}S_{SO4}$ for the Minntac basin and surrounding waters, including Mountain Iron Pit (red square), basin pool waters (grey diamonds), seepage collection pumps (triangles), wells (Xs), and stream waters (circles). For all data except for the stream locations, mean values for the five sampling rounds are plotted with error bars representing the standard deviation. For the sites outside of the basin, symbols that are green represent the west, or Dark River, side of the basin, while blue symbols represent the east, or Sand River, side. All wells are labeled for clarity. The arrow depicts a general bacterial sulfate reduction trend associated with increasing isotopic values.

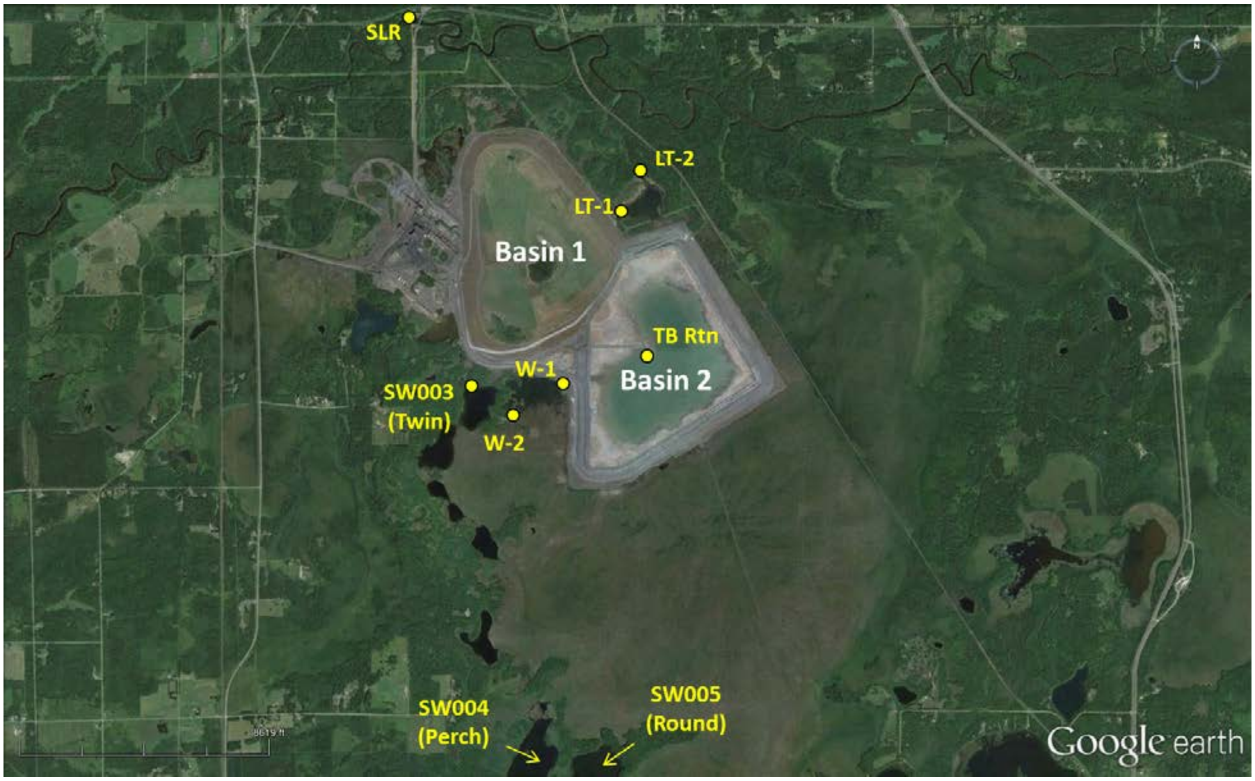

Figure 14. United Taconite (Utac) basin area map. Sampling locations are labeled accordingly.

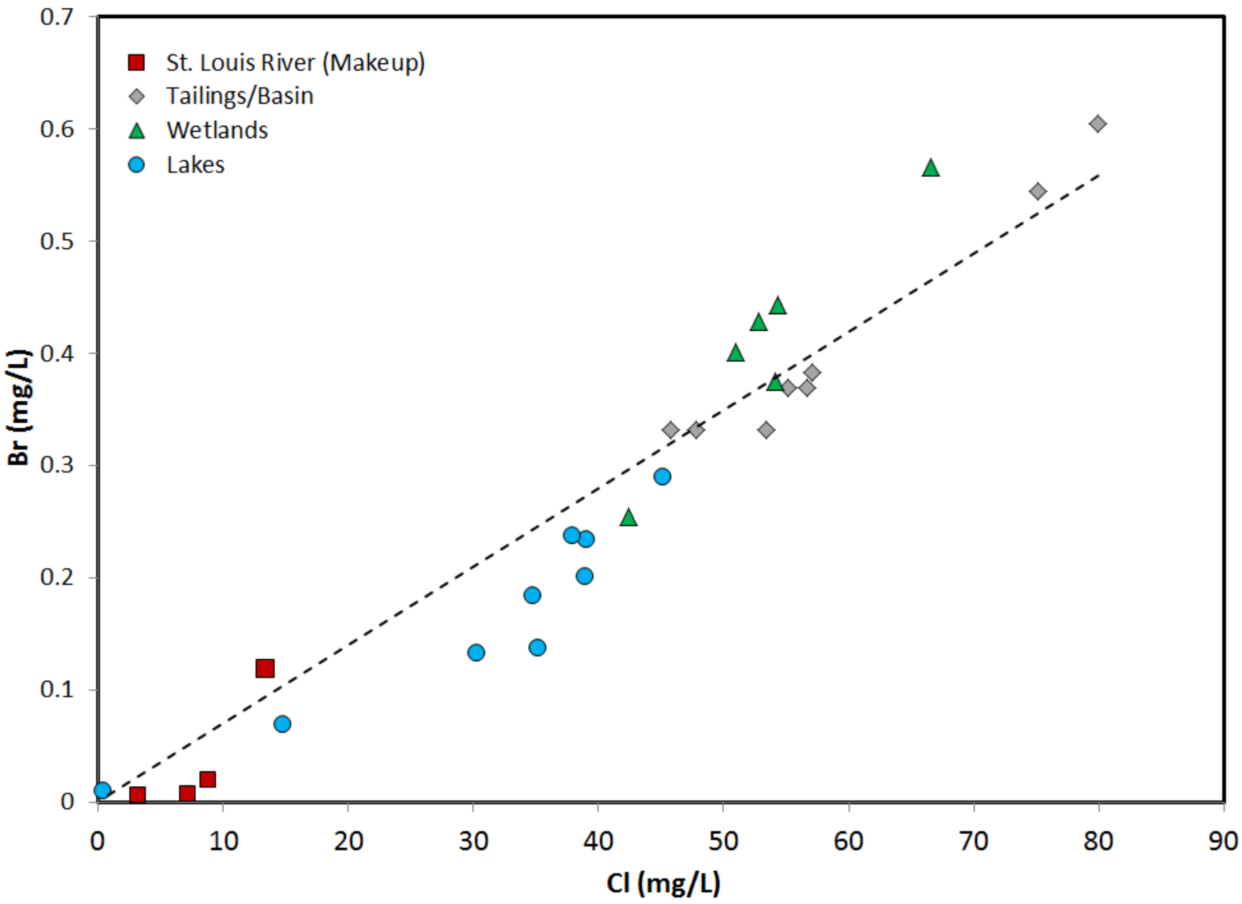

Figure 15. Chloride (Cl) versus bromide (Br) concentrations measured in Utac tailings and basin waters (grey diamonds) and all downstream wetland (green triangles) and lake (blue circles) sampling locations.

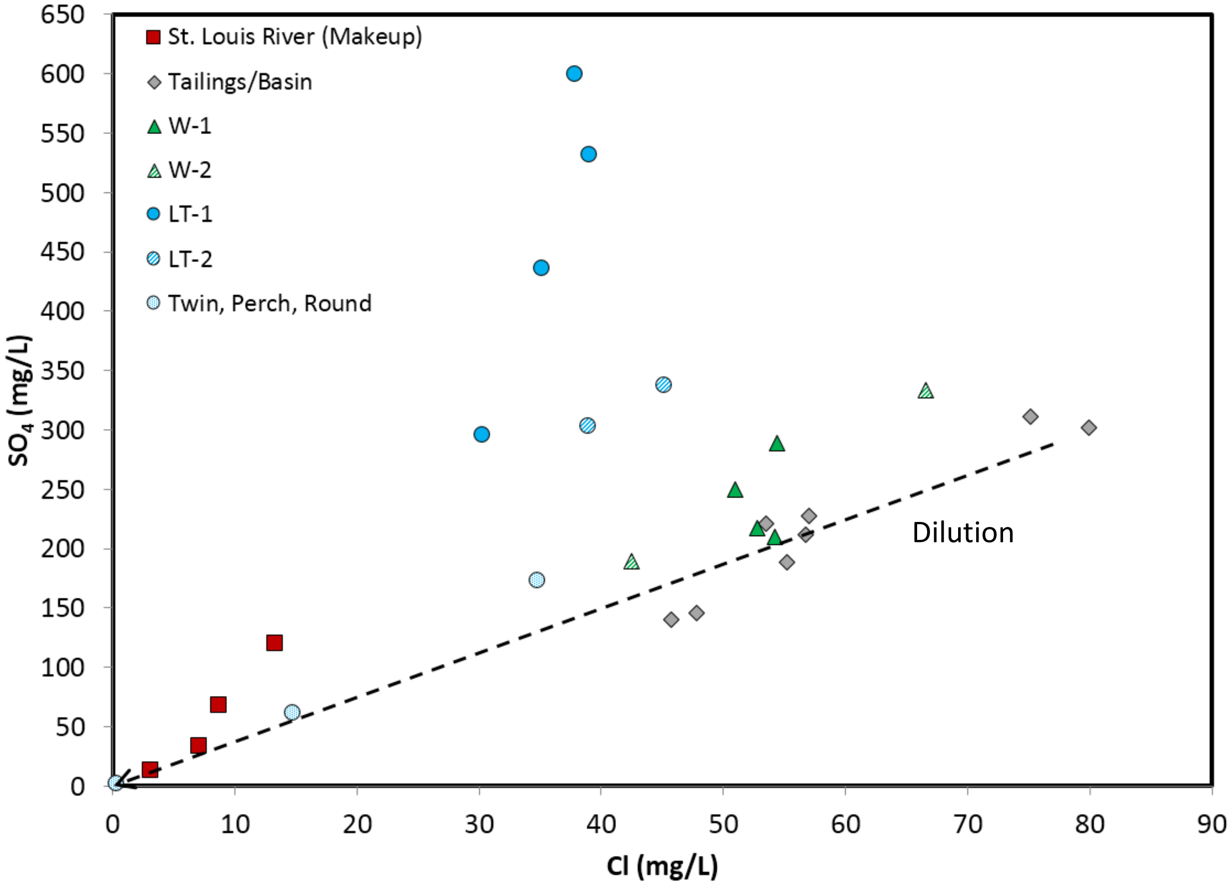

Figure 16. Chloride (Cl) concentration plotted relative to sulfate (SO_4) concentration for all Utac basin area sampling locations. Downstream locations (wetland and lake) mainly plot on or above the process water dilution trend, indicating a net gain in sulfate as water moves from the basin into the surrounding environment.

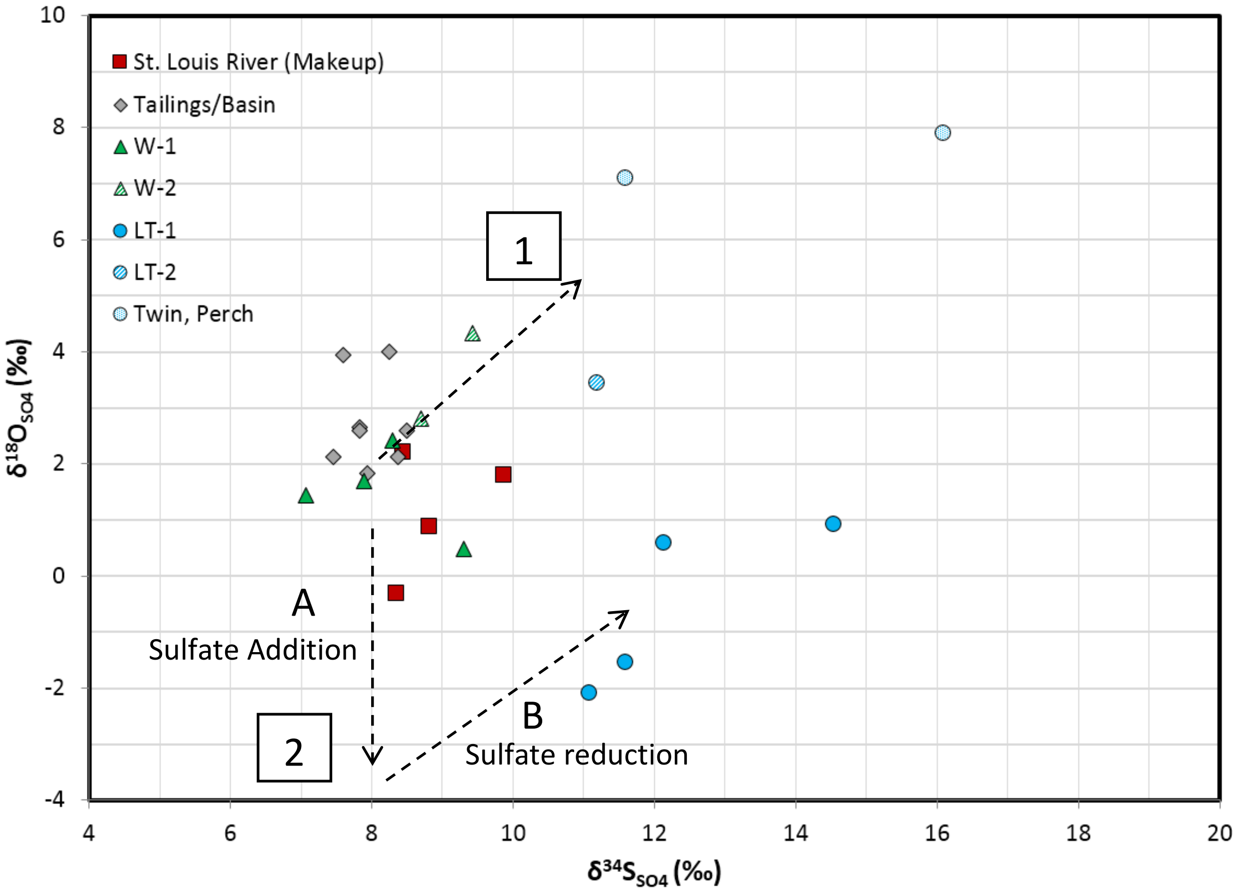

Figure 17. Plot of $\delta^{18}O_{SO4}$ versus $\delta^{34}S_{SO4}$ for the Utac source water (St. Louis River), tailings basin, and surrounding wetland and lake locations. Path 1 represents the bacterial sulfate reduction trend in the wetland area to the west of Basin 1 towards Twin and Perch Lakes. Path 2 depicts the potential two-part isotopic trend involving first (A) the addition of new sulfate with an oxygen isotope composition close to that of meteoric water, ~10‰, followed by (B) sulfate reduction and the associated increase in both $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$.

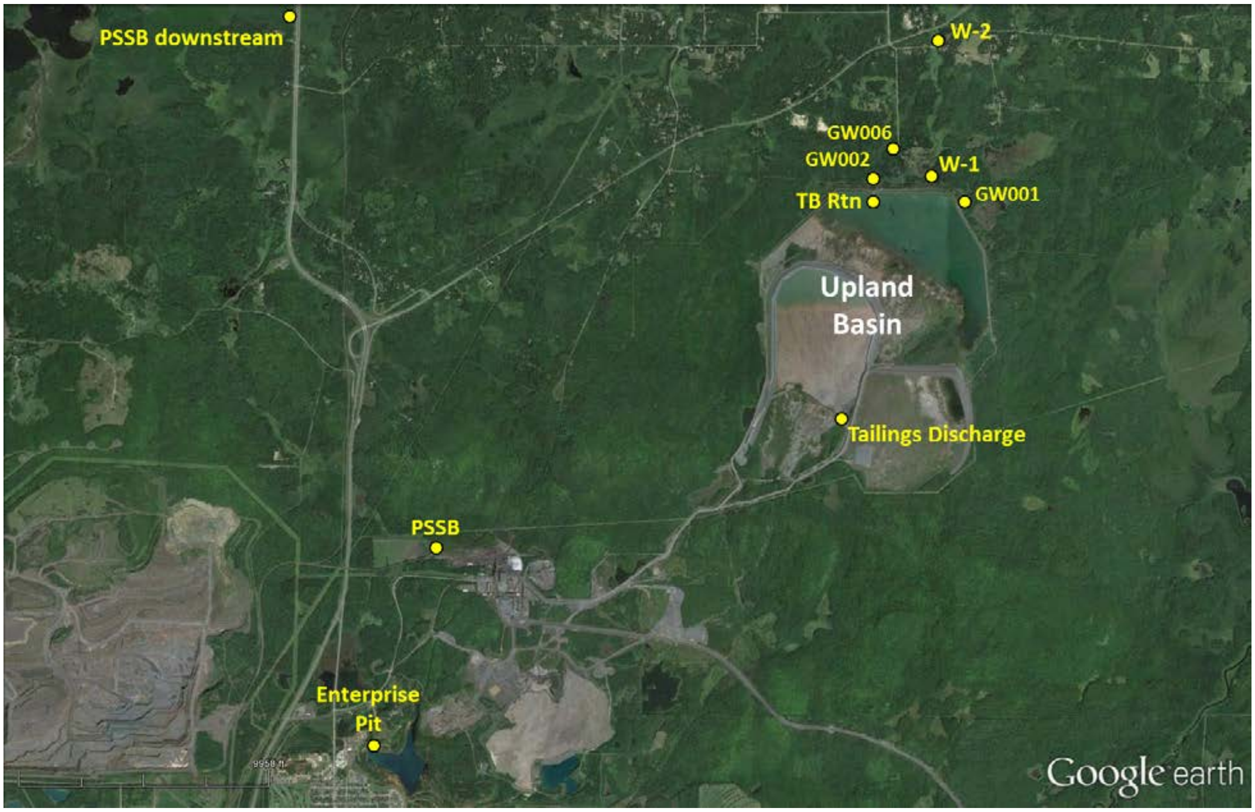

Figure 18. ArcelorMittal Minorca basin area map. Select sampling locations are labeled.

