An updated isotopic analysis of sulfur cycling and mixing processes in the St. Louis River Watershed

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Summary

River, lake, and wetland sites were sampled during 2012-2013 as part of the Mine Water Research Advisory Panel (MWRAP) study of the relationships between sulfate and methylmercury in St. Louis River Watershed. This report details work related to MWRAP Project 2, focusing on sulfate behavior as waters travel from the mining region through various environments within the watershed to the St. Louis River. Stable isotopes of sulfur and oxygen were used as a tool to trace source mixing, sulfate reduction, and additional processes taking place in the St. Louis River and in parts of its watershed where mine waters containing SO₄ interact with organic matter in wetlands and lakes on their way. This document provides sulfur and oxygen isotope data and proposed interpretations for surface waters from 2012, along with a limited data set for select 2013 sampling sites.

Previous work has shown that SO₄ in the St. Louis River is composed mostly of mining derived SO₄ that has been partially reduced in its head water regions that is mixed with relatively small and variable amounts of SO₄ derived from non-mining watersheds. Watershed-wide increases in $\delta^{18}O_{SO4}$ without correspondingly large $\delta^{34}S_{SO4}$ changes, referred to here as oxygen re-equilibration or cryptic sulfur cycling, also appears to be a common although still little understood process. Several sites in the watershed reveal additional sulfur cycling processes that can impact $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ systematics on at least a local scale. For example, the Long Lake Creek wetland area was flooded by high-SO₄ mine water during two consecutive fall seasons. During periods of low flow substantial reduction and loss of SO₄ occurred within the wetland watershed. During the artificial flooding event in the fall, however, the wetland served as a source of SO₄ rather than a sink. Additionally, it was found that an intermediate sulfur species, thiosulfate, played an important role in the sulfur cycle in the hypolimnion of a lake with high productivity and mining inputs. Partial reduction and/or oxidation reactions involving the intermediate sulfur species resulted in an overall shallowing of the $\delta^{18}O_{SO4}$ versus $\delta^{34}S_{SO4}$ slope compared to that observed during sulfate reduction processes elsewhere in the watershed.

1. Introduction

In 2008, the MN Department of Natural Resources began investigating sulfur and mercury cycling in both mining and non-mining watersheds in NE Minnesota. These studies showed that the St. Louis River receives high sulfate waters from the mining region as a result of drainage from mine stockpiles, pit dewatering, and tailings seepage (Berndt and Bavin, 2009; 2012). This sulfate mixes with substantial amounts of sulfate from non-mining portions of the watershed and reacts in various ways that depend on inter-related environmental factors such as redox conditions, hydrology, availability of labile organics, and temperature. Much of the motivation for the DNR's recent sulfate research relates to the fact that the St. Louis River and its estuary are considered to be impaired with respect to mercury concentration in fish tissue (MPCA, 2013). There is widespread evidence that in reducing environments there is a link between the bacterial sulfate reduction process and the formation of toxic methyl mercury which bioaccumulates in fish (Gilmour et al., 1992; Branfireun et al., 1999; Jeremiason et al., 2006). Thus, it is important to determine the degree to which increased sulfate loads from the mining industry contribute to mercury methylation in the river and whether lowering the amounts of SO₄ delivered to the river can lead to decreased methylmercury in fish.

This document represents one of a series of linked studies conducted in the St. Louis River (Berndt et al., 2014; Jeremiason et al., 2014a; Jeremiason et al., 2014b; Jeremiason et al., 2014c) and mine impacted watersheds (Bailey et al., 2014a; Bailey et al., 2014b; Johnson et al., 2014) in 2012 and 2013. While the other studies focused on a range of topics detailing major and trace element chemistry, this study focuses on the stable isotopic ratios of oxygen and sulfur (δ^{18} O and δ^{34} S) in surface waters and lake sediments. Stable isotope techniques have previously been used by the DNR to trace sulfur and oxygen transformations as sulfate (SO_4^{2-}) produced in the iron mining region of NE Minnesota travels through the St. Louis River watershed (Berndt and Bavin, 2009; 2011; 2012). These studies have shown that mining waters are geochemically and isotopically distinct from non-mining waters, and that a simultaneously rise in $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values can be used to quantify sulfate reduction taking place in wetland and lakes downstream from the mining region. Within the tributary stream channels and the St. Louis River itself, sulfate largely behaves in a conservative manner (Berndt and Bavin, 2012). However, an additional trend in $\delta^{18}O_{SO4}$ has been identified within certain mine-impacted tributary streams, where increases in $\delta^{18}O_{SO4}$ are unaccompanied by increases in $\delta^{34}S_{SO4}$, suggesting that an additional cycling process is affecting the isotopic makeup of the sulfate molecules (Berndt, 2011; Berndt and Bavin, 2012). If sulfate is indeed reacting downstream of the mining region, it is important to understand this process and the associated impacts.

The present study expands the previous isotopic dataset for the St. Louis River basin, using updated sampling and processing techniques for surface waters and sediments collected during the 2012 and 2013 field seasons. This report provides an updated interpretation of the sequential framework model developed by Berndt (2011) to describe the previously observed isotopic

trends, and provides detailed, site-specific interpretations of sulfur cycling based on the trends in $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ along with any relevant geochemical data. In addition to the isotopic results presented here, a significant number of samples were collected from the Minntac Tailing basin and surrounding wells in 2012 and those data are provided and discussed in Kelly et al. (2014). Isotopic data from tailing leach experiments, also conducted in 2012, are provided and discussed in Von Korff et al. (2014).

2. Methodology

2.1. Site Descriptions

Sampling sites were selected with a particular focus on areas where sulfate and mercury cycling may be linked (see Figure 1A, Table 1). Thus, samples for isotope analysis were obtained from locations along the St. Louis River, Long Lake Creek, East Two River watershed (Lake Manganika), and West Two River watershed (Lake McQuade), corresponding to locations where other related studies were being conducted. Three locations were sampled on the St. Louis River itself. Mile 179 (Site 3) is situated upstream from the mining region, near Hoyt Lakes, and has characteristically low sulfate concentrations (<5mg/L) representative of background conditions in the watershed. Site 2, at river mile 94, is located just downstream of the iron formation and includes most of the mining inputs to the St. Louis River. The final St. Louis River site at river mile 36 (Site 1) near Cloquet is located downstream of most major mine-impacted and non-impacted tributary inputs. Chemical data, maps, geochemical context, and conclusions for these three sites are provided by Berndt et al. (2014) and Jeremiason et al. (2014a).

The Long Lake Creek wetland is located south of the city of Eveleth, and, under normal conditions, receives drainage waters at its inlet from United Taconite's (UTAC) South Pit area. The inlet and outlet of the Long Lake Creek wetland were studied previously, and results indicated that a substantial amount of sulfate reduction occurs within the wetland (Berndt and Bavin, 2011). In 2012, the same two sites were sampled (Sites 4 and 5), along with an additional location further downstream on Long Lake Creek near its confluence with the St. Louis River (Site 6). This wetland was artificially flooded with high-sulfate mine water during consecutive fall seasons, providing the unique opportunity to examine the geochemical response to both natural and artificial flooding events. Johnson et al. (2014) also sampled surface waters, peat sediments and pore waters at the Long Lake Creek wetland and provide an analysis of methyl mercury production and release mechanisms within the wetland complex.

Two lakes were included in the study: Lake Manganika, located in the East Two River watershed, and Lake McQuade, located in the West Two River watershed. Lake Manganika (Site 10), situated just south of Virginia, MN, receives water from the city waste treatment plant (Inlet 1) and from United Taconite (Inlet 2). Both inlets deliver high sulfate water to the lake. The DNR collected water samples from the two inlets (when possible), surface and bottom water

of the lake itself, the lake outlet, and approximately 0.5 miles further downstream on the East Two River. Lake McQuade is located 8 miles east of Hibbing, MN, and is impacted by the Minntac mining operation in Mountain Iron, MN. Lake surface and bottom waters were sampled (Site 16), as well as the lake inlet (Site 14) and outlet (Site 15). Sampling also took place downstream of the West Two River Reservoir (site 12) and the West Two River near its confluence with the St. Louis River (Site 13). Chemical data and insights for these sites are provided here, and additional interpretations of the lake waters and sediments are provided by Bailey et al. (2014a, 2014b).

The remaining two sites are located in the Swan River watershed, influenced by draining from the mining region as well as wastewater runoff and discharge from the Hibbing/Chisholm area. The West Swan River was sampled near the Highway 73/Highway 16 intersection (Site 17), as was the Swan River just above its confluence with the St. Louis River (Site 18). Data for these sites has not been presented elsewhere, but sulfur isotopic and chemical data are provided in this report.

An additional suite of sites were also sampled for sulfate isotopes on two occasions during the summer of 2013. These sites correspond to a watershed study that was being conducted by the MPCA during the same period. These include samples collected at Sites 1 and 3 and at the Forbes Dam in the St. Louis River and at the confluences of a number of important tributaries (Partridge, Embarrass River, East Two, West Two, Swan, Whiteface, Floodwood, and Cloquet Rivers) (Figure 1B).

2.2. Sample Processing and Analytical Methods

Sampling during the 2012 season occurred on a bi-weekly basis from early May though mid-October. This period was characterized by high rainfall and flooding during June, followed by prolonged dry period through October. Field parameters were measured with a YSI sensor at the time of sampling, including pH, temperature, dissolved oxygen concentration, and conductivity. Water samples were collected for major cations/anions, alkalinity, total and methyl mercury, dissolved organic carbon (DOC), stable isotopes of sulfate, and when applicable, sulfide (see Appendix A for full data set). This discussion focuses mainly on sulfate concentration and isotope data beginning in mid-July 2012, when isotope samples began to be processed as described below. An additional suite of sites were also sampled for sulfate isotopes on two occasions during the summer of 2013 (Figure 1B, Table 1B), and isotopic data along with sulfate concentration for these sites is reported in Table 3.

Prior to 2012, water samples collected by the DNR for S and O isotopic analysis of sulfate were stored for varying amounts of time in collection bottles prior to processing and analysis, raising the possibility that some of the observed isotope patterns were actually reflecting in-bottle reactions during storage rather than the true conditions in the surface waters at the time of sampling. To explore the risk of in-bottle reactions, a number of test samples were analyzed in

2012-13 once processing techniques were in place at the Hibbing laboratory. The tests indicated that isotopic shifts due to delays in sample processing are small, but may have had a minor influence on past isotopic results. In particular, we found that samples should be filtered as soon as possible after collection. In-bottle storage after filtration appears to be less problematic, with test results falling within the bounds of analytical error.

As a precaution, the DNR implemented new in-house techniques for extracting dissolved sulfate from waters as solid barium sulfate (BaSO₄), based on methods described in Carmody et al. (1998). Beginning in July of 2012, samples intended for isotope analysis were filtered the day of collection at the DNR laboratory in Hibbing, MN, and, in most cases, fully processed within 1 to 2 days. The filtrate was acidified with 1M HCl to a pH of 3-4 and heated at 90°C for ~ one hour so that any carbonate present would be degassed as CO₂. Approximately 6 ml of 6% hydrogen peroxide (H₂O₂) was also added to each sample prior to heating to oxidize and degas any dissolved organic matter. After heating, ~5 ml of 20% BaCl₂ was added (in excess) and the samples were allowed to cool for several hours or overnight. The BaSO₄ precipitate was collected on pre-weighed 0.45 μ m PES membrane filters, and was dried overnight at 90°C. Once dry, the BaSO₄ powder was weighed, scraped into glass vials, and stored until shipment to the University of Waterloo Environmental Isotope Laboratory in Ontario, CA for isotopic analysis.

Each BaSO₄ sample was analyzed for $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$. Relative ³⁴S and ³²S 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 ¹⁸O and ¹⁶O 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. $\delta^{34}S_{SO4}$ values are reported in ‰ units against the primary reference scale of Vienna-Canyon Diablo Troilite meteorite (VCDT), with an analytical precision of 0.3‰. $\delta^{18}O_{SO4}$ is reported relative to VSMOW, with analytical precision of 0.5‰.

In addition to isotopic analysis of dissolved sulfate, the DNR employed techniques in the summer of 2012 to collect anoxic waters and sediments for analysis of $\delta^{34}S_{H2S}$. Samples were collected in air-tight syringes to limit oxygen exposure during transport to the Hibbing DNR laboratory. Samples were injected into nitrogen-purged glass sample jars and any H₂S present was carried by N₂ gas into a vial containing 20% AgNO₃, where sulfide precipitated as an Ag₂S solid. Samples were collected on pre-weighed 0.45 µm PES membrane filters, rinsed with dilute NH₄OH to dissolve any AgCl precipitate, and dried in an oven at 90° for approximately 1 hr. The Ag₂S samples were then weighed, scraped into glass vials, and stored prior to shipment to the University of Waterloo Environmental Isotope Laboratory for analysis of δ^{34} S as described above.

Low sulfate concentrations at background sites previously prohibited isotopic analysis, as large volumes of water would be required to collect enough sulfate for analysis. Sulfate

concentrations in non-mining background streams are <10 mg/L, and in many cases are as low as 1-2 mg/L. A limited isotopic data set of non-mining tributaries from the region (Whiteface River, Cloquet River) was obtained as part of 2010-11 sampling campaign (Berndt and Bavin. 2012). However, in an effort to gain a better representation of background isotope compositions in the watershed, improved techniques were used in 2012 (after Carmody et al., 1998; Révész and Qi, 2006) in which multiple liters of water are passed through a cartridge containing an anion exchange resin to capture a sufficient amount of sulfate for isotope analysis. The sulfate can then be eluted from the resin using a small volume of 3M KCl solution, and the eluted samples are subsequently processed as with other sulfate isotope samples. This technique was fully in place beginning in September of 2012. Sulfate yields using the ion-exchange resin method, however, were initially much lower than measured concentrations, suggesting that sulfate capture by the resin was incomplete. Non-mining waters tend to have high DOC and in some cases high chloride/sulfate ratios, which can interfere with the capacity of the resin (Carmody et al., 1998). Extra precautions were taken during 2013 sampling to address this issue. The resin loaded cartridges were flushed with copious amounts of DI water until the conductivity of water passing through the cartridge approached that of DI water itself. It appears as though this additional treatment improved the ability of the resin to capture sulfate.

2.3. Isotope background

Isotopes are measured in terms of the ratio of heavier atoms (³⁴S, ¹⁸O) to the lighter and more common atoms (³²S, ¹⁶O) in the sample, and reported as delta (δ) values relative to a standard where

$$\delta^{34}S(\%) = \left[\binom{^{34}S}{^{32}S}_{sample} / \binom{^{34}S}{^{32}S}_{standard} - 1 \right] \times 1000$$
(1)

Positive δ -values indicate that the sample is enriched in the heavy isotope with respect to the reference material, and vice versa. Note that δ -values are in units of per mil (‰), as deviations from unity are typically quite small.

The isotopic signature of dissolved sulfate is modified during certain biogeochemical processes. Sulfur can exist in a number of oxidation states, and kinetic transformations between different oxidation states are often associated with isotope fractionation effects, leading to shifts in the δ^{34} S of the various sulfur species. For example, bacterial dissimilatory sulfate reduction (BSR) involves the uptake of sulfate (+6) by the cell, conversion to various intermediates, and ultimately, the release of sulfide (-2). This process is generalized as follows:

$$2(CH_2O) + SO_4^{2-} = 2(HCO_3) + H_2S$$
⁽²⁾

Through the BSR process, organisms gain energy for growth, organic carbon is oxidized, and alkalinity is produced. If iron is present, the product sulfide may precipitate as Fe-sulfide minerals.

Molecules containing the lighter isotopes have a lower vibrational energy and thus the bonds are more easily broken. Focusing first on sulfur, this means that the lighter ${}^{32}SO_4{}^{2-}$ is preferentially utilized by the bacteria during metabolism, leaving the residual pool of $SO_4{}^{2-}$ relatively enriched in the heavy isotopes. The product sulfide will be depleted in the heavy ${}^{34}S$ isotope relative to the original pool of sulfate. In a closed system, we can model the isotopic evolution of the sulfate pool as a function of "*f*," the fraction of the original substrate ($SO_4{}^{2-}$) remaining,

$$\delta^{34} S_{SO4} = (\delta^{34} S_{SO4,init} + 1000) f^{(\alpha - 1)} - 1000$$
(3)

As *f* decreases, the residual SO_4^{2-} pool becomes progressively more enriched in the heavier ³⁴S. The isotope fractionation factor (α) is defined as the ratio of the isotopic ratios of the element of interest in source (in this case, sulfate) and product (H₂S) during a reaction or process

$$\alpha = R_{SO4}/R_{H2S} \tag{4}$$

This is related to an alternate term to describe fractionation, the isotope fractionation effect, ε , where

$$\varepsilon (\%_0) = 1000 (\alpha - 1) \approx \Delta = \delta_{SO4} - \delta_{H2S}$$
(5)

We assign a value of 17‰ for the sulfur isotope fractionation effect during BSR, based on a study by Berndt and Bavin (2011) where alternative methods existed to estimate the fraction of sulfate remaining (*f*), thereby allowing the calculation of the fractionation factor (α) using the Rayleigh equation. While this value falls within the range of values reported in the literature (Detmers et al., 2001), the magnitude of isotope fractionation in nature is variable and depends on a number of factors, including the type of bacteria and the rate of sulfate reduction (slower rates generally lead to higher fractionations), which in turn is controlled by temperature, sulfate concentration, and type and quality of organic substrate (Brüchert et al., 2001; Canfield, 2001; Detmers et al., 2001; Kleikemper et al., 2004; Sim et al., 2011). The 17‰ value appears to be appropriate in several settings in NE Minnesota (Berndt and Bavin, 2011; Kelly et al., 2014). Therefore, the adopted 17‰ value is used empirically, here, but can and should be modified if and where evidence becomes available to support a different value.

A similar fractionation process also impacts the isotopic signature of sulfate-oxygen (Lloyd, 1968), though the net fractionation effect can relate to a number of additional factors. Dissimilatory sulfate reduction proceeds through multiple steps, all of which are potentially reversible (Rees, 1973; Brunner and Bernasconi, 2005). The overall kinetic oxygen isotope fractionation effect involves the sum of the fractionations during each forward and backward step and the ratio between the forward and backward fluxes. Additional isotopic processes may be involved, however, including oxygen isotope exchange between intermediate species and ambient water, an equilibrium process, and isotope effects during the internal re-oxidation of sulfite, indicating that the isotopic composition of ambient water is also an important factor (Fritz et al., 1989; Brunner et al., 2005; Mangalo et al. 2007). The relationship between δ^{18} O and

 $\delta^{34}S_{SO4}$ reflects the specifics of the sulfate reduction pathway in a particular environment. Thus, the paired isotopic analysis of both sulfur and oxygen can provide information regarding the origin and fate of sulfate in the St. Louis River watershed that may not be accessed in any other way.

