Sulfate and Mercury Chemistry of the St. Louis River in Northeastern Minnesota

A Report to the Minerals Coordinating Committee

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Abstract

The St. Louis River and its major tributaries were sampled upstream from Cloquet during periods of high, medium, and low flow between September 2007 and October 2008. Special emphasis was placed on measuring sulfate (SO_4) and mercury (Hg) distributions as well as other chemical parameters that might help to determine whether SO_4 releases from the Iron Range have an impact on Hg speciation in the St. Louis River. These included, but were not limited to, dissolved organic carbon (DOC), dissolved iron (Fe), and the isotopic ratios for sulfur and oxygen atoms in dissolved SO_4 ($\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$). Dissolved and particulate fractions of methyl mercury (MeHg), total mercury (THg), and bioavailable mercury (AHg) were additionally determined over a range of hydrologic conditions to identify primary source regions and transport mechanisms for Hg species.

Results confirm that the majority of SO_4 is derived from the iron mining district, and that SO_4 added in the upstream portion of the St. Louis River is generally diluted downstream by waters from larger watersheds containing high percentages of wetlands. SO_4, magnesium (Mg), calcium (Ca), sodium (Na), and chloride (Cl) concentrations all increase in the river, especially in the mining region, during periods of low-flow when groundwater inputs dominate chemistry of dissolved components. Variations in the relative concentrations of major elements and in $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ among the tributaries provide important clues to specific SO_4 sources for each of the individual watersheds under varying flow conditions. Chemical data indicate that most SO_4 from the mining region is derived from oxidation of small amounts of iron sulfide minerals present in stock piles, tailings, and pit walls containing Mg-rich carbonate minerals that are common in the Biwabik Iron Formation. Comparison with stream chemistry from 1955 to 1961 indicates SO_4 sources were commonly present in the mining region before taconite mining became widespread in the region. Other chemical parameters in these data, particularly Ca and Mg, indicate the primary source for this SO_4 was different from today.

In contrast to SO_4, Hg appears to be derived predominantly from wetlands, and is highest during periods of increased flow in the rivers. THg is well correlated to DOC concentration under most conditions, but quite variable during precipitation events when dissolved AHg and particulate SHg become more abundant in the rivers. MeHg concentrations in the St Louis River and its tributaries are also strongly correlated to DOC. Four sources of DOC are preliminarily inferred to be present in the river depending on the season and watershed characteristics, and it is believed that the relative amounts of DOC from each source may control the MeHg concentrations present in the river. These include: (1) DOC released from surface wetland areas containing low Fe (approximately 0.2 ng/mg Hg and 0.02 ng/mg MeHg in the DOC), (2) DOC containing almost no MeHg that is either produced in-stream or present in small amounts in natural groundwater, (3) DOC released from deep wetland areas following a major summer rain event containing very high MeHg and high Fe, and (4) DOC containing almost no MeHg in waters containing elevated dissolved Fe that seep slowly from deep within wetland areas under dry conditions. MeHg systematics appear to be very similar to those reported in two well-studied low-SO_4 tributaries of the Rum River in east-central Minnesota. Additional sampling is planned to verify the above model and to more fully characterize mercury speciation during the warm summer months, particularly during periods when high Fe concentrations are present in the streams.

1. Introduction

The St. Louis River basin serves multiple purposes ranging from recreational fishing and boating to agriculture and forestry as well as hydroelectric power generation, but it is also well known for its vast mineral resources. The Mesabi Iron Range, which lies along the northern fringe of the basin (Fig. 1), is a world class mining district that has supplied iron to the U.S. continuously since the 1890s and could continue to do so for another century or more. Along the eastern edge of the St. Louis River watershed lies a series of undeveloped Cu-Ni sulfide/ precious metal deposits that, although relatively low in grade, are sufficiently large to be considered an important future U.S. metals resource.

It has long been known that mining activities on the Iron Range result in release of SO_4 to the St. Louis River (Moyle and Kenyon, 1947; Maderak, 1963; Peterson, 1979; Lindgren et al., 2006; Waters, 1977). While SO_4 is typically not toxic to aquatic organisms, a growing body of research supports a link between bacterial SO_4 reduction and conversion of mercury (Hg) to methylmercury (MeHg) (Gilmour, 1992; Benoit et al., 1999; Jeremiason et al., 2006). MeHg is the type of Hg that accumulates in fish. High Hg concentrations in fish have led to issuance of fish consumption advisories throughout the state, including the St. Louis River. As a result, the MPCA has recently issued guidance that is to be used for permitting SO_4 discharges into the environment (MPCA, 2006). This guidance attempts to eliminate or reduce SO_4 discharge to environments that bring SO_4 into contact with labile organic matter and Hg under reducing conditions, especially when SO_4 concentration is the limiting factor for SO_4 reduction.

In the St. Louis River basin, situations that have the potential to increase Hg methylation might include SO_4 discharge to wetlands that drain to a river, discharge to streams where flooding may result in inundation of high organic wetlands, or SO_4 loading to lakes or impoundments in which anoxic conditions are produced within the water column or at the sediment/water interface. Until more detailed studies are conducted, virtually all SO_4 releases within the St. Louis River basin can be considered high risk because wetlands, flood plains, and lakes are common in the region.

The MPCA's new guidance presents a serious issue for the mining industry as well as many other industries in the state. To assist the state of Minnesota in deciding which kinds of mining discharges really do and do not influence MeHg levels, the Minnesota DNR began studying SO_4 and Hg behavior in the St. Louis River in 2007. This report details the existing SO_4 and Hg distributions in the St. Louis River watershed and attempts to develop a mechanistic approach for understanding what causes the concentrations of Hg species, and MeHg in particular, to vary seasonally along the St. Louis River and within each of its component watersheds.

2. Background

2.1. Geography

Mining activities affect several major watersheds in Northeastern Minnesota. These include: the St. Louis River, the Mississippi River near Grand Rapids, the Little Fork River, the Vermilion River, and the Rainy River headwaters, which cover a total area of approximately

11,100 mi^2. Most of the mining is concentrated within the St. Louis River watershed, but much of the mineral processing takes place in the other watersheds. When the St. Louis River watershed is separated into its major tributaries, approximately 24% of its land area or ten major tributaries have mining activities located within their boundaries (Fig. 2). Of these, the Swan River watershed is the largest, covering approximately 241 mi^2 and Otter Creek is the smallest, covering approximately 11.4 mi^2. With the exception of the areas near Duluth and Cloquet, the aforementioned watersheds contain the majority of the population in the St. Louis River watershed. As a result, these watersheds may also be impacted by other non-mining related sources.

Whereas mining activities and population centers are potential sources of SO_4 and Cl, wetlands are typically the most important sources of dissolved organic carbon and mercury (Sorensen et al., 1990; Kolka et al., 1999). The average area covered by wetlands in sub-watersheds where at least some mining takes place is equal to approximately 165.6 mi^2 or 16.1% of the total land area. However, total and percent wetland areas vary considerably among the individual watersheds (Fig. 2; Table 1). Of the watersheds with mineland areas in them, the Swan River watershed has the largest wetland area (61.6 mi^2) whereas Otter Creek has the smallest area covered by wetlands (0.8 mi^2). When total wetland area is compared to the total watershed area, the Stony Creek watershed has the largest percentage of land classified as wetlands (53.1%) as compared to East Two River, which has the smallest percentage of wetlands (5.0%). In contrast, average wetland cover in the non-mining watersheds totals approximately 26.0%.

From its headwaters above Seven Beaver Lake, the St. Louis River winds a counter-clockwise semicircular path over 180 miles in length, dropping approximately 1100 feet to its mouth in Lake Superior and draining approximately 3584 square miles of land (Waters, 1977). The upper St. Louis River parallels the Iron Range mining district from east to west for approximately 100 miles. Heavily influenced by groundwater inputs, the water in this portion is generally lighter in color and harder in character (that is, higher concentrations of Ca and Mg) compared to typical waters from more wetland rich areas. The river eventually turns south to meet up with three of its largest tributaries, the Whiteface, Floodwood, and Cloquet Rivers. Input from these and other smaller tributaries darkens, softens, and dilutes the water before it flows through the lower portion of the St. Louis River and into Lake Superior (Waters, 1977).

2.2. Mining Resources

The iron mining industry began in Minnesota around the middle of the nineteenth century with the discoveries of iron ore in Northeastern Minnesota. Not long after, mining began on the Vermilion Range in the early 1890's and rapidly expanded to the Mesabi Iron Range and the Cuyuna Range in the early 1910's (Emmons and Grout, 1943; Hatcher, 1950; Engesser and Niles, 1997). Most of the ore mined during the first half of the 20th century was of high grade having been enriched by extensive weathering near the surface and therefore needed little processing before being shipped to iron and steel manufacturing facilities in the Great Lakes Region. However, as the reserves of high quality ore were slowly exhausted, beneficiation began to increase, reaching approximately 50% by 1940 (Emmons and Grout, 1943).

Today, mining and beneficiation of taconite forms the backbone of the iron mining industry in the Minnesota. It was estimated in 1982 that there was still over 200 years of taconite reserves on the Iron Range (Ojakangas and Matsch, 1982). Active and inactive taconite pits and tailings basins currently occupy approximately 75 square miles of land in NE Minnesota. The pits and tailings basins are spread along either side of the Biwabik Iron Formation, a narrow belt of iron ore that that extends 120 miles along the Iron Range. In 2007, there were six active taconite mining and processing facilities on the Iron Range (Fig. 1). These included: U.S. Steel Keewatin Taconite (formerly National Steel Pellet Company) near Keewatin; Hibbing Taconite (HibTac) located near Hibbing; U.S. Steel Minntac located near Mt. Iron; Arcelor-Mittal Steel near Virginia; United Taconite with a mine located near Eveleth and processing facility near Forbes; and Northshore Mining, with a mine located near Babbitt and processing facility located on the North Shore of Lake Superior in Silver Bay.

In more recent developments, Essar Steel will re-open the old Butler Taconite mine and tailings basin areas on the west end of the Iron Range near Nashwauk. The project will combine ore processing, direct reduced iron (DRI) production, and steel-making into an integrated facility to provide steel for the domestic and world markets (Essar Steel 2007). It is estimated that the mine will process 13,100,000 metric tons of raw ore per year and the DRI processing facility and produce 2,800,000 metric tons of iron or approximately 2,500,000 metric tons of steel slabs per year (Minnesota Steel 2007). Mesabi Nugget LLC is currently in Phase II of Environmental Review and is slated to open in the Hoyt Lakes Mining Area. The facility will be unique in that it will produce iron nuggets, which are almost pure iron and can be used to feed electric arc furnaces. U.S Steel is also planning to expand its Keewatin facility.

Besides iron mining, there is extensive Cu-Ni sulfide mineralization in parts of the Duluth Gabbro within this watershed (Naldrett, 2004). A new copper-nickel and precious metals mine has been proposed close to the former LTV mine operation near Hoyt Lakes. The PolyMet mine project (shown on Figure 1) is still undergoing environmental review. However, if opened, this ore processing facility and mine would be located on approximately 14,400 acres straddling the boundary between the Embarrass and Partridge River watersheds (PolyMet 2007a). Other copper/nickel sulfide deposits are also being explored near Birch Lake and at other sites along the edge of the Duluth Complex.