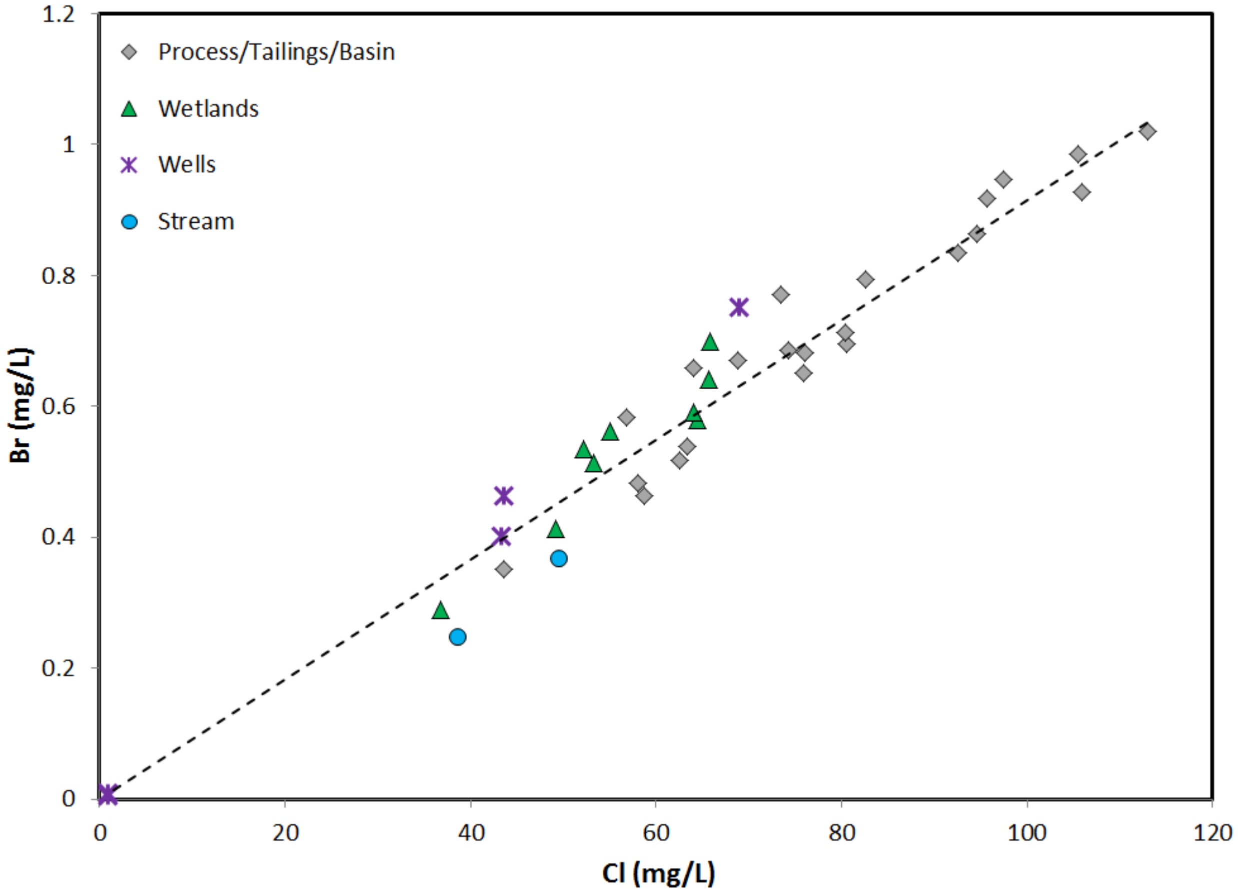

Figure 19. Chloride (Cl) versus bromide (Br) concentrations measured in ArcelorMittal tailings and basin waters (grey diamonds) and all surrounding locations, including wetland (green triangles), wells (purple Xs) and streams (blue circles). All data follows the process water dilution trend reasonably well, indicating that chloride and bromide are relatively conservative in water moving through the environment.

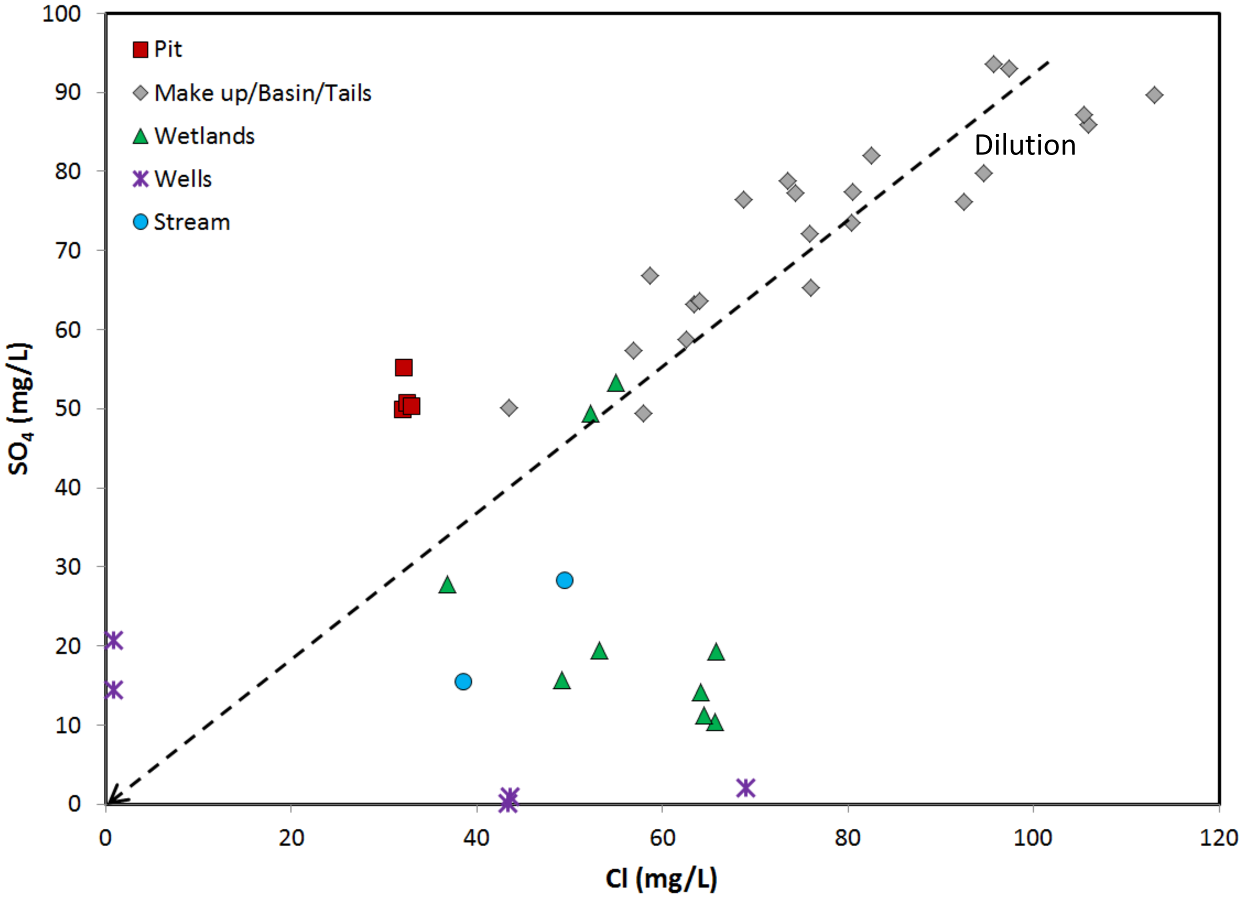

Figure 20. Chloride (Cl) concentration plotted relative to sulfate (SO_4) concentration for all ArcelorMittal basin area sampling locations. Downstream locations (wetland, wells, streams) mainly plot on or below the process water dilution trend, indicating a net loss in sulfate as water moves from the basin into the surrounding environment.

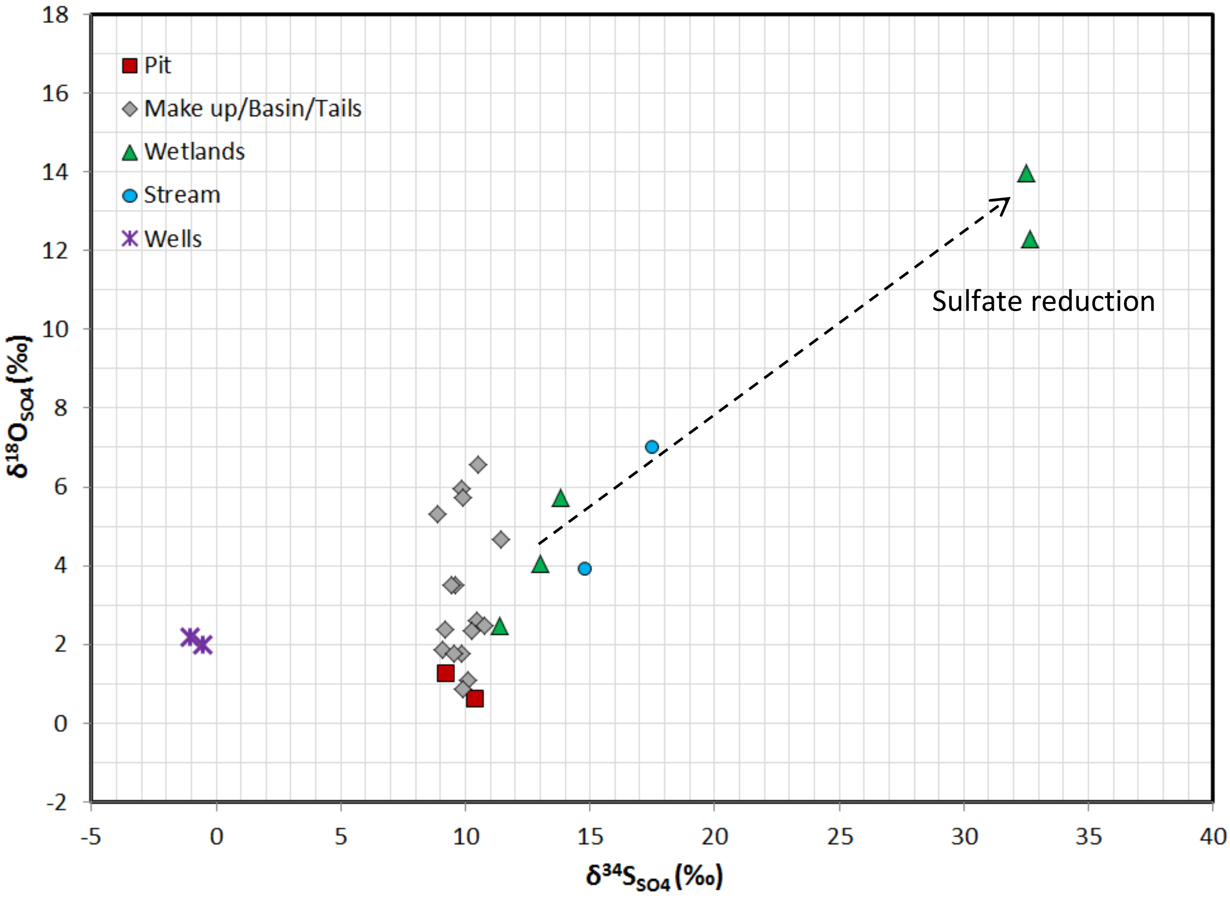

Figure 21. Plot of $\delta^{18}O_{SO4}$ versus $\delta^{34}S_{SO4}$ for the ArcelorMIttal sampling locations, including the Enterprise Pit source, plant makeup and tailings basin, and surrounding wetlands, wells, and streams. The arrow depicts an increasing isotopic trend associated with bacterial sulfate reduction.

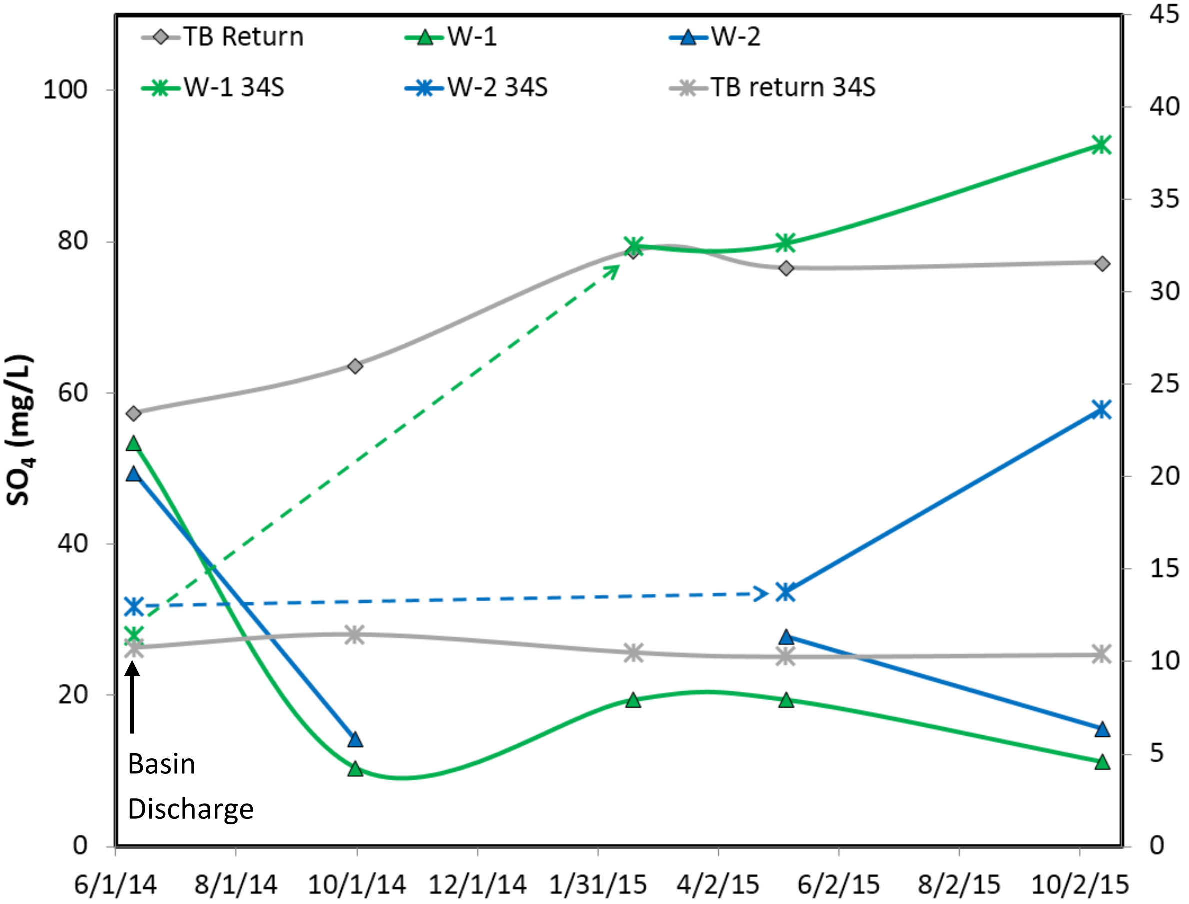

Figure 22. Plot of sulfate (SO_4) concentration and $\delta^{34}S_{SO4}$ values (34S) by sampling date for the ArcelorMIttal basin and wetland locations. Dashed line segments connect data points when isotopic values were unavailable due to low sulfate concentrations.

Appendix – Analytical Results

Data results for all physical and chemical parameters measured at each sampling location. All values are in mg/L unless otherwise noted. See individual basin maps for sampling locations.

Table A-1. U. S. Steel – Keetac. Analytical results for all Keetac sites.

Table A-2. Hibbing Taconite. Analytical results for all Hibtac sites.

Table A-3. U. S. Steel – Minntac.

A-3a. Analytical results for Minntac process and basin water sites.

A-3b. Analytical results for Minntac downstream surface water sites.

A-3c. Analytical results for Minntac monitoring wells and piezometers.

Table A-4. United Taconite.

A-4a. Analytical results for all DNR-sampled Utac sites.

A-4b. Analytical results for supplemental Utac lake sites.

Table A-5. ArcelorMittal Minorca. Analytical results for all ArcelorMittal sites.

Table A-1. **U. S. Steel – Keetac.** Analytical results for all Keetac sites.