3. Results

All measured physical and chemical parameters for waters collected as part of this study, are listed in Appendix A, while Tables 2-4 focus on including concentrations and sulfate isotope values. Figure 2 presents the $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ data for all of the samples collected during the 2012-2013 sampling seasons. Also shown is the sequential framework isotope model developed by Berndt (2011), which portrays the potential range of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values associated with specific cycling processes. Positive trending $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values are associated with the bacterial sulfate reduction process, as described in the previous section. Data that plots towards the upper right of the graph (relatively "heavy" $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$) tend to be wetland sites, where sulfate reduction takes place as waters pass through anoxic, organic rich soils. The vertical edge of the framework represents what Berndt (2011) referred to as the "oxygen reequilibration" trend within the St. Louis River watershed, where $\delta^{18}O_{SO4}$ increases between upstream and downstream locations without a corresponding increase in $\delta^{34}S_{SO4}$. In particular, this trend has been observed in tributary waters close to the mining region, where high-sulfate mine waters come into contact with low-sulfate, high-DOC background waters (Berndt and Bavin, 2012). The unaccompanied positive shift in oxygen values can only partially be explained by mixing with a different sulfate source, as the mining source overwhelmingly dominates the sulfate load. Each suite of sampling sites has unique characteristics and displays different isotopic trends, adding to our understanding of sulfate behavior in the St. Louis River watershed. Several of these locations and trends will be examined in more detail in the following sections of this document.

4. Discussion

4.1. Sequential Framework Model

Berndt (2011) developed what he referred to as "a sequential framework model" as a qualitative or semi-quantitative guide to help interpret $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values for mine-water dominated samples collected from the St. Louis River watershed. This model describes the isotopic composition of dissolved sulfate in the St. Louis River watershed in relation to the original source (oxidation of sulfides in the mining region) and subsequent cycling (sulfate reduction, oxygen re-equilibration). The distribution of sulfate isotope values observed throughout the watershed requires that the processes described by the framework model occur in a sequential manner: (1) oxidation of sulfide minerals in the iron formation, (2) sulfate reduction along the flow path as waters migrate into surface water streams, and (3) re-equilibration of $\delta^{18}O_{SO4}$ toward

a value of approximately +8 by a little understood process that occurs as waters migrate downstream in the St. Louis River and its tributaries towards the estuary. Here, we re-evaluate these steps in light of more recent data and observations.

The "starting point" of the framework model is the approximate composition of mineland sulfate, set at $\delta^{34}S_{SO4} = +5\%$ and $\delta^{18}O_{SO4} = -10\%$, which was and still remains guite distinct from the composition of sulfate commonly measured elsewhere in the watershed. The sulfate in mine waters is likely produced by the oxidation of primary sulfide minerals in the iron formation exposed during processing, and most high-sulfate mine pit and discharge waters collected by the DNR to date have $\delta^{34}S_{SO4}$ values between 4 and 12‰ (Theriault, 2011; Berndt, 2011; Berndt and Bavin, 2012; Kelly et al., 2014), most commonly in the lower end of this range. The source of the oxygen atoms in the mine-derived sulfate is water, which has a $\delta^{18}O_{H2O}$ of about -10% in NE Minnesota (Theriault, 2011; Berndt, 2011; Kelly et al., 2014). More detail regarding the isotopic composition of newly formed sulfate in mines is provided in Berndt (2011) and Kelly et al. (2014). Generally, the value corresponds to the average $\delta^{18}O_{H2O}$ for regional meteoric water. Pyrite weathering under oxidizing conditions is a complex process involving oxidation of both Fe and S atoms accompanied by electron transfer between the elements and oxygen in the aqueous solution (Rimstidt and Vaughan, 2003). The end result is that the released sulfate molecules obtain there S atoms from pyrite and O atoms from ambient water, which in this case, appears to be infiltrating, largely unevaporated, meteoric water. This process was recently confirmed in our own laboratory by Von Korff and Bavin (2014).

According to the model, the mine-derived, high-sulfate water then moves into the watershed along flow paths where sulfate reduction may occur, promoted by the presence of reduced organic matter (Step 2 in the sequential framework model). The method applies a Rayleigh fractionation model to calculate the % reduction associated with the isotopic increases. Any sulfide produced is removed completely from the water and no longer exchanges with dissolved sulfate. The framework depicted in Figures 2 and 3 assumes a sulfur isotope fractionation of 17‰, which provides a good empirical fit of data obtained from several areas in the watershed (Berndt and Bavin, 2011; Kelly et al., 2014). The slope of the sulfate reduction trend was set to 1, implying that the fractionation factor for oxygen is approximately the same as for sulfur. This, too, was consistent with observed isotope trends at DNR sites impacted by sulfate reduction. Since fractionation values used in this case for δ^{18} O and δ^{34} S are empirically based, site-specific situations involving different mechanisms could result in much higher or lower fractionation values for either or both elements (Mizutani and Rafter, 1969; Mizutani and Rafter, 1973; Aharon and Fu, 2000; Mandernack et al., 2003; Brunner et al., 2005; Mangalo et al., 2007; Turchyn et al. 2010; Antler et al., 2013). As will be discussed later, some instances appear to occur in the St. Louis River watershed, specifically associated with the formation of an intermediate species, thiosulfate, in lake-bottom waters.

As mentioned previously, Berndt and Bavin (2012) also found that $\delta^{18}O_{SO4}$ in most mining tributaries appeared to increase significantly with little or no corresponding increase in $\delta^{34}S_{SO4}$ (Step 3 in the sequential framework model). No such similar data were collected in the present data set, but Figures 3 to 5 illustrate how it remains difficult to account for St. Louis River watershed $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values without incorporating such a step.

First, Figure 3 shows that background and mine waters have fairly similar $\delta^{34}S_{SO4}$ but widely disparate $\delta^{18}O_{SO4}$ and that $\delta^{34}S_{SO4}$ values at SLR Mile 36 are always elevated with respect to both. Thus, at least some sulfate reduction is required, in addition to mixing, to account for the isotopic composition of waters at Mile 36. Similarly, Figure 4 indicates that this impact extends across seasons, as the mixing of mine waters with background waters (shaded region, diamonds) in this watershed always results in a slight positive shift in $\delta^{34}S_{SO4}$ and a negative shift in $\delta^{18}O_{SO4}$ downstream along the SLR (circles). The question, then, is how much of this shift is related to mixing, and how much can be attributed to sulfate reduction in the watershed or to some type of oxygen re-equilibration process? Figure 5A and 5B show, respectively, the expected $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$ if SO₄ from mines that has undergone a partial reduction process (0, 10, and 40% removed) is mixed into waters containing background sulfate levels and isotopic ratios. While 10% watershed-wide reduction is sufficient to produce the $\delta^{34}S_{SO4}$ vs sulfate mixing trends, an unlikely 40% reduction is required to account for the $\delta^{18}O_{SO4}$ vs sulfate mixing trends.

One possible means to account for this discrepancy is to mix background waters into mine waters that have been impacted by a reduction process involving much greater fractionation of oxygen isotopes than of sulfur isotopes. However, this type of model is inconsistent with the general direction of isotopic exchange observed in the region at sites where sulfate reduction is known to occur (Berndt and Bavin, 2011; Kelly et al., 2014). Alternatively, the possibility exists whereby $\delta^{18}O_{SO4}$ values in the watershed are modified by so-called "cryptic" sulfur cycling, which is known to occur in areas where active sulfate-reducing and sulfur-oxidizing microbial populations coexist (Holmkvist et al., 2011; Reese et al., 2014). In such cases, any sulfide produced is subsequently re-oxidized, resulting in no net change to sulfate concentration (or to $\delta^{34}S_{SO4}$). However, because the process effectively removes and replaces some or all of the O atoms from the original sulfate molecules, the $\delta^{18}O_{SO4}$ is substantially impacted. This process appears to occur within mining tributaries, since trends at their confluences fall on the same mixing trends as "composited" values for St. Louis River Miles 36 and 94. Overall, the framework displayed in Figures 2 and 3 remains a useful qualitative guide to describe St. Louis River watershed isotopic trends in the context of the sulfate reduction and re-equilibration/reoxidation processes, though as previously cautioned, there are likely other processes affecting isotope composition in certain settings that preclude direct application of the model without collection of confirming information.

4.2. Sulfur cycling in a sulfate-impacted wetland: Long Lake Creek

Isotopic data for samples from the Long Lake Creek wetland (see map, Figure 6) and associated sampling sites sampled in 2012 are highlighted in Figures 7 and 8. This site was flooded by mine-waters in the fall of 2011, prior to the present study. During the study, there were several large rainfall events in May and June, but the impact of these was small compared to the flooding that occurred when mine waters were pumped through the wetland (see Johnson et al., 2014).

Water entering the wetland inlet (Site 4) prior to the flooding event had an average $\delta^{34}S_{SO4}$ of +7.7‰ and an average $\delta^{18}O_{SO4}$ of -5.4‰. These values are consistent with derivation from the oxidation of primary sulfide minerals within the iron formation, possibly followed by a small amount of sulfate reduction. Examination of the area by air photos suggest this water is derived from runoff and seepage from extensive mine-wastes in the region north of the wetland. Consequently, sulfate concentrations averaged 269 mg/L. At the wetland outlet (Site 5), approximately 0.7 miles to the south, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values prior to mine-water flooding averaged +16.5‰ and +6.6‰, respectively, with average sulfate concentration of 174 mg/L. The positive shift in both $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ compared to the wetland inlet suggest that a significant amount of sulfate reduction occurs as the waters pass through this portion of the wetland. Between the wetland outlet and the confluence sites (Site 6), $\delta^{34}S_{SO4}$ values continued to increase, averaging +18.9% just above the confluence with the St. Louis River. However, $\delta^{18}O_{SO4}$ values at this site are lower than at the outlet. Sulfate concentration at the confluence during this period is only about 10% of that measured at the wetland outlet (avg. ~15 mg/L). indicating that the high-sulfate water from the wetland outlet is diluted by a large volume of lowsulfate water along its path to the confluence. Thus, both mixing and continued sulfate reduction are likely important processes in this part of the watershed.

A 2010 study at Long Lake Creek showed a similar pattern of increasing $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ between the wetland inlet and outlet (Berndt and Bavin, 2011). The authors applied the Rayleigh model using average sulfate isotopic compositions at the wetland inlet and outlet and a 17‰ fractionation effect (as in the isotope framework), and results indicated that approximately 25% of the sulfate was lost due to reduction (*f*=0.75) as water moved through the wetland. In this study, however, conditions were quite different from those in 2010, owing to the sequence of flooding events. Flooding with mine-waters has provided additional insights on mixing and reduction processes in this wetland complex that were not apparent in the previous study. More specifically, it was found that when this wetland is flooded periodically by mine waters from nearby pits, it receives (and stores) a large amount of sulfate that is isotopically distinct from that brought into the wetland during other periods (See Johnson et al., 2014).

The presence of this additional sulfate component became especially conspicuous when the supplemental pumping began in September 2012. At this point, the $\delta^{34}S_{SO4}$ values at all 3 sites converged at approximately +12.0‰ (Figure 8A), dominated apparently by sulfate from the source pit waters which had sulfate concentrations around 500 mg/L. A +12.0‰ value for

 $\delta^{34}S_{SO4}$ is distinctly elevated for Iron Range source waters having such negative $\delta^{18}O_{SO4}$ values of -5 to -6‰ (refer to Figure 3). Finding the reason for this would require further study, but it is evidently a persistent characteristic for the water pumped into the wetland.

Interestingly, the $\delta^{18}O_{SO4}$ of the water at the confluence during the pumping period is elevated compared to upstream sites, while $\delta^{34}S_{SO4}$ at all three sites is approximately the same. Does this imply the presence of cryptic sulfur cycling processes taking place in the region between the wetland outlet and confluence? To examine this question, we plot SO₄/Mg ratios for the three Long Lake Creek sites for samples collected both prior to and following flooding of the wetland complex by the mine-water (Figure 9). Because magnesium is abundant in mine waters and typically conservative (e.g., remains in solution) in this region, SO₄/Mg ratios can be used to determine if sulfate is lost or gained (see Berndt et al., 2014 and Johnson et al., 2014). If a truly cryptic sulfur cycling process occurred in the area between the wetland outlet and the confluence, we would expect SO₄/Mg ratios for the sites to be constant. Instead, SO₄/Mg ratios were higher at the confluence then they were at either wetland site during the mine-water pumping event. This indicates that SO₄ must have been mobilized from the wetland by the flooding event.

Some fraction of the sulfate in mine waters that previously inundated the area may be stored in between flooding events, and then remobilized during subsequent flooding events. Isotopically, the sulfate mobilized from the wetland must have $\delta^{34}S_{SO4}$ values close to those of the mine water, but $\delta^{18}O_{SO4}$ values that are much higher. Such a process is consistent with the complete reduction of the stored fraction of sulfate (to preserve the $\delta^{34}S_{SO4}$ value, similar to that of the flood water) and then subsequent re-oxidation of this pool during the period between flooding events.

4.3. Sulfur cycling in sulfate-impacted lakes

4.3.1. Lake Manganika

Past investigations at and around Lake Manganika revealed periodically high MeHg concentrations at the lake outlet and downstream on the East Two River (Berndt and Bavin, 2009; 2011), prompting additional studies to determine if/where sulfate reduction occurs, and whether sulfate reduction is linked to mercury methylation and demethylation processes in the lake environment. Previously, it appeared as though the lake remained fairly well mixed throughout the summer months, despite reduced O₂ levels in the bottom waters. The standing theory was that sulfate reduction and mercury methylation occurred within the sediments and then diffused into the overlying waters, where H₂S was rapidly oxidized and MeHg circulated towards the outlet (Berndt and Bavin, 2011). The site was revisited in 2012 and 2013 to evaluate this interpretation, with the addition of intensive lake water and sediment sampling (see map Figure 10). Bailey et al. (2014a; 2014b) present a detailed look at methylmercury production and transport in the lake environment, while this study focuses on sulfate concentrations and

isotopic signatures of sulfur species in the lake and surrounding waters. During 2012 and likely during 2013, the lake became temporarily but strongly stratified, isolating the bottom waters, where MeHg was produced from the outlet stream. Thus, rather than the high MeHg concentrations observed previously for this lake, the outlet from the lake had very low MeHg concentrations (Bailey et al., 2014a; 2014b).

The sulfate isotope data for the East Two River watershed sampling sites, including lake waters, are shown in Figure 11. Inlet 2, which receives drainage from a nearby mining area, has values consistent with primary sulfide oxidation, averaging +5% for $\delta^{34}S_{SO4}$ and -10.8% for $\delta^{18}O_{SO4}$. Inlet 1, the municipal water source, has slightly more positive $\delta^{34}S_{SO4}$ values, averaging +6.9%, but considerably more positive $\delta^{18}O_{SO4}$, averaging -2.2%. Lake surface and outlet waters approximately overlap, with $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values representing a mix between the compositions of the two inlets. Surface water $\delta^{34}S_{SO4}$ is relatively consistent throughout the sampling season. Bottom water $\delta^{34}S_{SO4}$, on the other hand, changed dramatically between the summer and fall sampling trips (see Figure 11 and Figure 12A). Peak bottom water $\delta^{34}S_{SO4}$ was +23.9% in mid-August, ~18% higher than surface water sulfate was at that time. Enrichment in the heavy isotopes of sulfur is expected with progressive sulfate reduction, according to the Rayleigh model described above. Early warm season conditions were not captured during 2012, but a return trip to Lake Manganika in early June 2013 found anoxic conditions were just beginning to develop in the bottom waters. Bottom water $\delta^{34}S_{SO4}$ was slightly more positive than surface water, then, suggesting that sulfate reduction was occurring but had so far only produced a minor influence on the isotopic composition of the water column's sulfur pool. Similar conditions likely existed at the lake in early 2012.

Bottom water and sediment samples from Lake Manganika were also collected for analysis of $\delta^{34}S_{H2S}$. Results are listed in Table 4. Dissolved iron concentrations are very low in Lake Manganika waters (Appendix A), and thus, the lake's bottom waters became "euxinic" or "sulfidic", with produced sulfide accumulating in the water column rather than combining with iron and precipitating out. A comparison of the $\delta^{34}S$ for each bottom water species, along with surface water $\delta^{34}S_{SO4}$, is shown in Figure 12A. Bottom water $\delta^{34}S_{SO4}$ and $\delta^{34}S_{H2S}$ generally track each other through early September. During the final two 2012 sampling trips, the lake began to turnover, oxygenating the bottom waters and rendering us unable to capture enough H₂S from the bottom waters for isotopic analysis. Bottom water sulfate isotopic composition equilibrated with surface waters at this time, along with sulfate concentrations. The linked evolution of sulfate and sulfide from Lake Manganika bottom waters provides compelling evidence that, at least when the lake is stratified, sulfate reduction is taking place in the water column rather than the sediments.

The average $\Delta_{SO4-H2S}$ in Lake Manganika bottom water during the summer of 2012 was 22.1‰, and similarly 20.2‰ at the start of the summer in 2013. One set of paired $\delta^{34}S$ data is available for pore waters from the top 8 inches of lake sediments sampled in October 2012 (Table 4). The $\Delta_{SO4-H2S}$ for the surface sediments (0-2inches) was 10.9‰, and increased to 16.3 ‰ at depth.

Though concurrent bottom water sulfide analysis was unavailable, these values are smaller than the isotope separation observed in the bottom waters and the dissolved sulfate isotope data appear to follow a different trend as well. Furthermore, a microbiological study of Lake Manganika waters and sediment was initiated during the June 2013 sampling trip, in partnership with Dr. Daniel Jones at the University of Minnesota, and preliminary results indicated that the makeup of the sulfate-reducing bacterial communities differed between the bottom waters and the sediments, potentially supporting the above interpretations.

A sulfur mass balance was performed, to determine if sulfur is generally conserved as it cycles between different oxidation states in the bottom water (Figure 12B). It was found that bottom and surface waters total sulfur concentrations generally tracked each other, but that some sulfur appeared to be lost from the water column when the lake was stratified and gained when the lake was not (Figure 12B). This indicates that although much of the interaction occurred within the sediment column, some interaction with sediments likely takes place throughout the year.

The appearance of thiosulfate coincided also with the formation of acetate, formate, and ammonium (see Appendix A), suggesting that the isolated bottom waters experienced a period of rapid bacterial processing not only of sulfate, but also of organic carbon, and nitrogen. Sulfate reducing bacteria sometimes only partially metabolize sulfate, producing intermediate sulfur oxyanions such as thiosulfate instead of sulfide (Fitz and Cypionka, 1990; Sass et al., 1992). Thiosulfate can also be produced by partial oxidation of sulfide (Goldhaber, 1983). If this was the case, these reactions may have occurred in-situ (i.e. within the lake) provided an oxidant (dissolved oxygen, nitrate) was available for sulfur oxidizing bacteria, or may have occurred later during sample processing. How and where the thiosulfate formed is an important distinction and at this point remains unclear from the information collected in this study.

If we assume that thiosulfate was the product of partial reduction reactions in the lake bottom waters, we may also have a reasonable interpretation for the observed isotopic trends. Once produced, thiosulfate can undergo disproportionation to $SO_4^{2^2}$ and H_2S , and/or re-oxidation to sulfate (Bak and Cypionka, 1987; Jorgensen, 1990). During this process, the newly produced sulfate molecules obtain their additional oxygen atoms from the surrounding water (Mangalo et al., 2007). We might expect, then, that this oxygen exchange would dominate the oxygen isotope signature of residual sulfate, potentially producing different isotopic trend than when sulfate is reduced completely and trapped as sulfide. While most of the DNR isotope samples collected over the years fall within the bounds of the isotope framework developed by Berndt (2011), the suite of samples collected from Lake Manganika bottom waters plots outside of the frame and along a trend with a relatively shallow slope (Figure 13). The isotopic composition of water-oxygen ($\delta^{18}O_{H2O}$) in Lake Manganika bottom waters, as measured in June 2013, was - 9.5‰, and the incorporation of these relatively negative oxygen atoms may contribute to the observed trend. Although the precise sulfate reduction and oxidation path is unknown, the combined evidence from sulfur speciation and the isotope trends indicates that sulfate reduction

does take place in the seasonally isolated bottom waters of Lake Manganika, and that the specific reduction pathway is distinct from that observed elsewhere in the watershed.