2.3. Sulfate Sources

Of importance in terms of potential SO_4 sources is the presence of generally small amounts of sulfide mineralization that might be exposed at or near the surface as a result of mining. When exposed to oxygen, sulfide minerals in tailings, stockpiles, and pit walls can be oxidized to SO_4 which can then be transported to surrounding watersheds in surface runoff, ground water outflow, pit-overflow, and during pit dewatering. Pyrite and pyrrhotite, when present in rock exposed to air, commonly dominate SO_4 generation processes, however, other sulfides can also oxidize and generate SO_4 when they are found in the host rock (Blowes and Ptacek, 2003). Reviews of pyrite oxidation rates and mechanisms are presented in Lowson (1982), Evangelou (1995), Evangelou and Zhang (1995), Nordstrom and Southam (1997), and Nordstrom and Alpers (1999).

Morey (1992) calculated a weighted average sulfur (S) content for sixty-seven samples collected from three cores in the Biwabik Iron Formation to be approximately 0.05 ± 0.02%. The S content of individual samples ranged from below detection limits to 12.8 wt% in one sample from a core near Keewatin (Morey and Morey, 1990). The 12.8%, however, appears to be an outlier compared to the rest of the samples, which ranged from below detection to 0.32

wt% S. The Virginia formation is known to contain regions of somewhat elevated S concentrations, especially in areas where it is close to the Duluth Gabbro.

The Biwabik Iron Formation is typically divided into four lithostratigraphic members which include the: 1) Lower Cherty, 2) Lower Slaty, 3) Upper Cherty, and 4) Upper Slaty (Gruner, 1946). The Upper and Lower Slaty units are generally not mined, but must be removed and stored in stockpiles to access the Upper and Lower Cherty units, respectively. Although some sulfide mineralization can occur in both the Upper and Lower Slaty units, the Lower Slaty unit, in particular, is becoming recognized as a source of elevated sulfide mineralization in some areas (Mesabi Nugget, 2009).

Most of the crude ore that is used to produce taconite pellets comes from the Upper and Lower Cherty Units. Sulfide minerals included in these units will typically be separated during the grinding process and thereby be found in tailings basins. When Morey and Morey (1990) examined the S wt% of three Lower Cherty samples taken from different locations on the Biwabik Iron Formation, they found that S tended to be higher near the center of the formation and lower in the east and west. Engesser and Niles (1997) obtained similar results when they measured crude ore S contents at various mines along the formation. Overall, S contents were highest at the Minntac facility (0.085%) and lowest at the Northshore facility (0.011%) (Engesser and Niles, 1997). Similarly, Lapakko and Jagunich (1991) also estimated that the S content of crude ore at the Minntac facility was about 0.09%.

Several stages of crushing and grinding are required to reduce the crude ore to a fine powder. During this stage, water is often added to reduce the dust and to make the powdered ore easier to transport. After crushing, processes such as gravity concentration, magnetic separation, and flotation are used to increase the total percentage of iron. In the last stage, the concentrate is agglomerated, or bound together, into pellets and fired in large kilns (Earney, 1969).

During the different processing stages, the waste material, termed *fine* and *coarse* tailings, and associated slurry water are removed and trucked or pumped to the tailings basin for disposal. The slurry water is accumulated from a variety of secondary sources including: return water, makeup water, crude ore feed, fluxstone moisture, and indurator combustion (Minntac, 2004a,b). After settling, most of the water is pumped back to the processing facility for re-use. Extensive reuse of water means that SO_4 generated by grinding, concentration, and firing of the pellets can become concentrated in the tailings basin and process water over time.

Between 1999 and 2000, approximately 10,700 tons of SO_4 in the Minntac tailings basin came from the induration scrubbers. When low sulfur fuels such as natural gas and wood are used for pellet induration process, sulfur in the raw pellets accounted for nearly all of the SO_4 released during induration (Lapakko and Jagunich, 1991; Minntac, 2004a,b). However, burning of coal can add significantly to the SO_4 inventory as can oxidation of sulfide in the tailings. Minntac (2004b) estimated that tailings oxidation was responsible for approximately 33% of the total SO_4 in their tailings basin, lower than the 60-72% estimate made by Lapakko and Jagunich (1991). Berndt et al. (1999) found that tailings oxidation contributed only small amounts of SO_4 to tailings basins at the National Steel Pellet Company (now Keewatin Taconite) and Inland Steel (now Arcelor-Mittal). Tailings oxidation made a significant contribution to the amount of SO_4 in the LTV Steel Mining Company tailings basin. However, this was considered a special case because previously oxidized, high-sulfide waste rock had been disposed in the basin and was likely a major source of SO_4 (Berndt et al., 1999).

Besides mining, rainfall also contributes to the SO_4 loading in the St. Louis River watershed. Sulfur dioxide (SO_2) in the atmosphere oxidizes and dissolves in precipitation as sulfuric acid (H_2SO_4). Currently, the National Atmospheric Deposition Program (NADP) measures SO_4 concentration and loading information for a network of stations located throughout the United States. The closest station to the Iron Range is located at the Marcell Experimental Forest near Grand Rapids, MN. SO_4 in precipitation at this station peaked at approximately 2.0 mg SO_4 L^{-1} in 1979 and has declined steadily to approximately 0.8 mg SO_4 L^{-1} in 2006 (NADP, 2006, Fig. 3). The reduction in rainfall SO_4 can largely be attributed EPA efforts to reduce SO_2 emissions from coal-fired power plants (EPA, 2000). Overall, the concentration of SO_4 in rainfall is considerably lower than that in most surface waters.

Power generation from coal burning utilities often produces SO_2 that is captured from gases and, depending on the method used, can result in high SO_4 waters that may or may not be entirely contained within the facility. The Laskin Energy Center operated by Minnesota Power near Aurora Minnesota uses low-sulfur sub-bituminous coal and wet scrubbers to control SO_2. There is potential for ash ponds to leak some SO_4 from this source into the Partridge River which, in turn, feeds the St. Louis River.

Oxidation of sulfide minerals in other naturally occurring geologic strata is not well characterized in this area. An example of this type of SO_4 source is provided by the Red River in western Minnesota where high SO_4 is introduced by oxidation of sulfides present in glacial sediments (Berndt and Soule, 2000). Waters in the Red River in Fargo and Grand Forks commonly have greater than 100 mg/L SO_4 (Maderak, 1963). Oxidation of sulfides in glacial sediments in the St. Louis River basin has not been identified as an important SO_4 source, but small occurrences of pyrite and other phases have been identified in till samples. In the western portion of the Iron Range thin, unconsolidated sediments of Cretaceous age overlaid parts of the Iron Formation prior to mining and this unit was potentially pyrtitic (Dennis Martin, DNR Geologist, personal communication). Clearing and piling of these materials either by glaciation or mining could potentially have led to elevated sulfate in waters draining from the area.

Stream SO_4 data from the period when mining of enriched hematic ores (natural ore) was ending and taconite mining industry was beginning (1955-1961) showed that SO_4 concentrations in the East Two, Embarrass, and Swan Rivers and Elbow Creek were elevated compared to other rivers in the area (Maderak, 1963). Sulfate in the St. Louis River at the Scanlon Dam ranged between 20 and 30 mg/L at that time, indicating that considerable SO_4 sources have existed in the St. Louis River basin for at least 50 years. High SO_4 waters in these streams, however, had much lower Mg/Ca ratios than they do today. As will be discussed later, sulfide oxidation in Biwabik Iron Formation stockpiles and tailings results in high Mg/Ca ratios for high-SO_4 waters, so this difference in Mg/Ca ratios suggests there has been a shift in SO_4 sources in the last 50 years.

2.4. Mercury and Methyl Mercury Sources

As is the case in most other regions in the world, Hg loading in Northeastern Minnesota is overwhelmingly dominated by atmospheric deposition, in both wet (dissolved in precipitation) and dry forms (sorbed from air). Most Hg that is deposited on land is revolatilized, but a significant fraction is incorporated into local soils with only a relatively small component transported into lakes (Grigal, 2002). Average mercury concentration in Northeastern Minnesota precipitation is higher than dissolved mercury in most streams and lakes, underscoring the importance of volatilization, sedimentation, and uptake by soils and vegetation in mercury cycles (Berndt, 2003). Lake sediment studies indicate that Hg is being delivered to lakes at rates much greater now than in pre-industrial times, but many lakes reveal recent declines (Engstrom and Swain, 1997; Engstrom et al., 1999).

Taconite processing in Northeastern Minnesota potentially contributes Hg to the environment in two primary ways, the most important of which is release of Hg to the atmosphere through stack emissions. Most of this Hg, which originated from the ore, is emitted in elemental form and adds to the national and global mercury inventories rather than to local landscapes (Berndt, 2003). The other form of Hg release is with waters discharged during taconite processing. This source appears to be small because the water sampled from tailings basins has Hg concentrations that are lower than average local precipitation and generally lower than in the surface waters to which it discharges (Berndt, 2003).

Of the different Hg species present in the environment, methylmercury (MeHg or CH_3Hg^+) has generated the most interest because it is magnified up the food chain such that concentrations in fish tissues are often over a million times greater than the water they live in (Boudou and Ribeyre, 1997). Mercury concentrations in fish inhabiting surface waters are sufficiently high to trigger consumption advisories. Recent analysis by Monson (2009) found that average fish-Hg has decreased since the early 1980s to the present, but since the mid-1990s the downward trend reversed, despite there being no evidence for increased atmospheric deposition. Deposition of Hg in precipitation is monitored, but there is not yet a practical method to monitor dry deposition, which may equal or exceed wet deposition (Grigal, 2002). Methylation of Hg is not only a function of total deposition, however, because it can be altered by local geochemical processes involving redox state and the presence of sulfate and organic matter.

Only a small fraction of the Hg in surface waters, usually on the order of 5 to 15 percent, is present as MeHg. The variation in methylation efficiency (the percentage of Hg converted to MeHg) may well be greater than the variation in mercury deposition across the United States. Generally, Hg methylation is mediated by SO_4-reducing bacteria in anoxic environments (Compeau and Bartha, 1985; Gilmour et al., 1992) and increased SO_4 loading has been shown to increase MeHg concentrations in some aquatic systems (Branfireun et al., 1999; Jeremiason et al., 2006). Besides SO_4, other physical and biogeochemical factors, such as changes in watershed hydrology, have been shown to impact MeHg concentrations in rivers. Balogh et al. (2004, 2008), for example, measured Hg and MeHg approximately twice weekly for several rivers in east central Minnesota. They found that the highest MeHg and MeHg/Hg ratios followed large summer precipitation events. The reducing chemistry of the high MeHg waters pointed to flooded wetlands as the primary source. Meanwhile, in a systematic study of four rivers located throughout the U.S., Brigham et al. (2009) concluded that benthic, in channel, production of MeHg was insignificant, compared to that delivered to the river during runoff from connected wetlands.