Sample Location	**Scrubber water input**			**Scrubber output**			**Tailings slurry**		**48" line from plant to Carlz Pit**			**Inner tailings basin decant tower**		
Sample Date	**5/21/14**	**10/7/14**	**2/23/15**	**5/21/14**	**10/7/14**	**2/23/15**	**5/21/14**	**2/23/15**	**5/21/14**	**10/7/14**	**2/23/15**	**5/21/14**	**10/7/14**	**2/23/15**
Temp (^{o}C)	10.57		3.87	39.6		44.59		12.52	10.05	13.09	3.55	12.65	5.29	0.18
D.O. (mg/L)	17.88		13.8	4.42		5.03		11.96	99	10.34	14.79	16.75	10.34	15.27
pH	8.73		8	9.8		2.85	8.35	8.31	6.87	8.58	8.04	8.68	8.58	8.35
Sp. Cond (uS/cm)	756		878	2057		3579	700	914	770	689	900	630	689	1134
ORP			252			457.5		185.4		444.8	300.7			212.4
Alk (mg/L $CaCO_3$)	235		280	80				300	267.5	230	287.5	182.5	222.5	335
$\delta^{18}O_{H2O}$	-8.7		-7.8	-3.0		-1.2	-8.5	-7.7	-9.7	-7.3	-8.0	-8.1	-6.6	-8.1
$\delta^{2}H_{H2O}$	-69.5		-65.6	-52.2		-46.4	-68.0	-65.5	-74.8	-61.7	-65.4	-64.7	-59.1	-67.9
$\delta^{34}S_{SO4}$	5.3		4.3	8.4		9.8	5.9	5.2	3.9	6.4	5.5	5.5	5.3	5.0
$\delta^{18}O_{SO4}$	3.9		4.3	4.7		6.8	3.5	3.9	0.8	5.2	4.3	3.4	4.8	3.8
Al	<0.01		<0.01	<0.01		0.16	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	0.01
Ba	0.012		0.020	0.032		0.054	0.019	0.014	0.009	0.015	0.020	0.012	0.021	0.022
Ca	32.9		44.3	385.2		306.3	31.5	39.8	42.1	26.7	41.6	24.8	25.6	49.3
Fe	0.009		0.011	0.022		37.432	0.020	0.022	0.006	0.015	<0.005	0.007	0.007	0.013
K	7.6		8.8	12.1		18.1	7.5	11.1	5.3	6.8	9.5	7.6	9.1	14.4
Li	0.012		0.020	0.021		0.043	0.016	0.027	0.010	0.012	0.020	0.012	0.016	0.029
Mg	56.4		65.0	7.3		125.6	54.0	69.2	63.8	53.8	66.9	45.0	53.5	82.7
Mn	0.007		0.096	0.001		3.315	0.050	0.138	0.012	0.019	0.109	0.022	0.003	0.106
Na	35.3		41.6	64.3		89.2	59.9	50.2	29.4	33.5	46.6	40.8	43.3	66.7
P	<0.01		0.01	0.07		0.26	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01
Si	6.4		6.7	0.7		28.3	14.5	8.8	5.4	4.3	6.9	5.6	6.7	12.4
Sr	0.090		0.121	0.367		0.403	0.087	0.113	0.098	0.077	0.121	0.067	0.081	0.141
F	1.37		1.33	8.68		102.33	1.97	1.85	0.86	1.19	1.53	1.64	1.62	2.27
Acetate	<0.01		<0.03	0.62		<0.03	<0.01	<0.03	<0.01	<0.01	<0.03	<0.01	<0.01	<0.03
Formate	<0.01		<0.03	0.76		0.42	0.02	<0.03	0.02	<0.01	<0.03	0.01	0.02	<0.03
Cl	22.7		28.5	137.5		225.5	27.6	32.8	21.2	21.5	31.7	22.4	26.4	40.4
Nitrite-N	0.017		0.052	0.494		0.054	0.153	0.147	0.049	0.052	0.069	0.083	0.126	0.187
Br	0.13		0.14	0.80		1.34	0.17	0.17	0.11	0.12	0.15	0.14	0.14	0.22
Nitrate-N	1.306		2.717	3.399		7.838	5.538	4.905	2.622	0.679	2.681	1.606	3.151	7.132
Sulfate	113.4		127.1	817.1		1317.2	132.7	137.6	99.7	95.6	131.0	110.5	126.5	185.7
Thiosulfate	0.02		<0.03	<0.03		<0.03	0.03	<0.03	<0.01	0.01	<0.03	0.02	0.03	<0.03
Phosphate-P	<0.01		<0.03	<0.03		0.276	<0.01	<0.03	<0.01	<0.01	<0.03	<0.01	<0.01	<0.03

Table A-1, continued. U. S. Steel – Keetac. Analytical results for all Keetac sites.

Sample Location	**Outer basin/stage 2 basin weir**			**Reservoir 2**			**Reservoir 6 pump house**			**MW1**		**MW 12**	**MW 11**
Sample Date	**5/21/14**	**10/7/14**	**2/23/15**	**5/21/14**	**10/7/14**	**2/23/15**	**5/21/14**	**10/7/14**	**2/23/15**	**5/21/14**	**10/7/14**	**5/21/14**	**10/7/14**
Temp (^{0}C)	10.54	9.82				1.1	10.07	11.47	0.73	6.66	10.46	7.21	11.29
D.O. (mg/L)	13.77	11.27				8.93	13.92	9.09	13	0.21	1.14	7.69	1.25
pH	8.66	8.82				7.81	8.57	8.76	8.08	8.09	7.59	7.7	7.08
Sp. Cond (uS/cm)	666	706				800	704	676	892	680	754	594	833
ORP		313.4				188		306	179.1	-163.3	-176.6	-48.7	173.3
Alk (mg/L $CaCO_3$)	210	230				290	230	240	275	230	260	340	320
$\delta^{18}O_{H2O}$	-8.6	-6.5				-8.4	-8.6	-7.1	-7.9	-6.5	-6.1	-8.3	-6.8
$\delta^{2}H_{H2O}$	-68.3	-58.3				-68.1	-69.0	-61.0	-64.7	-53.7	-51.5	-63.6	-56.7
$\delta^{34}S_{SO4}$	5.9	6.2				7.0	6.0	6.6	5.8	35.7	28.7	14.6	15.3
$\delta^{18}O_{SO4}$	5.0	6.0				5.0	5.3	5.9	4.5	16.7	26.6	10.5	15.4
Al	<0.01	<0.01				<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01
Ba	0.010	0.013				0.028	0.010	0.016	0.022	0.046	0.065	0.077	0.089
Ca	25.8	21.0				48.0	28.5	25.7	39.0	49.7	62.7	85.6	87.8
Fe	0.006	0.005				0.025	0.006	<0.005	0.009	17.809	25.349	0.016	0.103
K	7.5	7.7				7.6	7.9	6.7	9.9	2.1	2.1	2.2	2.4
Li	0.011	0.013				0.018	0.012	0.012	0.020	0.001	0.001	0.007	0.010
Mg	52.5	56.2				56.1	56.3	53.9	67.2	22.6	23.1	34.1	35.6
Mn	<0.001	<0.001				0.267	0.001	<0.001	0.081	3.938	6.428	0.046	0.054
Na	37.3	38.6				35.0	37.7	32.5	47.6	46.2	46.3	40.4	36.1
P	<0.01	<0.01				0.04	<0.01	<0.01	0.01	<0.01	0.02	<0.01	<0.01
Si	5.9	3.9				4.8	6.2	4.0	6.8	2.3	3.4	10.0	10.3
Sr	0.072	0.060				0.137	0.079	0.070	0.118	0.411	0.465	0.161	0.151
F	1.46	1.42				1.04	1.48	1.15	1.63	0.09	0.08	0.93	0.87
Acetate	<0.01	<0.01				<0.03	<0.01	<0.01	<0.03	<0.01	<0.01	<0.01	<0.01
Formate	<0.01	0.01				<0.03	<0.01	<0.01	<0.03	<0.01	<0.01	<0.01	<0.01
Cl	21.1	23.1				27.6	22.1	21.2	30.1	23.3	23.8	17.2	23.3
Nitrite-N	0.038	0.036				0.060	0.039	0.012	0.059	0.004	<0.002	<0.004	<0.002
Br	0.13	0.13				0.11	0.14	0.12	0.16	0.11	0.12	0.08	0.14
Nitrate-N	1.346	1.075				2.716	1.291	0.169	4.193	0.026	<0.005	<0.002	<0.002
Sulfate	106.2	111.9				90.1	112.4	94.1	130.1	43.8	65.9	57.4	93.1
Thiosulfate	0.02	0.02				<0.03	0.02	0.01	<0.03	<0.01	<0.01	0.01	0.02
Phosphate-P	<0.01	<0.01				<0.03	<0.01	<0.01	<0.03	<0.01	<0.01	<0.01	<0.01

Table A-1, continued. U. S. Steel – Keetac. Analytical results for all Keetac sites.

Sample Location	**Carlz Pit**			**Russell Pit**			**Section 18 Pit**		
Sample Date	**5/21/14**	**10/7/14**	**2/23/15**	**5/21/14**	**10/7/14**	**2/23/15**	**5/21/14**	**10/7/14**	**2/23/15**
Temp (^{o}C)	10.32	12.63	3.59	9.73	11.55	1.87	8.31	14.93	1.97
D.O. (mg/L)	12.09	9.09	13.44	10.76	9.93	12.09	13.1	8.88	16.26
pH	8.5	8.35	7.92	6.44	8.1	7.91	6.05	8.15	7.89
Sp. Cond (uS/cm)	735	776	818	766	855	881	801	854	987
ORP		352.8	118.7		382	263.1		376.3	289.2
Alk (mg/L $CaCO_3$)	232.5	270	272.5	285	350	330	310	322.5	392.5
$\delta^{18}O_{H2O}$	-8.6	-8.8	-9.1	-10.2	-9.2	-9.3	-11.4	-9.8	-10.2
$\delta^{2}H_{H2O}$	-67.7	-69.3	-69.2	-77.2	-70.9	-73.3	-82.8	-74.4	-78.8
$\delta^{34}S_{SO4}$	-3.2	0.3	-1.0	3.9	3.4	2.1	3.8	4.8	2.4
$\delta^{18}O_{SO4}$	2.4	-0.4	1.5	-0.2	-2.4	-0.2	-4.8	-7.1	-4.6
Al	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	0.019	0.014	0.018	0.004	0.006	0.006	0.006	0.007	0.008
Ca	59.8	47.1	57.9	44.3	44.2	55.0	41.9	36.8	57.3
Fe	0.013	<0.005	<0.005	<0.005	<0.005	0.006	0.006	0.008	<0.005
K	3.9	4.8	5.4	4.7	5.4	5.6	3.4	4.6	4.0
Li	0.011	0.012	0.016	0.009	0.012	0.015	0.008	0.011	0.011
Mg	48.9	61.3	61.2	64.1	74.7	70.9	77.0	83.4	92.6
Mn	0.033	0.003	0.062	0.003	0.001	0.018	0.027	0.005	0.052
Na	23.2	22.2	24.9	28.4	24.4	27.3	15.7	16.6	18.1
P	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Si	6.3	4.8	5.8	4.6	4.7	5.6	3.9	3.6	4.3
Sr	0.152	0.118	0.146	0.097	0.103	0.119	0.082	0.080	0.115
F	0.41	0.40	0.46	0.72	0.47	0.60	0.18	0.14	0.17
Acetate	<0.01	<0.01	<0.03	<0.01	<0.01	<0.03	<0.01	<0.01	<0.03
Formate	<0.01	0.02	<0.03	0.02	0.02	<0.03	0.03	0.05	<0.03
Cl	26.4	20.5	24.7	17.4	15.9	20.8	13.5	11.1	11.4
Nitrite-N	0.006	0.023	0.032	0.009	0.005	<0.01	0.027	0.059	<0.010
Br	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.1
Nitrate-N	1.053	3.168	2.898	1.995	2.858	1.786	8.765	12.083	7.751
Sulfate	115.6	104.5	120.4	96.1	95.7	116.8	71.8	90.3	116.5
Thiosulfate	<0.01	<0.01	<0.03	<0.01	<0.01	<0.03	<0.01	<0.01	<0.03
Phosphate-P	<0.01	<0.01	<0.03	<0.01	<0.01	<0.03	<0.01	<0.01	<0.03

Table A-2. Hibbing Taconite. Analytical results for all Hibtac sites.

Sample Location	Plant Make-up from Morton Pit					Plant Make-up from Scranton Pit					Pipeline from Group 5 Pits to tailings basin				
Sample Date	**6/24/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**	**6/24/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**	**6/24/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**
Temp (°C)	23.01	14.94	1.16	12.47	16.86	15.11	12.9	0.62		13.48	19.81	11.52	1.15	13.31	13.54
D.O. (mg/L)	9.26	8.67	13.38	11.46	8.53	10.85	9.51	15.57		9.67	7.33	10.1	15.53	11.49	10.39
pH	8.26	8.07	7.48	8.05	8.12		8.01	7.77		7.84	7.57	8.1	7.52	8.21	8.18
Sp. Cond (uS/cm)	557	558	583	555	608	704	720	656		724	917	1069	825	706	1161
ORP		318.9	281	197.4	-5.7		363.7	288.5		43.5		242.2	0.1	124.6	10.9
Alk (mg/L CaCO3)	185	205	180	212.5	190	247.5	270	230		270	300	407.5	290		365
$\delta^{18}O_{H2O}$	-10.1	-9.7	-9.7	-10.1	-9.5	-10.7	-10.0	-9.7		-9.1	-9.9	-9.9	-9.5	-9.3	-10.1
$\delta^{2}H_{H2O}$	-75.6	-73.8	-74.1	-75.4	-71.2	-78.5	-75.0	-73.9		-69.2	-73.0	-74.4	-73.3	-71.3	-71.4
$\delta^{34}S_{SO4}$	2.2	4.9	3.4	2.2	2.0	4.6	4.6	4.3		4.4	7.4	5.2	6.6	7.0	1.5
$\delta^{18}O_{SO4}$	0.3	2.1	1.8	0.2	-0.4	-3.7	-2.2	0.2		-3.2	-4.2	-5.5	0.8	-0.4	-9.1
Al	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	0.016	0.017	0.019	0.019	0.017	0.007	0.008	0.005		0.009	0.024	0.023	0.031	0.012	0.022
Ca	45.3	49.3	52.8	51.8	48.8	46.0	43.2	51.7		40.6	45.0	41.9	58.4	50.1	35.3
Fe	0.005	0.011	<0.005	0.027		<0.005	<0.005	<0.005		<0.005	0.048	0.022	0.200	0.037	<0.005
K	3.0	3.3	3.5	3.3	3.7	3.7	4.3	3.7		4.6	5.6	7.5	5.2	4.8	7.9
Li	0.007	0.009	0.010	0.010	0.008	0.008	0.013	0.011		0.011	0.011	0.014	0.013	0.012	0.013
Mg	33.7	35.6	34.8	35.2	41.7	52.5	57.7	45.4		57.8	75.8	97.6	59.4	53.7	114.1
Mn	0.074	0.074	0.011	0.056	0.025	0.041	0.023	0.017		0.022	0.078	0.036	0.314	0.050	0.039
Na	13.0	11.3	13.1	14.5	14.9	20.2	19.3	14.3		22.6	35.2	41.5	22.8	20.9	41.2
P	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Si	6.6	7.1	7.6	7.3	7.0	5.1	5.1	5.2		5.1	3.1	4.6	6.6	3.1	5.3
Sr	0.132	0.133	0.139	0.102	0.139	0.104	0.094	0.117		0.112	0.173	0.138	0.158	0.112	0.113
F	0.12	0.14	0.15	0.12	0.15	0.20	0.23	0.21		0.21	1.43	1.51	1.04	0.82	0.17
Acetate	<0.01	<0.01	<0.03	<0.02	<0.02	<0.01	<0.01	<0.03		<0.02	<0.01	<0.02	<0.03	<0.02	<0.02
Formate	0.01	<0.01	<0.03	<0.02	<0.02	<0.01	<0.01	<0.03		<0.02	<0.01	<0.02	<0.03	<0.02	0.09
Cl	10.3	11.4	11.7	11.3	12.5	24.0	26.2	21.9		22.9	29.6	31.5	28.4	27.4	19.0
Nitrite-N	0.010	0.009	0.010	0.005	0.004	0.007	0.011	<0.010		0.004	0.022	0.013	<0.01	<0.003	<0.074
Br	0.03	0.05	0.05	0.04	0.05	0.06	0.08	0.05		0.06	0.12	0.16	0.12	0.06	0.11
Nitrate-N	3.072	1.223	4.001	1.043	1.448	3.236	4.009	2.106		3.271	4.970	9.459	4.163	0.322	19.699
Sulfate	59.8	71.4	72.7	67.9	66.7	68.8	79.0	70.4		65.4	89.7	136.2	86.7	72.3	167.9
Thiosulfate	<0.01	<0.01	<0.03	<0.02	<0.02	<0.01	<0.01	<0.03		<0.02	<0.01	<0.02	<0.03	<0.02	<0.02
Phosphate-P	<0.01	<0.01	<0.03	<0.01	<0.02	<0.01	<0.01	<0.03		<0.02	<0.01	<0.02	<0.03	<0.01	<0.02

Table A-2, continued. Hibbing Taconite. Analytical results for all Hibtac sites.