4.3.2. Lake McQuade

Previous sampling efforts in the West Two Rivers watershed provided evidence that oxygen isotope re-equilibration was taking place between the mining stream headwaters and the downstream locations (Berndt and Bavin, 2012). The 2012 MWRAP study did not include the mining headwaters sites, so we are unable to adequately evaluate this interpretation with the updated data set. However, based on the data that was collected, it appears as though sulfate reduction and mixing are largely responsible for the observed trends within the West Two River watershed and within Lake McQuade. The map in Figure 14 highlights the associated sampling locations, with the isotopic data presented in Figure 15. For an expanded discussion on Lake McQuade water and sediment chemistry profiles, see Bailey et al. 2014a and 2014b.

Water entering Lake McQuade at its inlet has sulfate concentrations ~50 mg/L early in the summer, rising to an average of 143 mg/L for the remainder of the sampling season between mid-July and mid-October. Within the lake surface waters, sulfate concentrations follow an approximately similar trend, ~30 mg/L in June but more gradually increasing over the late summer/fall to ~112 mg/L (Table 2). Despite gradually increasing surface water sulfate concentration, the bottom water sulfate concentration dropped to a low of ~1 mg/L between June and early August, which precluded isotope sampling for several sampling rounds. Decreasing SO₄/Mg ratios though mid-August, along with a minor shift towards more positive $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$ values at the outlet as compared to the inlet, suggests that sulfate is lost in Lake McQuade bottom waters as a result of active bacterial sulfate reduction (refer to Appendix A). A minor, late-summer turnover event injected sulfate from the oxygenated surface waters into the previously low-sulfate hypolimnion. Bottom water $\delta^{34}S_{SO4}$ values from the subsequent sampling round in early September were more positive than the surface water (10.9% vs. 8.3%), suggesting that sulfate reduction again took place in the bottom waters following the brief turnover event. These multiple lines of evidence imply that sulfate was being reduced in Lake McQuade bottom water during the summer of 2012.

As described by Bailey et al. (2014b), the lake bottom waters had relatively high dissolved iron concentrations, so it is reasonable to conclude that much of the sulfide produced was removed in the form of iron-sulfide precipitates. This condition is referred to as ferruginous, meaning that although anoxic conditions are present, sufficient Fe is available to combine with and precipitate out any sulfide that forms. Because the sulfide is likely segregated from the residual sulfate, however, we should be able to test a Rayleigh fractionation model to quantify the proportion of the sulfate pool that was reduced. Accordingly, a 2.6% difference in δ^{34} S between bottom water and surface water (initial) sulfate for early September correlates to approximately 14% reduced to sulfide, assuming a 17% fractionation effect. This amount is consistent with that expected based on sulfate mass lost for the same time period. No isotope samples were obtained earlier in

the summer when a much larger percentage of the sulfate was reduced. A final lake turnover event occurred in mid-September, and the bottom water geochemical profile again approached that of the surface water. The isolation of the reduced sulfur pool, along with a lack of evidence of sulfur intermediates in the bottom waters, suggests that partial oxidation/reduction reactions are less important here, under ferruginous conditions, than at Lake Manganika, which became sulfidic in the bottom waters.

The West Two River Reservoir sits to the NE of Lake McQuade (Figure 14) and is heavily impacted by mining activity. The $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$ values measured downstream of the reservoir (Site 12) are elevated relative to typical mine waters, suggesting that both sulfate reduction and cycling occur within the reservoir. Based on the isotope ratio data for this site, the cycling that occurred took place under ferruginous conditions, rather than sulfidic. Further downstream, at the West Two River confluence, the isotopic composition of sulfate at the confluence site looks like a variable mixture of sulfate from Lake McQuade and West Two River Reservoir, with no clear evidence for additional sulfur reduction or cycling.

5. Summary

In sum, isotopic sampling during 2012-2013 has provided an updated understanding of sulfate cycling in the St. Louis River watershed.

- The implementation of several techniques for in-house sample treatment/preparation has improved our ability to analyze low-sulfate background waters for $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$, and has also enabled the analysis of sulfidic waters and sediments for $\delta^{34}S_{H2S}$.
- The 2012-2013 sulfate isotope data generally plots within the framework model presented by Berndt (2011), which illustrates the expected isotope trends associated with sulfate reduction and oxygen re-equilibration processes.
- A simple mixing model supports the idea that oxygen re-equilibration, in the form of a cryptic sulfur cycle, is necessary to account for the observed $\delta^{18}O_{SO4}$ values at locations within the St. Louis River watershed.
- Confirming previous results, the large positive shift in $\delta^{34}S_{SO4}$ between the Long Lake Creek wetland inlet and outlet is evidence that a significant amount of sulfate reduction occurs within the wetland complex. However, additional processes involving sulfate storage and re-oxidation of product sulfide within the wetland areas prevents a simple interpretation of the isotopic signal.
- At Lake Manganika, which had bottom waters that became sulfidic over the summer months, the paired analysis of sulfate-sulfide isotopes provides compelling evidence that sulfate reduction occurs mostly within the water column. However, a sulfur balance analysis indicates that sediments were still a sink for sulfur during summer stratification and a sulfur source at other times. Thiosulfate appeared in some of the analyzed samples from the bottom water and it is unclear whether the thiosulfate was produced during

partial reduction or partial oxidation reactions. The $\delta^{18}O/\delta^{34}S$ trend, however, suggest that the reduction (and/or oxidation) pathway is distinct from that occurring in the majority of the watershed.

• At Lake McQuade, where bottom waters remained ferruginous during summer stratification, sulfate reduction also took place with product sulfide combining with reduced iron and precipitating out. Based on the late summer/early fall bottom water isotopic results, approximately 14% of the sulfate was reduced in Lake McQuade bottom waters during the time interval when the samples were collected, consistent with mass-based estimates. Overall, the West Two River watershed data set can be characterized by a combination of sulfate reduction and cycling under largely ferruginous conditions, and mixing.

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Figure 1: (A) Map of the Saint Louis River watershed in NE Minnesota. Mining features associated with the iron formation are shaded brown. 2012 sampling locations are numbered, including site 1-3 on the St. Louis River itself. See Table 1 for a list and description of numbered sites.



Figure 1, continued: (B) Map of the Saint Louis River watershed as in Figure 1A, with color-coded sub-watersheds. Tributary and St. Louis River sites sampled during summer 2013 are labeled. See Table 1 for a list of sites.



Figure 2: All 2012-2013 $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ results plotted with the isotope framework model of Berndt (2011), which serves as a guide to describe both the sulfate reduction and oxygen re-equilibration trends. A Rayleigh model was used to calculate "*f*," the fraction of sulfate remaining, using a 17‰ fractionation effect.



Figure 3: All 2012-2013 $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ data (black triangles) plotted with all previously collected by the DNR from the St. Louis River Watershed (grey circles). The isotope framework model (Berndt, 2011) is also shown. Characteristic compositions of background (non-mining) and mine pits/discharge waters are circled and color coded, along with the data collected from Site 1 along the St. Louis River (SLR) at mile 36.



Figure 4: 2012 SLR and background tributary (**A**) δ^{34} S_{SO4} and (**B**) δ^{18} O_{SO4} data, plotted by date and color coded by site or site type. Grey bars envelop the non-mining data set (SLR 179, Cloquet, Whiteface, and Floodwood Rivers), in general agreement with previously available background data from the Whiteface and Cloquet Rivers (Berndt and Bavin, 2012).



Jul-12 Aug-12 Sep-12 Oct-12 Nov-12 Dec-12 Jan-13 Feb-13 Mar-13 Apr-13 May-13 Jun-13 Jul-13 Aug-13

Figure 5: SLR mixing model for (**A**) $\delta^{18}O_{SO4}$ and (**B**) $\delta^{34}S_{SO4}$. We assign $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$ values for the mining component of -8‰, and +7.5‰, respectively. When mixing "mining" water with "background" water to incrementally double the sulfate load, the model always predicts more negative $\delta^{18}O_{SO4}$, implicating a cryptic sulfur cycle/oxygen re-equilibration process. See text for discussion.



Figure 6: Map showing the MWRAP sampling locations with an emphasis on the Long Lake Creek sites, including the wetland inlet (site 4), wetland outlet (site 5), and confluence (site 6) sites.



Figure 7: $\delta^{18}O_{SO4}$ vs. $\delta^{34}S_{SO4}$ for the 3 Long Lake Creek sites, prior to supplemental pumping (July-early September) from the UTAC mine pits. See Figures 1 and 6 for map locations. The associated full suite of data is presented in Table 2 and Appendix A. The positive trend between the wetland inlet and outlet suggests that a significant amount of sulfate reduction as water moves through the wetland area.



Figure 8: (A) $\delta^{34}S_{SO4}$ and (B) $\delta^{18}O_{SO4}$ for the 3 Long Lake Creek sites, before and during supplemental pumping. Average SO₄ concentrations are indicated in parenthesis. During the summer months, the positive $\delta^{34}S_{SO4}$ shift between the inlet and outlet reflects the impact of sulfate reduction. Once pumping began $\delta^{34}S_{SO4}$ values at all 3 sites converge, while $\delta^{18}O_{SO4}$ at the confluence site had a gradually decreasing, positive offset from the other two upstream locations. See text for discussion.







Figure 10: Map showing the MWRAP sampling locations with an emphasis on the Lake Manganika/East Two River watershed sampling locations, including the lake itself (site 10), two lake inlets (site 7; site 8), the lake outlet (site 9), and the East Two River confluence (site 11).



Figure 11: $\delta^{18}O_{SO4}$ vs. $\delta^{34}S_{SO4}$ for samples from the East Two Rivers watershed, including Lake Manganika surface and bottom waters. See Figures 1 and 12 for map locations.







(**B**) Bottom water sulfur mass balance, including the contribution from sulfate, sulfide, and thiosulfate, compared to surface water sulfate concentration.



Figure 13: Framework model with $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$ data as in Figure 2. The Lake Manganika bottom water trend is highlighted by the green arrow. The slope of this trend is shallower than that seen at other upstream/downstream sites within the watershed, around 0.5, potentially due to the presence and cycling of the intermediate thiosulfate species, S₂O₃.



Figure 14: Map showing the MWRAP sampling locations with an emphasis on the Lake McQuade/West Two River watershed sampling locations, including the lake itself (site 16), lake inlets (site 14), lake outlet (site 15), downstream of the West Two River Reservoir (site 12), and the West Two River confluence near the St. Louis River (site 13).



Figure 15: $\delta^{18}O_{SO4}$ vs. $\delta^{34}S_{SO4}$ for samples from the West Two River watershed, including Lake McQuade surface and bottom waters. See Figures 1 and 10 for map locations. The associated full suite of data is presented in Appendix A. For additional discussion of Lake McQuade water and sediments, see Bailey et al. 2014a and 2014b.



Table 1: (A) 2012 and (B) 2013 MWRAP sampling sites and associated site numbers. For amap of sampling locations, see Figure 1A and 1B, respectively.

(A)

2012 Site #	Description	MWRAP Reference
1	St. Louis River Mile 36, Cloquet	1, 2
2	St. Louis River Mile 94, Forbes	1, 2
3	St. Louis River Mile 179, Skibo	1, 2
4	Long Lake Creek Wetland Upstream	3
5	Long Lake Creek Wetland Downstream	3
6	Long Lake Creek Confluence	3
7	Lake Manganika Inlet 1 (City Wastewater)	
8	Lake Manganika Inlet 2 (Mine discharge)	
9	Lake Manganika Outlet	
10	Lake Manganika	4
11	East Two River Confluence	
12	West Two River Downstream of Reservoir	
13	West Two River Confluence	
14	Upstream of Lake McQuade	
15	Downstream of Lake McQuade	
16	Lake McQuade	4
17	West Swan River	
18	Swan River Confluence	

- 1. Berndt et al, 2014
- 2. Jeremiason et al., 2014a; 2014b
- 3. Johnson et al., 2014
- 4. Bailey et al., 2014a; 2014b

(B)

2013 Site #	Description
S003-973	St. Louis River Mile 36, Cloquet
S000-119	St. Louis River Mile 94, Forbes
S000-631	St. Louis River Mile 179, Skibo
S005-147	Cloquet River
S005-755	Floodwood River
S005-763	Whiteface River
S005-770	Swan River
S004-601	West Two River
S007-615	East Two River
S005-751	Embarrass River
S005-752	Partridge River

Site	Site 1, St. Louis River Mile 36		Site 2	2, St. Louis R	iver Mile 94	Site 3	, St. Louis Ri	ver Mile 179	
Data	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O _{SO4}	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O _{SO4}	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O _{SO4}
Date	mg/L	‰ VCDT	‰ VSMOW	mg/L	‰ VCDT	‰ VSMOW	mg/L	‰ VCDT	‰ VSMOW
16-May-12	10.4			25.3			4.0		
4-Jun-12	8.0			18.5			2.6		
27-Jun-12	4.4			13.4			1.3		
18-Jul-12	10.3			23.5			1.1		
30-Jul-12	10.7			34.1	7.9	-1.6	0.9		
13-Aug-12	13.6	8.6	2.1	36.0	8.0	-0.5	0.9		
28-Aug-12	17.7	8.7	0.74	53.5	7.8	-0.3	1.6		
11-Sep-12	16.0	8.2	1.1	65.2	8.4	0.2	2.1		
25-Sep-12	15.2	8.2	0.59	94.3	8.7	-1.4	3.0	5.0 (R)	2.1 (R)
15-Oct-12	21.7	8.6	0.26	134.3	9.4	-1.5	3.0	5.1 (R)	2.4 (R)
29-Oct-12	38.7	9.5	0.04	104.1	9.3	-0.5	2.7	6.9 (R)	5.5 (R)
17-Dec-12	26.7	9.0	0.90	86.6	9.1	0.08	2.6	5.7 (R)	7.3 (R)
30-Jan-13	21.7			100.4			3.1		
26-Feb-13	20.5			90.2			3.3		

Table 2: SO_4 concentration and SO_4 isotope data for the 2012 MWRAP sampling sites. An (R) indicates that the sample was collected by passing multiple liters of water through anion exchange resin to capture SO_4 . For a map of sampling locations, see Figure 1A. The full data set is presented in Appendix A.

Site	Site 4, Long Lake Creek Inlet		Site 5	Site 5, Long Lake Creek Outlet			Site 6, Long Lake Creek Confluence		
Data	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O _{SO4}	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O ₅₀₄	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O _{SO4}
Date	mg/L	‰ VCDT	‰ VSMOW	mg/L	‰ VCDT	‰ VSMOW	mg/L	‰ VCDT	‰ VSMOW
16-May-12	246.4			135.1			33.7		
6-Jun-12	262.2			78.4			24.3		
26-Jun-12	280.6			74.3			21.5		
17-Jul-12	291.3			140.2			19.1		
31-Jul-12	197.3	9.0	-6.0	143.1	15.2	6.1	17.0	6.2	5
14-Aug-12	273.8	6.6	-4.8	170.6	16.5	6.3	16.7	18.1	4.1
27-Aug-12	298.7	7.4	-5.4	185.0	17.2	6.5	12.4	19.4	4.4
10-Sep-12	306.3	7.9	-5.5	197.7	17.1	7.4	14.8	19.2	4.7
19-Sep-12	519.0	11.8	-6.0	482.5	12.0	-4.8	363.7	11.8	-1.9
24-Sep-12	520.2	11.6	-5.5	494.3	11.6	-4.9	402.5	12.0	-2.9
2-Oct-12	528.2	11.7	-5.5	519.3	11.6	-4.8	480.3	11.7	-3.4
9-Oct-12	532.2	11.7	-6.1	518.9	14.5	-5.0	488.7	11.9	-3.8
16-Oct-12	384.5	11.7	-5.2	412.3	12.0	-4.9	384.2	12.1	-3.2
30-Oct-12	493.0	12.3	-5.5	395.4	12.38	4.71	347.3	12.4	-3.3
17-Dec-12							344.8	13.4	-3.8

Table 2, continued:

Site	Site 7, Inlet 1 Lake Manganika			Site 8	Site 8, Inlet 2 Lake Manganika			Site 9, Outlet Lake Manganika		
Data	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O _{SO4}	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O _{SO4}	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O _{SO4}	
Date	mg/L	‰ VCDT	‰ VSMOW	mg/L	‰ VCDT	‰ VSMOW	mg/L	‰ VCDT	‰ VSMOW	
17-May-12	111.0			537.9			295			
6-Jun-12	116.5			529.0			230			
28-Jun-12	121.3			604.0			212			
17-Jul-12	122.0			655.4	3.9	-10.7	275	-6.3	-6.9	
1-Aug-12	123.1	7.0	-3.7	719.5	5.1	-11.1	305	5.9	-6.3	
15-Aug-12	113.1	6.6	-3.8	711.3	5.0	11.0				
29-Aug-12	122.1	7.3	-2.4	656.1	5.1	-10.8				
12-Sep-12	126.4	6.6	-1.6							
26-Sep-12	128.1	7.1	-2.2							
16-Oct-12	108.4	7.1	0.3	715.3	6.1	-10.5	445	7.6	-5.3	

Site	Site 10-1	S, Lake Manganika	a, surface*	Site 10-1	Site 10-1B, Lake Manganika, bottom*			
Data	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O ₅₀₄	SO4 [#]	$\delta^{34}S_{SO4}$	$\delta^{18}O_{SO4}$		
Date	mg/L	‰ VCDT	‰ VSMOW	mg/L	‰ VCDT	% VSMOW		
25-Jun-12	212.6			266.6				
10-Jul-12	250.3			280.3				
24-Jul-12	287.2	-6.9	5.3	201.3	-2.4	14.0		
7-Aug-12	331.4	-6.6	5.5	105.8	1.7	23.8		
21-Aug-12	370.1	-7.2	5.6	106.6	-2.3	15.4		
5-Sep-12	391.0	-6.3	5.4	229.2	-3.3	12.9		
17-Sep-12	408.1	-5.6	5.6	461.6	-6.5	5.9		
6-Oct-12	450.8	-6.0	6.3	482.6	-6.8	5.7		
4-Jun-13	322.0	-5.4	7.6	395.0	-3.8	9.8		

*See Table 4 for additional Lake Manganika isotope data. [#]Samples were purged with N_2 gas to remove H_2S

Site	Site 11,	East Two Rivers C	onfluence
Data	SO4	δ ³⁴ S ₅₀₄	δ ¹⁸ O _{SO4}
Date	mg/L	‰ VCDT	‰ VSMOW
16-May-12	128.4		
5-Jun-12	104.9		
27-Jun-12	98.2		
16-Jul-12	112.0		
31-Jul-12	131.2	7.0	-3.0
13-Aug-12	157.6	6.5	-3.7
27-Aug-12	167.4	6.5	-3.5
10-Sep-12	192.7	6.4	-3.7
24-Sep-12	214.9	5.7	-4.2
15-Oct-12	217.1	5.6	-4.0

Table 2, continued:

Site	Site 12	, Downstrea	am West Two	Site	e 13, West T	wo Rivers	Site	14, Upstrear	n McQuade
Site		Rivers	5		Conflue	nce		Lake	
Data	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O ₅₀₄	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O ₅₀₄	SO4	$\delta^{34}S_{SO4}$	δ ¹⁸ O ₅₀₄
Date	mg/L	‰ VCDT	‰ VSMOW	mg/L	‰ VCDT	% VSMOW	mg/L	‰ VCDT	% VSMOW
17-May-12	141.7			49.4			51.7		
7-Jun-12	149.3			73.5			71.9		
28-Jun-12	130.0			70.1			56.5		
18-Jul-12	117.9			73.8			127.9		
31-Jul-12	112.4	11.2	4.5	66.3	2.1	9.9	137.1	-5.0	6.3
14-Aug-12	112.2	11.5	3.6	74.7	0.4	10.0	157.5	-4.6	6.7
27-Aug-12	109.5	11.6	4.1	84.7	0.2	9.7	133.7	-3.8	8.2
10-Sep-12	114.1	11.1	3.7	81.5	2.4	10.7	162.0	-3.5	7.8
24-Sep-12	117.2	11.0	3.8	104.2	-0.1	9.0	145.3	-2.9	7.2
15-Oct-12	103.1	11.0	4.6	70.9	5.0	10.8	137.4	-3.4	6.9

Site	Site Site 15, Downstream McQuade Lake					
Data	SO4	δ ³⁴ S ₅₀₄	$\delta^{18}O_{SO4}$			
Date	mg/L	‰ VCDT	‰ VSMOW			
16-May-12	51.9					
7-Jun-12	45.1					
28-Jun-12	32.2					
18-Jul-12	61.8					
31-Jul-12	69.9	7.9	-2.6			
14-Aug-12	84.1	7.9	-2.5			
27-Aug-12	97.2	8.2	-2.3			
10-Sep-12	107.9	9.7	-2.0			
24-Sep-12	118.5	8.0	-2.1			
15-Oct-12	118.6	8.9	-0.2			

Site	Site 16-	1S, McQuade Lake	e, surface	Site 16-1B, McQuade Lake, bottom			
Data	SO ₄	δ ³⁴ S ₅₀₄	δ ¹⁸ O ₅₀₄	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O ₅₀₄	
Date	mg/L	% VCDT	‰ VSMOW	mg/L	‰ VCDT	‰ VSMOW	
25-Jun-12	31.2			15.6			
10-Jul-12	35.3			15.4			
25-Jul-12	57.0	7.56	-2.01	6.2			
7-Aug-12	77.5	7.89	-2.73	1.4			
21-Aug-12	89.1	8.04	-2.66	71.1	8.5	-2.0	
6-Sep-12	101.8	8.29	-2.86	78.8	10.9	-1.5	
17-Sep-12	106.3	8.75	-2.58	106.7	8.7	-2.8	
4-Oct-12	112.5	8.68	-1.5	111.9	8.6	-1.1	

Table 2, continued:

Site	Site 17,	West Swan River	@ Hwy 73	Site 1	8, Swan River Con	fluence
Data	SO ₄	$\delta^{34}S_{SO4}$	$\delta^{18}O_{SO4}$	SO ₄	$\delta^{34}S_{SO4}$	δ ¹⁸ O _{SO4}
Date	mg/L	‰ VCDT	‰ VSMOW	mg/L	‰ VCDT	% VSMOW
15-May-12	14.2			19.1		
7-Jun-12	5.9			10.0		
27-Jun-12	7.5			7.8		
16-Jul-12	1.1			27.0		
30-Jul-12	3.9			17.2	0.8	4.7
13-Aug-12	4.9			27.3	-0.9	4.9
28-Aug-12	3.1			48.3	0.0	4.0
11-Sep-12	1.1			55.9	-1.2	4.1
25-Sep-12	1.5	12.5 (R)	4.2 (R)	57.6	0.5	4.1
16-Oct-12	7.1	18.0 (R)	4.3 (R)	44.0	2.4	4.3

64-	Data Canadad	SO ₄	δ ³⁴ S ₅₀₄	δ ¹⁸ Ο ₅₀₄
Site	Date Sampled	mg/L	‰ VCDT	‰ VSMOW
SLR mile 36 (Cloquet)	5-Jun-13	8.7	7.23	3.32
	7-Aug-13	12.7	7.90	2.86
SLR mile 94 (Forbes)	5-Jun-13	19.5	8.77	2.37
	7-Aug-13	35.0	9.56	0.74
SLR mile 179 (Skibo)	5-Aug-13	1.1	5.83 (R)	2.58 (R)
		2.6	C (D (D)	2.50 (D)
Cloquet River	7-Aug-13	2.6	6.60 (R)	2.59 (R)
	7 4	27	2 74 (D)	6 21 (D)
Floodwood River	7-Aug-13	5.7	5.74 (K)	0.21 (K)
Whiteface River	7-Aug-13	1.8	7.01 (R)	3.21 (R)
			()	
Swan River	3-Jun-13	10.9	5.00	4.03
	6-Aug-13	25.2	4.15	3.50
West Two River	5-Jun-13	46.9	9.53	0.66
	6-Aug-13	69.8	9.72	0.80
East Two River	6-Aug-13	148.7	6.89	-2.16
		24.4	0.64	4.40
Embarrass River	4-Jun-13	24.4	9.64	1.48
	6-Aug-13	26.3	8.89	0.15
Doutuidae Diver	2 1	28.6	7 75	2 55
Partriuge River	5-JUII-13	20.0	7.75	2.33 -7 37
	o-Aug-13	00.0	1.30	-2.37

Table 3: SO_4 concentration and SO_4 isotope data for sampling sites visited in 2013. An (R) indicates that the sample was collected by passing multiple liters of water through anion exchange resin to capture SO_4 . For a map of sampling locations, see Figure 1B.

Table 4: Isotopic data for samples collected from Lake Manganika waters and sediments dur	ing
2012-2013. The full suite of physical and geochemical parameters measured for Lake	
Manganika surface and bottom waters are provided in Appendix A.	

Lake Mar	nganika	Date	δ ³⁴ S _{so4} ‰ VCDT	δ ¹⁸ O _{so4} ‰ VSMOW	δ ³⁴ S _{H2S} ‰ VCDT
Surface		June 4, 2013	+7.6	-5.4	
"Chemocline	9"	Trip 11	+7.0	-6.1	
Bottom			+9.8	-3.8	-10.4
Sediments	(0-2cm)		+16.7	+1.4	-3.2
	(2-4cm)		+13.6		+1.2
(4-8cm					+3.0
Surface		October 6, 2012	+6.3	-6.0	
Bottom		Trip 10	+5.7	-6.8	
Sediments	(0-2cm)		+14.9	+3.4	+4.0
	(2-4cm)		+13.1	+1.5	+1.7
	(4-8cm)		+8.7		-7.6
Surface		September 17,	+5.8	-5.6	
Bottom		Trip 9	+5.9	-6.5	
Surface		September 5.	+5.4	-6.3	
Bottom		Trip 8	+12.9	-3.3	-8.9
Surface		August 21, 2012	+5.6	-0.2	
Bottom		Trip 7	+15.5	-2.3	-1.2
Surface		August 7, 2012	+5.5	-6.6	
Bottom		Trip 6	+23.8	+1.7	-4.1
Surface		July 24, 2012	+5.3	-6.9	
Bottom		Trip 5	+14.0	-2.4	-7.8
Sediments	(0-2cm)				+1.3
	(2-4cm)				+6.6
	(4-8cm)				+6.0

Appendix A: Physical and chemical parameters measured at MWRAP sampling sites in May-October 2012. All values are in mg/L unless otherwise noted. Isotope values marked with an (R) indicates that the sample was collected by passing multiple liters of water through anion exchange resin to capture SO₄. For a map of sampling locations, see Figure 1A.

Site 1, St. Louis River Mile 36

Temperature (°C) 16.9 17.1 19.6 24.4 25.6 22.3 23.6 18.4 12.9 7.2 5.2 pH 7.55 7.05 6.85 7.47 7.4 7.03 7.91 7.88 8.12 8.43 6.28 7.82 7.24 7.29 Sp Cond (µS/cm) 167 115 90 153 175 197 218 223 210 241 315 7.24 7.29 Alkalinity (mg/L) 55 35 17.5 50 62.5 55 77.5 80 80 90 105 80 80 78 DO (mg/L) 9.6 7.6 5.9 5.5 6.5 6.5 7.7 7.9 10.2 13.2 13.5 78 ORP (mv) 87 64 119 233 100 135 150 88 -72 111 153 SUVA (L/mg C/m) 3.9 4.2 4.3 4.3 4.1 3.8 <th>Date</th>	Date
pH 7.55 7.05 6.85 7.47 7.4 7.03 7.91 7.88 8.12 8.43 6.28 7.82 7.24 7.29 Sp Cond (µS/cm) 167 115 90 153 175 197 218 223 210 241 315 155 355 35 17.5 50 62.5 55 77.5 80 80 90 105 80 80 78 D0 (mg/l) 9.6 7.6 5.9 5.5 6.5 6.5 7.7 7.9 10.2 13.2 13.5 78 78 ORP (mv) 87 64 119 233 100 135 150 88 -72 111 153 75 50 6.5 6.5 7.7 7.9 10.2 13.2 13.5 75 75 80 80 90 10.5 10.5 16.3 17.1 13.5 83 6.2 3.3 3.6 3.8 3.6	Temperature (°C)
Sp Cond (µS/cm) 167 115 90 153 175 197 218 223 210 241 315 Alkalinity (mg/L) 55 35 17.5 50 62.5 55 77.5 80 80 90 105 80 80 78 D0 (mg/L) 9.6 7.6 5.9 5.5 6.5 6.5 7.7 7.9 10.2 13.2 13.5 78 78 ORP (mv) 87 64 119 233 100 135 150 88 -72 111 153 75 50 6.5 77 7.9 10.2 13.2 13.5 78 78 SUVA (L/mg C/m) 3.9 4.2 4.3 4.3 4.1 3.8 3.6 3.8 3.6 73 73 73 73 73 73 73 73 73 73 73 73 73 73 73 73 73 73 73 <	рН
Alkalinity (mg/L) 55 35 17.5 50 62.5 77.5 80 80 90 105 80 80 78 D0 (mg/L) 9.6 7.6 5.9 5.5 6.5 6.5 7.7 7.9 10.2 13.2 13.5 15.5 15.5 6.5 7.7 7.9 10.2 13.2 13.5 15.5	Sp Cond (µS/cm)
D0 (mg/L) 9.6 7.6 5.9 5.5 6.5 6.5 7.7 7.9 10.2 13.2 13.5 ORP (mv) 87 64 119 233 100 135 150 88 -72 111 153 SUVA (L/mg C/m) 3.9 4.2 4.3 4.5 4.3 4.3 4.1 3.8 3.6 3.8 3.6 AI 0.05 0.12 0.16 0.11 0.09 0.06 0.03 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.03 0	Alkalinity (mg/L)
ORP (mv) 87 64 119 233 100 135 150 88 -72 111 153 SUVA (L/mg C/m) 3.9 4.2 4.3 4.5 4.3 4.3 4.1 3.8 3.6 3.8 3.6 AI 0.05 0.12 0.16 0.11 0.09 0.06 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.03 0.06 0.35 0.66	DO (mg/L)
SUVA (L/mg C/m) 3.9 4.2 4.3 4.5 4.3 4.1 3.8 3.6 3.8 3.6 AI 0.05 0.12 0.16 0.11 0.09 0.06 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.01 0.01 0.01 0.01 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.01 0.01 0.02 0.02 0.02 0.02 0.0	ORP (mv)
Al 0.05 0.12 0.16 0.11 0.09 0.06 0.03 0.02 0.03 0.02 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.03 0.02 0.02 0.03 0.03 0.02 0.02 0.02 0.03 0.02 0.02 0.02 0.03 0.02 0.02 0.02 0.03 0.02 0.02 0.02 0.01 0.01 Ca 15.0 11.6 10.5 16.3 17.1 17.9 19.3 17.9 19.1 20.5 25.2 21.28 21.03 20.29 Fe 0.40 0.52 0.83 2.18 1.71 1.51 0.79 0.37 0.29 0.35 0.36 0.53 0.60 <th>SUVA (L/mg C/m)</th>	SUVA (L/mg C/m)
Ba 0.01 0.06 0.10 0.03 0.07 0.02 0.02 0.03 0.03 0.02 0.02 0.03 0.03 0.02 0.02 0.01 0.01 Ca 15.0 11.6 10.5 16.3 17.1 17.9 19.3 17.9 19.1 20.5 25.2 21.28 21.03 20.29 Fe 0.40 0.52 0.83 2.18 1.71 1.51 0.79 0.37 0.29 0.35 0.36 0.53 0.60 0.53 K 0.93 0.85 0.93 1.28 1.33 1.29 1.39 1.31 1.50 1.91 1.64 1.69 1.44 Mg 6.0 6.0 4.4 9.3 9.8 11.4 13.1 12.0 12.2 14.4 21.1 16.02 14.08 13.34 Mn 0.09 0.07 0.06 0.12 0.09 0.06 0.01 0.01 0.03 0.04 0.04	AI
Ca 15.0 11.6 10.5 16.3 17.1 17.9 19.3 17.9 19.1 20.5 25.2 21.28 21.03 20.29 Fe 0.40 0.52 0.83 2.18 1.71 1.51 0.79 0.37 0.29 0.35 0.36 0.53 0.60 0.53 K 0.93 0.85 0.93 1.28 1.33 1.29 1.39 1.31 1.50 1.91 1.64 1.69 1.44 Mg 6.0 6.0 4.4 9.3 9.8 11.4 13.1 12.0 12.2 14.4 21.1 16.02 14.08 13.34 Mn 0.09 0.07 0.06 0.12 0.09 0.06 0.01 0.01 0.03 0.04 0.04 0.05 0.05	Ва
Fe 0.40 0.52 0.83 2.18 1.71 1.51 0.79 0.37 0.29 0.35 0.36 0.53 0.60 0.53 K 0.93 0.85 0.93 1.28 1.33 1.29 1.39 1.31 1.50 1.91 1.64 1.69 1.44 Mg 6.0 6.0 4.4 9.3 9.8 11.4 13.1 12.0 12.2 14.4 21.1 16.02 14.08 13.34 Mn 0.09 0.07 0.06 0.12 0.09 0.06 0.01 0.01 0.03 0.04 0.04 0.05 0.05	Са
K 0.93 0.85 0.93 1.28 1.33 1.29 1.39 1.31 1.50 1.91 1.64 1.69 1.44 Mg 6.0 6.0 4.4 9.3 9.8 11.4 13.1 12.0 12.2 14.4 21.1 16.02 14.08 13.34 Mn 0.09 0.07 0.06 0.12 0.09 0.06 0.01 0.01 0.03 0.04 0.04 0.05 0.05	Fe
Mg 6.0 6.0 4.4 9.3 9.8 11.4 13.1 12.0 12.2 14.4 21.1 16.02 14.08 13.34 Mn 0.09 0.07 0.06 0.12 0.09 0.06 0.01 0.01 0.03 0.04 0.04 0.05 0.05	к
Mn 0.09 0.07 0.06 0.12 0.09 0.06 0.01 0.01 0.01 0.03 0.04 0.04 0.05 0.05	Mg
	Mn
Na 5.2 3.5 2.6 5.0 5.1 6.0 6.7 6.2 6.3 7.3 9.9 7.64 7.61 7.01	Na
P 0.01 0.02 0.03 0.04 0.04 0.03 0.02 0.00 0.00 0.01 0.01 0.02 0.01 0.01	Р
Si 1.8 2.8 3.1 4.5 4.9 4.9 4.1 3.1 3.6 4.1 4.0 5.10 5.53 5.25	Si
Sr 0.04 0.04 0.03 0.05 0.05 0.06 0.06 0.06 0.06 0.06 0.07 0.06 0.07 0.06	Sr
Fluoride 0.08 0.08 0.07 0.09 0.11 0.14 0.12 0.12 0.14 0.13 0.13 0.11	Fluoride
Acetate <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 <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 <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 <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 <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 <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 <0.01 <0.01 <0.01 <	Acetate
Formate <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 <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 <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 <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 <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 <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 <0.01 <0.01 <0.01 <	Formate
Chloride 5.2 2.7 1.7 4.0 4.6 4.8 5.5 5.7 5.6 6.4 9.69 6.9 7.4 6.7	Chloride
Nitrite-N <0.002 <0.002 <0.002 0.005 0.005 0.003 <0.002 <0.002 <0.002 <0.002 <0.002 0.000 0.00 0.	Nitrite-N
Bromide <0.006 <0.006 <0.005 0.008 0.011 0.009 0.008 <0.005 <0.005 <0.005 <0.005 0.01 0.01 0.01	Bromide
Nitrate-N 1.04 0.08 0.06 0.22 0.54 0.21 0.047 <0.001 0.025 <0.001 0.041 0.37 0.40 0.34	Nitrate-N
Sultate 10.4 8.0 4.4 10.3 10.7 13.6 17.7 16.0 15.2 21.7 38.7 26.7 21.7 20.5	Sulfate
	Thiosulfate
Phosphate-P <0.006 0.21 <0.005 <0.005 <0.005 <0.005 <0.005 <0.005 <0.005 <0.005 <0.001 <0.01 <0.01	Phosphate-P
Ammonia-N 0.025 0.040 0.042 0.068 0.041 0.043 0.022 0.026 < 0.020 < 0.020 < 0.020	Ammonia-N
Nitrate/Nitrite $\langle 0.40 \rangle \langle 0$	Nitrate/Nitrite
IKN 0.91 1.2 1.4 1.4 1.3 1.1 0.84 0.64 0.68 0.71 <0.50	TKN
Total P 0.04 0.08 0.09 0.08 0.06 0.05 0.03 0.02 0.02 0.02 0.02	
r-Weng (ng/L) 0.22 0.51 0.42 0.72 0.42 0.59 0.21 0.12 0.07 0.09 0.07	F-IVIENg (ng/L)
ring (ing) (j 3.3 3.3 0.6 0.7 3.1 4.0 3.1 2.0 1.7 1.6 1.4	
100 25.2 25.7 25.3 41.9 25.5 26.1 26.7 15.5 17.7 10.7 15	δ ¹⁸ O ₂₀₁ (‰)
$\delta^{44}S_{504}$ (%) 8.6 8.7 8.2 8.6 9.5 9.0	$\delta^{34}S_{SO4}(\%)$