For the St. Louis River Basin, an important question is whether the elevated SO_4 can cause greater MeHg concentrations than those observed in lower SO_4 basins such as those studied by Balogh et al (2004, 2006 2008). Although SO_4 reduction can stimulate MeHg production, its conversion to sulfide ($S^=$) can, in theory, limit Hg availability through precipitation of HgS or formation of non-bioavailable Hg-sulfide species (Compeau and Bartha, 1985). Compeau and Bartha (1985) and Choi and Bartha (1994) attributed a reduction in Hg methylation to HgS precipitation. Consistent with this hypothesis, Benoit et al (1998) found a positive correlation between Hg and pore-water sulfide and a decrease in bulk MeHg with increasing HgS. However, it is now thought that the availability of uncharged Hg-S complexes could be the primary factor regulating methylation under high sulfide conditions (Drott et al. 2007; Benoit et al., 1999). King et al. (2002) found a positive correlation between pore-water sulfide and MeHg but sulfide concentrations were likely too low to inhibit Hg methylation in that study. In an experimental wetland in Northern Minnesota, Mitchell et al. (2008) measured elevated MeHg levels in wetland mesocosms fertilized with SO_4 at rates 4 and 10 times that of annual atmospheric deposition; however, MeHg concentrations were not significantly higher in the 10X mesocosms. Mitchell et al. discuss the sulfide inhibition hypothesis for their data and reject it, concluding that methylation was no higher with higher sulfate because the bacteria had run out of labile organic matter.

Although SO_4 reduction is linked to MeHg generation in many studies, the range of SO_4 values studied is often small (e.g., 0 – 10 mg/L) (Jeremiason et al., 2006, Selvendiran et al. 2008). SO_4 concentrations can be well above 10 mg/L in wetlands if SO_4 from other sources such as mining. In such cases, there may be a threshold value above which further increases do not impact Hg methylation rates (Harmon et al., 2004) or may even inhibit MeHg production.

Whatever the SO_4 threshold is, many studies have shown that wetlands are sinks for Hg and sources of MeHg to surrounding watersheds. Indeed, because of strong complexation between DOC and Hg species, positive correlations between total Hg (THg), MeHg, and DOC are often found in water flowing from wetlands (St. Louis et al., 1996; Branfireun et al., 1998; Galloway and Branfireun, 2004; Selvendiran et al. 2008). The present study examines such correlations for multiple locations in the St. Louis River watershed with variable amounts of SO_4 loading. The purpose of this project is to determine whether the additional SO_4 loading in mining areas affects MeHg production in individual watersheds and whether there is evidence that it contributes to MeHg production within the St. Louis River itself.

3. Approach

The chemical composition of water in a stream is determined by the chemistry and relative volumes of surface and ground waters that feed into it and by subsequent chemical reactions that take place. The approach used here was to evaluate the most important influences by providing periodic chemical “snapshots” on a basin-wide scale, encompassing all major tributaries and numerous selected locations along the St. Louis River itself.

Underlying the diverse geographical characteristics of individual watersheds are common geochemical processes and, thus, an important aspect of the “snapshot” approach is that it affords the ability to compare tributary chemistries to each other across a range of hydrologic settings and with differing amounts of natural and anthropogenic effects. In the case of the St. Louis River, its component watersheds are diverse, containing differing amounts of wetland influence, urban development, and mining impact. Hypothetically, the influence of wetlands can be evaluated by comparing water chemistry as a function of wetland percentage in otherwise similar watersheds. The concentration of Dissolved Organic Carbon (DOC) can be used as an index of the wetland percentage of watersheds (Schiff et al., 1998). The influence of mining, meanwhile, can be evaluated by comparing watersheds with similar wetland percentages, or DOC concentrations, but with and without mining present. Alternatively, the MeHg concentration can be normalized to DOC concentration and a comparison made between watersheds containing and not containing significant SO_4 sources.

For the following analysis, tributaries to the St. Louis River (Table 1) are categorized first on the basis of whether they have taconite mining features in them. Major tributaries in this study that may be influenced by drainage from mining regions include the Partridge, Embarrass, East Two, West Two, and Swan Rivers. Long Lake and Elbow Creeks also drain mining areas, but these are small in size so less effort was focused on these watersheds. East Two and Swan Rivers also receive significant runoff and wastewater discharges from Iron Range cities, Eveleth/Virginia/Mountain Iron and Hibbing/Chisholm, respectively.

The other tributaries studied are distinctly more rural in character, and do not include mining features or any major towns or cities. These include Mud Hen, Stony Creek, Floodwood, Whiteface, and Cloquet Rivers. Whiteface and Cloquet Rivers both include major reservoirs that are used to control flow through hydroelectric generating facilities and it is possible that water level fluctuations within these reservoirs affect methylation efficiency in them. Of these two, the Whiteface River has a much higher percentage of wetlands than does the Cloquet River. Mud Hen Creek and Floodwood River basins, meanwhile, have no reservoirs, but the former has a low wetland percentage compared to the latter. The Stony Creek watershed hosts a portion of the United Taconite processing plant in its northern-most tip. However, no mine dewatering occurs in this district and it was found, during sampling, that water flow near its confluence with the St. Louis River appeared to be completely independent of the mining operation. Thus, for this study, it is considered a non-mining-impacted stream. This watershed has the highest wetland percentage of all of the sites (53.4%) and is the smallest of the non-mining impacted streams that was sampled here.

The sampling plan for this study was developed by balancing the available budget constraints with the high cost of Hg analyses and the need for wide geographic coverage. To provide adequate spatial coverage, 17 locations were selected for sampling but only four full sampling periods could be accommodated. An initial reconnaissance sampling trip was conducted in fall 2007, and spring, summer, and expanded fall sampling campaigns were conducted in 2008. Sampling locations for the St. Louis River (Tables 1 and 2) were selected to be as far downstream from major tributaries as possible, usually at locations just above the next major tributary. The reason for this was to allow as much time as possible for the waters from the St. Louis River and its tributary to fully mix before the sample was collected. For tributaries, sampling points were selected where there was access to the stream as close to its confluence with the St. Louis River as possible.

For the first reconnaissance survey in September 2007, seven St. Louis River locations and eight major tributaries were sampled under relatively low flow conditions for SO_4, sulfate-sulfur and sulfate-oxygen isotope ratios ($\delta^{34}S(SO_4)$, $\delta^{18}O(SO_4)$), total Hg (THg), methyl Hg (MeHg), dissolved organic carbon (DOC), and many other dissolved species. In 2008, the SO_4 isotopes were not included during most sampling periods, but mercury speciation and other chemistry was measured for ten tributaries and at seven locations along the river. This sampling took place in May, July, and October during periods representing relatively high, moderate but declining, and moderate but increasing flow conditions, respectively (Fig 3). Of particular importance was the timing of the July sampling, which occurred following a period of significant summer precipitation. Studies conducted by Balogh et al. (2004 2008) on other Minnesota rivers found that such conditions are ideal for transport of MeHg from recently flooded wetlands.

To learn more about the relative sizes of each sulfate source, an additional sampling survey, focusing on SO_4 concentrations, SO_4 isotopes, and many dissolved cations and anions, was conducted for an even larger set of locations in June (2008). Hg and DOC analyses were not conducted on these samples because the focus of this part of the study was not to evaluate Hg chemistry. This additional round included stream gauging at each site in addition to sample collection. A brief discussion of the stream flow and isotopic measurements from this June 2008 survey is provided in this report, but greater detail on this specific part of the study will be provided in future reports.

4. Methods

4.1. Field Methods and Dissolved Cations and Anions

The temperature and pH of each sample were measured in the field using a portable temperature and pH meter (Beckman Model 255). Conductivity was determined using a conductivity meter (Myron L Conductivity Meter, Model EP-10).

For cation and anion analysis, 60 mL samples for each were filtered in the field. A portable vacuum pump was used to pull the sample through acid-washed, 0.45 μm Nalgene filters. The cation samples were preserved with nitric acid and were shipped cold for analyses by the University of Minnesota – Twin Cities Research Analytical Lab (St. Paul, MN). This lab uses inductively coupled plasma (ICP) atomic emission spectrometry (Perkin Elmer Optima 3000 consisting of an echelle polychrometer and two solid-state detectors). The anion samples were not preserved but were shipped cold to the Aqueous Geochemistry Lab at the University of Minnesota Geology Department (Minneapolis, MN). This lab used ion-chromatography to analyze anions (Dionex ICS-2000 Ion Chromatograph consisting of an AS11 analytical column, AMMS III suppressor, AS40 autosampler, and integrated dual piston pump and conductivity detector).

An additional 50 mL sample was filtered in the field and used for measurement of dissolved organic carbon (DOC). The DOC samples were preserved with sulfuric acid and shipped to the Minnesota Department of Health (St. Paul, MN) where they were analyzed using a non dispersive-infrared analyzer (reference method SM 5310c).

An additional 500 mL aliquot of unfiltered water was collected at each site and shipped to the Minnesota Department of Agriculture (St. Paul, MN) for nutrient analysis where EPA method 353.2 was used to analyze for nitrate-nitrite, and standard methods 4500N, 4500PE, and 4500F were used to analyze for total nitrogen, phosphorus, and ammonia, respectively. A 60 mL sample was also filtered in the field, and taken to the Minnesota Department of Natural Resources Hibbing Lab where alkalinity was measured by titration with 0.02 N sulfuric acid.

4.2. Sulfate Isotopes

Isotopic measurements often provide a useful tool for identifying source and fate relationships for the targeted species in relatively complex geochemical systems. SO_4 is potentially useful in this regard because it contains two elements, sulfur and oxygen, both of which are common in the environment, have considerable variation among the various reservoirs, and can fractionate during many chemical processes (Van Stempvoort and Krouse, 1994; Taylor and Wheeler, 1994; Eimers, et al., 2004; 2007). Samples were collected for SO_4

isotope analyses ($\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$) in September 2007 and June 2008, representing relatively dry and wet conditions in the basin, respectively.

SO_4 isotopic ratios were analyzed at the University of Waterloo Environmental Isotope Laboratory in Ontario, Canada. Two methods were used for sample preparation: direct $BaSO_4$ precipitation and column concentration preceding $BaSO_4$ precipitation. The method of choice was determined by the analytical facility, as was the determination of whether enough SO_4 was available in the sample to complete the analysis (generally, about 5 mg is needed). An Element Analyzer was used for the analysis. A total of 1000 mL were sampled and shipped to the laboratory. Because dissolved SO_4 ions are considered stable in oxidizing waters, no preservation was required.

$\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values are reported using per mil notation (‰) which is a convenient means for reporting small ratios that vary by small amounts. For sulfur, the reported value represents the difference between the $^{34}S/^{32}S$ ratio measured in the sample and an accepted standard value (FeS in Canyon Diablo meteorite) multiplied by a factor of 1000/($^{34}S/^{32}S$ in the standard). A $\delta^{34}S_{SO4}$ value of 1 ‰ means, for example, that the $^{34}S/^{32}S$ ratio in the sample is 0.1% higher than the measured standard value. For oxygen in SO_4 ($\delta^{18}O_{SO4}$) the reported values represent the difference between $^{18}0/^{16}0$ ratio measured in the sample and the $^{18}0/^{16}0$ ratio for H_2O in Standard Mean Ocean Water (SMOW), also multiplied by a factor of 1000/($^{18}O/^{16}O$ in the standard).