Sample Location	**Fine tailings**					**Agglomerator/floorwash discharge**					**Weir structure inside basin**				
Sample Date	**6/24/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**	**6/24/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**	**6/24/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**
Temp (^{o}C)			9.69	21.5	19.93	30	25.51	11.53	25.22	26.67	22.32	12.6	0.6	13.9	14.46
D.O. (mg/L)			13.88		6.29	6.15	6.66	9.8	7.58	6.65	9.66	10.51	17.8	11.1	10.76
pH	8.37		8.3	8.5	8.32	7.56	8	7.95	8.38	7.87	8.18	8.65	8.41	8.68	8.61
Sp. Cond (uS/cm)	875		1238	726	965	896	938	1207	983	976	844	905	1280	1009	943
ORP			94.7	194.8	-43		195.6	220	150.6	-31		205.2	208.4	130	-37.2
Alk (mg/L CaCO3)	187.5	210	290	255	205	165	187.5	240		157.5	180	220	282.5	262.5	200
$\delta^{18}O_{H2O}$	-7.6	-6.2	-7.2	-7.0	-5.3	-7.8	-6.4	-7.2	-7.1	-5.4	-7.5	-6.3	-6.9	-6.8	-5.2
$\delta^{2}H_{H2O}$	-63.1	-55.9	-61.7	-60.2	-48.9	-64.0	-56.8	-62.2	-60.9	-49.6	-60.7	-55.2	-61.2	-58.6	-47.1
$\delta^{34}S_{SO4}$	7.4	7.2	7.0			6.8	6.6	7.3			7.4	7.0	7.0		
$\delta^{18}O_{SO4}$	-0.1	2.4	2.4			0.6	3.4	2.4			0.7	3.5	2.8		
Al	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	0.003	0.012	0.012	0.019	0.012	0.006	0.009	0.010	0.011	0.011	0.002	0.014	0.011	0.014	0.013
Ca	31.1	31.4	45.4	36.4	33.5	34.0	33.1	47.0	39.6	36.0	29.5	30.5	45.3	36.0	35.0
Fe	<0.005	0.008	<0.005	0.032	<0.005	0.022	<0.005	<0.005	0.007	<0.005	<0.005	<0.005	0.011	0.007	<0.005
K	11.5	13.5	16.3	12.4	12.6	9.3	11.6	15.1	12.2	13.1	9.9	13.6	17.6	13.9	14.5
Li	0.013	0.019	0.027	0.024	0.016	0.013	0.017	0.024	0.022	0.015	0.013	0.018	0.030	0.023	0.015
Mg	59.8	67.2	97.4	76.8	68.0	62.6	67.4	92.2	75.2	67.9	58.6	66.0	98.3	79.8	65.8
Mn	0.033	0.027	0.096	0.031	0.045	0.035	0.025	0.094	0.031	0.047	0.002	0.014	0.070	0.021	0.017
Na	48.5	54.7	72.2	56.0	57.3	48.5	51.1	65.8	49.7	52.4	49.0	51.0	73.3	56.3	54.8
P	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Si	7.8	7.2	10.2	9.9	8.3	5.0	5.3	9.5	8.0	6.9	7.1	6.9	10.2	9.7	9.2
Sr	0.101	0.103	0.142	0.123	0.120	0.110	0.101	0.144	0.111	0.123	0.097	0.097	0.134	0.107	0.129
F	7.03	9.36	13.17	9.15	10.73	11.39	14.34	17.22	11.41	20.28	6.85	9.21	13.22	9.47	10.43
Acetate	<0.01	<0.02	<0.03	<0.02	<0.02	<0.01	<0.02	<0.03	<0.02	<0.02	<0.01	<0.02	<0.03	<0.02	<0.02
Formate	<0.01	<0.02	<0.03	<0.02	<0.02	<0.01	<0.02	<0.03	<0.02	<0.02	<0.01	0.07	<0.03	<0.02	<0.02
Cl	45.7	54.7	68.0	53.0	53.5	48.8	55.6	66.0	52.2	55.6	44.5	54.6	68.2	54.1	54.0
Nitrite-N	0.090	0.071	0.152	0.079	0.237	0.115	0.128	0.217	0.111	0.121	0.114	0.091	0.139	0.091	0.150
Br	0.28	0.33	0.43	0.30	0.30	0.27	0.31	0.39	0.26	0.29	0.27	0.33	0.43	0.30	0.30
Nitrate-N	2.673	1.665	5.965	2.998	2.326	2.252	1.702	3.948	2.587	1.446	3.511	1.503	6.474	3.159	1.591
Sulfate	143.3	172.8	224.0	173.6	178.7	157.9	190.2	232.8	168.6	205.2	139.4	171.0	225.5	178.9	177.1
Thiosulfate	<0.01	<0.02	<0.03	<0.02	<0.02	<0.01	<0.02	<0.03	<0.02	<0.02	<0.01	<0.02	<0.03	<0.02	<0.02
Phosphate-P	<0.01	<0.02	<0.03	<0.01	<0.02	<0.01	<0.02	<0.03	<0.01	<0.02	<0.01	<0.02	<0.03	<0.01	<0.02

Table A-2, continued. Hibbing Taconite. Analytical results for all Hibtac sites.

Sample Location	Tailings basin return					Culvert outfall 220; SD002					Culvert outfall 230; SD003				
Sample Date	**6/24/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**	**6/24/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**	**6/24/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**
Temp (^{o}C)	21.4	13.67		12.93	15.32	15.05	11.56		13.42	6.67	16.58	11.15		9.01	9.33
D.O. (mg/L)	8.93	9.75		11.24	9.41	8.94	8.07		9.96	10.91	7.12	8.94		9.21	9.76
pH	8.35	8.76		8.65	8.72	7.8	7.19		7.43	7.16	7.79	8		7.79	7.91
Sp. Cond (uS/cm)	850	900		987	935	902	953		863	960	643	787		644	793
ORP		190.9		118.2	-39		209.8		132.8	83.7		207.5		66.4	-2.6
Alk (mg/L CaCO3)	187.5	205.0		252.5	210.0	322.5	327.5		307.5	360	302.5	397.5		297.5	372.5
$\delta^{18}O_{H2O}$	-7.7	-6.4		-7.0	-5.4	-8.6	-6.8		-7.8	-7.1	-9.7	-8.2		-9.0	-8.2
$\delta^{2}H_{H2O}$	-62.5	-55.9		-60.2	-48.8	-65.8	-60.6		-61.6	-60.7	-71.8	-67.0		-69.6	-64.4
$\delta^{34}S_{SO4}$	7.4	7.3		7.5	6.9	12.3	12.0		12.0	13.7					
$\delta^{18}O_{SO4}$	0.5	2.7		0.8	1.3	4.8	7.5		5.9	6.5					
Al	<0.01	<0.01		<0.01	<0.01	<0.01	<0.01		<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Ba	0.005	0.010		0.014	0.011	0.086	0.083		0.077	0.072	0.024	0.024		0.037	0.024
Ca	30.8	29.6		36.7	32.5	88.5	91.3		81.4	93.6	71.8	88.4		69.7	88.9
Fe	<0.005	<0.005		0.026	<0.005	0.018	0.030		0.039	0.029	0.030	0.034		0.053	0.044
K	9.6	12.1		13.2	13.9	2.9	3.7		4.1	3.9	1.2	3.3		4.1	3.5
Li	0.013	0.017		0.021	0.015	0.014	0.019		0.020	0.016	0.006	0.011		0.012	0.008
Mg	61.8	66.9		79.0	68.5	48.7	51.8		47.9	53.4	34.2	44.5		35.2	44.1
Mn	0.002	0.003		0.008	<0.001	1.051	0.336		0.730	0.303	0.079	0.035		0.053	0.110
Na	48.9	53.4		54.3	53.4	30.4	31.5		32.2	34.2	13.1	15.4		15.8	17.3
P	<0.01	<0.01		<0.01	<0.01	<0.01	<0.01		<0.01	<0.01	0.03	0.04		0.02	0.04
Si	4.2	4.1		7.7	5.8	11.3	11.9		10.6	12.8	11.8	12.6		10.6	12.8
Sr	0.104	0.093		0.097	0.113	0.323	0.314		0.283	0.316	0.228	0.272		0.211	0.273
F	7.45	9.38		9.35	10.72	0.64	0.80		0.76	0.86	0.27	0.32		0.29	0.33
Acetate	<0.01	<0.02		<0.02	<0.02	<0.01	<0.02		<0.02	<0.02	<0.01	<0.01		<0.02	<0.02
Formate	<0.01	<0.02		<0.02	<0.02	<0.01	<0.02		<0.02	<0.02	<0.01	<0.01		<0.02	<0.02
Cl	45.6	53.9		52.5	52.8	38.8	49.7		45.3	45.6	15.7	37.0		30.9	31.4
Nitrite-N	0.096	0.055		0.074	0.082	<0.002	<0.006		<0.003	<0.004	<0.002	<0.004		<0.003	<0.004
Br	0.27	0.32		0.29	0.29	0.24	0.27		0.24	0.27	0.14	0.24		0.18	0.21
Nitrate-N	3.501	1.471		2.896	1.428	0.652	<0.003		0.022	0.044	2.167	<0.002		0.031	0.004
Sulfate	144.5	169.9		174.1	176.1	79.8	105.7		96.5	87.7	0.2	0.5		2.3	0.3
Thiosulfate	<0.01	<0.02		<0.02	<0.02	<0.01	<0.02		<0.02	<0.02	<0.01	<0.01		<0.02	<0.02
Phosphate-P	<0.01	<0.02		<0.01	<0.02	<0.01	<0.02		<0.01	<0.02	<0.01	<0.01		<0.01	<0.02

Table A-2, continued. Hibbing Taconite. Analytical results for all Hibtac sites.

Sample Location	Culvert outfall 240; SD004					Surface water sample at Day Lake Rd					Surface water sample at HW 5; Culvert outfall 100; SD001				
Sample Date	**6/24/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**	**6/25/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**	**6/25/14**	**10/2/14**	**2/19/15**	**5/7/15**	**9/29/15**
Temp (^{o}C)	16.08	10.35	0.1	7.34	8.51	18.56	12.02	0.09	16.15	16.37	16.66	11.98	0.18	12.06	13.17
D.O. (mg/L)	4.64	3.07	6.42	4.27	5.7	5.27	6.42	8.22	8.23	8.55	4.39	7.13	7.25	8.52	8.18
pH	7.81	7.48	7.03	7.41	7.33	9.75	7.56	7.21	7.68	7.44	9.64	7.61	7.13	7.58	7.45
Sp. Cond (uS/cm)	1012	997	1069	816	1121	241	474	774	346	321	581	728	1142	671	739
ORP		95.3	-24.9	102.9	63.4		201.9	34.8	112.6	7.3		102.5	48	70.4	5.7
Alk (mg/L CaCO3)	435	455	480	375	480	97.5	190	245		130	162.5	270	385	220	267.5
$\delta^{18}O_{H2O}$	-9.2	-8.1	-8.3	-8.3	-8.2	-10.1	-8.7	-10.4	-10.1	-7.8	-9.5	-7.9	-8.1	-8.7	-7.3
$\delta^{2}H_{H2O}$	-68.8	-66.5	-67.1	-65.0	-65.1	-71.4	-67.4	-79.3	-76.5	-57.3	-71.8	-64.3	-68.0	-68.7	-57.4
$\delta^{34}S_{SO4}$		22.9	27.0	28.3	22.9			22.4	19.2		28.9	34.7	20.0	21.2	27.4
$\delta^{18}O_{SO4}$		9.6	8.0	8.0	4.6			7.9	5.0		7.6	14.0	10.0	10.6	9.7
Al	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01
Ba	0.086	0.101	0.106	0.082	0.097	0.031	0.038	0.067	0.037	0.030	0.045	0.054	0.112	0.058	0.058
Ca	102.0	109.8	131.9	92.2	117.4	24.5	44.0	68.3	31.9	32.2	40.7	48.2	79.6	46.3	48.1
Fe	0.025	0.013	1.266	<0.005	<0.005	1.964	0.319	0.337	0.326	0.501	0.235	0.155	0.445	0.062	0.153
K	3.3	5.4	4.8	5.6	4.9	0.9	2.1	4.4	3.2	2.0	3.4	5.3	8.2	5.8	5.2
Li	0.009	0.014	0.017	0.013	0.012	0.003	0.007	0.012	0.006	0.003	0.007	0.009	0.014	0.010	0.009
Mg	64.4	55.7	52.8	45.6	63.6	12.3	23.8	40.2	17.2	16.3	33.8	45.0	73.3	41.2	46.2
Mn	0.132	0.061	0.829	0.471	0.680	0.195	0.062	1.258	0.114	0.075	0.177	0.231	2.332	0.078	0.197
Na	23.3	15.9	16.9	15.4	21.2	7.5	13.2	25.2	12.4	9.4	26.0	31.7	46.5	29.1	34.7
P	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.01	<0.01	<0.01	0.02	0.01	0.01	<0.01	0.01	0.01
Si	9.1	10.0	12.9	9.8	12.9	4.5	6.2	9.4	1.5	6.6	5.5	7.6	10.2	3.5	7.4
Sr	0.314	0.294	0.313	0.246	0.322	0.092	0.150	0.208	0.085	0.110	0.150	0.169	0.256	0.148	0.170
F	0.27	0.41	0.32	0.28	0.40	0.15	0.17	0.22	0.12	0.17	1.94	2.64	3.39	2.57	2.69
Acetate	<0.01	<0.02	<0.03	<0.02	<0.02	<0.01	<0.01	<0.03	<0.02	<0.02	<0.01	<0.01	<0.03	<0.02	<0.02
Formate	<0.01	<0.02	<0.03	<0.02	<0.02	<0.01	<0.01	<0.03	<0.02	<0.02	<0.01	<0.01	<0.03	<0.02	<0.02
Cl	15.7	39.0	38.2	32.4	33.0	9.8	38.7	52.3	22.8	14.6	37.2	52.3	63.0	42.1	50.2
Nitrite-N	<0.002	<0.006	<0.010	0.007	0.004	<0.002	<0.004	<0.010	<0.003	<0.004	<0.002	<0.004	<0.010	<0.003	<0.004
Br	0.14	0.26	0.30	0.21	0.23	0.04	0.10	0.19	0.05	0.04	0.13	0.21	0.32	0.14	0.20
Nitrate-N	2.163	0.107	1.443	0.068	0.088	0.008	<0.002	0.962	0.014	0.005	<0.001	0.013	3.252	0.045	0.013
Sulfate	0.2	26.5	25.0	21.5	50.3	1.3	3.1	32.3	12.2	2.3	14.0	37.3	103.5	64.8	33.1
Thiosulfate	<0.01	<0.02	<0.03	<0.02	<0.02	<0.01	<0.01	<0.03	<0.02	<0.02	<0.01	<0.01	<0.03	<0.02	<0.02
Phosphate-P	<0.01	<0.02	<0.03	<0.01	<0.02	<0.01	<0.01	<0.03	<0.01	<0.02	<0.01	<0.01	<0.03	<0.01	<0.02

Table A-3a. U. S. Steel – Minntac. Analytical results for Minntac process and basin water sites.

Sample Location	Plant make-up water; Mt. Iron Pit at 23 MG Reservoir					Plant Makeup Transfer Sump			WS002; Line 3 scrubber input; raw water					WS003; Line 3 scrubber
Sample Date	**5/28/2014**	**10/8/2014**	**2/24/2015**	**5/13/2015**	**10/8/2015**	**2/24/2015**	**5/13/2015**	**10/8/2015**	**5/28/2014**	**10/8/2014**	**2/24/2015**	**5/13/2015**	**10/8/2015**	**5/28/2014**
Temp (°C)	5.8	5.7	3.44	4.69	5.05	0.82	9.66	11.81	23.6		8.74	9.28	14.4	39.5
D.O. (mg/L)	13.2	10.28	12.45	12.08	10.58	12.35	11.28	9	6.1		11.05	11.81	9.83	4.44
pH	6.38	8.12	8.31	8.29	8.27	7.83	7.73	8.21	6.85		8.27	8.49	8.33	10.08
Sp. Cond (uS/cm)	1386	1311	1445	1453	1422	1097	1312	1393	1833		2398	2325	2060	4239
ORP	-6	209.9	161.2	97	-101.3	156.2	82.6	-101.7	-80		-33.3	87.9	-109.7	
Alk (mg/L CaCO3)	307	302.5	327.5	300	310	320	290	407.5	227.5		325	275	267.5	
$\delta^{18}O_{H2O}$	-10.2	-10.7	-10.5	-10.8	-10.6	-10.9	-10.2	-10.4	-8.5		-7.9	-7.6	-7.2	-2.4
$\delta^{2}H_{H2O}$	-76.6	-79.1	-79.6	-79.9	-78.9	-80.5	-77.5	-74.8	-69.9		-68.7	-66.2	-62.4	-60.6
$\delta^{34}S_{SO4}$	4.9	5.6	6.7	5.6	5.1	7.5	8.8	5.3	7.5		8.7			6.1
$\delta^{18}O_{SO4}$	-6.9	-6.8	-7.3	-8.7	-8.3	-4.4	-1.4	-8.9	-1.6		0.1			2.6
Al	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		0.02	<0.01	<0.01	<0.01
Ba	0.025	<0.001	0.020	0.019	0.018	0.087	0.071	0.056	0.029		0.030	0.021	0.026	0.089
Ca	67.8	67.4	65.3	64.9	65.1	71.1	82.5	53.0	111.2		129.7	118.2	87.7	903.7
Fe	<0.005	0.023	<0.005	0.055	<0.005	<0.005	0.051	<0.005	0.013		0.026	0.071	<0.005	<0.005
K	12.4	11.9	16.0	16.4	15.2	14.0	15.1	17.3	20.4		26.0	24.9	23.1	34.9
Li	0.012	0.000	0.018	0.019	0.013	0.016	0.020	0.013	0.022		0.035	0.035	0.022	0.031
Mg	116.2	112.5	131.9	132.0	128.6	84.2	108.1	130.1	177.0		226.6	221.5	200.0	5.2
Mn	0.012	<0.001	0.005	0.001	<0.001	1.264	0.612	0.369	0.067		0.406	0.036	0.017	<0.001
Na	52.6	48.0	54.6	52.7	53.9	34.6	43.0	57.0	83.5		91.2	84.7	82.7	114.2
P	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01		<0.01	0.02	<0.01	0.02
Si	4.6	4.5	4.9	5.0	5.0	6.5	5.2	5.5	4.5		6.3	1.5	5.3	0.51
Sr	0.225	0.200	0.210	0.187	0.211	0.275	0.273	0.216	0.343		0.364	0.301	0.236	0.856
F	0.37	0.25	0.31	0.25	0.29	0.46	0.83	0.25	2.60		2.44	2.02	1.81	9.35
Acetate	<0.03	<0.01	<0.03	<0.03	<0.04	<0.03	<0.02	<0.04	<0.03		<0.03	<0.03	<0.04	<0.05
Formate	0.09	0.20	0.07	<0.03	<0.04	0.03	<0.02	<0.04	0.09		0.04	<0.03	<0.04	0.93
Cl	29.5	28.6	32.0	31.1	29.9	22.4	48.4	12.4	119.2		137.0	139.1	110.796	519.0
Nitrite-N	<0.010	<0.004	0.051	0.013	0.021	0.045	0.036	0.095	0.029		0.051	0.058	0.031	0.137
Br	0.11	0.11	0.14	0.10	0.11	0.17	0.37	0.06	0.90		1.22	1.07	0.87	2.96
Nitrate-N	10.377	9.603	12.053	10.984	10.438	5.376	2.513	17.169	7.374		5.839	3.107	5.252	11.487
Sulfate	365.4	343.1	410.7	400.6	407.7	238.0	350.3	302.0	740.4		904.2	862.1	763.6	1648.6
Thiosulfate	<0.03	<0.01	<0.03	<0.03	<0.04	<0.03	<0.02	<0.04	<0.03		<0.03	<0.03	<0.04	<0.05
Phosphate-P	<0.03	<0.01	<0.03	<0.02	<0.04	<0.03	<0.01	<0.04	<0.03		<0.03	<0.02	<0.04	<0.05

Table A-3a, continued. U. S. Steel – Minntac. Analytical results for Minntac process and basin water sites.