Site 2,	St. Louis	River Mile 94	

Date	5/15/12	6/5/12	6/27/12	7/16/12	7/30/12	8/13/12	8/28/12	9/11/12	9/25/12	10/15/12	10/29/12	12/17/12	1/28/13	2/26/13
Temperature (°C)	17.4	18.1	20.3	24.7	23.8	20.9	20.1	16.9	9.2	6.6	4.4			
рН	7.9	7.3	7.1	7.5	7.8	7.9	8.1	8.3	8.3	8.4	7.7	7.98	7.42	7.42
Sp Cond (µS/cm)	254	168	140	221	262	282	412	503	581	673	582			
Alkalinity (mg/L)	65	45	45	72.5	75	97.5	135	160	187.5	190	175	140	170	175
DO (mg/L)	9.9	8.1	6.8	6.4	7.3	8.8	8.2	11.3	12.3	15.7	15.6			
ORP (mv)	186	145	124	133	92	121	141	52	-41	137	127			
SUVA (L/mg C/m)	3.7	4.1	4.3	4.4	4.4	4.2	4.0	3.6	3.1	3.3	3.2			
AI	0.04	0.31	0.18	0.14	0.10	0.07	0.04	0.01	0.01	0.01	0.01	0.02	0.01	0.02
Ва	0.02	0.07	0.05	0.04	0.02	0.03	0.02	0.04	0.04	0.03	0.02	0.03	0.03	0.02
Ca	17.4	13.6	12.5	17.2	18.1	20.8	26.0	27.6	33.4	37.9	36.7	32.48	38.99	39.39
Fe	0.33	0.93	1.1	2.7	2.1	1.9	0.95	0.28	0.14	0.19	0.23	0.48	0.49	0.46
к	1.61	1.48	1.30	1.95	1.99	2.41	3.24	3.58	4.96	4.80	4.59	4.04	4.85	4.26
Mg	13.0	9.8	8.2	14.7	17.8	20.6	28.8	31.0	43.1	53.2	44.6	37.29	43.33	39.26
Mn	0.06	0.10	0.08	0.08	0.07	0.08	0.05	0.04	0.06	0.08	0.06	0.05	0.09	0.10
Na	8.4	6.0	4.9	8.3	9.1	11.2	16.0	19.2	23.0	22.9	21.6	18.11	25.22	21.42
Р	0.01	0.03	0.02	0.04	0.03	0.03	0.02	< 0.004	0.00	0.01	0.01	0.01	0.01	0.01
Si	2.0	3.6	3.7	4.6	4.9	4.9	3.3	2.7	3.3	3.7	4.0	5.60	6.95	6.93
Sr	0.06	0.05	0.05	0.06	0.07	0.08	0.10	0.10	0.13	0.13	0.13	0.12	0.15	0.14
Fluoride	0.093	0.080	0.077	0.111	0.143	0.162	0.185	0.213	0.221	0.265	0.217	0.16	0.22	0.21
Acetate	<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
Formate	<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
Chloride	8.1	4.9	3.7	6.3	6.6	8.4	12.3	17.0	16.5	19.3	18.4	15.37	23.70	20.85
Nitrite-N	<0.002	<0.002	<0.002	0.005	0.003	0.003	< 0.002	<0.002	<0.002	<0.002	<0.002	0.00	0.01	0.00
Bromide	<0.006	<0.006	<0.005	0.012	0.016	0.017	0.020	0.025	0.025	<0.005	0.019	0.03	0.04	0.03
Nitrate-N	0.186	1.09	0.077	0.331	0.590	0.299	0.199	0.203	0.073	0.169	0.274	0.61	0.98	0.94
Sulfate	25.3	18.5	13.4	23.5	34.1	36.0	53.5	65.2	94.3	134	104	86.56	100.36	90.19
Thiosulfate	<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
Phosphate-P	<0.006	0.021	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.01	0.01	0.01
Ammonia-N	0.024	0.042	0.045	0.061	0.040	0.044	< 0.020	0.025	< 0.020	< 0.020	0.022			
Nitrate/Nitrite	<0.4	<0.4	<0.4	<0.4	<0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4			
TKN	0.89	1.2	1.5	1.5	1.4	1.1	0.70	0.56	0.58	0.52	< 0.5			
Total P	0.04	0.07	0.11	0.09	0.07	0.04	0.03	0.04	0.02	0.01	0.02			
F-MeHg (ng/L)	0.20	0.35	0.68	1.14	0.56	0.40	0.28	0.08	0.07	0.06	0.09			
F-THg (ng/L)	3.5	6.8	8.3	7.8	5.6	4.3	2.1	2.7	1.2	0.8	0.9			
DOC	21.4	31.2	40.9	42.4	37.3	31.3	20.8	14.8	11.8	9.6	9.3			
δ U _{s04} (‰)					-1.6	-0.5	-0.3	0.2	-1.4	-1.5	-0.5	0.08		
δ ^{~~} S _{sO4} (‰)					7.9	8.0	7.8	8.4	8.7	9.4	9.3	9.1		

Site 3, St.	Louis River Mile 179

Date	5/15/12	6/6/12	6/28/12	7/17/12	8/1/12	8/15/12	8/29/12	9/12/12	9/26/12	10/16/12	10/30/12	12/17/12	1/28/13	2/26/13
Temperature (°C)	16.3	18.6	22.0	25.5	23.8	19.6	19.2	15.3	6.4	5.9	1.9			
рН	7.1	6.4	6.5	6.9	6.7	7.1	7.2	7.4	7.8	8.0	8.7	7.25	6.87	6.84
Sp Cond (µS/cm)	55	46	42	54	63	63	74	89	94	92	72			
Alkalinity (mg/L)	15	12.5	15	17.5	20	25	25	35	40	40	25	25	40	40
DO (mg/L)	9.5	8.8	7.5	6.8	7.5	8.3	8.0	8.7	10.8	12.6	14.4			
ORP (mv)	180	189	149	152	89	102	83	82	-48	155	95			
SUVA (L/mg C/m)	3.7	4.2	4.6		4.6	4.5		4.2	3.9	3.9	3.8			
Al	0.12	0.27	0.31	0.36	0.30	0.27	0.23	0.17	0.12	0.11	0.12	0.21	0.26	0.22
Ва	0.01	0.09	0.05	0.06	0.05	0.03	0.02	0.05	0.03	0.02	0.02	0.01	0.01	0.01
Са	5.1	5.0	5.5	7.0	7.7	8.5	8.6	8.1	8.9	8.1	6.3	7.8	11.2	10.9
Fe	0.5	0.9	1.3	3.1	3.0	4.2	3.6	2.7	1.8	1.8	2.1	2.9	3.2	2.5
к	0.2	0.3	0.4	0.5	0.4	0.6	0.6	0.5	0.6	0.5	0.4	0.6	0.8	0.8
Mg	3.7	3.3	3.1	4.3	5.0	6.0	6.4	5.8	6.4	5.6	4.8	5.9	8.7	8.3
Mn	0.02	0.06	0.10	0.19	0.12	0.09	0.09	0.08	0.06	0.04	0.03	0.0	0.0	0.0
Na	1.9	1.5	1.4	1.6	1.4	1.5	1.9	1.8	2.4	2.3	2.3	2.2	3.2	3.0
Р	0.01	0.01	0.01	0.03	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.0	0.0	0.0
Si	0.3	1.7	2.2	3.5	4.5	5.2	5.1	4.4	5.6	5.5	4.1	6.2	8.3	8.1
Sr	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.04	0.04
Fluoride	0.04	0.05	0.06	0.08	0.08	0.08	0.08	0.07	0.06	0.08	0.06	0.07	0.06	0.06
Acetate	<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
Formate	<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
Chloride	0.39	0.26	0.22	0.27	0.32	0.41	0.63	0.60	0.88	0.58	1.17	0.82	1.28	1.04
Nitrite-N	<0.002	<0.002	<0.002	<0.002	0.003	0.003	<0.002	<0.002	<0.002	<0.002	<0.002	0.00	0.00	0.00
Bromide	<0.006	<0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.01	0.01	0.01
Nitrate-N	0.03	0.06	0.04	0.17	0.38	0.28	0.25	0.15	0.12	0.10	0.10	0.64	0.82	0.46
Sulfate	4.0	2.6	1.3	1.1	0.9	0.9	1.6	2.1	3.0	3.0	2.7	2.6	3.1	3.3
Thiosulfate	< 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
Phosphate-P	<0.006	0.009	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.01	0.01	0.01
Ammonia-N	0.025	0.058	0.060	0.147	0.095	0.062	0.033	0.042	0.041	0.022	0.023			
Nitrate/Nitrite	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40			
TKN	1.08	1.35	1.57	1.76	1.92	1.71	1.48	1.11	0.89	0.77	0.76			
Total P	0.021	0.042	0.039	0.049	0.047	0.048	0.034	0.033	0.026	0.022	0.036			
F-MeHg (ng/L)	0.23	0.49	0.88	1.10	0.81	0.50	0.37	0.15	0.11	0.10	0.09			
F-THg (ng/L)	5.2	11.2	11.8	9.9	10.2	9.0	4.2	3.8	2.6	2.4	2.3			
DOC	30.2	41.7	46.6	54.4	58.8	57.7	47.2	37.2	26.7	22	24.2	= = (=)		
0 U _{SO4} (‰)									2.1 (K)	2.4 (R)	5.5 (R)	7.3 (R)		
δ S _{SO4} (‰)									5.0 (R)	5.1 (R)	ь.9 (R)	5.7 (R)		

Site 4, Long Lake Creek Inlet

Date	5/16/12	6/6/12	6/26/12	7/17/12	7/31/12	8/14/12	8/27/12	9/10/12	9/19/12	9/24/12	10/2/12	10/9/12	10/16/12	10/30/12
Temperature (°C)	5.87	8.28	9.51	9.84	11.88	8.14	7.68	7.02	6.61	6.12	6.62	6.07	9.22	5.28
рН	7.64	7.72	7.84	7.62	7.71	7.67	7.71	7.82	7.93	7.85	7.89	8.04	7.99	8.03
Sp Cond (µS/cm)	1365	1400	1423	1997	1133	1505	1532	1556	1649	1601	1590	1617	1254	1528
Alkalinity (mg/L)	467.5	485	510	570	512.5	600	600	605	430	425	415	417.5	322.5	397.5
DO (mg/L)	11.57	9.5	10.24	8.65	8.92	9.7	10.73	10.08	12.27	12.24	12.92	13.12	12.39	13.67
ORP (mv)				78	50	24	77	-133	104	23	38	2	95	142
SUVA (L/mg C/m)	2.4	2.5	2.3	2.2	2.6	2.2	2.2	1.9	0.9		1.0	0.9	0.9	1.0
Al	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Ва	0.00	0.01	0.02	0.01	0.01	0.01	0.01	0.03	0.01	0.02	0.02	0.02	0.01	0.01
Са	63.8	60.4	58.4	66.9	51.2	69.0	76.2	68.3	89.7	89.6	88.1	87.9	67.2	84.2
Fe	0.03	0.01	0.01	0.03	0.02	0.04	0.03	0.01	0.00	0.02	-0.01	0.00	0.02	0.01
к	14.5	15.7	17.2	18.3	14.8	17.7	17.9	16.0	11.4	11.8	11.7	11.9	10.9	11.6
Mg	130.4	147.6	153.6	155.6	135.0	153.8	161.2	146.2	174.5	176.5	175.3	175.6	133.6	169.5
Mn	0.07	0.04	0.02	0.14	0.05	0.19	0.32	0.23	0.82	0.96	1.06	0.69	0.40	0.51
Na	27.8	25.3	27.6	34.3	23.5	35.5	40.3	38.4	27.9	28.6	28.4	28.4	24.0	27.9
Р	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Si	4.4	4.3	4.2	5.0	4.7	5.5	5.7	5.0	5.4	5.4	5.2	5.2	4.2	5.0
Sr	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2
Fluoride	0.14	0.14	0.14	0.13	0.16	0.16	0.19	0.15	0.06	0.08	0.06	0.06	0.10	0.09
Acetate	< 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	<0.02
Formate	< 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	<0.02
Chloride	3.0	2.7	2.3	2.2	2.6	2.5	2.4	2.6	39.2	39.5	38.9	38.5	31.8	35.7
Nitrite-N	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.004
Bromide	<0.006	<0.006	0.009	0.010	0.013	0.014	0.018	0.015	0.046	0.043	0.045	0.044	<0.005	<0.01
Nitrate-N	0.71	0.73	1.18	1.27	1.52	1.44	1.68	1.54	0.07	0.13	0.17	0.16	0.05	0.16
Sulfate	246.4	262.2	280.6	291.3	197.3	273.8	298.7	306.3	519.0	520.2	528.2	532.2	384.5	493.0
Thiosulfate	< 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	<0.02
Phosphate-P	<0.006	<0.006	<0.005	<0.005	<0.005	< 0.005	<0.005	< 0.005	<0.005	<0.005	<0.005	<0.005	< 0.005	<0.01
Ammonia-N	<0.02	< 0.02	<0.02	0.054	< 0.02	0.021	< 0.02	0.021	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Nitrate/Nitrite	<0.4	0.76	1.14	1.24	0.76	1.47	1.62	1.6	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40
TIKN	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Iotal P	0.018	0.021	0.022	0.025	0.021	0.026	0.019	0.026	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
F-IVIENg (ng/L)	0.02	0.37	0.05	0.08	0.05	0.09	0.07	0.03	0.01	0.00	0.02	0.03	0.02	0.01
F-THg (ng/L)	2.3	1.27	0.99	3.29	1.07	0.63	0.44	0.33	0.22	0.24	0.22	0.23	0.18	0.18
δ ¹⁸ Ο (%-)	5.9	5.5	4.1	5	4.4	5.8 _/L 9	-5.4	4.3	1.8	-5.5	1.6	1./ -6.1	1.4 -5.2	1.5
$\delta^{34}S_{34}(\%)$					-0.0	-4.0	-3.4	-3.5	-0.0	-3.5	-3.5	-0.1	-3.2 11 7	-3.5
U J _{SO4} (700)					5.0	0.0	/.4	1.5	11.0	11.0	11./	11./	11./	12.5

Site 5, Long Lake Creek Outlet

Date	5/16/12	6/6/12	6/26/12	7/17/12	7/31/12	8/14/12	8/27/12	9/10/12	9/19/12	9/24/12	10/2/12	10/9/12	10/16/12	10/30/12
Temperature (°C)	15.2	19.5	21.6	26.0	24.5	18.2	18.2	12.7	9.7	7.9	8.7	5.2	8.5	3.9
рН	8	8	7	8	8	8	8	8	8	8	8	8	8	8
Sp Cond (µS/cm)	751	604	564	816	800	1006	1047	1086	1649	1590	1623	1629	1385	1305
Alkalinity (mg/L)	220	165	185	320	320	365	395	412.5	420	400	405	410	350	335
DO (mg/L)	7.5	5.4	3.1	3.5	6.2	5.0	2.3	3.6	4.6	6.9	8.8	10.1	10.8	12.6
ORP (mv)				-99	-65	-61	59	-71	121	-62	26	2	89	142
SUVA (L/mg C/m)	3.3	4.1	4.5	4.1	3.7	3.3	3.3	3.1	3.3	2.5		2.5	2.6	2.2
AI	0.01	0.13	0.11	0.02	0.01	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Ва	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.03	0.02	0.02	0.02	0.02	0.01	0.01
Са	42.1	27.3	27.9	44.1	44.2	49.1	50.2	42.0	85.6	86.9	88.2	87.3	72.0	69.4
Fe	0.08	0.73	0.64	0.11	0.06	0.05	0.06	0.04	0.05	0.03	0.01	0.00	0.02	0.02
к	6.7	5.0	5.6	8.6	8.0	9.0	9.8	9.5	11.0	11.1	11.4	11.5	10.9	10.8
Mg	61.3	47.7	52.2	80.9	84.0	96.5	107.7	98.8	165.3	166.4	170.9	170.1	140.2	137.6
Mn	0.11	0.09	0.16	0.37	0.19	0.26	0.62	0.28	0.10	0.05	0.03	0.03	0.02	0.01
Na	14.3	9.0	9.2	17.1	17.6	21.6	24.3	24.0	27.8	28.0	28.2	28.1	25.1	24.6
Р	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Si	2.14	2.68	3.85	7.52	10.57	11.73	12.79	10.73	6.49	5.78	5.18	5.10	4.30	4.15
Sr	0.15	0.10	0.11	0.16	0.16	0.18	0.19	0.17	0.26	0.26	0.25	0.24	0.21	0.20
Fluoride	0.095	0.084	0.09	0.116	0.1375	0.145	0.147	0.134	0.103	0.109	0.076	0.0795	0.12	0.096
Acetate	< 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	<0.02
Formate	< 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	<0.02
Chloride	9.1	3.7	2.4	5.3	5.5	6.6	7.6	9.1	35.4	37.4	38.4	38.3	32.8	31.9
Nitrite-N	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.004
Bromide	<0.006	<0.006	<0.005	0.015	0.020	0.018	0.026	0.025	0.039	0.037	0.038	0.04	<0.005	0.01
Nitrate-N	0.488	0.006	<0.001	<0.001	0.003	0.013	0.006	0.005	<0.002	0.003	0.016	0.029	< 0.001	0.018
Sulfate	135.1	78.4	74.3	140.2	143.1	170.6	185.0	197.7	482.5	494.3	519.3	518.9	412.3	395
Thiosulfate	< 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	0.02
Phosphate-P	<0.006	<0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.01
Ammonia-N	0.033	0.044	0.025	0.105	0.044	0.05	0.071	0.053	0.036	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020
Nitrate/Nitrite	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40
TKN	0.72	0.98	0.97	0.94	0.84	0.75	0.86	0.82	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Total P	0.02	0.021	0.037	0.034	0.021	0.023	0.021	0.026	0.01	< 0.010	< 0.010	0.014	< 0.010	< 0.010
F-MeHg (ng/L)	0.26	1.32	2.26	1.01	0.27	0.19	0.38	0.12	0.24	0.09	0.07	0.09	0.11	0.07
F-THg (ng/L)	1.17	5.63	6.61	3.87	2.17	1.05	0.96	0.74	0.73	0.40	0.40	0.53	0.47	0.30
DOC	19.4	31.3	31.5	25.2	20.3	16.4	16.6	17.9	5.9	4.2	2.9	2.8	2.7	2.4
δ ¹⁸ Ο _{SO4} (‰)					6.1	6.3	6.5	7.4	-4.8	-4.9	-4.8	-5.0	-4.9	4.71
δ ³⁴ S ₅₀₄ (‰)					15.2	16.5	17.2	17.1	12.0	11.6	11.6	14.5	12.0	12.38