4.3. Mercury Speciation

In 2007, one unfiltered sample was collected for Hg analysis at each location using a modified clean hands/dirty hands technique (Method 1631) and a clean Teflon sampling cup. Double bagged, 250 ml glass bottles with Teflon-lined caps were used to store the samples for Hg analysis. After each day, the samples were shipped overnight to Cebam Analytical (Seattle, WA) where they were quickly analyzed for THg, MeHg, and reactive Hg (AHg, described below). Per instruction from the analytical laboratory, the samples were not preserved prior to shipment. In 2008, both filtered and unfiltered samples were collected for each mercury species. The filtered Hg samples were processed in the field by pulling ~250 mL of water through a disposable, 0.45 μm Nalgene filter that was stored in a sealed bag prior to use. Four method blanks and two unfiltered duplicates were included with each day's samples. In 2008, a filtered blank was added to the daily sampling list.

Two relatively novel Hg measurements that were made in this study include "AHg" and "SHg". AHg is the non-methylated fraction of Hg that can be directly ethylated in the laboratory without pre-digestion (Liang et al., 2009). SHg is determined by subtracting AHg and MeHg from THg. It is thought that the AHg fraction consists of loosely bound, charged Hg species that are much more bio-available than the SHg fraction, which is tightly bound to organic thio-species (Liang et al., 2009). In this study, AHg and MeHg were determined together, using ethylation, Tenax trap collection, GC separation, and cold vapor fluorescent atomic spectrometry (CVAFS) detection (modified EPA 1630). THg was oxidized with BrCl then analyzed by $SnCl_2$ reduction, gold trap collection, and CVAFS detection (modified EPA 1631).

Hg in the filtered samples was considered to be present as dissolved Hg species. Particulate Hg fractions were determined by subtracting Hg values measured in the filtered sample from that of a separate unfiltered sample from the same site.

Measured and calculated Hg parameters are summarized as follows:

Total Hg (THg_u): Total mercury measured in unfiltered samples

Total dissolved Hg (THg_f): THg measured in filtered samples

Total particulate Hg (THg_p): Calculated as difference between THg_u and THg_f

Total MeHg ($MeHg_u$): MeHg measured in unfiltered samples

Dissolved MeHg ($MeHg_f$): MeHg measured in filtered samples

Particulate MeHg ($MeHg_p$): Calculated as difference between $MeHg_u$ and $MeHg_f$

Total Bioavailable Hg (AHg_u): AHg measured in unfiltered samples

Dissolved Bioavailable Hg (AHg_f): AHg measured in filtered samples

Particulate Bioavailable Hg (AHg_p): Calculated as difference between AHg_u and AHg_f

Total Non-Bioavailable Hg (SHg_u): Calculated as THg_u-$MeHg_u$-AHg_u

Dissolved Non-Bioavailable Hg (SHg_f): Calculated as THg_f-$MeHg_f$-AHg_f

Particulate Non-Bioavailable Hg (SHg_P): Calculated as difference between SHg_u and SHg_f.

While THg and MeHg values are based on EPA-approved analytical methods, no accepted protocol exists to distinguish between bioavailable and non-bioavailable Hg fractions. AHg and SHg numbers presented in this report are included as a means to distinguish between mercury pools that are thought to be more available and less available for methylation. Although they were determined using quantitative techniques, they should only be treated as semi-quantitative, relative indicators of bio-availability. It was felt that this method for distinguishing between mercury pools would offer a distinct advantage to evaluate mercury chemistry changes compared to the more usual methods of reporting only THg and MeHg.

Sampling, shipment, and delivery were all synchronized between the field sampling crew and the receiving laboratory to permit all samples to be processed at the analytical facility in Seattle within 48 hours of sample collection. However, an internal contract issue emerged within the DNR in early July 2008, specifically at a time when water levels were decreasing within the St. Louis River. A decision was reached to collect the samples and ship them to the laboratory as the contract issues were being resolved. Those samples were processed following a one week delay, a period thought to be within the normal holding time for these types of samples, except possibly for AHg, where no holding time had been previously established.

4.4. Stream Flow Measurements

In an effort to provide an inventory of the relative importance of different sulfate sources in the watershed, extensive stream flow gauging was included during the June 2008 sample period. Flow rate was determined at the same time the samples were collected. The DNR uses standard mechanical meters for stream gauging, including Price AA and Pygmy meters, Acoustic Doppler Current Profilers, and Acoustic Velocity Meters, depending on equipment availability and stream size. The DNR Division of Waters follows the standards and quality control procedures for discharge measurement and computation provided in Rantz et al (2005).

5. Results

5.1. *Sulfate and Sulfate Isotopes*

SO_4 and other major element concentrations and parameters for waters collected from the St. Louis River during this study are presented in Tables 3 to 7 and those for the tributaries are reported in Tables 8 to 12. For the St. Louis River, concentrations of most major cations and anions increased downstream from Mile 179 to a peak value at Mile 98 or 115, and then decreased downstream to Mile 36. The one exception was in July 2008, when the highest SO_4 concentration along the river was found at Mile 142.

The highest SO_4 concentration overall for St. Louis River samples was found at Mile 98 in September 2007, following a relatively long dry period (e.g., when water flow at the Scanlon Dam was also low). The lowest SO_4 concentration for each sample period was always found at Mile 179 where concentrations ranged from approximately 2 to 5 mg/L. The lowest concentrations occurred during wet periods (May and June 2008) and highest during the other drier periods.

SO_4 and major element compositions for tributary waters sampled during the present study are presented in Tables 8 to 12. The highest SO_4 concentration for tributaries was found in the Partridge River in July 2008, when the measured value was 189 mg/L. This high value likely explains the upstream shift in the St. Louis River SO_4 peak measured in July. More typically, the highest SO_4 concentrations were found in East Two and West Two Rivers, where concentrations remained elevated even in relatively wet periods. A high SO_4 concentration (155 mg/L) was also found in Elbow Creek in June 2008, the only time this creek was sampled. Sulfate concentrations in tributaries whose watersheds have no mining features (Mud Hen and Stony Creeks; Whiteface, Floodwood, and Cloquet Rivers) have SO_4 concentrations similar to the St. Louis River at Mile 179, with the highest value of 7.1 mg/L for the Floodwood River in September/October 2008. SO_4 concentrations for these rivers were sometimes less than 1 mg/L during wet periods.

Sulfate isotope data for September 2007 and June 2008 are provided in Tables 3, 5, 8, and 10. Sufficient dissolved SO_4 was available to permit measurement of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ in samples from all but one site in the St. Louis River (Mile 179). However, insufficient SO_4 was available for measurement of sulfate isotopes in samples from the Floodwood and Cloquet Rivers in September 2007 and for samples collected from Stony and Mud Hen Creeks and Floodwood River in June 2008.

For the St. Louis River, the $\delta^{34}S_{SO4}$ values in September 2007, ranged from 11.8 to 14.3 ‰, approximately 4 to 5 units higher than the 7.9 to 8.9 ‰ range measured in June 2008. This shift may signal a change in the relative dominance of SO_4 sources delivered to the river during dry and wet periods, respectively. More surprising was that fact that the $\delta^{34}S_{SO4}$ values measured for the river did not overlap the range of $\delta^{34}S_{SO4}$ measured for its tributaries during the September sampling period (3.1 to 10.1 ‰). However, two tributaries sampled in June 2008, but not in September 2007, extended the range of tributary $\delta^{34}S_{SO4}$ values up to 16.6 ‰ (Elbow and Long Lake Creeks).

$\delta^{18}O_{SO4}$ values for the St. Louis River ranged between 2.1 and 7.1 in September 2007, and between 0.5 and 3 ‰ in June 2008. For tributaries, the range was between 0.3 and 8.0 ‰ in September 2008, and from –1.7 to 7.0 in the tributaries in June 2008. Unlike $\delta^{34}S_{SO4}$, the tributary $\delta^{18}O_{SO4}$ values for tributaries bracketed those of the St. Louis River samples during both seasons.

5.2. *Ca, Mg, Na, and Cl*

Ca, Mg, and Na dominated the cation chemistry of the St. Louis River, and like SO_4 and Cl, the concentrations of these elements were typically greatest in the center part of the mining district (Tables 3 to 7). However, the relative concentrations of the major cations in the river were subject to considerable variation during wet and dry periods, respectively. For example, Ca>Mg>Na (mg/L basis) throughout the St. Louis River during wet periods, but Mg>Ca>Na (mg/L basis) during dry periods in sections where the river traversed the mining district.

For the tributaries, the Ca, Mg, and Na characteristics were much more variable. For example, in the Embarrass, East Two, and Swan Rivers, it was found that Na concentrations assumed a much greater importance relative to Ca and Mg. Thus, in September 2007, the relative concentrations in the East Two River was Na>Mg>Ca (mg/L basis), opposite to what was seen in upstream and downstream portions of the St. Louis River. For tributaries with high SO_4, generally with mine lands in their watershed, Mg concentrations are typically elevated compared to Ca, while the reverse is true for those districts with no mine lands.

Cl concentrations in the St. Louis River paralleled the observed SO_4 trends, although the peak concentration extended further downstream to Mile 80. The highest concentration was 21.1 mg/L at Mile 98 in September 2007. The lowest concentration was always found at Mile 179, where Cl concentration ranged between 0.04 and 0.6 mg/L during wet and dry periods, respectively. For tributaries, the highest Cl concentrations were found in East Two and Swan Rivers in September 2007, a dry period, when the concentrations were 78 and 27 mg/L, respectively. In addition, it was found that Cl concentration in the East Two River was more resistant to dilution than in most of the other tributaries, with a lowest concentration of 42.7 mg/L occurring in May 2008.

5.3. *DOC and Fe*

DOC distribution in the St. Louis River is quite distinct from that of the major dissolved cations and anions in the river. This parameter was typically elevated at Mile 179 compared to the next several stations downstream (Miles 80 to 142), with differences most pronounced during dry periods. The DOC concentration then increased again by Mile 53 but was sometimes found to decrease again at Mile 36, downstream from the Cloquet/St. Louis River confluence. For the tributaries, the highest DOC values were found in the July sample set, when the Partridge River, Mud Hen Creek, Stony Creek, Whiteface River, and Floodwood River had DOC concentrations of 23, 23, 43, 25, and 43 mg/L, respectively. By contrast, DOC concentrations at this time in the Embarrass, East Two, West Two, Swan, and Cloquet Rivers were only 14, 11, 10, 17, and 13 mg/L, respectively. These values occurring after a relatively wet summer period in the St. Louis River basin, provide information on which streams may contain water derived from recently flooded wetlands – conditions thought to be most conducive for MeHg formation. Of these rivers, the Partridge and Swan Rivers are the only high DOC streams from watersheds where mining is taking place. The Cloquet River, meanwhile, is the only tributary sampled with low DOC that comes from a watershed where no mining has taking place.