Sample Location	**Composite tailings sample from steps 1, 2, and 3**					**Composite agglomerator sample from steps 1/2 and 3**					**Tailings basin Cell 2**				
Sample Date	**5/28/2014**	**10/8/2014**	**2/24/2015**	**5/13/2015**	**10/8/2015**	**5/28/2014**	**10/8/2014**	**2/24/2015**	**5/13/2015**	**10/8/2015**	**5/28/2014**	**10/8/2014**	**2/24/2015**	**5/13/2015**	**10/8/2015**
Temp (°C)			17.97	11.88	8.9	28.56	19.92	12.49	18.64	22.21	17.89	9.27	0.75	10.06	13.11
D.O. (mg/L)			8.99	9.63		7.89	7.24	9.83	8.92	6.69	14.1	11.18	10.13	11.57	9.29
pH	8.03	8.15	8.4	8.31	8.46	8.45	9.03	8.88	8.93	9.08	8.09	8.51	7.82	8.76	8.51
Sp. Cond (uS/cm)	2100	2150	2486	2290	2080	2091	2169	2449	2349	2068	2259	2356	2850	2386	2353
ORP			64.6	54.4	281.8	-17.1	162.9	44.6	56.2	-155.5	-3.9	157	175.4	25.2	-139.6
Alk (mg/L CaCO3)	148.5	172.5	222.5	215	180	112	135	135	167.5	110	307.5	305	370	292.5	282.5
$\delta^{18}O_{H2O}$	-8.2	-7.6	-7.6	-7.4	-6.8	-8.1	-7.1	-7.4	-6.8	-6.7	-8.2	-6.8	-7.3	-7.4	-6.0
$\delta^{2}H_{H2O}$	-69.0	-66.3	-67.9	-65.4	-61.4	-68.9	-65.2	-66.9	-64.2	-60.8	-68.7	-62.4	-65.2	-64.7	-56.2
$\delta^{34}S_{SO4}$	7.3	8.5	8.7			7.1	9.2	8.8			8.4	8.3	8.9	8.5	8.5
$\delta^{18}O_{SO4}$	-1.4	-1.0	0.1			-0.4	-0.4	0.4			-1.2	0.0	2.1	-1.4	0.1
Al	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01
Ba	0.062	0.000	0.041	0.049	0.045	0.035	0.025	0.025	0.026	0.021	0.015	0.022	0.025	0.016	0.022
Ca	106.3	99.0	113.0	103.4	87.6	116.8	116.0	125.7	107.3	89.4	131.4	120.9	158.2	122.9	104.6
Fe	<0.005	0.015	<0.005	0.049	<0.005	<0.005	0.020	<0.005	0.052	<0.005	<0.005	0.021	0.012	0.049	<0.005
K	26.7	20.8	26.0	26.5	25.1	21.4	22.6	26.3	24.9	24.0	21.8	24.9	30.1	25.0	24.5
Li	0.039	0.000	0.052	0.045	0.032	0.024	0.031	0.038	0.038	0.024	0.022	0.031	0.042	0.037	0.029
Mg	171.9	183.3	226.7	214.5	184.1	177.7	180.5	230.4	222.1	190.7	208.8	217.9	270.4	228.7	232.5
Mn	0.29	0.10	0.18	0.23	0.20	0.07	0.08	0.07	0.03	0.01	0.10	0.00	0.41	0.15	0.00
Na	101.2	108.9	118.0	97.3	99.9	84.9	88.1	97.1	96.2	86.5	82.2	88.2	109.3	94.4	94.5
P	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.02	<0.01	0.01	<0.001	<0.01	<0.01	<0.01	0.08	<0.01
Si	10.0	9.7	8.2	5.9	7.8	6.3	6.9	7.6	4.4	7.1	<0.1	4.57	6.34	0.54	5.83
Sr	0.477	0.400	0.410	0.332	0.406	0.374	0.332	0.360	0.304	0.233	0.320	0.318	0.401	0.307	0.271
F	3.16	2.74	2.59	1.94	2.87	4.81	4.57	3.74	2.95	4.21	1.91	1.80	2.44	1.77	1.97
Acetate	<0.03	<0.02	<0.03	<0.03	<0.04	<0.03	<0.02	<0.03	<0.03	<0.04	<0.03	<0.03	<0.03	<0.03	<0.04
Formate	0.13	0.11	0.06	<0.03	<0.04	0.08	0.07	0.05	<0.03	<0.04	0.06	0.05	0.05	<0.03	<0.04
Cl	152.0	153.7	169.9	143.0	137.1	148.9	154.1	165.1	160.2	137.5	129.0	134.8	164.0	138.4	145.2
Nitrite-N	0.848	0.833	0.641	0.345	0.685	0.252	0.290	0.229	0.191	0.250	0.056	0.081	0.080	0.078	0.055
Br	1.17	1.21	1.58	1.10	1.12	1.16	1.19	1.51	1.26	1.13	1.00	1.05	1.50	1.07	1.14
Nitrate-N	11.517	7.348	8.750	4.158	7.921	7.518	5.251	5.835	3.348	5.310	3.121	1.933	5.270	3.306	0.904
Sulfate	786.2	798.6	949.2	863.2	796.8	838.8	849.0	990.0	924.8	847.5	844.5	885.2	1087.0	886.0	933.4
Thiosulfate	0.05	0.05	<0.03	<0.03	<0.04	0.06	0.04	<0.03	<0.03	<0.04	<0.03	<0.03	<0.03	<0.03	<0.04
Phosphate-P	<0.03	<0.02	<0.03	<0.02	<0.04	<0.03	<0.02	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04

Table A-3a, continued. U. S. Steel – Minntac. Analytical results for Minntac process and basin water sites.

Sample Location	**Basin return water (Cell 1) at 23 MG Reservoir**					**Pump 2; Catch basin 10**					**Pump 1; Catch basin 5**				
Sample Date	**5/28/2014**	**10/8/2014**	**2/24/2015**	**5/13/2015**	**10/8/2015**	**6/2/2014**	**10/8/2014**	**2/24/2015**	**5/13/2015**	**10/8/2015**	**5/28/2014**	**10/8/2014**	**2/24/2015**	**5/13/2015**	**10/8/2015**
Temp (^{o}C)	17.3	8.49	3.91	9.92	13.59		8.33	4.33	9.18	10.91	12.45	8.46	4.26	9.43	10.39
D.O. (mg/L)	10.9	10.89	13.3	11.68	9.42		9.65	11.36	10.89	8.49	10.9	11.55	11.07	10.22	9.07
pH	7.64	8.35	8.05	8.53	8.39		7.42	7.65	7.38	7.44	7.65	7.52	7.76	7.46	7.71
Sp. Cond (uS/cm)	2206	2237	2670	2407	2281		2820	2665	2712	2679	2478	2589	2455	2482	2466
ORP		219.2	145.5	82.7	-121.8		88.7	23.7	51.8	-83.2	-55.3	20.9	-6.1	-14.4	-107.7
Alk (mg/L CaCO3)	207.5	227.5	295	272.5	235		652.5	555	577.5	625	350	397.5	367.5	360	385
$\delta^{18}O_{H2O}$	-8.1	-6.9	-7.3	-7.3	-6.2		-8.5	-8.2	-8.8	-8.5	-7.4	-7.5	-7.5	-7.8	-7.2
$\delta^{2}H_{H2O}$	-68.1	-62.9	-65.8	-64.4	-57.4		-69.7	-67.7	-69.8	-70.2	-63.2	-64.9	-65.1	-65.9	-64.8
$\delta^{34}S_{SO4}$	7.7	8.5	8.7	8.5	9.2	11.6	12.3	11.9	12.6	11.9	10.3	12.4	10.8	10.7	9.9
$\delta^{18}O_{SO4}$	-0.5	-0.8	0.5	-0.9	0.4	-1.1	-2.7	-0.1	-1.2	-1.1	0.7	0.1	1.2	0.2	0.4
Al	<0.01	<0.01	<0.01	0.01	<0.01		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	<0.01
Ba	0.025	0.026	0.026	0.018	0.022		0.040	0.040	0.035	0.033	0.065	0.062	0.059	0.065	0.058
Ca	122.0	115.5	143.2	121.9	99.8		184.6	172.9	177.3	180.1	151.3	155.5	141.9	146.4	146.1
Fe	<0.005	0.020	0.015	0.050	<0.005		0.313	0.029	0.196	0.208	0.014	0.813	0.094	1.001	0.883
K	22.3	25.3	27.7	25.2	23.1		15.4	18.4	17.3	16.2	22.3	23.1	23.3	24.6	23.8
Li	0.02	0.03	0.04	0.04	0.03		0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01
Mg	191.3	198.6	250.1	233.4	223.7		307.6	280.1	299.0	292.7	234.6	250.3	233.2	236.7	239.9
Mn	0.14	0.01	0.35	0.02	0.00		1.32	1.49	1.14	1.07	1.6	1.6	1.6	1.5	1.3
Na	90.9	89.0	102.5	92.4	91.7		58.5	67.6	62.6	60.1	81.6	81.4	82.1	83.9	80.1
P	<0.01	0.01	<0.01	0.02	<0.01		<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01
Si	4.6	4.8	6.6	1.2	5.4		7.8	7.0	7.5	7.9	6.6	7.0	6.4	6.6	6.9
Sr	0.373	0.348	0.393	0.309	0.248		0.387	0.385	0.376	0.384	0.403	0.388	0.352	0.365	0.373
F	3.02	2.60	2.94	2.11	2.41		1.20	1.58	1.18	1.27	2.67	2.35	2.67	2.43	2.58
Acetate	<0.03	<0.03	<0.03	<0.03	<0.04		<0.03	<0.03	<0.03	<0.04	<0.03	<0.03	<0.03	<0.03	<0.04
Formate	0.09	0.07	0.04	<0.03	<0.04		<0.03	<0.03	<0.03	<0.04	<0.03	<0.03	<0.03	<0.03	<0.04
Cl	141.9	142.0	163.1	143.4	146.7		86.0	102.2	91.3	93.1	134.4	132.4	130.3	131.9	134.4
Nitrite-N	0.056	0.094	0.056	0.053	0.039		<0.010	<0.010	<0.005	<0.008	<0.010	0.013	<0.010	<0.005	<0.008
Br	1.09	1.10	1.49	1.11	1.15		0.65	0.91	0.68	0.72	1.04	1.04	1.18	1.04	1.06
Nitrate-N	6.778	3.983	5.321	3.033	1.534		0.074	0.847	0.082	0.110	0.293	0.211	0.410	0.118	0.140
Sulfate	835.3	850.1	1038.1	905.5	922.7		1044.3	984.0	956.7	997.1	942.5	972.6	912.8	893.7	944.1
Thiosulfate	<0.03	<0.03	<0.03	<0.03	<0.04		<0.03	<0.03	<0.03	<0.04	<0.03	<0.03	<0.03	<0.03	<0.04
Phosphate-P	<0.03	<0.03	<0.03	<0.02	<0.04		<0.03	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04

Table A-3b. U. S. Steel – Minntac. Analytical results for Minntac downstream surface water sites.

Sample Location	**Sand River at HW 53**					**Dark River at CR 668**				
Sample Date	**5/28/2014**	**10/8/2014**	**2/24/2015**	**5/13/2015**	**10/8/2015**	**5/28/2014**	**10/8/2014**	**2/24/2015**	**5/13/2015**	**10/8/2015**
Flow (gpm)	11,983	8,597	779*	17,754	3,078		2,239	2,346*	9,639	4,561
Temp (^oC)	20.17	5.99	0.2	5.86	9.84	22.84	7.37	0.22	6.95	9.65
D.O. (mg/L)	2.43	5	4.57	8.72	7.34	8.07	11.44	7.61	11.96	9.67
pH	7.33	7.33	7.48	7.63	7.79	7.6	8	7.61	7.96	8.48
Sp. Cond (uS/cm)	334	442	1863	478	579	1069	1797	2729	1252	2048
ORP	-10.7	95.1	22.5	88	-92.1	1.6	75.4	62.8	-72.1	-124.2
Alk (mg/L CaCO3)	65	95	342.5	52.5	110	235	432.5	600	225	407.5
$\delta^{18}O_{H2O}$	-12.0	-8.2	-10.6	-10.2	-7.4	-10.7	-8.5	-8.6	-9.7	-7.5
$\delta^{2}H_{H2O}$	-89.1	-66.8	-80.5	-75.9	-58.7	-80.5	-68.6	-69.4	-73.5	-62.3
$\delta^{34}S_{SO4}$	16.9	20.7	17.7	15.5	17.6	12.5	16.6	10.9	11.0	10.4
$\delta^{18}O_{SO4}$	5.7	11.1	9.9	6.5	8.4	0.9	5.2	1.2	2.0	1.8
Al	0.03	0.02	<0.01	0.02	<0.01	0.02	0.01	<0.01	0.02	<0.01
Ba	0.028	0.028	0.081	0.024	0.025	0.034	0.036	0.054	0.026	0.032
Ca	19.2	27.1	118.0	24.0	31.6	64.9	104.0	184.9	75.2	123.3
Fe	1.033	0.532	0.288	0.402	0.372	0.253	0.072	0.032	0.172	0.013
K	3.3	2.8	14.7	4.4	3.7	7.4	10.8	17.5	9.5	14.9
Li	0.002	0.004	0.013	0.005	0.003	0.005	0.009	0.018	0.008	0.010
Mg	21.0	31.1	157.4	30.0	42.0	96.9	180.1	275.3	114.6	204.8
Mn	0.210	0.030	1.862	0.046	0.083	0.159	0.141	1.616	0.048	0.086
Na	12.0	12.0	61.6	18.8	20.3	20.4	38.6	63.1	27.6	55.1
P	0.01	<0.01	<0.01	0.01	<0.01	0.03	0.01	<0.01	0.02	0.03
Si	2.1	5.4	12.3	1.9	4.4	1.3	6.4	9.6	2.7	5.4
Sr	0.072	0.083	0.354	0.054	0.106	0.161	0.217	0.361	0.139	0.257
F	0.46	0.40	1.53	0.46	0.63	0.40	0.47	0.95	0.39	0.86
Acetate	<0.01	<0.01	<0.03	<0.02	<0.01	<0.01	<0.03	<0.03	<0.02	<0.04
Formate	<0.01	<0.01	<0.03	<0.02	<0.01	<0.01	<0.03	<0.03	<0.02	<0.04
Cl	20.9	21.9	106.8	37.3	37.8	29.9	62.4	102.3	43.4	86.2
Nitrite-N	<0.002	<0.002	<0.010	<0.003	<0.002	<0.004	<0.010	0.026	<0.003	<0.008
Br	0.10	0.13	0.92	0.17	0.20	0.20	0.41	0.91	0.27	0.62
Nitrate-N	0.427	<0.001	0.288	0.022	0.017	0.497	<0.005	2.811	0.105	0.008
Sulfate	57.6	89.3	568.6	108.6	121.1	290.3	555.9	940.9	398.2	719.7
Thiosulfate	<0.005	<0.005	<0.025	<0.015	<0.01	<0.01	<0.025	<0.025	<0.015	<0.04
Phosphate-P	<0.005	<0.005	<0.025	<0.009	<0.01	<0.01	<0.025	<0.025	<0.009	<0.04

* Flow measurements taken on 3/5/2015

Table A-3c. **U. S. Steel – Minntac.** Analytical results for Minntac monitoring wells and piezometers.