Site 6, Long Lake Creek Confluence

Date	5/16/12	6/5/12	6/26/12	7/17/12	7/31/12	8/14/12	8/27/12	9/12/12	9/19/12	9/24/12	10/2/12	10/9/12	10/15/12	10/30/12	12/17/12
Temperature (°C)	12.0	22.3	22.3	24.8	21.6	15.2	16.1	13.0	8.1	7.21	6.84	4.3	5.7	1.7	
рН	7.9	8.0	7.4	8.1	8.1	8.1	7.9	7.4	8.0	8.0	8.0	7.8	8.0	7.4	7.9
Sp Cond (µS/cm)	378	327	307	304	285	335	326	328	1254	1283	1463	1505	1264	1167	
Alkalinity (mg/L)	112.5	102.5	107.5	107.5	107.5	115	132.5	125	300	287.5	340	350	307.5	285	270
DO (mg/L)	11.9	8.8	7.4	8.7	10.2	10.8	10.4	8.3	11.5	12.3	13.1	13.9	13.2	15.4	
ORP (mv)				64	50	111	93	181	170	-27	92	8	142	158	
SUVA (L/mg C/m)	3.6	3.6	4.1	3.6	3.3	2.8	2.7	2.5	3.4	3.1	3.4	3.2	3.0	3.0	
AI	0.04	0.05	0.10	0.04	0.06	0.02	0.01	0.02	0.01	0.01	0.00	0.01	0.01	0.01	0.00
Ba	0.02	0.03	0.03	0.03	0.02	0.03	0.03	0.04	0.05	0.04	0.04	0.04	0.03	0.02	0.03
Ca	27.8	25.9	24.6	26.3	25.9	27.9	31.8	27.5	69.0	70.6	80.9	80.8	71.1	62.5	62.7
Fe	0.25	0.23	1.75	1.25	0.39	0.22	0.15	0.28	0.10	0.06	0.03	0.03	0.06	0.04	0.03
к	2.1	1.9	1.8	1.9	1.8	2.2	2.2	2.1	7.9	9.1	9.5	10.7	8.9	9.3	9.3
Mg	21.1	17.8	17.4	16.7	16.9	18.3	16.5	14.5	115.0	125.5	147.8	153.1	124.1	118.1	116.7
Mn	0.32	0.11	0.13	0.08	0.09	0.06	0.10	0.09	0.18	0.11	0.08	0.06	0.28	0.05	0.12
Na	11.6	10.7	10.2	11.8	11.3	11.9	12.3	11.7	24.4	25.1	27.0	27.0	24.1	22.8	23.6
Р	0.02	0.01	0.03	0.04	0.02	0.03	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01
Si	3.2	3.5	4.2	4.6	4.8	4.9	6.0	5.5	6.6	5.8	4.9	4.8	5.0	4.1	4.9
Sr	0.10	0.10	0.10	0.10	0.10	0.11	0.14	0.12	0.24	0.24	0.26	0.25	0.22	0.19	0.19
Fluoride	0.09	0.09	0.09	0.10	0.12	0.13	0.19	0.16	0.11	0.10	0.11	0.11	0.12	0.08	0.09
Acetate	< 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	0.02	0.02
Formate	<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	0.02	0.02
Chloride	15.0	15.4	14.0	17.2	16.6	16.9	12.6	14.9	24.2	31.1	35.9	37.4	32.6	30.1	30.0
Nitrite-N	<0.002	<0.002	< 0.002	<0.002	<0.002	<0.002	0.009	0.004	<0.002	<0.002	<0.002	< 0.002	<0.002	< 0.004	0.00
Bromide	<0.006	0.007	0.008	<0.005	0.0085	<0.005	<0.005	<0.005	0.025	0.025	0.0275	0.0305	<0.005	0.01	0.01
Nitrate-N	0.604	0.006	0.008	0.029	0.017	0.033	0.220	0.169	0.003	0.004	0.001	< 0.001	< 0.001	0.00	0.23
Sulfate	33.7	24.3	21.5	19.1	17.0	16.7	12.4	14.8	363.7	402.5	480.3	488.7	384.2	347.3	344.8
Thiosulfate	<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	0.02	0.02
Phosphate-P	<0.006	<0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.01	0.01
Ammonia-N	0.059	0.029	0.034	0.061	0.03	0.028	0.032	0.033	0.03	0.021	< 0.020	< 0.020	0.021	< 0.020	
Nitrate/Nitrite	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	
TKN	0.81	0.88	1.05	0.7	0.66	0.53	< 0.50	< 0.50	0.86	0.54	< 0.50	< 0.50	< 0.50	< 0.50	
Total P	0.052	0.044	0.054	0.057	0.04	0.035	0.033	0.034	0.048	0.032	0.024	0.02	0.036	0.019	
F-MeHg (ng/L)	0.24	0.6	1.43	0.27	1.05	0.45	0.12	0.10	0.50	0.33	0.22	0.18	0.17	0.10	
F-THg (ng/L)	2.44	2.58	4.74	2.02	2.27	2.01	0.47	0.51	1.69	1.20	0.11	0.94	0.86	0.60	
DOC	17.2	14.8	25.1	14.2	14.6	10.8	8.3	8.9	15.5	12.1	8	6.7	7	5.2	2.0
0 U _{SO4} (‰)					5	4.1	4.4	4./	-1.9	-2.9	-3.4	-3.8	-3.2	-3.3	-3.8
0 S _{SO4} (‰)					6.2*	18.1	19.4	19.2	11.8	12.0	11./	11.9	12.1	12.4	13.4

 $\ensuremath{^*}$ This data point is considered an anomaly and is not addressed in the discussion

Site 7, Inlet 1 Lake Manganika

Date	5/17/12	6/6/12	6/28/12	7/17/12	8/1/12	8/15/12	8/29/12	9/12/12	9/26/12	10/16/12
Temperature (°C)	14.1	17.3	18.7	20.0	20.2	18.5	19.6	18.8	15.8	18.2
рН	7.8	7.8	7.8	7.6	7.7	7.8	7.7	7.8	7.5	7.7
Sp Cond (µS/cm)	1638	1531	1309	1375	1344	1333	1570	1561	1564	1383
Alkalinity (mg/L)	427.5	387.5	337.5	377.5	397.5	447.5	425	450	400	382.5
DO (mg/L)	3.1	5.6	5.9	1.3	1.0	0.3	0.7	3.5	2.1	1.2
ORP (mv)				85	-72	-143	-152	4	-19	-133
SUVA (L/mg C/m)	1.4	2.3	1.9	2.0	1.9	1.7		1.8	1.4	1.5
Al	0.05	0.06	0.11	0.07	0.06	0.04	0.08	0.10	0.06	0.11
Ва	0.01	0.05	0.04	0.03	0.02	0.02	0.03	0.04	0.03	0.02
Са	60.9	61.8	62.8	59.8	64.6	64.2	68.3	55.2	62.3	57.1
Fe	0.07	0.39	0.09	0.10	0.11	0.11	0.08	0.08	0.13	0.10
к	11.2	11.5	11.5	12.8	12.2	13.0	13.6	13.0	13.7	12.1
Mg	82.5	82.7	76.7	74.6	79.5	81.0	82.7	68.7	74.3	67.4
Mn	0.27	0.27	0.23	0.26	0.28	0.34	0.28	0.28	0.30	0.20
Na	92.2	95.5	84.4	75.0	96.0	83.2	105.6	84.9	106.4	96.2
Р	0.57	0.27	0.24	0.36	0.67	1.33	1.01	0.38	0.45	0.41
Si	6.0	5.6	6.5	6.3	6.9	7.0	6.6	5.5	6.1	5.8
Sr	0.18	0.20	0.21	0.19	0.20	0.18	0.19	0.16	0.18	0.15
Fluoride	0.55	0.30	0.37	0.41	0.55	0.60	0.62	0.64	0.86	0.76
Acetate	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	< 0.01	<0.01
Formate	0.02	0.07	0.04	0.05	0.13	0.07	0.08	0.04	0.03	<0.01
Chloride	148.4	147.7	131.6	112.3	147.1	118.9	169.6	150.5	184.5	145.7
Nitrite-N	0.02	0.05	0.08	0.05	0.04	0.04	0.02	0.02	0.023	<0.002
Bromide	0.11	0.11	0.09	0.10	0.14	0.18	0.16	0.16	0.15	0.12
Nitrate-N	5.12	1.96	0.81	0.21	0.49	0.24	0.25	0.27	0.12	0.02
Sulfate	111.0	116.5	121.3	122.0	123.1	113.1	122.1	126.4	128.1	108.4
Thiosulfate	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	< 0.01	<0.01
Phosphate-P	0.53	0.17	0.16	0.22	0.33	1.06	0.18	0.13	0.19	0.05
Ammonia-N	21	13	8.3	11	13	22	17	30	26	20
Nitrate/Nitrite	< 0.40	1.9	0.8	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40
TKN	21.5	16.7	10.1	12.4	13.8	24.5	19.8	29.2	25.1	20.9
Total P	1.4	0.62	0.49	0.72	0.94	1.9	1.5	0.53	0.57	0.62
F-MeHg (ng/L)	0.5	0.9	0.4	1.1	2.5	2.9		1.3	0.8	1.8
F-THg (ng/L)	1.1	3.3	1.7	2.3	3.6	2.8	3.7	2.2	1.0	2.3
DOC	11.6	14.9	10.6	10.0	11.5	15.2	16.9	10.6	10.0	13.1
δ O _{sO4} (‰)					-3.7	-3.8	-2.4	-1.6	-2.2	0.3
δ ^{~~} S _{SO4} (‰)					7.0	6.6	7.3	6.6	7.1	7.1

Site 8, Inlet 2 Lake Manganika

Date	5/17/12	6/6/12	6/28/12	7/17/12	8/1/12	8/14/12	8/29/12	10/16/12
Temperature (°C)	15.3	17.1	20.2	23.0	20.8	19.4	19.3	8.9
рН	8.4	8.4	8.3	8.3	8.4	8.4	8.3	8.3
Sp Cond (µS/cm)	2016	2104	2133	2322	2209	2403	2170	2177
Alkalinity (mg/L)	517.5	582.5	625	647.5	635	605	560	572.5
DO (mg/L)	12.4	10.1	8.7	7.7	8.0	9.1	8.5	12.8
ORP (mv)				104	75	42	99	86
SUVA (L/mg C/m)	2.7	2.5	2.4	3.3	2.5	2.3	2.6	1.7
AI	0.00	0.01	0.01	0.03	0.00	0.00	0.02	0.00
Ва	0.00	0.01	0.02	0.01	0.01	0.01	0.01	0.01
Ca	42.5	28.0	22.8	20.5	27.3	21.8	19.2	36.7
Fe	0.02	0.01	0.02	0.05	0.00	0.01	0.01	0.01
К	17.1	22.2	27.3	31.4	26.1	26.2	22.1	18.9
Mg	214.0	226.7	248.3	266.8	277.4	276.6	257.0	263.7
Mn	0.03	0.01	0.02	0.05	0.01	0.01	0.01	0.01
Na	86.5	105.2	113.0	114.6	124.0	116.2	112.0	89.4
Р	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.00
Si	3.9	4.6	4.7	5.4	5.9	5.6	6.2	5.7
Sr	0.16	0.12	0.10	0.08	0.11	0.09	0.07	0.12
Fluoride	0.09	0.10	0.10	0.10	0.11	0.10	0.10	0.09
Acetate	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	<0.01
Formate	0.24	0.51	0.65	0.70	1.68	0.75	0.54	0.19
Chloride	36.2	24.2	20.4	23.3	25.3	26.4	28.2	33.4
Nitrite-N	0.008	0.023	0.037	0.039	0.022	0.023	0.015	<0.002
Bromide	0.05	0.04	0.04	0.04	0.06	0.06	0.06	0.05
Nitrate-N	3.90	11.96	18.51	19.64	31.28	14.43	10.66	6.71
Sulfate	537.9	529.0	604.0	655.4	719.5	711.3	656.1	715.3
Thiosulfate	<0.01	< 0.01	< 0.01	<0.01	< 0.01	< 0.01	< 0.01	< 0.01
Phosphate-P	<0.006	<0.006	< 0.005	<0.005	<0.005	<0.005	< 0.005	<0.005
Ammonia-N	0.03	0.03	0.03	0.05	0.03	0.03	0.03	< 0.020
Nitrate/Nitrite	3.8	12	17.9	18.9	16.1	14.7	11	6.8
TKN	0.52	0.68	< 0.50	0.61	0.55	0.53	< 0.50	< 0.50
Total P	0.05	0.02	0.03	0.03	0.02	0.02	0.02	< 0.010
F-MeHg (ng/L)	<0.01	0.12	0.06	0.13	0.06	0.06	0.07	0.02
F-THg (ng/L)	1.44	0.87	0.82	1.3	1.03	0.44	0.02	0.23
DOC	3.7	3.5	3.6	5.1	3.3	3.2	2.5	2
δ ¹⁸ O _{SO4} (‰)				-10.7	-11.1	11.0	-10.8	-10.5
δ ³⁴ S _{SO4} (‰)				3.9	5.1	5.0	5.1	6.1

Site 9, Outlet Lake Manganika

Date	5/17/12	6/6/12	6/28/12	7/17/12	8/1/12	10/16/12
Temperature (°C)	14.7	20.2	24.1	23.9	22.7	7.6
рН	9.1	9.3	9.2	9.1	9.1	8.8
Sp Cond (µS/cm)	1401	1162	1026	1226	1223	1693
Alkalinity (mg/L)	290	270	292.5	351.25	355	470
DO (mg/L)	13.6	16.5	15.1	12.3	10.0	11.9
ORP (mv)				43	0	111
SUVA (L/mg C/m)	2.0	2.8	3.2	3.0	2.7	2.1
Al	0.01	0.03	0.05	0.01	0.00	0.00
Ва	0.01	0.01	0.02	0.03	0.04	0.02
Са	17.6	25.5	29.3	30.5	21.5	25.7
Fe	0.00	0.03	0.17	0.01	0.00	0.01
К	12.1	10.1	10.2	13.2	13.5	16.7
Mg	124.5	99.3	93.0	117.8	131.7	179.8
Mn	0.04	0.03	0.05	0.02	0.01	0.05
Na	84.2	68.8	61.7	70.3	76.7	94.5
Р	0.02	0.02	0.02	0.02	0.02	0.02
Si	0.22	2.32	4.08	5.02	5.50	6.48
Sr	0.04	0.08	0.10	0.10	0.06	0.07
Fluoride	0.16	0.14	0.13	0.14	0.17	0.20
Acetate	< 0.01	<0.01	<0.01	< 0.01	<0.01	<0.01
Formate	0.07	0.06	0.08	0.13	0.37	0.11
Chloride	86.4	72.7	59.3	56.3	57.4	63.7
Nitrite-N	0.06	0.00	0.03	0.10	0.12	0.16
Bromide	0.07	0.06	0.05	0.05	0.07	0.08
Nitrate-N	1.37	0.04	0.37	0.78	1.94	1.22
Sulfate	295	230	212	275	305	445
Thiosulfate	< 0.01	<0.01	<0.01	< 0.01	<0.01	<0.01
Phosphate-P	<0.006	<0.006	<0.005	<0.005	<0.005	<0.005
Ammonia-N	0.09	0.02	0.03	0.39	0.25	1.68
Nitrate/Nitrite	0.82	<0.4	0.42	0.85	0.98	1.29
TKN	3.3	4.3	3.7	4.9	5.1	5.5
Total P	0.28	0.22	0.20	0.23	0.26	0.30
U-MeHg (ng/L)				0.8		0.2
U-THg (ng/L)				6.1	4.9	4.1
F-MeHg (ng/L)	0.05	0.09	0.10	0.06	0.10	0.03
F-THg (ng/L)	1.47	1.43		1.57	0.69	0.48
DOC	6.5	9.6	13.3	9.4	8.5	6.6
δ ¹⁸ O _{SO4} (‰)				-6.9	-6.3	-5.3
δ ³⁴ S _{SO4} (‰)				-6.3	5.9	7.6

Site 10-1S, Lake Manganika, surface*

Date	6/25/12	7/10/12	7/24/12	8/7/12	8/21/12	9/5/12	9/17/12	10/6/12	6/4/2013
Temperature (°C)	21.4	23.9	25.0	23.3	20.7	21.8	16.4	9.2	
pН	9.1	9.2	9.1	9.0	9.0	8.9	8.9	8.9	
Sp Cond (µS/cm)	1076	1113	1204	1426	1461	1553	1614	1677	
Alkalinity (mg/L)	262.5	327.5	342.5	385	410	430	455	485	
DO (mg/L)	18.8	15.5	13.8	13.0	14.8	11.1	9.9	12.2	
ORP (mv)	163.2	123	134	78	74	130	125	125	
SUVA (L/mg C/m)	2.9	2.8	2.9	2.7	2.5	0.2	2.3	2.2	
Al	0.04	0.03	0.01	0.02	0.00	0.00	0.00	0.01	0.01
Ва	0.02	0.02	0.03	0.02	0.01	0.02	0.04	0.02	0.05
Ca	28.7	30.0	20.0	24.0	22.1	17.2	19.3	23.8	29.1
Fe	0.06	0.02	0.002	0.00	0.00	0.00	0.00	0.00	0.00
К	9.9	11.9	13.8	14.6	15.8	16.6	15.3	16.9	11.8
Mg	92.7	108.5	123.9	141.6	156.1	167.1	158.1	183.0	130.6
Mn	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.00	0.00
Na	61.4	66.1	72.1	80.6	85.6	90.7	81.1	95.1	83.2
Р	0.03	0.03	0.02	0.03	0.03	0.02	0.03	0.02	0.00
Si	3.7	4.4	5.0	5.7	6.0	6.4	5.9	6.6	0.0
Sr	0.10	0.10	0.05	0.07	0.06	0.04	0.05	0.07	0.08
Fluoride	0.13	0.14	0.14	0.18	0.17	0.17	0.18	0.19	0.20
Acetate	< 0.01	< 0.01	<0.01	<0.01	< 0.01	< 0.01	<0.01	<0.01	< 0.03
Formate	0.09	0.13	0.16	0.45	0.23	0.22	0.21	0.14	0.08
Chloride	59.7	55.6	56.5	57.2	56.9	58.3	61.1	62.0	86.4
Nitrite-N	0.04	0.08	0.08	0.14	0.15	0.11	0.13	0.12	0.10
Bromide	0.05	0.05	0.05	0.08	0.08	0.08	0.08	0.08	<0.03
Nitrate-N	0.07	1.09	1.22	2.19	1.15	0.93	0.55	1.14	1.84
Sulfate	212.6	250.3	287.2	331.4	370.1	391.0	408.1	450.8	322.0
Thiosulfate	< 0.01	< 0.01	<0.01	<0.01	< 0.01	< 0.01	< 0.01	<0.01	<0.03
Phosphate-P	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	-0.005	<0.005	<0.015
Ammonia-N	0.03	0.05	0.04	0.76	0.46	0.49	1.53	1.59	
Nitrate/Nitrite	0.54	0.98	1.18	1.09	1.14	0.94	0.56	1.17	
TKN	3.61	4.34	4.87	5.2	5.82	5.94	6.44	6.53	
Total P	0.233	0.22	0.24	0.245	0.302	0.292	0.325	0.3	
U-MeHg (ng/L)				0.89					
U-THg (ng/L)			3.71		4.25	3.14	3.93	3.44	
F-MeHg (ng/L)	0.03	0.05		0.057	0.13	0.03	0.19	0.13	
F-THg (ng/L)	1.42	1.21	1	0	0.97	0.56	0.50	0.44	
DOC	10.8	9.8	8.1	8.5	7.3	7	7.3	6.5	
δ ¹⁸ Ο _{SO4} (‰)			-6.9	-6.6	-7.2	-6.3	-5.6	-6.0	-5.4
δ ³⁴ S _{SO4} (‰)			5.3	5.5	5.6	5.4	5.6	6.3	7.6

 \ast For additional data results from Lake Manganika, see Bailey et al. 2014a and 2014b