The concentration of dissolved Fe (Fe measured in filtered samples) is an important indicator of source region owing to the low solubility of $Fe(OH)_3$ under neutral-pH oxidizing conditions. Fe can become stabilized for transport in high DOC solutions, however, by formation of colloidal organo-metallic species. The highest dissolved Fe concentrations were observed in July 2008, shortly after wet conditions were present in the basin. Mud Hen Creek, Stony Creek, Whiteface River, and Floodwood tributaries had Fe concentrations of 1.2, 1.3, 1.2, and 2.5 mg/L, respectively, at this time, which compares to values of 0.4, 0.07, 0.2, 0.6, and 0.3 mg/L for Embarrass, East Two, West Two, Swan, and Cloquet Rivers, respectively. A higher dissolved Fe concentration indicates that a greater fraction of the water in the river is draining from submerged wetland areas, perhaps recently flooded, where conditions are sufficiently reducing to mobilize dissolved Fe. The Partridge River had an Fe concentration of 0.9 mg/L at this time, potentially suggesting greater sensitivity to wetland influence compared to other streams draining mine lands. The Cloquet River, meanwhile, had an Fe concentration of only 0.3 mg/L, consistent with a relatively small direct input from wetland drainage.

Fe concentrations and metal mobility can be affected by pH if conditions become weekly to moderately acidic. Neither case was present in the St. Louis River. Field pH values in the St. Louis River were lowest during periods of high flow when values ranged between approximately 7.1 and 7.7. In contrast, the pH of water in the St. Louis River in September 2007, was lowest upstream from the mining district (7.6 at mile 170) but increased to 8.4 by Mile 98 before decreasing to 8.2 at sites downstream. Interestingly, the pH in the East Two and West Two Rivers, in the center of the mining district where the pH in the St. Louis River was peaking at the time, were 7.0 and 7.1, respectively, among the lowest values measured during the study. Measured pH values for these two streams were 8.0 or above during all of the other times they were sampled, suggesting a potential pH measurement problem in calibration during the September 2007, visit. Outside of those two measurements, samples with elevated SO_4 from the mining district generally had pH values that were relatively high compared to the low-SO_4 streams. This is the expected case for a watershed containing both high alkalinity (carbonate-buffered) and low alkalinity, DOC-rich streams (e.g., Drever, 1988).

Most other elements are present at relatively low concentrations or are of lesser concern to this study, which is focused on relationships affecting SO_4 and Hg concentrations. Hg species are discussed separately, below, but concentrations of other selected components of potential interest to readers are included in Tables 3 to 12.

5.4. Mercury Speciation

Mercury species are present in water at very low concentrations and can easily be contaminated, although more likely by inorganic Hg than MeHg, unless there is an unusual source of organic Hg. Thus, extensive use was made of sample and procedural blanks and blind duplicates. Mercury analysis for samples submitted in September 2007, May 2008, and September/October 2008 (Tables 13-20) all met data quality expectations, with very low or undetectable concentrations for blanks and excellent agreement among blind duplicate samples. The samples from July 2008 (Tables 15 and 19), however, had some very high analyzed THg and MeHg concentrations, but the blank samples that were analyzed were still all within acceptable ranges. Importantly, duplicate samples collected from the same sites had measured concentrations that varied considerably during this period.

Dr. Liang conducted an exhaustive internal study to determine why the duplicate samples from July did not agree and why some of the samples from this batch had very high THg and MeHg concentrations. It was found that all of the samples with unusually high THg and MeHg contained the compound dimethyl mercury (DMM), which although not unprecedented in the natural environment is quite rare. The DMM was eventually traced to an unfortunate contamination event that is discussed in greater detail in Appendix 1. Only those samples that were found to contain little or no DMM are retained in Tables 15 and 19, but the complete data set for this period is reported in Appendix 1. The values in Tables 15 and 19 are considered to represent maximum concentrations owing to the possibility that DMM converted to MeHg within the bottles.

In September 2007 and September/October 2008, the THg and AHg values for unfiltered samples were lower than in May 2008 (Figures 5 and Fig. 6). The highest concentrations were measured in May at Mile 179 of the St. Louis River, upstream from the mining district (THg = 12.3 and AHg = 8.9 ng/L). For almost all sites in this study, MeHg concentrations in unfiltered samples were also higher in May 2008, than they were in either September 2007, or September/October 2008. The two exceptions were Swan and East Two Rivers, the only two sites with large cities in their watersheds. These rivers had MeHg concentrations of about 0.4 and 0.6 ng/L, respectively, in September 2007. In May 2008, the highest MeHg concentrations were found in Stony Creek and Floodwood River, the two streams with the highest wetland percentages and highest DOC concentrations. MeHg concentrations in these two sites were 0.57 and 0.52 ng/L, respectively. During the same period, Whiteface River and Mudhen Creek each had a MeHg concentration of 0.37 ng/L, while all other tributaries had MeHg concentrations between 0.24 and 0.35 ng/L. Unfiltered MeHg in the St. Louis River during the same time periods ranged from 0.27 to 0.39 ng/L. The typical unfiltered MeHg values for the St. Louis River and tributaries in the fall months were approximately 0.2 ng/L or less.

In July 2008, despite the DMM issue, a few locations had relatively low MeHg. These included the Cloquet and Embarrass Rivers, where the reported MeHg concentrations were approximately 0.2 ng/L. Mud Hen Creek, on the other hand, had a dissolved MeHg concentration of 0.6 ng/L. This is similar to values reported for the minimally contaminated July samples from the St. Louis River (Miles 179, 142, 53, and 36), which had dissolved or total MeHg concentrations from 0.48 to 0.65 ng/L. The values above 0.6 ng/L are among the highest found during this study.

Full partitioning of Hg among particulate and non-particulate fractions, as well as between MeHg, AHg, and SHg was only possible for the May and September/October samples from 2008 (Figures 8-11) when both filtered and unfiltered samples were collected and analyzed. Because particulate Hg fractions are calculated rather than measured directly, the values can be slightly negative if most of the Hg is dissolved because variability in samples can lead to instances where the filtered fraction can have higher Hg concentration than the unfiltered fraction. Despite this difficulty, relatively few samples had significantly negative values for particulate THg or any of its component species.

Within the St. Louis River, particulate THg was highest during May, when river levels and runoff were high. Otherwise, particulate Hg accounted for a relatively small fraction of the

Hg present in water during periods of reduced flow. For tributaries, particulate THg concentrations were more variable. West Two and Swan Rivers had a relatively high particulate fraction compared to most tributaries. Typically, filtered and unfiltered AHg and MeHg measurements agreed with each other more closely than THg measurements, indicating that mercury filtered from the solution was mostly present as non-bioavailable SHg. Although significant SHg also exists in the dissolved fraction, this component usually has a larger particulate fraction than either AHg or MeHg. Possible exceptions to this include MeHg in East Two River and Mud Hen Creek samples from May 2008, which had a high particulate fraction. Also, Swan River had a relatively high particulate fraction for AHg in May 2008 and Mile 115 of the St Louis River had a comparatively high particulate AHg fraction in September/October 2008, samples.

6. Discussion

The mining industry in Minnesota began in the 1890s, long before MeHg generation and fish-Hg were considered problematic. Now, more than a century later, mine pits and stockpiles dot the entire northern fringe of the St. Louis River basin, and it is clear that these features contribute the majority of SO_4 presently found in the St. Louis River. Of much greater concern than determining if SO_4 is derived from mine lands, is the task of evaluating whether SO_4 mobilized by past or present mining is responsible for elevated MeHg loading to surface waters. For this to be the case, this SO_4 must first reach an environment where it is reduced to sulfide in the presence of both a labile carbon food source and bioavailable Hg. To affect MeHg production, the added SO_4 must increase the rate or the cumulative amount of SO_4 reduction that takes place, and accomplish this without converting the bioavailable Hg to non-bioavailable sulfidic forms. Finally, to affect river chemistry, the MeHg produced as a by-product of additional SO_4 reduction must also be transported to the rivers.

In this area of Minnesota, SO_4 reduction and associated MeHg may occur in wetlands, river sediments, or impoundments downstream. From wetlands, MeHg will not contaminate fish unless it is transported from the wetland into the river and it is possible for MeHg to be produced in a wetland and never affect fish. Similarly, MeHg produced in river sediments does not enter the food chain unless it diffuses into overlying water or it is absorbed by benthic invertebrates. It is generally thought that loading from wetlands is the bigger concern, both because of greater production of organic matter and because the lateral movement of water from a wetland can be much faster than molecular diffusion of MeHg from sediment.

Before conducting detailed studies of each of the detailed links of the SO_4-MeHg chain it is important to empirically examine the distributions of SO_4 and MeHg to determine if, where, and, perhaps when the whole methylation and transport chain is complete. This is not an easy task, however, owing to the diverse and dynamic nature of the river environment especially when, as in this case, the river is superimposed onto a wetland-rich landscape that for more than a century has hosted a large mining industry. The following treatment is, in effect, a survey of what is present here and now in the district, but with focus on dissolved species most closely tied to SO_4 and Hg reactions. The distributions and sources of SO_4 are examined in relation to the other measured parameters in the hopes of providing a more mechanistic understanding of how and where SO_4 is delivered to the St. Louis River. Later, the distributions of DOC and dissolved Fe are used to infer the nature of wetland involvement in river chemistry, specifically relating to MeHg generation. SO_4 and MeHg distributions are then finally compared to help establish a better understanding of the degree to which SO_4 from past and present mining activities affects MeHg generation in this watershed.

6.1. *Sulfate Source Considerations*

Present SO_4 loading in the St. Louis River upstream from Cloquet can be estimated using flow data available in the USGS hydrograph for Scanlon Dam and data from this and other studies (Lindgren et al, 2006) (Figure 12). Loading is estimated in each case using SO_4 concentration from a point immediately upstream of the Scanlon Dam and multiplying this value by the flow at the time that the measurement was made. An additional independent data point was computed, for comparison, using flow measurements and SO_4 data from this report for June 2008 and calculated for the point where the St. Louis and Cloquet Rivers meet.

These loading data (Fig. 12) indicate a general trend of increasing SO_4 load with increasing flow in the river. Thus, it would be a mistake to represent SO_4 loading to this river as being derived from a constant groundwater source that is periodically diluted by precipitation and snowmelt events. Similarly, it would be a mistake to link seasonal changes in SO_4 loading to simple changes in flow because, as shown in Figure 4, SO_4 concentrations across the watershed obviously respond to change in water availability. Whatever the SO_4 release mechanisms are, the overall loading to the river increases from about 25-50 tons/day under relatively dry periods to over 200 tons/day under relatively wet conditions.

Under high flow conditions, as in June 2008, the SO_4 sources are relatively evenly spread throughout the region (Fig. 13), but loading from the sampled tributaries only accounted for 2/3 of the total SO_4 loading. The remaining 1/3 has not been accounted for in this study, but this missing component, from a relatively wet period, is as great in mass as the total load for the St. Louis River during dry periods. Thus, further study will be needed if we are to gain a complete understanding of SO_4 sources to the St. Louis River during all periods.