Sample Location	**MW 1**					**MW 3**					**MW 4**				
Sample Date	**5/28/14**	**10/9/14**	**4/28/15**	**7/15/15**	**10/7/15**	**5/28/14**	**10/9/14**	**4/28/15**	**7/15/15**	**10/7/15**	**5/28/14**	**10/9/14**	**4/28/15**	**7/15/15**	**10/7/15**
Temp (^oC)	10.46	9.02	10.43	11.04	9.71	9.77	9.62	8.04	10.6	9.77	6.41	7.76	4.59	12.4	10.95
D.O. (mg/L)	10.9	0.21	1.01	0.48	0.48	0.25	0.57	0.81	1.01	0.49	0.97	0.76	1.56	1.48	1.77
pH	6.77	7.09	7.14	7.36	7.12	7.01	6.88	6.83	7	6.82	6.6	6.26	6.26	6.23	6.29
Sp. Cond (uS/cm)	2455	2469	2344	2362	2412	2174	2177	2119	2207	2245	1499	1505	1486	1517	1533
ORP	-5.4	121.5	63.7	54.8	170.4	-104.7	-58.4	-40.2	-99.5	-93.5	-97.8	98	134.5	114.9	84.5
Alk (mg/L CaCO3)	229.5	250	262.5	255	265	309.5	312.5	300	310	302.5	187.5	197.5	185	192.5	190
$\delta^{18}O_{H2O}$	-6.45	-7.12	-7.46	-7.25	-7.39	-7.12	-7.01	-7.34	-7.18	-6.79	-7.24	-7.45	-7.29	-7.26	-7.09
$\delta^{2}H_{H2O}$	-58.69	-63.41	-64.48	-64.78	-65.03	-61.65	-61.42	-62.09	-61.99	-61.38	-60.96	-61.97	-60.83	-61.03	-61.15
$\delta^{34}S_{SO4}$	8.35	9.70	8.28	8.29	8.1	15.11	15.60	14.79	13.51	14.39	14.32	14.80	14.04	14.14	14.35
$\delta^{18}O_{SO4}$	-0.94	0.70	-0.14	-0.14	-0.43	5.83	8.00	6.91	6.62	6.26	1.30	3.70	2.13	2.40	2.09
Al	<0.01	<0.01	0.06	<0.01	<0.01	0.02	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	0.118	0.122	0.104	0.081	0.079	0.119	0.095	0.099	0.115	0.096	0.029	0.028	0.030	0.031	0.031
Ca	149.3	147.0	138.2	142.1	142.9	145.1	144.6	148.1	150.7	151.3	205.0	204.3	211.5	212.4	211.9
Fe	<0.005	0.011	<0.005	0.012	<0.005	15.902	16.696	11.922	17.501	18.084	<0.005	0.044	0.020	0.086	<0.005
K	21.0	21.8	22.5	22.2	22.5	17.1	16.5	18.6	18.4	18.0	6.6	7.3	7.4	7.5	7.7
Li	0.006	0.009	0.011	0.010	0.007	0.005	0.008	0.010	0.009	0.006	0.013	0.019	0.020	0.019	0.015
Mg	220.9	216.7	212.6	212.8	213.5	174.6	173.6	178.7	180.6	180.3	66.8	65.9	68.6	68.6	68.0
Mn	1.220	1.307	0.891	1.149	1.297	2.231	2.088	2.598	2.048	2.036	0.102	0.097	0.099	0.103	0.100
Na	87.8	94.4	90.9	91.4	89.5	72.2	74.0	77.6	76.7	76.2	24.8	22.7	26.6	28.7	28.9
P	<0.01	<0.01	0.02	0.01	<0.01	0.04	0.03	0.02	0.06	0.08	<0.01	<0.01	0.01	0.01	<0.01
Si	4.2	4.2	4.1	4.1	4.1	10.0	9.9	9.9	10.1	10.1	8.7	9.7	8.5	9.0	9.6
Sr	0.425	0.377	0.358	0.376	0.376	0.490	0.433	0.459	0.473	0.473	0.755	0.695	0.731	0.740	0.731
F	3.11	2.75	2.91	2.87	3.40	2.48	2.08	2.20	2.25	2.58	0.06	0.04	0.03	0.03	0.04
Acetate	<0.03	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04
Formate	<0.03	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04
Cl	159.9	151.7	145.5	145.9	150.7	130.8	128.6	132.0	132.6	137.330	90.5	84.7	92.2	92.1	91.7
Nitrite-N	0.130	0.139	0.079	0.055	0.028	<0.010	<0.010	<0.005	<0.004	<0.008	<0.010	<0.010	<0.005	<0.004	<0.008
Br	1.28	1.22	1.14	1.16	1.19	0.92	0.93	0.98	0.99	1.035	0.71	0.68	0.74	0.76	0.75
Nitrate-N	1.409	2.633	0.979	1.190	0.938	0.007	0.021	0.026	0.054	0.020	<0.005	0.077	0.018	0.037	0.022
Sulfate	966.8	953.9	898.0	913.3	948.8	720.3	723.5	738.4	756.9	778.2	507.6	503.0	513.9	515.2	528.0
Thiosulfate	<0.03	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04
Phosphate-P	<0.03	<0.03	<0.02	<0.02	<0.04	<0.03	<0.03	<0.02	<0.02	<0.04	<0.03	<0.03	<0.02	<0.02	<0.04

Table A-3c, continued. **U. S. Steel – Minntac.** Analytical results for Minntac monitoring wells and piezometers.

Sample Location	**PZ-5S**					**PZ-5D**					**MW 6**				
Sample Date	**5/28/14**	**10/9/14**	**4/28/15**	**7/15/15**	**10/7/15**	**5/28/14**	**10/9/14**	**4/28/15**	**7/15/15**	**10/7/15**	**5/28/14**	**10/9/14**	**4/28/15**	**7/15/15**	**10/7/15**
Temp (^{o}C)	6.93	9.97	6.07	12.69	12.4	6.01	9.62	5.62	8.93	10.11	15.33	9.65	9.18	12.15	12.75
D.O. (mg/L)	1.28	0.24	0.98	0.26	0.72	0.37	0.57	0.79	0.32	0.53	2.44	0.24	1.44	1.2	1.54
pH	5.85	6.91	7.35	7.18	6.92	6.17	6.88	7.45	7.29	6.69	6.55	6.61	6.56	6.58	6.59
Sp. Cond (uS/cm)	2289	2501	2436	1946	2652	2244	2177	2274	2332	2339	2183	2323	2176	2241	2266
ORP	-27.4	-55.3	-92.2	-107.6	-85	-39.2	-58.4	-160.3	-171.4	-83	30.5	95.7	87.4	45.5	46.3
Alk (mg/L CaCO3)	205	240	380	300	375	242	242.5	297.5	295	277.5	300	330	310	322.5	310
$\delta^{18}O_{H2O}$	-9.29	-8.27	-9.78	-8.43	-8.99	-6.75	-6.54	-6.73	-7.00	-7.03	-7.77	-7.42	-7.56	-7.54	-7.29
$\delta^{2}H_{H2O}$	-74.12	-66.33	-75.71	-62.52	-70.24	-58.89	-57.93	-59.36	-59.80	-60.42	-62.9	-62.24	-62.97	-63.01	-62.63
$\delta^{34}S_{SO4}$	2.14	3.10	10.06	10.31	10.58	13.80	14.02	14.05	13.98	13.84	10.96	12.50	10.85	10.08	10.14
$\delta^{18}O_{SO4}$	2.55	4.00	2.06	4.99	3.42	4.48	7.20	5.49	5.19	4.07	-0.61	1.60	-0.57	-0.69	-0.84
Al	<0.01	<0.01	0.03	0.02	<0.01	0.02	0.03	0.04	0.04	<0.01	<0.01	<0.01	0.02	<0.01	<0.01
Ba	0.072	0.073	0.067	0.070	0.094	0.088	0.085	0.047	0.047	0.077	0.028	0.032	0.028	0.031	0.026
Ca	197.6	222.2	219.9	177.9	218.9	217.5	216.0	201.2	174.8	222.0	249.8	256.3	258.4	260.0	260.1
Fe	3.590	7.990	2.632	5.882	12.133	46.283	47.450	27.557	24.193	47.356	0.179	0.720	0.263	0.449	0.072
K	5.0	5.7	8.7	5.8	5.9	7.7	8.2	60.0	88.4	18.8	5.3	5.7	6.3	6.0	6.0
Li	0.009	0.013	0.011	0.012	0.008	0.017	0.022	0.075	0.094	0.026	0.024	0.031	0.034	0.033	0.029
Mg	187.9	200.7	243.2	154.5	223.3	131.4	129.6	129.6	128.1	142.0	142.0	148.3	149.6	150.0	149.7
Mn	0.535	0.771	0.312	0.460	0.788	2.888	2.884	2.375	2.291	2.837	0.952	1.375	0.800	1.416	0.718
Na	63.2	74.8	62.5	54.2	80.9	79.8	82.6	104.0	114.4	84.8	60.0	61.3	63.5	61.9	62.6
P	0.02	0.12	0.06	0.05	0.05	<0.01	0.02	0.02	<0.01	0.03	<0.01	<0.01	0.02	0.01	<0.01
Si	5.0	7.2	6.9	8.0	7.2	11.8	12.0	10.2	9.4	11.9	8.8	9.0	8.7	9.0	9.2
Sr	0.802	0.855	0.716	0.694	0.888	0.701	0.662	0.624	0.586	0.698	0.576	0.571	0.560	0.566	0.568
F	0.24	0.20	0.31	0.25	0.30	0.20	0.14	0.12	0.14	0.25	0.12	0.08	0.07	0.08	0.10
Acetate	0.03	<0.03	<0.03	<0.02	<0.04	0.16	<0.03	<0.03	<0.02	<0.04	0.04	<0.03	<0.03	<0.02	<0.04
Formate	0.03	<0.03	<0.03	<0.02	<0.04	0.10	<0.03	<0.03	<0.02	<0.04	0.10	<0.03	<0.03	<0.02	<0.04
Cl	100.6	103.9	83.5	60.7	88.7	130.2	130.4	131.8	128.6	130.9	106.1	105.1	105.9	106.1	108.5
Nitrite-N	<0.010	<0.010	<0.005	<0.004	<0.008	<0.010	<0.010	<0.005	<0.004	<0.008	<0.010	<0.010	<0.005	<0.004	<0.008
Br	0.58	0.56	0.48	0.40	0.61	0.98	0.97	0.99	1.01	1.02	0.76	0.78	0.78	0.81	0.85
Nitrate-N	<0.005	<0.005	0.016	0.031	<0.008	0.017	0.005	0.011	0.060	<0.008	0.016	0.011	0.052	0.057	0.088
Sulfate	997.4	1114.2	1081.3	783.4	1107.1	799.3	795.1	794.6	800.6	865.0	845.7	880.7	865.0	877.2	904.4
Thiosulfate	0.03	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04
Phosphate-P	<0.03	<0.03	<0.02	<0.02	<0.04	<0.03	<0.03	<0.02	<0.02	<0.04	<0.03	<0.03	<0.02	<0.02	<0.04

Table A-3c, continued. **U. S. Steel – Minntac.** Analytical results for Minntac monitoring wells and piezometers.

Sample Location	**MW 7**					**MW 8**					**MW 9**				
Sample Date	**5/28/14**	**10/9/14**	**4/28/15**	**7/15/15**	**10/7/15**	**5/28/14**	**10/9/14**	**4/28/15**	**7/15/15**	**10/7/15**	**5/28/14**	**10/8/14**	**4/28/15**	**7/15/15**	**10/7/15**
Temp (^{o}C)	6.4	10.0	6.6	9.3	9.0	7.2	9.4	7.1	15.0	10.5	6.4	8.2	6.1	11.3	11.4
D.O. (mg/L)	0.10	0.35	0.82	1.00	1.47	0.13	0.35	1.08	0.77	0.77	0.74	0.30	1.2	0.71	0.56
pH	6.9	6.8	6.8	7.0	6.9	6.7	6.7	6.6	6.5	6.6	6.9	6.1	5.9	5.47	5.65
Sp. Cond (uS/cm)	2595	2499	2393	2451	2284	2031	2107	1976	2022	2128	71	60	87	73	68
ORP	-4.4	134.2	136.6	115.8	30.4	-39.7	-10.6	-6.8	-44.2	-43	34.0	-8.7	68.4	57.1	54.6
Alk (mg/L CaCO3)	497.0	467.5	465.0	495.0	450.0	490.0	487.5	500.0	500.0	472.5	22.0	15.0	27.5	25	
$\delta^{18}O_{H2O}$	-8.1	-7.5	-8.1	-8.0	-7.8	-8.6	-8.2	-8.0	-8.2	-8.1	-9.9	-10.9	-10.5	-10.7	-10.7
$\delta^{2}H_{H2O}$	-64.3	-64.2	-67.1	-66.4	-65.7	-66.8	-66.4	-66.1	-66.3	-66.1	-72.2	-80.8	-78.8	-79.4	-79.2
$\delta^{34}S_{SO4}$	10.4	12.1	10.8	9.8	11.7	17.7	17.6	18.0	17.5	16.0					
$\delta^{18}O_{SO4}$	0.4	1.7	0.0	-0.7	0.8	5.9	7.5	6.1	6.7	5.7					
Al	<0.01	<0.01	0.12	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.45	0.44	0.43	0.48	0.35
Ba	0.082	0.078	0.048	0.070	0.039	0.207	0.222	0.172	0.139	0.198	0.013	0.013	0.017	0.015	0.013
Ca	179.0	193.7	178.8	164.9	147.4	197.0	204.5	205.7	206.8	224.4	6.2	4.6	8.1	6.6	6.8
Fe	<0.005	0.018	<0.005	0.009	<0.005	4.887	4.798	5.502	6.143	6.542	5.968	5.475	7.533	6.133	5.463
K	15.0	15.6	16.7	16.3	16.0	3.0	3.5	4.5	3.7	4.1	0.4	0.5	0.4	0.3	0.4
Li	<0.001	0.002	0.002	<0.001	<0.001	0.017	0.025	0.030	0.028	0.027	<0.001	0.001	0.002	0.001	<0.001
Mg	256.4	229.9	245.8	243.0	220.1	166.3	163.1	158.9	154.9	160.7	1.8	1.3	1.9	2.0	2.6
Mn	2.943	3.742	3.394	4.158	2.755	3.351	3.689	3.877	4.016	4.584	0.139	0.141	0.163	0.152	0.162
Na	66.6	60.5	63.7	68.0	57.6	40.7	42.3	41.0	44.2	48.0	1.6	1.3	3.3	1.7	1.9
P	0.03	0.02	0.04	0.03	0.02	0.07	0.07	0.05	0.03	0.06	0.04	<0.01	0.03	0.02	<0.01
Si	6.0	7.2	6.5	6.5	6.8	11.3	11.4	11.4	11.5	11.5	4.4	4.4	7.2	5.1	4.5
Sr	0.454	0.456	0.432	0.443	0.360	0.434	0.412	0.404	0.418	0.449	0.030	0.026	0.004	0.031	0.020
F	1.21	0.87	0.92	0.92	1.05	0.46	0.36	0.34	0.32	0.44	0.07	0.04	0.04	0.04	0.06
Acetate	<0.03	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04	0.023	<0.01	<0.01	<0.01	<0.01
Formate	<0.03	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04	0.031	<0.01	<0.01	<0.01	<0.01
Cl	109.3	103.2	105.4	100.8	98.4	87.0	93.3	91.7	91.1	95.2	0.3	0.5	0.3	0.2	1.5
Nitrite-N	<0.010	<0.010	<0.005	<0.004	<0.008	<0.010	<0.010	<0.005	<0.004	<0.008	<0.002	<0.002	<0.001	<0.001	<0.002
Br	0.83	0.79	0.81	0.79	0.79	0.66	0.70	0.70	0.72	0.75	0.01	0.01	<0.00	<0.01	<0.01
Nitrate-N	<0.005	<0.005	0.028	0.012	0.095	<0.005	<0.005	0.030	0.043	<0.008	<0.001	0.006	0.008	0.012	0.009
Sulfate	940.2	898.3	883.7	883.4	786.2	601.5	624.1	576.0	570.3	658.1	0.1	0.9	0.1	0.1	7.3
Thiosulfate	<0.03	<0.03	0.030	<0.02	<0.04	<0.03	<0.03	<0.03	<0.02	<0.04	<0.005	<0.005	<0.005	<0.005	<0.01
Phosphate-P	<0.03	<0.03	0.020	<0.02	<0.04	<0.03	<0.03	<0.02	<0.02	<0.04	<0.01	0.02	0.01	0.01	<0.01

Table A-3c, continued. **U. S. Steel – Minntac.** Analytical results for Minntac monitoring wells and piezometers.