Site 10-1B, Lake Manganika, bottom*

Date	6/25/12	7/10/12	7/24/12	8/7/12	8/21/12	9/5/12	9/17/12	10/6/12	6/4/2013
Temperature (°C)	14.0	14.9	15.7	15.9	16.6	16.8	15.3	9.1	
рН	7.7	7.3	7.5	7.4	7.4	7.1	6.8	8.9	
Sp Cond (µS/cm)	1457	1755	1447	1650	1687	1844	1867	1680	
Alkalinity (mg/L)	395	472.5	550	682.5	767.5	655	495	492.5	
DO (mg/L)	-0.1	-0.3	-0.3	-0.3	-0.5	-0.4	4.6	11.4	
ORP (mv)	-315	-288	-330	-344	-350	-312	-281	114	
SUVA (L/mg C/m)	2.4	2.6				2.4	2.3	2.2	
AI	0.02	0.03	0.04	0.01	0.01	0.01	0.01	0.02	0.08
Ва	0.03	0.03	0.04	0.07	0.04	0.02	0.05	0.02	0.08
Ca	30.1	32.3	36.8	43.4	46.6	34.7	20.1	24.5	51.8
Fe	0.03	0.04	0.02	0.01	0.01	0.01	0.00	0.01	0.03
к	13.8	14.4	14.7	14.8	16.3	17.3	16.1	17.2	16.6
Mg	124.8	128.6	129.5	134.9	146.1	164.6	174.9	193.3	177.4
Mn	1.04	1.09	1.11	1.16	1.06	0.75	0.27	0.01	0.95
Na	74.5	74.5	74.5	76.9	79.8	86.7	82.5	95.3	122.1
Р	0.61	0.79	1.07	1.70	2.06	1.16	0.04	0.02	0.03
Si	4.8	5.5	6.6	8.0	8.9	8.1	6.0	6.5	6.0
Sr	0.11	0.11	0.13	0.15	0.16	0.08	0.09	0.07	0.16
Fluoride	0.13	0.13	0.13	0.18	0.17	0.16	0.17	0.19	0.33
Acetate	< 0.01	< 0.01	< 0.01	6.2	13.4	0.6	< 0.01	<0.01	13.3
Formate	0.13	0.14	0.14	0.34	0.26	0.21	0.24	0.15	0.097
Chloride	63.8	60.0	58.7	58.2	56.5	52.7	56.3	58.9	115.1
Nitrite-N	<0.002	<0.002	<0.002	< 0.002	0.003	< 0.002	0.295	0.115	0.006
Bromide	0.06	0.06	0.06	0.09	0.09	0.09	0.07	0.07	< 0.03
Nitrate-N	<0.001	< 0.001	<0.001	0.005	0.009	<0.001	0.957	1.72	<0.003
Sulfate [#]	266.6	280.3	201.3	105.8	106.6	229.2	461.6	482.6	395.0
Thiosulfate [#]	< 0.01	< 0.01	33.4	43.0	59.0	< 0.01	< 0.01	< 0.01	14.0
Phosphate-P	0.41	0.48	0.71	1.09	1.80	0.13	< 0.005	< 0.005	<0.015
Ammonia-N	8.0	9.4	13	21	28	17	2.5	1.5	
Nitrate/Nitrite	<0.40	<0.40	< 0.40	<0.40	< 0.40	< 0.40	1.11	1.69	
TKN	9.4	10.4	14.6	22.8	29.4	18.3	6.6	5.9	
Total P	0.85	0.95	1.35	2.08	2.46	1.26	0.36	0.27	
U-MeHg (ng/L)			2.1	4.7					
U-THg (ng/L)			6.5		<0.1	0.0	4.9	3.7	
F-MeHg (ng/L)	2.3	3.1	1.4	4.3	5.2	3.2	0.8	0.0	
F-THg (ng/L)	3.4	6.3	<0.03		0.2	<0.04	1.7	0.5	
DOC	9.7	10.1	10.1	13.2	16.4	9.6	7.3	6.1	
δ ¹⁸ O _{SO4} (‰)			-2.4	1.7	-2.3	-3.3	-6.5	-6.8	-3.8
δ ³⁴ S _{so4} (‰)			14.0	23.8	15.4	12.9	5.9	5.7	9.8
δ ³⁴ S _{H2S} (‰)			-7.8	-4.1	-1.2	-8.9			-10.4
Sulfide			36.0	58.4	64.9	47.0			11.1

* For additional data results from Lake Manganika, see Bailey et al. 2014a and 2014b $^{\#}$ Samples were purged with N $_2$ gas to remove H $_2$ S

Site 11, East Two Rivers Confluence	
Site 11, East Two Rivers Confluence	

Date	5/16/12	6/5/12	6/27/12	7/16/12	7/31/12	8/13/12	8/27/12	9/10/12	9/24/12	10/15/12
Temperature (°C)	14.9	20.5	23.1	25.2	21.4	21.7	20.4	14.8	9.0	5.4
рН	8.3	8.0	8.0	8.2	8.2	8.5	8.4	8.4	8.4	8.6
Sp Cond (µS/cm)	903	725	694	763	832	933	951	1009	1035	1044
Alkalinity (mg/L)	215	215	175	220	232.5	257.5	295	295	297.5	300
DO (mg/L)	11.9	8.7	9.8	9.2	9.0	12.1	10.4	10.4	12.0	14.2
ORP (mv)				122	70	54	56	-160	-55	157
SUVA (L/mg C/m)	2.9	3.7	4.0	3.7	3.1	2.8	2.6	2.5	2.1	
Al	0.01	0.08	0.04	0.03	0.02	0.00	0.02	0.02	0.01	0.16
Ва	0.02	0.04	0.03	0.04	0.03	0.02	0.02	0.04	0.03	0.03
Са	34.8	27.6	28.1	31.3	27.5	29.7	30.5	26.4	30.5	32.7
Fe	0.08	0.47	0.65	0.39	0.12	0.04	0.03	0.01	0.03	0.23
к	6.72	5.59	5.44	6.86	7.32	8.32	9.32	8.80	9.30	9.15
Mg	63.2	51.2	48.8	59.8	66.7	77.0	84.4	80.9	93.3	95.2
Mn	0.32	0.29	0.21	0.23	0.13	0.11	0.11	0.07	0.05	0.03
Na	45.1	38.0	34.7	38.9	41.7	45.7	48.0	45.4	51.3	50.8
Р	0.05	0.04	0.03	0.10	0.08	0.07	0.11	0.07	0.03	0.07
Si	0.8	2.6	4.0	4.4	3.6	1.6	3.7	3.3	2.8	2.2
Sr	0.10	0.09	0.09	0.10	0.09	0.10	0.09	0.08	0.09	0.10
Fluoride	0.155	0.126	0.136	0.1435	0.1675	0.1675	0.18	0.1805	0.188	0.1955
Acetate	<0.01	< 0.01	<0.01	<0.01	<0.01	< 0.01	<0.01	<0.01	< 0.01	<0.01
Formate	0.02	0.02	0.03	0.04	0.09	0.05	0.06	0.07	0.07	0.04
Chloride	56.7	46.3	39.5	40.0	40.3	41.1	41.3	42.7	44.3	42.7
Nitrite-N	0.007	0.007	0.003	0.004	0.005	0.003	0.008	0.01	0.004	<0.002
Bromide	0.05	0.36	0.03	0.04	0.05	0.05	0.06	0.05	0.05	0.06
Nitrate-N	0.25	0.24	0.09	0.27	0.55	0.04	0.34	0.42	0.63	0.77
Sulfate	128.4	104.9	98.2	112.0	131.2	157.6	167.4	192.7	214.9	217.1
Thiosulfate	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Phosphate-P	<0.006	<0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ammonia-N	0.028	0.028	0.029	0.037	0.029	0.032	0.159	0.081	0.037	0.023
Nitrate/Nitrite	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	0.43	0.62	0.76
TKN	1.21	2.1	2.38	1.65	1.19	0.84	0.75	1.03	1.05	1.14
Total P	0.16	0.23	0.24	0.23	0.15	0.12	0.04	0.14	0.11	0.09
F-MeHg (ng/L)	0.08	0.31	0.31	0.24	0.15	0.12	0.07	0.07	0.04	0.05
F-THg (ng/L)	1.44	2.84	3.34	2.08	1.41	0.96	0.91	0.73	0.51	0.46
DOC	10.7	17.9	22.3	15.8	12.0	10.1	9.5	8.6	8.5	
δ U _{s04} (‰)					-3.0	-3.7	-3.5	-3.7	-4.2	-4.0
δ [°] S _{SO4} (‰)					7.0	6.5	6.5	6.4	5.7	5.6

Site 12, Downstream West Two Rivers

Date	5/17/12	6/7/12	6/28/12	7/18/12	7/31/12	8/14/12	8/27/12	9/10/12	9/24/12	10/15/12
Temperature (°C)	12.9	18.4	23.2	24.8	20.1	17.1	17.1	13.9	8.7	5.5
рН	7.7	8.3	8.4	8.0	7.5	7.5	7.6	7.6	7.8	7.5
Sp Cond (µS/cm)	755	721	631	584	624	643	628	627	646	569
Alkalinity (mg/L)	192.5	175	157.5	162.5	167.5	167.5	180	185	175	165
DO (mg/L)	5.7	7.2	9.0	7.1	3.6	3.5	2.5	5.0	8.1	8.4
ORP (mv)				115	46	163	139	23	29	179
SUVA (L/mg C/m)	2.5	2.5	2.7	2.9	2.8	2.8	2.6	2.6	2.3	1.5
Al	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.01
Ва	0.05	0.04	0.04	0.04	0.03	0.04	0.04	0.06	0.05	0.04
Са	40.4	34.2	31.6	31.8	32.9	36.2	38.8	34.7	38.7	35.8
Fe	0.13	0.13	0.33	0.20	0.22	0.21	0.23	0.14	0.20	0.45
к	6.0	6.2	5.7	5.6	5.3	5.3	5.5	5.1	5.3	4.9
Mg	54.6	57.4	49.6	46.4	45.8	45.5	45.4	40.2	44.1	39.9
Mn	0.45	0.18	0.17	0.21	0.38	0.25	0.25	0.12	0.12	0.09
Na	24.4	24.9	22.5	21.9	21.6	22.0	22.2	21.1	22.0	19.9
Р	0.01	0.01	0.02	0.03	0.03	0.02	0.02	0.00	0.00	0.01
Si	2.1	0.6	1.2	1.9	2.4	2.6	3.4	2.9	3.2	3.6
Sr	0.17	0.14	0.14	0.14	0.14	0.16	0.17	0.16	0.17	0.15
Fluoride	0.14	0.11	0.11	0.12	0.15	0.16	0.17	0.17	0.17	0.17
Acetate	< 0.01	<0.01	<0.01	<0.01	<0.01	<0.01	< 0.01	<0.01	< 0.01	<0.01
Formate	< 0.01	< 0.01	<0.01	<0.01	< 0.01	<0.01	< 0.01	< 0.01	< 0.01	<0.01
Chloride	19.6	21.3	21.3	20.9	20.2	20.3	20.1	20.4	21.1	17.9
Nitrite-N	<0.002	<0.002	<0.002	0.008	0.032	0.019	0.021	<0.002	0.005	<0.002
Bromide	0.04	0.03	0.03	0.03	0.04	0.03	0.04	0.03	0.03	<0.005
Nitrate-N	0.72	0.01	0.01	0.03	0.11	0.06	0.10	0.04	0.13	0.06
Sulfate	141.7	149.3	130.0	117.9	112.4	112.2	109.5	114.1	117.2	103.1
Thiosulfate	< 0.01	<0.01	<0.01	<0.01	<0.01	<0.01	< 0.01	<0.01	<0.01	<0.01
Phosphate-P	<0.006	<0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ammonia-N	0.058	0.052	0.046	0.108	0.204	0.157	0.054	0.033	0.030	0.042
Nitrate/Nitrite	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40
TKN	0.61	0.82	0.96	0.78	0.93	0.76	0.8	0.56	0.52	0.71
Total P	0.05	0.05	0.07	0.04	0.06	0.04	0.17	0.03	0.02	0.02
F-MeHg (ng/L)	0.03	0.21	0.15	0.30	0.41	0.26	0.27	0.05	0.04	0.06
F-THg (ng/L)	0.88	1.27	1.17	1.29	0.99	0.96	0.68	0.45	0.44	0.61
DOC	8.9	10.4	11.7	11.3	11.8	11.2	10.6	10.7	11	12.4
δ ¹⁰ O _{SO4} (‰)					4.5	3.6	4.1	3.7	3.8	4.6
δ ³⁴ S _{SO4} (‰)					11.2	11.5	11.6	11.1	11.0	11.0

Site 13, West Two Rivers Confluence

Date	5/16/12	6/5/12	6/27/12	7/16/12	7/31/12	8/13/12	8/27/12	9/10/12	9/24/12	10/15/12
Temperature (°C)	16.3	20.6	23.5	25.2	21.5	22.2	19.2	15.2	9.9	5.2
рН	8.3	7.9	7.8	8.2	8.1	8.3	8.1	8.3	8.3	8.3
Sp Cond (µS/cm)	445	470	448	479	485	577	605	574	665	492
Alkalinity (mg/L)	132.5	130	125	150	155	192.5	222.5	205	220	165
DO (mg/L)	10.8	9.0	8.3	7.9	8.4	9.9	8.8	10.7	11.2	13.7
ORP (mv)				129	78	66	92	-134	-81	152
SUVA (L/mg C/m)	3.3	3.7	3.8	3.6	3.4	3.3	3.0	2.9	2.6	2.6
Al	0.02	0.05	0.05	0.08	0.04	0.02	0.06	0.03	0.01	0.02
Ва	0.03	0.04	0.04	0.03	0.03	0.04	0.04	0.06	0.05	0.04
Ca	26.8	24.8	24.3	27.0	26.4	30.5	33.0	31.2	35.0	34.4
Fe	0.30	0.39	0.58	0.31	0.31	0.11	0.16	0.10	0.07	0.210
К	4.6	4.7	4.3	5.1	5.0	6.6	7.6	6.0	8.8	4.5
Mg	26.7	32.6	30.9	35.2	34.4	42.5	46.9	37.2	52.5	32.7
Mn	0.26	0.21	0.16	0.08	0.07	0.06	0.06	0.05	0.03	0.03
Na	15.5	16.6	15.5	18.1	18.1	21.3	23.3	20.0	25.8	16.6
Р	0.02	0.02	0.03	0.04	0.03	0.03	0.03	0.01	0.02	0.01
Si	1.2	2.2	2.9	1.5	1.6	2.1	2.1	1.9	3.5	3.8
Sr	0.10	0.10	0.10	0.11	0.11	0.12	0.14	0.13	0.14	0.13
Fluoride	0.12	0.10	0.10	0.11	0.14	0.16	0.17	0.18	0.16	0.20
Acetate	< 0.01	<0.01	<0.01	< 0.01	< 0.01	< 0.01	< 0.01	<0.01	<0.01	< 0.01
Formate	< 0.01	<0.01	<0.01	< 0.01	0.016	0.014	0.015	<0.01	0.017	< 0.01
Chloride	13.9	13.7	13.3	13.6	12.6	10.0	10.5	12.9	10.8	13.2
Nitrite-N	<0.002	0.004	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Bromide	< 0.01	0.160	0.017	0.016	0.018	0.017	0.016	0.010	0.017	<0.005
Nitrate-N	0.969	0.69	0.077	-0.001	-0.001	0.151	0.0595	-0.001	-0.001	-0.001
Sulfate	49.4	73.5	70.1	73.8	66.3	74.7	84.7	81.5	104.2	70.9
Thiosulfate	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Phosphate-P	<0.006	<0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ammonia-N	0.024	0.025	0.035	0.027	0.033	0.026	0.022	0.024	< 0.020	0.028
Nitrate/Nitrite	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40
TKN	0.75	0.90	1.03	0.80	0.72	0.59	0.53	< 0.50	0.53	< 0.50
Total P	0.05	0.07	0.09	0.06	0.06	0.05	0.05	0.03	0.04	0.021
F-MeHg (ng/L)	0.1	0.32	0.55	0.18	0.11	0.14	0.07	0.05	0.07	0.04
F-THg (ng/L)	1.8	2.72	2.99	1.54	1.28	0.84	0.36	1.00	0.65	0.45
DOC	13.6	16.1	19.2	13.6	12.3	11.3	10.8	9.4	9.9	8.1
δ ⁻ °O _{so4} (‰)					2.1	0.4	0.2	2.4	-0.1	5.0
δ ³⁴ S _{SO4} (‰)					9.9	10.0	9.7	10.7	9.0	10.8

Site 14, Upstream McQuade Lake

Date	5/16/12	6/7/12	6/28/12	7/18/12	7/31/12	8/14/12	8/27/12	9/10/12	9/24/12	10/15/12
Temperature (°C)	14.4	18.7	24.3	24.2	21.2	18.2	19.0	13.1	7.2	5.0
рН	8.0	7.9	8.1	8.2	7.9	8.0	8.1	8.0	8.2	6.8
Sp Cond (µS/cm)	521	556	450	801	836	958	852	967	858	823
Alkalinity (mg/L)	170	187.5	150	315	290	322.5	310	367.5	325	305
DO (mg/L)	8.7	6.9	8.1	8.7	6.3	6.8	4.9	7.5	9.9	12.9
ORP (mv)				79	173	183	154	204	77	180
SUVA (L/mg C/m)	3.3	3.5	3.7	3.4	3.2	3.1	2.9	3.1	2.5	2.6
Al	0.01	0.03	0.23	0.03	0.02	0.01	0.03	0.04	0.01	0.01
Ва	0.03	0.04	0.04	0.06	0.05	0.05	0.05	0.07	0.06	0.05
Ca	30.2	30.6	26.6	38.4	38.4	40.3	37.2	38.2	40.3	41.1
Fe	0.20	0.45	1.07	0.11	0.11	0.05	0.08	0.08	0.05	0.07
К	6.2	7.2	5.5	12.5	11.7	13.6	13.3	14.5	13.2	12.7
Mg	33.1	40.8	33.3	72.1	68.0	80.3	73.9	75.2	74.0	68.3
Mn	0.31	0.20	0.23	0.09	0.08	0.05	0.12	0.08	0.09	0.05
Na	17.8	19.5	16.5	32.5	31.7	37.4	34.3	36.1	33.1	30.1
Р	0.017	0.023	0.048	0.046	0.034	0.014	0.025	0.028	0.010	0.006
Si	0.9	1.3	3.7	4.1	4.5	3.0	2.0	3.9	0.8	1.8
Sr	0.11	0.12	0.11	0.16	0.15	0.16	0.15	0.16	0.16	0.15
Fluoride	0.12	0.11	0.11	0.14	0.16	0.17	0.20	0.18	0.18	0.18
Acetate	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Formate	< 0.01	0.04	0.03	0.05	0.14	0.07	0.05	0.05	0.03	0.02
Chloride	12.1	7.2	6.8	7.3	7.7	8.2	9.0	9.1	8.8	10.2
Nitrite-N	<0.002	0.014	0.011	0.014	0.014	0.019	0.007	0.010	<0.002	<0.002
Bromide	0.01	0.16	0.02	0.03	0.03	0.03	0.02	0.03	0.02	-0.01
Nitrate-N	1.09	0.71	0.52	1.15	2.28	1.60	0.61	1.20	0.04	0.91
Sulfate	51.7	71.9	56.5	127.9	137.1	157.5	133.7	162.0	145.3	137.4
Thiosulfate	< 0.01	<0.01	<0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	<0.01	<0.01
Phosphate-P	<0.006	<0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ammonia-N	0.02	0.06	0.05	0.05	0.05	0.04	0.05	0.04	0.02	0.04
Nitrate/Nitrite	<0.4	0.76	0.53	1.05	1.13	1.60	0.61	1.16	< 0.40	0.91
TKN	0.68	0.76	0.97	0.84	0.70	0.76	0.63	0.63	< 0.50	< 0.50
Total P	0.06	0.05	0.06	0.07	0.07	0.06	0.06	0.06	0.03	0.02
F-MeHg (ng/L)	0.08	0.36	0.50	0.16	0.13	0.10	0.06	0.14	0.07	0.06
F-THg (ng/L)	1.58	1.92	3.03	1.10	1.30	0.91	0.62	0.85	0.56	0.54
DOC	12	12.6	17	7.8	9.2	7.7	7.4	7.3	5.9	5.4
δ ¹⁸ O _{sO4} (‰)					-5.0	-4.6	-3.8	-3.5	-2.9	-3.4
δ ³⁴ S _{SO4} (‰)					6.3	6.7	8.2	7.8	7.2	6.9