One of the most important known and more quantifiable SO_4 loads to the St. Louis River involves the pumping of water from mine pits that are being dewatered. Examples where this type of source applies include West and East Two Rivers. In each case, SO_4 concentration decreased during periods of high flow, but not by nearly as much as might be expected when compared to the relative increase in flow shown in the hydrograph in Figure 3. Although not all of the SO_4 in these rivers comes from mines, these two rivers collectively produced a load of approximately 25.5 tons of SO_4 during the June sampling round, corresponding to about 20% of the 126 tons/day at the time the measurements were made (Table 10; Fig. 12). Two important aspects of this type of pumping are (1) that it is continuous, owing to the fact that the pits are deep and receive inflow of groundwater even when conditions are dry and (2) the rate of pumping increases during wet periods, owing to the fact that the pit must be kept dry in order to continue mining. Although this is an important source of SO_4, capable of increasing load with increasing flow, other sources must also be present.

Another important source of SO_4 to the St. Louis River is the SO_4 that seeps from tailings basins. Tailings basins have high SO_4 due to collection of SO_2 by scrubber systems and also due to oxidation of sulfide minerals in tailings basins. This SO_4 can concentrate in the tailings water over time and loading due to tailings seepage tends to increase over time (Lapakko and Jagunich, 1991; Minntac, 2004b). The only tailings basins that lie within the watershed are those from the former LTV mining operation that contributes probably no more than 2 to 3 metric tons/day of

SO_4 to the Embarrass River watershed (Polymet 2007b) and an unknown amount from the active United Taconite processing plant that is located just south of the St. Louis River near the northern tip of the Stony Creek watershed (Fig. 2). In addition, Arcelor-Mittal deposits tailings into a pit system that is currently not overflowing. Although the exact contribution from United Taconite's tailings basin is not known, detailed analysis of the results in the St. Louis River flow data and SO_4 concentrations in Tables 5 and 10 for the area around the basin suggest that loading from this source was approximately 0.5 metric tons/day in June 2008 when the samples were collected. It appears that only a small percentage of the SO_4 in the river during the June sampling came from tailings basins and, thus, over 3/4 of the sulfate loading to the St. Louis River is derived from sources other than mine pit dewatering and tailings basin seepage under relatively wet conditions.

A primary source of SO_4 from mining activities on the Iron Range is that which drains from rock and overburden stockpiles that are piled in or near to both active and abandoned mine pits. Sulfide minerals present in amounts of only 0.5 to 2% can generate elevated SO_4 concentrations in water that penetrates a stockpile. This water can soak into the local groundwater systems or fill nearby pits and eventually find its way into nearby rivers and lakes. The amounts of sulfide mineralization in stockpiles on the Iron Range are not well known, but the widespread nature of this source is likely illustrated by the relatively large size of the loadings from all of the tributaries with mining in the watersheds compared to those without mines. The Elbow Creek watershed (19.9 mi^2), for example, accounted for 6.5 tons/day SO_4 during the June 2008 sampling round. By comparison, the nearby Mud Hen Creek watershed (99.3 mi^2) is five times larger than this and generated only 0.8 metric tons SO_4/day. Further studies will better refine the understanding of SO_4 loading to the river. However, it is currently estimated that the extensive network of stockpiles exceeds mine dewatering and tailings seepage as a source of SO_4 to the St. Louis River.

6.1.1. SO_4 Isotopes

SO_4 isotopes (Figure 13) and major element composition (Figures 14 and 15) can be used to help determine the relative amounts of SO_4 from individual sources. Eimers et al. (2004) found that $\delta^{34}S_{SO4}$ in surface waters sampled in central Ontario was dominated by oxidation and mobilization of sulfide minerals present in the rocks undergoing weathering. During most periods, wetlands were found to be net sinks for SO_4, although it has also been found that some of the sulfide formed and stored in wetlands by SO_4 reduction can be exposed to oxidizing conditions during drought periods and remobilized into streams during wet periods (Eimers et al., 2007).

Some reduction and oxidation occurs in the St. Louis River watershed, but such processes cannot account for the fact that the $\delta^{34}S_{SO4}$ for the St. Louis River samples collected in September were all greater than $\delta^{34}S_{SO4}$ for tributaries sampled during the same period. Furthermore, $\delta^{34}S_{SO4}$ for most of the tributaries increased between September and May, while that for the St. Louis River decreased substantially. If seasonally driven oxidation and reduction processes accounted for the changing $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values in the St. Louis River, it is difficult to understand why the same seasonal processes were not observed within all of the watersheds where SO_4 was derived. A more likely explanation for the changing $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values in the St. Louis River is that there is a change in the relative mix of sources when the conditions change from wet to dry.

During sulfide oxidation, the $\delta^{34}S$ for dissolved SO_4 should be similar to $\delta^{34}S$ of the oxidizing sulfide minerals (Taylor and Wheeler, 1994). $\delta^{18}O_{SO4}$ of SO_4 from dissolving sulfides is much more difficult to use as a marker, because this value reflects the composition of the water and O_2 that is present during oxidation and is also sensitive to the specific oxidation mechanism (Van Stempvoort and Krouse, 1994). For this discussion, therefore, we focus on $\delta^{34}S_{SO4}$ only.

Sulfur isotopic composition of the Biwabik Iron and Virgina Formations and the stratigraphically equivalent Gunflint and Rove Formations have been reported by Johnston et al. (2006). $\delta^{34}S$ values for three samples from the upper slaty member the Biwabik Iron Formation minerals ranged from 3.26 to 9.83 ‰. $\delta^{34}S_{SO4}$ values for samples collected from locations stratigraphically higher in the iron formation had a larger range than this, and extended to $\delta^{34}S$ values above 20 ‰ for many of the samples. The highest $\delta^{34}S_{SO4}$ samples were all for sulfide minerals collected from the Rove Formation which is equivalent to the Virginia Formation that overlies the Biwabik Iron Formation, with the two units only separated by igneous intrusions from the Duluth Complex. From this source, it is difficult to establish the values expected for rock in stockpiles, except that $\delta^{34}S_{SO4}$ could be higher for waters derived by oxidation of sulfide minerals in the Virginia Formation compared to those derived from the Biwabik Iron Formation.

$\delta^{34}S_{SO4}$ has also been measured in waters where SO_4 was obviously derived by oxidation of Biwabik Iron Formation sulfide in stockpiles at the former LTV mine site (Mesabi Nugget, 2009). The $\delta^{34}S_{SO4}$ values ranged from approximately 4 to 9 ‰, similar to the $\delta^{34}S_{SO4}$ values found in sulfide minerals in the Biwabik Iron Formation reported by Johnston et al. (2006). This range is also similar to $\delta^{34}S_{SO4}$ in most of the tributaries, except for two tributaries that were only sampled in June 2008, which had $\delta^{34}S_{SO4}$ values of 15.1 ‰ (Elbow Creek, confluence at Mile 123) and 16.6 ‰ (Long Lake Creek, confluence at Mile 128), respectively.

Elbow Creek, in particular, had the highest SO_4 concentration of tributaries measured during this sample period (155 mg/L) indicating there is potential to provide a large contribution of high-$\delta^{34}S_{SO4}$ SO_4 to the St. Louis River specifically in this region. The $\delta^{34}S_{SO4}$ value for the St. Louis River increased between Mile 142 and 125 from 12.5 to 14.3 ‰, respectively, as SO_4 concentrations increased from 24.7 to 67.9 mg/L. Between miles 125 and 98, as the St. Louis River moved through the rest of the mining region, $\delta^{34}S_{SO4}$ decreased to 13.0 ‰ as the SO_4 concentration increased again to 97 mg/L.

During the September 2007 sampling period, the $\delta^{34}S_{SO4}$ of the St. Louis River reached a high value between Miles 125-98 presumably due to SO_4 contribution from a high $\delta^{34}S_{SO4}$ source. The high $\delta^{34}S_{SO4}$ source from this region was quantitatively less important compared to the lower $\delta^{34}S_{SO4}$ sources entering the river both up- and down-stream from in June 2008, and thus the isotopic composition of SO_4 in the whole river appeared to shift. Future studies will be required to determine the significance of this (e.g., intermittent or constant ground water source for the SO_4 with high $\delta^{34}S_{SO4}$) and to better identify the high $\delta^{34}S_{SO4}$ source in the area around Elbow and Long Lake Creeks.

6.1.2. Ca, Mg, Na, and Cl

Further insight on the sources of SO_4 in the region can be gained by examining the elements that accompany SO_4 in the waters. Ca and Mg concentrations are closely linked to SO_4

owing to the crucial role these elements play in neutralizing sulfuric acid that is generated by sulfide oxidation in carbonate-bearing rocks such as those in the Biwabik Iron Formation.

Release of SO_4 from stockpiles and tailings basins begins with the oxidation of pyrite (FeS_2) to produce SO_4 and acid by reactions such as:

$$FeS_2 + 3.75O_2 + 3.5\ H_2O = Fe(OH)_3 + 4H^+ + 2SO_4^= \qquad (1)$$

where $Fe(OH)_3$ is an insoluble ferric hydroxide mineral. Despite the generation of acid, drainage in waste rock piles that contain carbonate minerals is not typically acidic, because the acid formed is neutralized by reaction with Ca or Mg-bearing carbonate minerals by reactions such as:

$$2H^+ + CaCO_3 = Ca^{++} + 2HCO_3^- \qquad (2)$$

or

$$2H^+ + MgCO_3 = Mg^{++} + 2HCO_3^- \qquad (3)$$

The net result of Reactions 1 through 3 is addition of Ca, Mg, and SO_4 to the water, as well as HCO_3^-.

Sulfide and carbonate minerals exposed to air and water in stockpiles provides an ideal source for Ca, Mg, and SO_4 release to the environment through reactions such as these. However, the relative Ca and Mg concentrations in waters can be variable, depending initially on the Ca and Mg ratios in the carbonate minerals being dissolved and, subsequently, on cation exchange processes in minerals and possible precipitation of calcium-rich carbonate minerals. The most important Ca and Mg-bearing carbonate minerals in the Biwabik Iron Formation include Mg-Ca-siderite and ankerite, the dissolution of which typically imparts a high Mg/Ca ratio on the water. Both siderite and ankerite are Fe-bearing carbonate minerals. Dissolution of the Fe-carbonate component does not, however, contribute Fe^{++} to solution, because Fe^{+2} is oxidized to insoluble Fe^{+++} species in the oxidizing environments where sulfide oxidation occurs.

Because of this link between high Mg/Ca ratio and sulfide oxidation in the Biwabik Iron Formation, some insight on present release mechanisms can be gained by examining the Ca and Mg chemistry of St. Louis River tributaries (Figure 15). In general, Mg increases with increasing SO_4 for tributaries, while Ca reaches relatively constant levels between about 20 and 40 mg/L, and never exceeds this. The reason for this is that calcite saturation places a limitation on Ca concentrations while no such limit exists for Mg until concentrations much higher than those observed in this study are reached. Although the waters may become saturated with respect to Mg-rich carbonates such as dolomite $CaMg(CO_3)_2$, kinetic limitations on nucleation and precipitation are difficult to overcome (Deelman, 2003). In June the streams containing elevated SO_4 and high Mg/Ca ratios included East and West Two Rivers and Elbow Creek. This source persisted through all seasons for East and West Two Rivers, but this can’t be established for Elbow Creek which was only sampled in June. Furthermore, when SO_4 concentrations in the Partridge River increased to high levels in July (due to pit dewatering; Mesabi Nugget, 2009), the stream switched from having a low Mg/Ca ratio to high Mg/Ca ratio, indicating the strong influence of oxidation of sulfides from the Biwabik Iron Formation on the SO_4 source in this stream.