Sample Location	**MW 10**					**MW 12**					**PZ-12S**				**PZ-12I**	
Sample Date	**5/28/14**	**10/9/14**	**4/28/15**	**7/15/15**	**10/7/15**	**5/28/14**	**10/9/14**	**4/28/15**	**7/15/15**	**10/7/15**	**5/28/14**	**10/9/14**	**7/15/15**	**10/7/15**	**5/28/14**	**10/9/14**
Temp (^{o}C)	5.7	8.83	5.31	12.17	10.04	5.68	6.85	3.5	7.27	8.54	5.22	8.38	8.56	9.35	5.42	6.58
D.O. (mg/L)	0.14	0.5	3.22	1.5	6.32	0.46	0.09	4.66	0.69	6.03	0.13	0.34	1.54	0.52	0.99	0.17
pH	5.95	6.31	6.4	7.01	6.35	6.5	6.61	6.64	6.45	6.83	6.48	6.5	6.46	6.44	6.48	6.56
Sp. Cond (uS/cm)	168	162	179	152	181	1044	1512	988	1481	1378	1759	1734	1776	1762	1671	1696
ORP	-5	-9.8	3.9	-26.5	-46.3	-14.5	-34.6	66.7	11.3	25.6	-40.9	-29.5	-41.4	-58	-23	-35.9
Alk (mg/L CaCO3)	26.5	32.5	47.5	42.5	32.5	150	137.5	97.5	160	122.5	127.5	105	125	122.5	126.5	120
$\delta^{18}O_{H2O}$	-11.7	-11.1	-10.8	-11.4	-11.0	-7.0	-6.6	-5.9	-7.0	-6.4	-6.0	-6.1	-6.3	-6.6	-6.0	-6.0
$\delta^{2}H_{H2O}$	-84.5	-81.7	-79.1	-83.0	-79.7	-58.6	-58.2	-53.3	-58.5	-56.8	-54.7	-55.5	-56.0	-56.9	-55.9	-55.5
$\delta^{34}S_{SO4}$	2.0	6.4	3.7	3.5	3.0	15.5	15.2	15.1	15.2	15.3	14.7	15.7	14.8	15.1	14.4	16.3
$\delta^{18}O_{SO4}$	5.3	6.8	5.2	8.8	3.7	4.1	7.6	5.0	5.3	4.6	6.2	7.5	6.7	6.1	5.2	7.1
Al	0.05	0.03	0.07	0.02	<0.01	0.01	0.01	0.02	<0.01	<0.01	0.03	0.04	0.03	<0.01	0.02	0.04
Ba	0.087	0.089	0.095	0.088	0.099	0.055	0.053	0.033	0.046	0.036	0.050	0.054	0.048	0.050	0.061	0.060
Ca	9.2	9.5	10.4	10.1	10.4	176.7	176.1	131.6	188.9	174.4	155.3	163.3	166.7	166.8	177.8	182.4
Fe	20.692	17.748	21.569	13.628	20.116	24.697	33.192	2.143	13.492	1.034	64.417	74.907	76.601	78.366	55.177	59.819
K	1.6	2.0	1.8	1.6	1.6	6.5	6.7	5.4	7.1	6.4	6.3	6.9	7.1	7.1	6.1	6.6
Li	<0.001	0.001	0.002	0.001	<0.001	0.027	0.033	0.026	0.035	0.027	0.017	0.028	0.026	0.024	0.025	0.033
Mg	3.6	3.5	3.7	4.0	4.1	66.4	67.4	48.8	70.6	64.9	89.9	80.9	94.5	83.6	77.1	76.9
Mn	1.527	1.454	1.669	1.483	1.574	4.558	4.489	3.353	4.729	4.217	2.372	2.536	2.526	2.521	3.792	4.008
Na	2.8	3.1	5.8	3.2	3.3	16.5	18.4	14.0	21.2	18.9	41.9	45.2	48.9	48.8	33.8	32.4
P	0.08	0.08	0.06	0.02	0.06	<0.01	0.02	<0.01	<0.01	<0.01	0.05	0.04	0.04	0.04	<0.01	0.02
Si	8.4	9.0	8.6	8.3	9.2	15.3	15.3	9.6	14.3	12.1	12.1	14.2	13.4	14.4	14.7	15.4
Sr	0.065	0.065	0.039	0.067	0.062	0.623	0.557	0.408	0.611	0.561	0.445	0.458	0.452	0.468	0.520	0.505
F	0.09	0.07	0.06	0.06	0.08	0.10	0.07	0.05	0.06	0.07	0.17	0.09	0.09	0.10	0.09	0.06
Acetate	0.03	<0.01	<0.01	<0.01	<0.01	0.03	<0.03	<0.02	<0.02	<0.04	0.07	<0.03	<0.02	<0.04	0.03	<0.03
Formate	0.06	<0.01	<0.01	<0.01	<0.01	0.03	<0.03	<0.02	<0.02	<0.04	0.07	<0.03	<0.02	<0.04	0.04	<0.03
Cl	1.2	1.4	1.4	1.4	1.3	100.9	107.9	77.8	110.3	103.5	126.1	130.7	133.2	135.7	119.6	125.4
Nitrite-N	<0.002	<0.002	<0.001	<0.004	<0.002	<0.004	<0.010	<0.004	<0.004	<0.008	<0.010	<0.010	<0.004	<0.008	<0.010	<0.010
Br	0.02	0.02	0.02	0.02	<0.01	0.81	0.85	0.63	0.91	0.87	0.99	1.01	1.07	1.07	0.92	0.97
Nitrate-N	<0.005	<0.001	0.008	0.028	<0.002	0.008	<0.005	0.019	0.057	0.254	0.014	0.005	0.050	0.008	0.004	0.005
Sulfate	25.3	17.4	20.2	19.0	21.1	435.7	473.3	338.0	484.0	452.4	565.7	579.9	610.1	597.9	535.8	566.1
Thiosulfate	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.03	<0.02	<0.02	<0.04	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03
Phosphate-P	<0.01	<0.01	<0.00	<0.01	<0.01	<0.01	<0.03	<0.01	<0.02	<0.04	<0.03	<0.03	<0.02	<0.04	<0.03	<0.03

Table A-3c, continued. **U. S. Steel – Minntac.** Analytical results for Minntac monitoring wells and piezometers.

Sample Location	**MW 13**					**MW 14**		**PZPT-06D**	
Sample Date	**5/28/14**	**10/9/14**	**4/28/15**	**7/15/15**	**10/7/15**	**5/28/14**	**10/9/14**	**7/15/15**	**10/7/15**
Temp (^{o}C)	6.7	6.18	6.06	9.2	7.93	5.26	7.85	7.24	9.6
D.O. (mg/L)	1.08	0.46	1.19	1.04	0.61	0.25	0.31	0.27	0.27
pH	6.38	6.42	6.36	6.46	6.26	6.57	7.26	7.46	7.48
Sp. Cond (uS/cm)	1078	1087	1025	1032	1126	653	653	1188	1198
ORP	-99.3	-47.1	-47.6	-69.1	-69.7	-125.8	-110.8	-227.6	-127.5
Alk (mg/L CaCO3)	137.5	105	87.5	100		327.5	330	412.5	397.5
$\delta^{18}O_{H2O}$	-10.7	-10.2	-10.4	-10.7	-10.3	-11.7	-11.4	-8.6	-8.7
$\delta^{2}H_{H2O}$	-77.2	-76.4	-77.3	-77.8	-76.0	-81.4	-80.4	-70.1	-70.3
$\delta^{34}S_{SO4}$	21.0	22.2	22.1	20.6	20.6			14.4	14.7
$\delta^{18}O_{SO4}$	2.8	4.7	3.2	4.1	2.6			3.1	2.4
Al	0.06	0.09	0.04	0.05	0.04	<0.01	<0.01	<0.01	<0.01
Ba	0.292	0.278	0.213	0.203	0.251	0.086	0.086	0.045	0.043
Ca	89.9	88.9	92.4	91.0	91.3	82.0	80.5	84.4	82.4
Fe	141.290	163.150	125.547	142.740	144.980	8.848	11.400	0.273	0.803
K	3.0	3.2	3.5	3.0	2.7	2.8	3.2	9.7	9.9
Li	0.012	0.015	0.017	0.015	0.012	0.009	0.013	0.020	0.016
Mg	25.0	23.8	25.1	24.8	25.1	31.0	28.8	102.9	103.0
Mn	4.420	4.464	4.554	4.486	4.544	1.668	1.648	1.166	1.146
Na	6.8	11.8	17.8	7.8	8.0	7.9	6.3	26.0	25.6
P	0.05	0.05	0.03	0.02	0.05	<0.01	0.06	<0.01	<0.01
Si	17.7	17.8	16.6	16.9	17.6	11.9	12.6	6.6	6.7
Sr	0.442	0.407	0.405	0.413	0.410	0.161	0.147	0.250	0.238
F	0.08	0.03	0.03	0.04	<0.02	0.41	0.34	0.19	0.24
Acetate	0.08	0.10	<0.02	<0.02	<0.04	2.30	<0.01	<0.02	15.19
Formate	0.35	0.39	<0.02	0.05	<0.04	0.02	<0.01	<0.02	0.11
Cl	35.8	36.1	39.2	37.9	39.3	2.7	2.7	29.6	29.5
Nitrite-N	<0.004	<0.004	<0.003	<0.004	<0.008	<0.002	<0.002	<0.004	<0.008
Br	0.26	0.27	0.29	0.29	0.30	0.02	0.03	0.24	0.25
Nitrate-N	0.003	0.002	0.013	0.041	<0.008	<0.001	<0.002	0.06	<0.008
Sulfate	305.7	298.6	311.9	308.6	320.3	6.2	9.8	219.1	218.6
Thiosulfate	<0.01	<0.01	<0.02	<0.02	<0.04	0.02	<0.01	<0.02	<0.04
Phosphate-P	<0.01	<0.01	<0.01	<0.02	<0.04	<0.01	<0.01	<0.02	<0.04

Table A-4a. United Taconite. Analytical results for all DNR-sampled Utac sites.

Sample Location	**Tailings basin return to plant**				**Fine tailings discharge to basin**				**St. Louis River at Forbes Dam**			
Sample Date	**6/11/14**	**10/1/14**	**2/17/15**	**5/12/15**	**6/11/14**	**10/1/14**	**2/17/15**	**5/12/15**	**6/11/14**	**10/1/14**	**2/17/15**	**5/12/15**
Temp (^{o}C)	19.24		1.6	8.44			4.73	21.3	19.23		0.15	9.39
D.O. (mg/L)	9.52		12.57	11.61			14.62		8.4		18.13	11.35
pH	8.08	8.63	8.25	8.6	8.38		8.43	8.29	8.43	8.15	7.54	7.69
Sp. Cond (uS/cm)	800	900	1414	1074	825		1335	1103	125	650	639	232
ORP	18.7		271	61			210.8	228.3	23.2		195.1	108.3
Alk (mg/L $CaCO_3$)	155	173	253	180	160	175	250	165	30	135	180	60
$\delta^{18}O_{H2O}$	-8.9	-6.7	-7.9	-7.7	-9.6	-7.1	-7.8	-8.5	-11.4	-9.1	-9.5	-10.2
$\delta^{2}H_{H2O}$	-70.2	-59.5	-70.4	-65.3	-73.8	-61.9	-69.5	-68.8	-84.3	-71.6	-74.6	-76.6
$\delta^{34}S_{SO4}$	7.8	8.5	7.6	7.9	7.5	7.8	8.3	8.4	8.8	9.9	8.4	8.4
$\delta^{18}O_{SO4}$	2.7	2.6	4.0	1.8	2.1	2.6	4.0	2.1	0.9	1.8	-0.3	2.2
Al	<0.01	<0.01	<0.01	0.03	<0.01	0.02	<0.01	<0.01	0.11	<0.01	<0.01	0.04
Ba	0.005	0.005	0.005	0.003	0.010	0.003	0.006	0.004	0.013	0.017	0.023	0.014
Ca	28.5	33.0	50.0	39.1	31.0	30.6	46.4	42.5	10.2	26.7	35.6	16.8
Fe	0.005	<0.005	0.010	<0.005	0.016	<0.005	0.007	0.006	0.843	0.284	0.402	0.492
K	11.9	12.2	17.4	15.6	21.6	16.3	18.3	18.1	1.3	3.0	5.5	2.2
Li	0.023	0.032	0.042	0.033	0.026	0.028	0.040	0.033	0.002	0.006	0.007	0.004
Mg	44.8	52.6	89.3	63.3	42.6	55.1	85.4	55.0	7.2	28.4	47.6	13.6
Mn	0.002	0.015	0.110	0.036	0.055	0.029	0.094	0.073	0.050	0.058	0.151	0.064
Na	61.7	83.1	116.0	80.7	63.0	92.8	122.6	73.2	4.3	10.6	19.9	8.2
P	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.02
Si	7.6	10.0	10.1	8.9	13.2	12.5	7.9	10.1	2.6	4.8	6.1	2.7
Sr	0.154	0.182	0.183	0.131	0.198	0.149	0.222	0.145	0.038	0.103	0.125	0.050
F	8.57	12.43	14.29	11.11	11.15	14.53	14.22	11.30	0.12	0.24	0.36	0.14
Acetate	<0.01	<0.02	<0.03	<0.02	<0.01	<0.02	<0.03	<0.03	<0.01	<0.01	<0.03	<0.01
Formate	0.06	0.09	0.08	<0.02	0.07	0.08	0.07	<0.03	<0.01	<0.01	<0.03	<0.01
Cl	45.8	55.2	80.0	57.0	47.8	53.5	75.2	56.7	3.1	8.8	13.4	7.1
Nitrite-N	0.353	0.798	0.905	0.604	0.857	1.491	0.712	1.187	<0.002	<0.004	<0.010	0.006
Br	0.33	0.37	0.60	0.38	0.33	0.33	0.54	0.37	0.01	0.02	0.12	0.01
Nitrate-N	4.085	6.876	7.455	4.684	3.995	6.547	6.957	4.372	0.076	0.007	0.399	0.143
Sulfate	139.9	188.3	302.3	228.0	146.0	221.0	311.1	212.2	13.1	67.9	120.1	33.7
Thiosulfate	0.04	<0.02	<0.03	<0.02	0.05	<0.02	<0.03	<0.03	<0.01	<0.01	<0.03	<0.01
Phosphate-P	<0.01	<0.02	<0.03	<0.01	<0.01	<0.02	<0.03	<0.02	<0.01	<0.01	<0.03	<0.00

Table A-4a, continued. United Taconite. Analytical results for all DNR-sampled Utac sites.

Sample Location	Unamed wetland near Twin Lakes (W-1)				Wetland downstream (W-2)		Little Tony Lake inlet near SD001 (LT-1)				Little Tony Lake outlet (LT-2)	
Sample Date	**6/11/14**	**10/1/14**	**2/17/15**	**5/12/15**	**2/17/15**	**5/12/15**	**6/11/14**	**10/1/14**	**2/17/15**	**5/12/15**	**2/17/15**	**5/12/15**
Temp (^{o}C)	10.59		2.5	8.86	0.47	6.8	15.41		3.68	8.96	1.82	8.38
D.O. (mg/L)	3.37		12.47	5.58	7.32	8.72	3.95		13.29	6.12	5.79	9.57
pH	7.48	7.61	7.41	7.57	7.39	8.42	7.1	7.32	7.28	7.73	7.15	7.95
Sp. Cond (uS/cm)	1465	1450	1331	1312	1951	1265	2160	2500	3048	2418	1826	1475
ORP	20.2		299.8	82	36	66.5	-11.4		48.8	18.7	98.6	90.8
Alk (mg/L CaCO$_3$)	415	485	385	367.5	610	405	785	1255	1322.5	917.5	685	480
$\delta^{18}O_{H2O}$	-7.31	-7.37	-7.49	-7.89	-8.46	-7.56	-10.07	-8.99	-9.04	-9.77	-8.49	-8.23
$\delta^{2}H_{H2O}$	-61.06	-60.19	-65.30	-63.85	-68.27	-61.87	-76.45	-70.32	-71.98	-70.86	-66.47	-65.74
$\delta^{34}S_{SO4}$	7.89	7.06	8.30	9.3	8.7	9.4	12.14	11.08	11.60	14.5	11.2	
$\delta^{18}O_{SO4}$	1.69	1.45	2.42	0.5	2.8	4.3	0.58	-2.1	-1.55	0.9	3.43	
Al	<0.01	<0.01	0.01	0.03	<0.01	0.06	<0.01	<0.01	<0.01	0.02	<0.01	0.02
Ba	0.006	0.008	0.006	0.010	0.022	0.018	0.033	0.043	0.043	0.024	0.161	0.067
Ca	57.0	65.2	52.1	50.1	83.8	45.2	74.7	91.5	98.6	55.4	156.4	98.7
Fe	0.008	<0.005	0.009	0.075	0.014	0.040	0.043	0.176	0.038	0.295	0.017	0.020
K	16.4	18.2	19.5	18.3	25.5	17.1	11.6	11.8	13.8	13.2	8.3	8.5
Li	0.020	0.023	0.029	0.024	0.029	0.018	0.006	0.009	0.010	0.007	0.024	0.020
Mg	118.6	129.1	101.3	91.7	168.6	107.1	224.7	356.6	437.4	308.1	133.0	121.0
Mn	1.902	1.993	0.783	1.063	0.963	0.066	0.874	2.399	2.348	0.699	4.901	0.194
Na	78.2	80.1	80.3	82.1	107.7	62.6	36.8	58.5	62.9	49.6	75.7	62.1
P	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.03	<0.01	<0.01
Si	6.2	6.5	5.9	5.9	7.9	0.5	8.3	10.4	9.3	6.6	12.5	5.9
Sr	0.327	0.368	0.255	0.246	0.427	0.242	0.414	0.651	0.735	0.446	0.743	0.536
F	9.79	9.90	9.90	9.66	11.11	6.07	4.71	6.72	6.00	4.10	2.30	1.84
Acetate	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.05	<0.03	<0.03	<0.03	<0.03
Formate	0.07	<0.03	0.06	<0.03	0.06	<0.03	<0.03	<0.05	<0.03	<0.03	<0.03	<0.03
Cl	51.0	54.4	52.8	54.2	66.6	42.5	30.3	39.1	37.9	35.2	45.2	39.0
Nitrite-N	0.102	0.133	0.028	0.019	0.507	0.023	<0.010	0.020	<0.010	0.039	0.109	0.027
Br	0.40	0.44	0.43	0.38	0.57	0.25	0.13	0.23	0.24	0.14	0.29	0.20
Nitrate-N	8.730	9.320	6.577	4.471	7.131	0.364	0.076	0.633	0.054	0.129	1.371	0.685
Sulfate	250.3	289.0	217.0	209.5	333.6	189.4	295.8	531.1	599.1	435.6	336.8	302.8
Thiosulfate	0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.05	<0.03	<0.03	<0.03	<0.03
Phosphate-P	<0.03	<0.03	<0.03	<0.02	<0.03	<0.02	<0.03	<0.05	<0.03	<0.02	<0.03	<0.02

Table A-4b. United Taconite. Limited analytical results for supplemental Utac lake sites, sampled by company-hired consultants as part of a scheduled annual sampling event.