Site 15, Downstream McQuade Lake

Date	5/16/12	6/7/12	6/28/12	7/18/12	7/31/12	8/14/12	8/27/12	9/10/12	9/24/12	10/15/12
Temperature (°C)	16.6	20.3	24.9	25.6	23.4	21.1	20.6	16.1	10.4	5.3
рН	7.6	7.6	7.6	7.7	8.1	7.8	8.0	7.3	7.5	7.4
Sp Cond (µS/cm)	500	396	294	462	550	644	688	749	757	778
Alkalinity (mg/L)	152.5	120	95	177.5	200	225	250	290	290	300
DO (mg/L)	5.2	6.1	7.5	5.0	5.2	4.5	1.7	0.8	6.7	8.7
ORP (mv)				74	315	205	172	209	117	174
SUVA (L/mg C/m)	2.9	3.5	3.8	3.8	3.5	3.3	2.8	2.8	2.8	2.7
Al	0.00	0.03	0.03	0.02	0.01	0.00	0.04	0.00	0.00	0.00
Ва	0.03	0.03	0.04	0.04	0.03	0.04	0.05	0.07	0.06	0.05
Са	27.2	22.3	18.2	25.3	26.9	30.1	33.7	31.3	35.3	36.6
Fe	0.11	0.29	0.34	0.12	0.06	0.05	0.09	0.04	0.03	0.04
К	6.3	5.3	4.0	6.8	7.0	8.7	10.3	10.4	11.4	11.7
Mg	31.4	26.2	20.1	37.6	41.7	49.8	57.2	54.8	63.7	64.9
Mn	0.351	0.205	0.083	0.142	0.084	0.127	0.600	0.180	0.085	0.106
Na	17.4	14.7	11.8	19.3	20.6	24.2	27.4	27.7	30.4	30.7
Р	0.02	0.02	0.03	0.04	0.02	0.02	0.05	0.03	0.02	0.01
Si	1.4	1.8	2.7	1.2	1.4	3.2	3.8	3.8	4.2	3.7
Sr	0.10	0.09	0.07	0.10	0.11	0.12	0.13	0.13	0.14	0.14
Fluoride	0.10	0.09	0.08	0.10	0.13	0.14	0.15	0.15	0.16	0.17
Acetate	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Formate	< 0.01	0.016	0.014	0.024	0.056	0.033	0.035	0.035	0.031	0.016
Chloride	14.1	9.6	7.3	7.4	7.5	7.8	8.1	8.3	8.6	9.0
Nitrite-N	0.009	0.010	0.010	0.010	0.008	0.008	0.014	0.006	0.006	< 0.002
Bromide	0.01	0.01	0.01	0.02	0.03	0.02	0.02	0.03	0.03	0.02
Nitrate-N	1.32	0.19	0.09	0.12	0.14	0.05	0.05	0.02	0.03	0.01
Sulfate	51.9	45.1	32.2	61.8	69.9	84.1	97.2	107.9	118.5	118.6
Thiosulfate	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Phosphate-P	<0.006	<0.006	<0.005	<0.005	<0.005	<0.005	< 0.005	<0.005	<0.005	<0.005
Ammonia-N	0.097	0.074	0.060	0.088	0.080	0.090	0.286	0.254	0.072	0.064
Nitrate/Nitrite	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40
TKN	0.72	0.84	1.00	1.02	0.99	1.12	1.38	0.99	0.69	0.72
Total P	0.06	0.04	0.06	0.07	0.05	0.05	0.06	0.05	0.04	0.03
F-MeHg (ng/L)	0.18	0.29	0.39	0.35	0.16	0.20	0.35	0.26	0.05	0.05
F-THg (ng/L)	0.96	2.7	3.24	1.95	1.16	0.62	0.68	0.60	0.63	0.39
DOC	11.8	15.3	19.3	14.9	14.2	13.0	13.6	12.1	10.6	9.7
δ ¹⁸ Ο _{SO4} (‰)					-2.6	-2.5	-2.3	-2.0	-2.1	-0.2
δ ³⁴ S _{SO4} (‰)					7.9	7.9	8.2	9.7	8.0	8.9

Site 16-1S, McQuade Lake, surface*

Date	6/25/12	7/10/12	7/25/12	8/7/12	8/21/12	9/6/12	9/17/12	10/4/12
Temperature (°C)	24.8	27.2	25.1	24.3	20.8	20.7	16.8	13.2
рН	7.8	8.6	8.5	8.4	8.5	8.4	8.4	8.3
Sp Cond (µS/cm)	301	254	440	539	633	732	732	737
Alkalinity (mg/L)	90	110	170	215	237.5	265	275	270
DO (mg/L)	8.2	10.4	8.3	8.9	9.7	5.7	9.9	10.7
ORP (mv)	72.2	33	117	0	140	115	44	134
SUVA (L/mg C/m)	3.9	3.8	3.5	3.4	3.2	3.0	2.9	2.8
Al	0.06	0.06	0.06	0.01	0.00	0.00	0.00	0.01
Ва	0.03	0.04	0.04	0.03	0.04	0.05	0.07	0.06
Са	17.5	18.6	18.6	28.8	30.9	32.8	30.9	34.9
Fe	0.37	0.18	0.18	0.03	0.04	0.02	0.01	0.05
К	4.2	4.4	4.4	8.0	9.1	10.2	10.2	11.1
Mg	18.7	22.1	22.1	45.9	52.2	58.8	53.9	62.7
Mn	0.11	0.02	0.02	0.05	0.26	0.05	0.01	0.18
Na	11.6	12.9	12.9	22.4	25.3	28.1	27.3	30.0
Р	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.02
Si	2.6	0.3	0.3	2.3	3.4	3.8	3.9	4.6
Sr	0.07	0.07	0.07	0.11	0.12	0.13	0.13	0.14
Fluoride	0.08	0.08	0.10	0.14	0.14	0.15	0.15	0.17
Acetate	< 0.01	< 0.01	< 0.01	<0.01	< 0.01	< 0.01	<0.01	< 0.01
Formate	0.01	0.01	0.02	0.07	0.04	0.04	0.04	0.01
Chloride	8.1	7.2	7.4	7.7	7.9	8.1	8.3	8.3
Nitrite-N	0.009	<0.002	<0.002	<0.002	0.004	<0.002	0.003	<0.002
Bromide	< 0.005	0.009	0.013	0.027	0.026	0.028	0.028	0.034
Nitrate-N	0.088	< 0.01	<0.01	<0.01	0.026	0.003	< 0.01	< 0.01
Sulfate	31.2	35.3	57.0	77.5	89.1	101.8	106.3	112.5
Thiosulfate	< 0.01	< 0.01	<0.01	<0.01	< 0.01	< 0.01	< 0.01	< 0.01
Phosphate-P	< 0.005	<0.005	<0.005	0.023	<0.005	<0.005	<0.005	<0.005
Ammonia-N	0.066	0.036	0.035	0.038	0.034	0.16	0.038	0.037
Nitrate/Nitrite	<0.40	<0.40	<0.40	<0.40	< 0.40	< 0.40	< 0.40	< 0.40
TKN	1.07	1.13	1.06	1.15	1.53	1.25	1.23	1.2
Total P	0.068	0.052	0.044	0.058	0.073	0.05	0.069	0.052
U-MeHg (ng/L)			0.47	0.40	0.42	0.16	0.25	0.33
U-THg (ng/L)			2.0		0.98	0.66	0.76	0.79
F-MeHg (ng/L)	0.31	0.29	0.36	0.18	0.13	0.08	0.09	0.01
F-THg (ng/L)	3.38		1.97		0.93	0.67	0.78	0.57
DOC	18.4	18.7	15.6	14.1	13	12.3	11.7	11
δ ¹⁸ Ο _{SO4} (‰)			-2.01	-2.73	-2.66	-2.86	-2.58	-1.5
δ ³⁴ S _{SO4} (‰)			7.56	7.89	8.04	8.29	8.75	8.68

* For additional data results from this site, see Bailey et al. 2014b

Site 16-1B, McQuade Lake, bottom*

Date	6/25/12	7/10/12	7/25/12	8/7/12	8/21/12	9/6/12	9/17/12	10/4/12
Temperature (°C)	13.8	13.8	14.4	15.0	16.4	16.7	16.7	13.2
рН	7.1	6.8	6.8	6.8	7.3	7.2	8.4	8.4
Sp Cond (µS/cm)	326	351	378	385	671	734	734	738
Alkalinity (mg/L)	115	123.75	150	185	242.5	290	280	275
DO (mg/L)	0.05	0.01	0.00	0.06	0.01	0.04	8.47	10.61
ORP (mv)	-183.7	-175	-221	-205	-241	-277	10	26
SUVA (L/mg C/m)	4.1	4.2		4.4	3.8		2.9	2.7
AI	0.10	0.11	0.10	0.07	0.02	0.01	0.00	0.03
Ва	0.04	0.08	0.07	0.14	0.10	0.12	0.07	0.06
Ca	19.9	19.2	20.9	23.7	31.5	34.3	31.1	34.7
Fe	2.0	1.8	3.0	2.0	0.24	0.13	< 0.001	0.05
К	4.6	4.7	5.2	5.8	8.9	9.7	10.2	11.1
Mg	19.0	19.3	20.7	23.7	48.9	54.8	54.1	62.8
Mn	1.19	1.40	2.95	6.59	3.09	3.10	0.06	0.17
Na	12.1	12.2	12.5	12.9	23.6	26.1	27.3	30.2
Р	0.80	0.70	1.25	1.78	0.59	0.67	0.01	0.02
Si	5.5	5.6	7.2	8.4	5.2	5.8	3.9	4.6
Sr	0.08	0.07	0.08	0.10	0.12	0.14	0.13	0.14
Fluoride	0.08	0.07	0.08	0.10	0.13	0.14	0.15	0.14
Acetate	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	<0.01
Formate	< 0.01	< 0.01	< 0.01	0.02	0.033	0.067	0.035	< 0.01
Chloride	10.4	8.9	8.8	8.6	8.1	8.1	8.3	8.2
Nitrite-N	<0.002	< 0.002	<0.002	< 0.002	0.006	<0.002	0.003	<0.002
Bromide	0.012	0.012	0.014	0.031	0.033	0.030	0.028	<0.005
Nitrate-N	< 0.001	< 0.001	<0.001	< 0.001	0.007	<0.001	< 0.001	<0.01
Sulfate	15.6	15.4	6.2	1.4	71.1	78.8	106.7	111.9
Thiosulfate	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	<0.01
Phosphate-P	0.68	0.38	0.97	1.30	0.54	0.12	< 0.005	<0.005
Ammonia-N	2.03	1.86	3.31	5.36	2.22	2.76	0.046	0.036
Nitrate/Nitrite	<0.40	<0.40	< 0.40	<0.40	< 0.40	< 0.40	< 0.40	< 0.40
TKN	3.06	2.74	4.29	7.01	3.43	3.64	1.32	1
Total P	1.02	0.754	1.39	2.24	0.638	0.786	0.063	0.046
U-MeHg (ng/L)			4.47	5.30	3.42	2.52	0.54	0.07
U-THg (ng/L)			8		4.16	3.46	0.90	1.00
F-MeHg (ng/L)	0.37		4.36	5.09	3.74	2.74	0.18	0.03
F-THg (ng/L)	5.91		6.45		3.41	3.21	0.76	0.70
DOC	20.2	20.7	22.9	23.0	14.6	13.3	11.7	11.3
δ ¹⁸ Ο _{SO4} (‰)					-2.0	-1.5	-2.8	-1.1
δ ³⁴ S _{sO4} (‰)					8.5	10.9	8.7	8.6

* For additional data results from this site, see Bailey et al. 2014b

Site 17, West Swan River @ Hwy 73

Date	5/15/12	6/7/12	6/27/12	7/16/12	7/30/12	8/13/12	8/28/12	9/11/12	9/25/12	10/16/12
Temperature (°C)	16.3	18.8	21.9	21.7	21.9	18.5	17.0	15.0	8.2	8.0
рН	7.3	7.3	7.4	7.4	7.6	7.6	7.5	7.6	7.5	7.9
Sp Cond (µS/cm)	281	181	200	339	374	462	520	512	457	500
Alkalinity (mg/L)	95	70	72.5	145	165	227.5	242.5	247.5	215	230
DO (mg/L)	7.5	6.7	6.8	4.8	5.9	6.2	3.9	5.2	9.3	11.4
ORP (mv)			0	166	63	185	108	144	19	97
SUVA (L/mg C/m)	3.4	3.9	3.9	3.8	3.6	3.5	3.4	2.9	3.1	3.0
Al	0.01	0.02	0.03	0.02	0.01	0.00	0.01	0.00	0.00	0.00
Ва	0.02	0.04	0.05	0.03	0.06	0.05	0.03	0.06	0.05	0.04
Ca	22.4	17.0	17.9	28.6	29.6	36.1	38.4	35.3	37.2	34.8
Fe	0.22	0.50	1.00	0.57	0.51	0.29	0.39	0.49	0.33	0.15
К	1.79	1.29	1.52	1.75	2.30	3.42	4.04	3.29	3.05	3.96
Mg	12.6	8.7	9.2	17.8	20.9	30.5	32.5	27.3	26.7	31.0
Mn	0.22	0.24	0.26	0.47	0.31	0.20	0.72	0.76	0.65	0.12
Na	9.4	6.7	8.1	12.4	16.8	24.4	25.3	21.7	20.8	25.2
Р	0.01	0.03	0.04	0.04	0.04	0.03	0.03	0.02	0.01	0.02
Si	0.7	1.9	3.1	3.8	4.3	4.0	3.7	3.3	3.8	1.7
Sr	0.07	0.06	0.07	0.09	0.10	0.12	0.14	0.12	0.12	0.11
Fluoride	0.08	0.08	0.08	0.12	0.15	0.17	0.17	0.15	0.13	0.17
Acetate	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Formate	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Chloride	8.5	5.3	5.6	8.4	10.7	13.8	14.7	14.8	15.3	16.1
Nitrite-N	<0.002	<0.002	< 0.002	<0.002	<0.002	<0.002	<0.002	<0.002	< 0.002	<0.002
Bromide	0.009	0.009	0.013	0.031	0.049	0.054	0.056	0.046	0.042	<0.005
Nitrate-N	0.250	0.01	0.004	0.004	<0.001	0.048	0.006	<0.001	< 0.001	< 0.001
Sulfate	14.2	5.9	7.5	1.1	3.9	4.9	3.1	1.1	1.5	7.1
Thiosulfate	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Phosphate-P	<0.006	<0.006	< 0.005	<0.005	<0.005	<0.005	<0.005	<0.005	< 0.005	<0.005
Ammonia-N	0.025	0.04	0.038	0.055	0.034	0.026	0.039	0.025	0.021	0.038
Nitrate/Nitrite	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40
TKN	0.65	0.85	0.99	0.91	0.98	0.71	0.7	0.63	0.53	0.53
Total P	0.05	0.05	0.03	0.07	0.11	0.04	0.05	0.05	0.06	0.02
F-MeHg (ng/L)	0.29	0.86	2.48	1.12	0.82	0.39	0.65	0.09	0.05	0.11
F-THg (ng/L)	1.7	3.5	4.9	2.7	2.2	1.1	1.7	0.74	0.73	0.77
DOC	14.1	19.3	20.9	16.6	14.4	12.0	13.0	14.5	12.0	10.5
δ ¹⁸ Ο _{SO4} (‰)									4.2 (R)	4.3 (R)
δ ³⁴ S _{so4} (‰)									12.5 (R)	18.0 (R)

Site 18, Swan River	Confluence

Date	5/15/12	6/5/12	6/27/12	7/16/12	7/30/12	8/13/12	8/28/12	9/11/12	9/25/12	10/15/12
Temperature (°C)	15.6	17.5	22.3	22.3	22.1	19.3	19.4	15.1	8.7	5.3
рН	7.8	7.4	7.7	7.7	7.8	8.2	8.3	8.3	8.5	8.4
Sp Cond (µS/cm)	309	183	373	392	293	374	556	634	596	551
Alkalinity (mg/L)	87.5	70	55	130	97.5	150	187.5	220	195	185
DO (mg/L)	9.2	8.6	6.6	6.6	7.0	8.4	7.8	10.9	11.4	14.2
ORP (mv)				147	96	147	144	155	15	137
SUVA (L/mg C/m)	3.7	4.1	4.3	4.1	4.1	3.9	3.3	3.1	2.7	2.6
Al	0.05	0.11	0.12	0.18	0.09	0.03	0.01	0.01	0.01	0.02
Ва	0.02	0.05	0.16	0.09	0.14	0.03	0.03	0.05	0.04	0.03
Ca	22.5	16.5	17.3	29.6	24.3	31.8	42.2	42.2	44.7	44.1
Fe	0.36	0.65	1.30	4.48	2.33	1.43	0.20	0.04	0.07	0.14
К	1.70	0.88	1.23	2.44	1.80	2.22	3.15	3.43	3.63	3.76
Mg	14.7	9.2	8.5	24.1	16.7	25.0	34.7	34.1	34.8	29.0
Mn	0.09	0.11	0.14	0.21	0.14	0.10	0.05	0.04	0.04	0.03
Na	10.8	6.6	6.0	14.3	12.1	14.7	21.4	23.4	26.1	24.9
Р	0.02	0.03	0.03	0.05	0.04	0.02	0.02	0.01	0.01	0.01
Si	2.0	2.7	3.7	5.5	4.7	3.7	3.1	2.9	1.5	2.0
Sr	0.06	0.05	0.06	0.08	0.08	0.10	0.13	0.13	0.13	0.13
Fluoride	0.10	0.08	0.08	0.15	0.22	0.18	0.24	0.27	0.29	0.28
Acetate	< 0.01	< 0.01	< 0.01	<0.01	< 0.01	<0.01	<0.01	<0.01	< 0.01	<0.01
Formate	< 0.01	< 0.01	< 0.01	<0.01	< 0.01	<0.01	<0.01	<0.01	< 0.01	< 0.01
Chloride	13.3	7.7	6.0	15.9	13.8	15.5	27.4	33.8	37.0	34.0
Nitrite-N	0.005	0.004	0.003	0.011	0.006	0.004	0.010	0.007	0.007	<0.002
Bromide	0.015	0.008	0.005	0.029	0.031	0.04	0.04	0.05	0.04	<0.005
Nitrate-N	1.0	0.4	0.4	1.9	2.2	1.0	1.4	1.8	1.7	1.6
Sulfate	19.1	10.0	7.8	27.0	17.2	27.3	48.3	55.9	57.6	44.0
Thiosulfate	<0.01	<0.01	<0.01	<0.01	<0.01	< 0.01	<0.01	<0.01	< 0.01	< 0.01
Phosphate-P	<0.006	<0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ammonia-N	0.034	0.044	0.046	0.075	0.050	0.036	0.025	0.022	< 0.020	0.030
Nitrate/Nitrite	0.92	0.46	<0.4	1.74	1.06	0.86	1.42	1.74	1.66	1.63
TKN	0.87	1.08	1.29	1.9	1.29	0.77	0.66	< 0.50	< 0.50	0.51
Total P	0.065	0.076	0.103	0.076	0.062	0.052	0.032	0.033	0.031	0.015
F-MeHg (ng/L)	0.28	0.41	0.57	0.82	0.37	0.22	0.34	0.08	0.07	0.04
F-THg (ng/L)	3.22	4.46	5.09	4.62	3.91	1.96	1.14	0.58	1.25	0.76
DOC	19.5	26.1	32.9	38.4	32.6	21	9.2	5.9	5.8	6.7
δ ¹⁸ Ο _{SO4} (‰)					0.8	-0.9	0.0	-1.2	0.5	2.4
δ ³⁴ S _{SO4} (‰)					4.7	4.9	4.0	4.1	4.1	4.3