The source of the sulfate in the Swan and Embarrass Rivers cannot clearly be identified using Mg/Ca ratio. These waters, however, appear to have Ca concentrations that vary similarly across seasons similar to those in the low-SO_4 Floodwood River. A high-Mg SO_4 source may also be present in the lower SO_4 streams, but if so, it is being dominated by calcite dissolution and precipitation processes that commonly control calcium concentrations in surface waters (e.g., Drever, 1988).

Though Ca appears to be limited by dissolution and precipitation processes, regardless of SO_4 concentration in this river, the case for Na is quite different. For the most part, Na release appears to be unrelated to SO_4 release except for a few samples whose SO_4 concentrations range from 100 to 130 mg/L in Figure 15. For these samples, there is a conspicuous increase in Na that accompanies the increase in SO_4, as well as for Mg mentioned previously. A close examination of these data reveal that all samples in this SO_4 concentration range are from East Two River but were sampled at different times. Further evaluation reveals that the Na increases are associated with conspicuous increases in Cl in Tables 8-12. A plot of Na versus Cl for all of the tributaries (Figure 16) reveals that Na and Cl sources are clearly linked in the East Two River and in many other streams on the Iron Range. The source of NaCl addition is unclear, but we note that the two rivers containing the highest Cl concentrations are the Swan and East Two Rivers. Among all the tributaries sampled in this study, these are the only two that have relatively large population centers in them: Hibbing and Chisholm for Swan River; Virginia, Mountain Iron, and Eveleth for East Two Rivers.

For East Two River, in particular, the data also imply that the dominant source of SO_4 in this river must also contain the added Na and Cl because SO_4, Cl, and Na concentrations in this river correlate to each other. Although the high Mg/Ca ratio suggests that the ultimate SO_4 source likely relates to oxidation of sulfides in stockpiles from the Biwabik Iron Formation, the relationship of SO_4, Mg, and Ca with NaCl suggests that the sulfide oxidation products are pooled with the Na and Cl into the same ground- or surface-water reservoir. Upon release to the watershed, concentrations of all of these components increase and decrease together depending on the amount of in-stream dilution that occurs.

An additional question that arises from close inspection of Figure 16 relates to the array of points with increasing Na concentration but relatively fixed Cl concentrations around 10 mg/L. These streams require an additional mechanism to generate increasing Na but without added Cl. Taconite processing plants sometimes add NaOH or Na_2CO_3 to their process streams, specifically to prevent their scrubber waters from becoming too acidic. The primary mechanism that generates acidity in a scrubber water stream is capture of SO_2 which arises from sulfide in the fuel source and greenball pellets that are fired in taconite furnaces. High Na without a correspondingly high value for Cl may thus be an indicator that some of the SO_4 is derived from this type of source. During this study, increasing Na without corresponding increase in Cl was found in the Embarrass and West Two Rivers, suggesting a processing water component may be present in those streams.

Finally, a comparison between current and past (1961) SO_4, Mg, Ca, Na, and Cl concentrations for East Two Rivers can be made to evaluate how SO_4 sources may have changed through time on the Iron Range (Figure 17). This year represents a point in time when taconite mining was relatively new to the area and mining of the softer “natural ore” deposits had been all but completed. The source of the sulfide in 1961 is not presently known by the authors of this report, but the high SO_4 concentrations suggest there may have been considerable sulfide mineralization in some of the rock and overburden stockpiles generated by mining at that time. Unlike what occurs in waste stockpiles from taconite mining today, however, Mg was released in amounts similar to SO_4 and Ca in 1961 (on a meq basis). Today, Mg greatly exceeds the concentration of Ca and SO_4 in the East Two Rivers. Although not shown in Figure 17, similar Ca-Mg-SO_4 relationships appear to hold for most of the Iron Range rivers in 1961. The nature of the SO_4 release in 1961 is not presently understood, but it cannot be forgotten that oxidation of sulfide grains in materials deposited on the surface by mining companies in the first half of the 20th century may still contribute SO_4 to streams today.

6.2. Wetlands and Hg Cycling

While most of the SO_4 in the St. Louis River is sourced ultimately in rocks, virtually all of the Hg is, or was, originally derived from the atmosphere (wet and dry precipitation). Furthermore, while SO_4 is a highly soluble major element, Hg is a relatively insoluble trace component that generally requires a ligand to promote its transport in aquatic systems. Hg that is transported into rivers is, therefore, typically bound to suspended particles and DOC (Brigham et al., 2009). For a low-sediment river such as the St. Louis River, Hg is almost certainly bound primarily to organic carbon and, thus, an important starting point for evaluating Hg transport involves understanding DOC transport.

Wetlands are usually important sources of DOC to rivers, but we have seen that most of the wetlands contribute water to the St. Louis River between Miles 71 to 119 (Table 1), where the major streams that join the St. Louis River have between 25.5 and 53.4 % wetland areas. By contrast, most of the SO_4 in the St. Louis River is added between miles 119 and 161 from streams traveling through watersheds composed of only 5 and 12.5% wetlands. From this perspective alone, it is easy to see that the majority of wetland-derived DOC in the St. Louis River does not contact SO_4 from mining, until the DOC actually enters the St. Louis River.

Wetlands are probably not the only source of DOC to a stream, however, because soil processes can lead to generation of DOC. In the May 2008 samples, for example, following a relatively wet spring, DOC concentrations were elevated in virtually all of the watersheds, regardless of wetland %. For the systems with low wetland %, the increase in DOC from dry to wet conditions was especially notable. This behavior is relatively common as indicated by studies of Hood et al. (2006) and Agren et al. (2008) who showed that DOC sources vary seasonally in forest/wetland watersheds. Agren et al. (2008), in particular, found that streams in forested catchments have higher concentrations of terrestrial-derived DOC during spring snow melt. Therefore, soil derived DOC was likely an important source of the increased DOC concentrations under high flow conditions in May.

Even higher DOC values than those found in May were found in some watersheds under moderate, but declining, flow conditions in July 2008. In this case, it was found that high Fe concentrations accompanied the high DOC and it is thought that the presence of this high Fe under these specific hydrologic circumstances provides an important clue to the source of the DOC. Fe is generally not soluble under oxidizing conditions that typically prevail in water under dry conditions in the upper vegetated regions in wetland areas and, like Hg, transport for this component requires a host ligand to carry it. Like Hg, the most common host species for Fe transport in water from wetlands is dissolved organic carbon. But because Fe concentrations in pore fluids from deep within a wetland tend to be higher than those in the shallow and surface portions, the elevated Fe concentration in streams at this time suggest that deeper, more reduced portions of wetlands were the source of the water.

Figure 19 shows how samples collected during the different seasons from the various watersheds display relatively systematic relationships between dissolved Fe and DOC. Although elevated DOC was observed throughout the system in May 2008, this DOC carried less Fe than samples with similar DOC in July. The elevated Fe/DOC ratio in July may be a strong indicator that much of the DOC in the St. Louis River came from deeper, more reduced portions of the wetlands as a result of wetland dewatering.

To evaluate the relative effect of different DOC source regions for transport of Hg and MeHg, these species are plotted against DOC in Figures 20 and 21. However, for the time being, data from the July sampling period is excluded, owing to the DMM contamination issue discussed in Appendix 1. Furthermore, additional available THg and DOC data have been added to these figures. These include THg reported by Lindgren et al. (2006) who collected and analyzed samples from the St. Louis River through the summer of 2005 and unpublished THg, MeHg, and DOC data collected during the summer of 2003 and 2004 for the Western Lake Superior Sanitary District (unpublished data provided by Tim Tuominen). All of these additional data are for samples collected various distances upstream from Mile 36 in the St. Louis River.

For THg, there is a relatively strongly developed array of samples where THg increases with DOC from a point extending from about 5 mg/l DOC and low THg (Fig. 20). Increasing DOC by 30 mg/L results in an increase in THg of about 6 ng/L. One interpretation of this trend is that it results from the mixing of waters containing DOC with low-Hg DOC (e.g., from groundwater and instream organic decomposition reactions) with high-Hg DOC derived from wetlands. To generate the observed slope, this wetland component would need to have a Hg concentration of approximately 0.2 ng Hg/mg DOC or about 0.2 ppm on a dry carbon basis. In May 2007 when abundant precipitation and recent runoff were present in the streams, both DOC and THg became elevated. Examination of Hg speciation for the May period (Figures 8-11 – high flow) reveals that much of this mercury was present as dissolved AHg and particulate SHg. This suggests, therefore, that Hg concentrations during this time period reflected a more diverse combination of sources, including particulate mercury from runoff, Hg attached to carbon derived from upland soils, and perhaps even unbound Hg^{++} from precipitation that has not yet interacted sufficiently with the particles to be fully removed from solution. Of these sources, only that attached to dissolved organic carbon would be expected to carry significant MeHg with it, because precipitation does not carry significant MeHg and because MeHg was not typically found on particulate carbon in the water samples collected during this study.

For MeHg concentrations during these same periods, a much tighter array is formed between samples collected during different seasons (Fig. 21). A possible interpretation for this pattern is that waters are composed of a mixture of components including DOC containing little or no MeHg (derived from groundwater and in-stream oxidation of organic matter) and DOC from wetlands containing about 0.02 ng MeHg/mg DOC (20 ppb on a dry carbon basis). Higher MeHg in May was due, largely, to a greater fraction of runoff from wetlands and the greater contribution of DOC from upland soil runoff. During such a period of high flow, it could be anticipated that the relative contribution from a low-MeHg groundwater component would be significantly decreased compared to that prevailing under dry conditions. Thus, MeHg samples from watersheds containing few wetlands could be shifted to the left on Figure 21. Meanwhile, flow from peaty wetlands can almost stop completely during dry periods. Thus, slow-flowing streams from watersheds containing high wetland percentages and sampled under dry conditions contain very high DOC but low MeHg and, therefore, plot to the right of the general trend. It is thought that these samples represent very old waters that may have once contained MeHg, but which lost MeHg via natural degradation in the pore fluid environment. Seeps of this type have relatively small impact on the St. Louis River chemistry as a whole because flow is limited, but they make it possible for streams with low flow and coming from wetland areas to have MeHg/DOC ratios much lower than waters arising from more actively flowing systems.

The processes discussed above are largely consistent with inferences made by Balogh et al. in 2004 and 2008 and by Selvendiran et al. (2008). Under most conditions it has been found that subsurface processes in peat lands have a limited impact on the chemical composition of surface waters draining through them. This is because hydraulic conductivity of deeper layers is typically low and thus, relatively shallow surface reactions control chemical processes in most cases. Transport of MeHg or Hg is the result of water flowing through the upper portions of the wetlands.