Sample Location	**Perch Lake SW004**	**Twin Lakes SW003**	**Round Lake SW005**
Sample Date	**6/11/14**	**6/11/14**	**6/11/14**
Temp ©			
D.O. (mg/L)			
pH			
Sp. Cond (uS/cm)			
ORP			
Alk (mg/L CaCO3)	205	407.5	15
$\delta^{18}O_{H2O}$	-7.98	-6.49	-8.74
$\delta^{2}H_{H2O}$	-64.68	-58.03	-69.47
$\delta^{34}S_{SO4}$	16.10	11.60	
$\delta^{18}O_{SO4}$	7.90	7.09	
Al			
Ba			
Ca			
Fe			
K			
Li			
Mg			
Mn			
Na			
P			
Si			
Sr			
F	2.47	5.24	0.07
Acetate	<0.01	<0.01	<0.01
Formate	<0.01	<0.01	<0.01
Cl	14.8	34.8	0.4
Nitrite-N	<0.004	<0.004	<0.004
Br	0.07	0.18	<0.01
Nitrate-N	0.019	0.007	<0.002
Sulfate	61.0	173.1	1.4
Thiosulfate	<0.02	<0.02	<0.02
Phosphate-P	<0.01	<0.01	<0.01

Table A-5. ArcelorMittal Minorca. Analytical results for all ArcelorMittal sites.

Sample Location	**Ditch entering PSSB**					**PSSB discharge**		**Raw water (PSSB, upland tailings, and enterprise pit water)**					**Downstream at HW 53**	
Sample Date	**6/10/14**	**9/30/14**	**2/18/15**	**5/6/15**	**10/13/15**	**6/10/14**	**9/30/14**	**6/10/14**	**9/30/14**	**2/18/15**	**5/6/15**	**10/13/15**	**6/10/14**	**9/30/14**
Temp (^oC)	22.94	17.53	3.08	16.76	15.54	20.27	15.37	22.25	16.16		15.57	14.59	18.1	11.32
D.O. (mg/L)	7.86	8.66	15.19	9.29	9.37	9.66	10.22	6.34	8.46		9.16	9.58	3.19	9.03
pH	8.55	8.88	8.78	8.56	8.68*	8.73	8.99	8.35	8.68		8.35	8.7*	7.95	7.35
Sp. Cond (uS/cm)	644	828	968	817	856	608	761	633	699		753	793	535	375
ORP	56.9		258	-6.2	-131.7	53.2					-9.1	-127.5	19.2	118.9
Alk (mg/L $CaCO_3$)	155	210	255	235	192.5	170	170	205	205	270	237.5	205	160	107.5
$\delta^{18}O_{H2O}$	-9.31	-7.33	-8.04	-8.48	-6.83	-9.52	-7.38	-9.45	-7.97	-8.15	-8.57	-6.92	-10.00	-9.33
$\delta^{2}H_{H2O}$	-73.50	-64.48	-67.63	-69.34	-60.36	-74.87	-64.93	-73.83	-66.90	-67.73	-70.24	-59.7	-77.47	-71.61
$\delta^{34}S_{SO4}$	9.07	10.45	9.85			9.19	9.58	9.85	10.1	9.90	9.92	9.15	14.81	17.5
$\delta^{18}O_{SO4}$	1.87	2.6	5.96			2.39	3.5	1.77	1.1	5.73	0.88	2.09	3.93	7
Al	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	0.011	0.009	0.013	0.011	0.007	0.010	0.010	0.009	0.007	0.019	0.007	0.008	0.016	0.033
Ca	33.3	39.5	47.8	45.4	47.5	30.7	33.0	38.6	36.7	41.5	44.3	35.6	28.7	24.3
Fe	0.023	0.016	<0.005	0.033	<0.005	0.006	<0.005	0.012	0.008	<0.005	0.028	<0.005	0.143	0.839
K	11.5	8.1	10.2	11.9	13.4	8.6	8.6	6.8	7.1	11.9	8.7	11.4	5.5	3.0
Li	0.018	0.025	0.029	0.028	0.028	0.018	0.025	0.012	0.017	0.026	0.020	0.019	0.014	0.006
Mg	42.6	59.2	69.7	58.2	57.0	40.9	53.6	44.7	50.6	70.1	54.1	60.4	33.1	20.3
Mn	0.034	0.105	0.137	0.135	0.255	0.003	0.009	0.002	0.003	0.046	0.003	0.007	0.022	0.106
Na	28.3	38.0	42.8	31.2	31.5	29.7	37.6	22.9	26.9	36.1	26.1	30.4	27.0	16.2
P	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01	0.01	<0.01	<0.01	<0.01	0.03	<0.01
Si	10.8	10.9	9.4	7.1	8.7	8.1	10.6	5.5	6.7	7.6	5.9	6.5	6.9	6.1
Sr	0.105	0.110	0.133	0.086	0.111	0.110	0.116	0.112	0.106	0.118	0.075	0.096	0.100	0.093
F	3.08	4.24	4.59	2.16	4.68	3.30	4.50	1.93	2.65	3.89	1.94	3.41	2.55	0.99
Acetate	<0.01	<0.01	<0.03	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.03	<0.02	<0.01	<0.01	<0.01
Formate	0.02	<0.01	<0.03	<0.02	<0.01	0.01	<0.01	<0.01	<0.01	<0.03	<0.02	<0.01	<0.01	<0.01
Cl	62.6	94.6	95.8	75.9	105.9	58.0	92.6	43.5	63.4	82.6	58.7	80.6	49.6	38.7
Nitrite-N	0.129	0.081	0.155	0.075	0.172	0.059	0.035	0.010	0.009	0.032	0.020	0.016	<0.004	<0.002
Br	0.52	0.86	0.92	0.65	0.93	0.48	0.83	0.35	0.54	0.79	0.46	0.70	0.37	0.25
Nitrate-N	1.050	1.278	2.364	1.012	1.759	0.635	0.970	0.408	0.346	1.007	0.533	0.459	0.057	0.073
Sulfate	58.7	79.8	93.6	72.2	85.9	49.5	76.1	50.1	63.2	82.1	66.8	77.5	28.2	15.4
Thiosulfate	0.03	<0.01	<0.03	<0.02	<0.01	0.02	<0.01	0.01	<0.01	<0.03	<0.02	<0.01	<0.01	<0.01
Phosphate-P	<0.01	<0.01	<0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	<0.01	<0.01	<0.01

Table A-5, continued. ArcelorMittal Minorca. Analytical results for all ArcelorMittal sites.

Sample Location	**Fine tailings discharge to upland basin**					**Upland basin return to plant**					**Enterprise Pit**			
Sample Date	**6/10/14**	**9/30/14**	**2/18/15**	**5/6/15**	**10/13/15**	**6/10/14**	**9/30/14**	**2/18/15**	**5/6/15**	**10/13/15**	**9/30/14**	**2/18/15**	**5/6/15**	**10/13/15**
Temp (^{o}C)			5.63	21.5	11.3	18.96	14.59	0.44	12.48	12.24	15.59	0.86	12.12	13.36
D.O. (mg/L)			12.24			10.58	9.91	12.62	11.09	10.22	10.15	13.35	11.65	10.46
pH	8.42		8.37	8.35	8.26	8.43	8.83	8.16	8.41	8.74*	8.13	7.54	7.96	8.03
Sp. Cond (uS/cm)	650		950	857	907	719	757	952	861	820	551	617	585	572
ORP			99.3	233.1	281.5	39.61		286.5	5.9	-157.6		247.8	5.3	-83.6
Alk (mg/L $CaCO_3$)	187.5	207.5	225	240	190	235	280	300	280	250	190	197.5	205	202.5
$\delta^{18}O_{H2O}$	-8.9	-7.4	-7.8	-8.4	-6.6	-8.3	-7.4	-8.0	-7.8	-6.4	-9.2	-9.9	-9.5	-8.9
$\delta^{2}H_{H2O}$	-71.0	-64.1	-66.3	-69.5	-59.0	-67.6	-63.3	-66.0	-66.6	-57.1	-72.1	-74.7	-73.6	-70.0
$\delta^{34}S_{SO4}$	9.5	9.5	8.9			10.8	11.5	10.5	10.3	10.5	10.4	9.2		9.6
$\delta^{18}O_{SO4}$	1.8	3.5	5.3			2.5	4.7	6.6	2.4	2.7	0.6	1.2		-0.8
Al	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	0.013	0.003	0.009	0.007	0.002	0.007	0.008	0.009	0.008	0.006	0.003	0.003	0.003	0.001
Ca	34.1	37.2	36.6	46.2	49.8	27.3	27.3	34.3	32.7	26.0	50.9	58.3	55.2	51.6
Fe	0.008	<0.005	0.022	0.024	<0.005	0.006	0.008	0.009	0.026	<0.005	0.005	<0.005	0.027	<0.005
K	16.9	8.1	10.0	15.1	15.5	9.6	10.0	12.1	11.9	12.0	3.1	3.6	3.5	3.3
Li	0.024	0.025	0.028	0.034	0.030	0.015	0.018	0.022	0.021	0.016	0.008	0.010	0.009	0.007
Mg	49.3	61.9	69.6	59.3	59.9	61.1	65.5	78.1	73.6	71.9	32.2	34.3	33.9	34.0
Mn	0.081	0.144	0.147	0.179	0.344	0.003	0.002	0.011	<0.001	<0.001	0.002	0.002	0.006	<0.001
Na	30.3	44.4	47.7	30.1	32.0	29.0	30.1	38.2	34.5	34.0	11.4	14.3	16.0	14.6
P	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Si	12.3	10.7	7.7	9.1	9.8	4.5	4.6	5.8	5.2	3.8	4.8	5.7	5.3	4.9
Sr	0.117	0.086	0.106	0.085	0.107	0.092	0.089	0.110	0.064	0.069	0.117	0.122	0.082	0.113
F	4.67	5.06	4.26	1.94	5.17	2.81	3.07	3.49	2.96	3.41	0.22	0.23	0.19	0.21
Acetate	<0.01	<0.01	<0.03	<0.02	<0.01	<0.01	<0.01	<0.03	<0.02	<0.01	<0.01	<0.03	<0.02	<0.01
Formate	0.03	<0.01	<0.03	<0.02	<0.01	<0.01	<0.01	<0.03	<0.02	<0.01	<0.01	<0.03	<0.02	<0.01
Cl	76.0	105.5	97.4	80.4	113.0	56.8	64.0	73.5	68.8	74.3	32.1	32.1	32.5	33.0
Nitrite-N	0.217	0.137	0.197	0.115	0.234	0.022	<0.004	<0.010	0.020	<0.002	<0.004	<0.010	<0.003	<0.002
Br	0.68	0.99	0.95	0.71	1.02	0.58	0.66	0.77	0.67	0.69	0.11	0.12	0.11	0.12
Nitrate-N	1.302	1.614	2.899	1.145	2.021	0.229	0.006	0.549	0.519	0.024	0.038	0.171	0.068	0.032
Sulfate	65.4	87.2	93.0	73.5	89.6	57.3	63.7	78.8	76.5	77.2	49.8	55.2	50.7	50.3
Thiosulfate	0.03	<0.01	<0.03	<0.02	<0.01	0.02	<0.01	<0.03	<0.02	<0.01	<0.01	<0.03	<0.02	<0.01
Phosphate-P	<0.01	<0.01	<0.03	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	<0.01	<0.01	<0.03	<0.01	<0.01

Table A-5, continued. ArcelorMittal Minorca. Analytical results for all ArcelorMittal sites.

Sample Location	**Wetland (W-2)**					**Wetland outlet (W-2)**					**GW001**		**GW002**		**GW006**	
Sample Date	**6/10/14**	**9/30/14**	**2/18/15**	**5/6/15**	**10/13/15**	**6/10/14**	**9/30/14**	**2/18/15**	**5/6/15**	**10/13/15**	**6/10/14**	**9/30/14**	**6/10/14**	**9/30/14**	**6/10/14**	**9/30/14**
Flow (cfs)									0.81							
Flow (gpm)																
Temp (^{o}C)	19.69	11.14	0.01	5.34	8.79	19.62	11.99		10.12	8.22	16.41	12.74		10.28	5.44	8.8
D.O. (mg/L)	6.73	2.36	8.15	5.85	6.3	7.36	9.72		10.73	6.42	0.51	0.47		0.18	2.86	4.41
pH	8.05	7.22	7.11	7.37	7.58*	7.85	7.96		7.73	7.54*	8.25	8.5		7.16	8.66	7.45
Sp. Cond (uS/cm)	727	835	887	691	805	685	793		470	610	420	643		782	97	93
ORP	58	-85	1	-30	-140	34	147		22	-113	-20	-87		-162	58	
Alk (mg/L $CaCO_3$)	242.5	327.5	332.5	263	320	220	310		155	215	170	235		212.5	30	25
$\delta^{18}O_{H2O}$	-8.2	-7.0	-8.3	-7.6	-7.5	-8.5	-7.1		-9.5	-8.0	-5.9	-7.2		-8.6	-11.6	-11.4
$\delta^{2}H_{H2O}$	-67.0	-59.7	-65.8	-63.9	-62.7	-67.7	-59.9		-74.5	-63.1	-50.3	-60.6		-67.9	-79.5	-79.5
$\delta^{34}S_{SO4}$	11.4		32.5	32.6	38.0	13.0			13.8	23.6					-0.5	-1.1
$\delta^{18}O_{SO4}$	2.5		14.0	12.3		4.1			5.7	5.0					2.0	2.2
Al	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		0.03	0.06	<0.01	<0.01		0.06	0.01	<0.01
Ba	0.013	0.109	0.076	0.050	0.040	0.015	0.032		0.023	0.037	0.112	0.030		0.193	0.081	0.016
Ca	28.6	44.2	46.8	38.2	42.9	27.4	40.6		25.4	32.3	22.4	20.6		53.5	7.6	8.1
Fe	0.039	5.816	1.283	1.163	0.805	0.087	0.073		0.323	0.225	1.712	0.008		92.463	0.017	0.016
K	9.2	5.7	6.7	7.5	8.3	8.3	5.9		5.5	5.5	4.2	6.2		3.5	1.8	1.8
Li	0.014	0.004	0.005	0.004	0.002	0.013	0.006		0.004	0.003	0.000	0.001		0.007	0.003	0.004
Mg	61.4	65.1	63.0	51.6	62.7	55.8	64.6		34.4	46.2	38.0	51.4		25.7	3.1	3.2
Mn	0.087	1.813	3.446	0.729	0.410	0.035	0.261		0.186	0.595	0.682	0.375		2.396	0.003	0.001
Na	28.8	25.7	29.2	24.9	28.2	27.1	24.9		18.0	21.6	19.7	26.9		13.8	6.9	6.1
P	<0.01	<0.01	<0.01	<0.01	0.01	0.01	<0.01		0.02	0.01	<0.01	<0.01		0.12	0.01	0.02
Si	4.4	8.5	8.6	5.9	7.4	4.2	8.0		4.0	7.1	1.0	0.6		14.3	10.2	10.6
Sr	0.101	0.198	0.197	0.127	0.188	0.104	0.177		0.068	0.141	0.102	0.080		0.261	0.035	0.034
F	2.69	2.32	2.14	1.85	2.08	2.55	2.22		1.14	1.48	1.40	2.15		1.21	0.15	0.12
Acetate	<0.01	<0.01	<0.03	<0.02	<0.01	<0.01	<0.01		<0.02	<0.01	<0.01	<0.01		<0.01	<0.01	<0.01
Formate	<0.01	<0.01	<0.03	<0.02	<0.01	<0.01	<0.01		<0.02	<0.01	<0.01	<0.01		<0.01	<0.01	<0.01
Cl	55.0	65.6	65.8	53.2	64.5	52.2	64.1		36.8	49.2	43.6	69.0		43.3	0.8	0.9
Nitrite-N	0.013	<0.004	<0.010	0.007	<0.002	<0.004	<0.004		0.004	<0.002	<0.002	<0.004		<0.004	<0.002	<0.002
Br	0.56	0.64	0.70	0.51	0.58	0.54	0.59		0.29	0.41	0.46	0.75		0.40	0.01	0.01
Nitrate-N	0.137	0.004	0.632	0.043	0.007	<0.002	<0.002		0.031	0.016	<0.001	0.010		0.009	0.042	0.044
Sulfate	53.4	10.4	19.4	19.4	11.2	49.4	14.2		27.8	15.6	0.9	2.0		0.0	14.5	20.8
Thiosulfate	0.01	<0.01	<0.03	<0.02	<0.01	0.01	<0.01		<0.02	<0.01	<0.01	<0.01		<0.01	<0.01	<0.01
Phosphate-P	<0.01	<0.01	<0.03	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01	<0.01	<0.01		<0.01	0.011	<0.01