On the other hand, when hydrologic conditions are upset by a period of high flow input, the deepening waters can have a smothering effect on the processes taking place in the upper surface layers of wetlands, where recent growth may have generated abundant labile carbon. In such cases, the O_2 may be quickly consumed, reduction of SO_4 can begin, and Hg may be converted to MeHg. Compounds produced in the uppermost layers of wetlands may be susceptible to transport to surrounding wetlands and streams both during and following high flow events.

Balogh et al. (2004) followed concentrations for Hg, MeHg, and other dissolved components in two tributaries of the Rum River in east-central Minnesota and found systematic variations that were attributed to a changeover from early surface flow in wetlands to deeper wetland derived drainage later. MeHg was not highly elevated during the periods of highest flow in the stream, apparently because reactions needing to form MeHg take time to occur. However, once the water levels began to decrease in the river MeHg concentration quickly peaked to a value of approximately 1 to 1.5 ng/L. Fe was not initially elevated in the high MeHg water but began increasing quickly as MeHg concentration continued to decline. DOC, Fe, and MeHg then all declined together indicating the volume of wetland-sourced water was decreasing relative to the normal groundwater component. Eventually, the system returned to normal base flow conditions with approximately 5 mg/l DOC containing very low MeHg and Fe concentrations.

While we are unable to compare all of our Hg data from July to the data from Balogh et al., owing to the problem with the July samples, the samples that had minimal DMM provide at least some basis for comparison (Tables 15 and 19). For example, filtered MeHg samples from SLR at Mile 53 contained 1.0 mg/L Fe, 26 mg/L DOC and a MeHg concentration of 0.6 ng/L. These values are all similar to the levels measured by Balogh et al. (2004) in the Rum River watershed. Mile 36, the most downstream point measured in our study, had MeHg, DOC, and Fe concentrations that were 0.5 ng/L, 24 mg/L, and 1.0 mg/L, respectively. These levels are all similar to what they were at Mile 53 and to the data reported by Balogh et al. By comparison, the highest MeHg values for these two sites in the St. Louis River in May and September/October was only 0.3 ng/L. Thus, it is believed that the elevated MeHg concentration observed in July were found under conditions similar to those observed by Balogh et al. (2004). Although it is tempting to use this similarity to conclude that the high SO_4 concentrations in the St. Louis River did not result in an increase in MeHg compared to the low SO_4 streams studied by Balogh, it is important to remember that much of the DOC in the St. Louis River in July was likely derived from low-SO_4, wetland-rich watersheds.

That such chemistry was found for the St. Louis River at Miles 36 and 53 implies that many tributaries within the St. Louis River Basin contributed DOC with increased MeHg and Fe concentrations to the river. Further upstream in the St. Louis River, at Miles 142 and 179 at locations upstream from where most of the SO_4 was added, Fe concentration was also elevated (0.8 and 0.9 mg/L, respectively), while DOC concentrations were 22 and 28 ng/L. These concentrations suggest a similar event-related MeHg contribution to surface waters might be present in this part of the river and, corresponding, the measured MeHg concentrations were 0.58 and 0.48 ng/L for the filtered samples.

Unfortunately, only four of the samples from tributaries sampled during July had low or undetectable DMM concentrations (Table 19): filtered and unfiltered samples from the Embarrass River and the filtered samples from the Cloquet River and Mud Hen Creek. The samples from the Embarrass River had relatively low Fe and were not likely derived from deeper wetlands within the watershed. The MeHg concentration was, correspondingly, low (0.2 ng/L) consistent with the low DOC concentration (13 ng/L). The Mud Hen Creek sample, by contrast, had elevated levels of DOC, Fe, and MeHg, suggesting this creek likely experienced a post-precipitation wetland drainage event. The Cloquet River, meanwhile, did not appear to experience a period of elevated MeHg and Fe during this time either, although this watershed has a relatively low wetland percentage.

A plot of MeHg versus SO_4 for samples collected in the St. Louis River watershed shows that under most conditions, waters in this basin typically have either elevated MeHg or elevated SO_4, but rarely both (Fig. 22). This is probably due, in part, to that fact that most DOC, and thus MeHg, is derived from watersheds that do not have a large SO_4 source in them. Futhermore, the majority of waters containing elevated SO_4 are derived from mining-influenced watersheds with few wetlands. Exacerbating this effect is the fact that wetlands typically produce DOC with lower MeHg concentrations under relatively dry conditions, precisely at a time when waters from mine lands have their greatest influence on SO_4 concentration in the St. Louis River.

During this study only a single sample was found to contain elevated levels of both MeHg and SO_4, and this was a sample collected from East Two River in September 2007. The source of this MeHg was originally thought to be related to high Cl in this stream. However, none of the subsequent samples from this or any other stream with elevated Cl had elevated MeHg concentrations. A Cl-MeHg link appears tenuous at this point (Bavin and Berndt, 2009) and the source of the elevated MeHg in this one case remains enigmatic.

7. Summary and Recommendations

SO_4 sources in the St. Louis River watershed are likely dominated by the oxidation of relatively small amounts of sulfide minerals in stockpiles that are found throughout the mined portions of the Mesabi Iron Range. Although the sulfide is present in relatively small amounts, more than a century of mining has generated an extensive array of stockpiles that cuts across the entire northern fringe of the St. Louis River watershed. Although mine dewatering and mineral processing on the Iron Range are also important sources of SO_4, evidence based on loading estimates and on the chemistry of other elements, including Ca, Mg, Na, and Cl, suggest that these sources are not as large as those from oxidation of sulfide minerals in stockpiles. A comparison with river chemistry data from 1955 to 1961 reveals that SO_4 concentrations have been elevated in streams for over 50 years in the region but the primary sources of SO_4 have changed during this time. The present source appears to be dominated by sulfide oxidation within stockpiles of the Biwabik Iron Formation while the specific SO_4 sources that were present 50 years ago are not well known.

MeHg concentrations in the river sites visited during this study appear to have little to do with SO_4 released to surface waters from the mining operations. MeHg appears to be produced primarily in extensive wetland areas located mostly downstream from the mining region. For the most part, the tributaries that have extensive wetlands in watersheds that have no mining activity taking place and the primary source regions for SO_4 have few wetlands. Thus, the MeHg levels in this relatively high-SO_4 river are controlled primarily by DOC levels which are, in turn, dictated by drainage from low-SO_4 watersheds. However, before such an interpretation can be accepted, it is important to remember that precipitation-event related processes, such as those reported by Balogh et al. (2004 and 2008) for tributaries of the Rum River, were not well covered in this study (owing to technical difficulties associated with analysis of the mercury samples during July 2008). Two samples from Miles 36 and 53 in the St. Louis River that were collected in July 2008, had DOC, Fe, and MeHg concentrations almost identical to two low-SO_4 tributaries of the Rum River under similar hydrologic condition. Although this provides some support for the hypothesis that SO_4 has minimal impact on MeHg concentrations in the St. Louis River, this will need to be verified with further sampling during the critical summer months.

Finally, because the approach used here relied on watershed-wide snapshots, the detail needed to evaluate MeHg production from direct SO_4 introduction to specific wetland or lake environments was not available. These effects need to be evaluated closer to the locations where SO_4 and MeHg interactions may be taking place, and without dilution from high-DOC waters derived from wetlands downstream. In this light, the most important contribution from the present study may not be the interpretation of MeHg arising from specific DOC-source areas, but rather the empirical results themselves. Presently, dissolved Fe and DOC appear to be among the most important measurements for assessing MeHg concentrations within the St. Louis River Basin. Data such as this can provide an initial framework that can begin to be used to distinguish "normal" from "abnormal" MeHg concentrations in the St. Louis River and each of its constituent watersheds.

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9. Tables

Table 1. Total area and wetland area for selected watersheds within the St. Louis River watershed. All areas were calculated using the most current GIS and watershed and wetland shape files available at the Minnesota Department of Natural Resources (2002). Confluence River miles are as measured from the mouth of the St. Louis River.

Watershed	*Confluence River Mile*	*Area (mi^2)*	*Wetland Area (mi^2)*	*% Wetland Area*
*Partridge River	160.6	161.8	20.3	12.5
*Embarrass River	139.2	180.8	19.3	10.7
Mud Hen Creek	133.0	99.3	13.1	13.2
*Long Lake Creek	128.0	21.5	1.5	7.0
*Elbow Creek	123.0	19.9	1.5	7.5
*East Two River	119.8	52.1	2.6	5.0
*West Two River	119.5	81.3	6.4	7.9
Stony Creek	98.5	88.4	47.0	53.4
*Swan River	97.0	241.4	61.6	25.5
Whiteface River	78.5	535.8	165.3	30.9
Floodwood River	71.7	231.1	108.4	46.9
Cloquet River	51.3	793.5	103.4	13.0

***** Denotes watershed that hosts iron mining features.

Table 2. Sampling locations for this study. Not all stations were sampled during each sample period (see data tables for specific dates). St. Louis River miles are as measured from the mouth of the St. Louis River.

River	*Location*
St. Louis River Mile 179	HW 110 bridge E of Hoyt Lakes
St. Louis River Mile 142	HW 95 bridge SE of Eveleth
St. Louis River Mile 135	HW 16 bridge SE of Eveleth
St. Louis River Mile 125	HW 7 bridge near Forbes
St. Louis River Mile 115	HW 27 bridge near Zim
St Louis River Mile 98	HW 83 bridge N of Toivola
St. Louis River Mile 80	HW 29 bridge NE of Floodwood
St. Louis River Mile 72	HW 8 bridge outside of Floodwood
St. Louis River Mile 53	HW 31 bridge in Brookston
St. Louis River Mile 36	HW 33 bridge in Cloquet
Partridge River	HW 110 bridge W of Hoyt Lakes
Embarrass River	HW 95 bridge SE of Eveleth
Mud Hen Creek	HW 16 bridge SE of Eveleth
Long Lake Creek	HW 16 bridge S of Eveleth
Elbow Creek	HW 16 bridge S of Eveleth
West Two Rivers	HW 16 bridge SW of Eveleth
East Two Rivers	HW 16 bridge SW of Eveleth
Stony Creek	HW 83 bridge N of Toivola
Swan River	HW 750 bridge N of Toivola
Whiteface River	HW 5 bridge NE of Floodwood
Floodwood River	HW 73 bridge in Floodwood
Cloquet River	HW 7 bridge NE of Brookston

Table 3. Values for selected parameters measured in samples collected from the St. Louis River in September 2007. DOC, cation, and anion concentrations are listed in mg/L.

Mile	*179*	*142*	*125*	*98*	*80*	*53*	*36*
Date	9/10/07	9/10/07	9/11/07	9/11/07	9/12/07	9/12/07	9/12/07
Time CDT	10:36	13:35	8:25	13:15	9:50	12:53	14:15
Temp. (C)	14.9	16.8	12.8	14.5	14.2	17	16.8
Cond (μS/cm)	95	225	380	550	430	275	260
pH	7.6	8.1	8.3	8.4	8.2	8.3	8.3
DOC	15.0	7.7	9.4	10.0	18.0	18.0	11.0
Cations							
Al	<0.03	<0.03	<0.03	<0.03	0.05	<0.03	<0.03
Si	3.0	6.1	5.0	4.1	3.3	2.5	2.8
Fe	0.3	0.3	0.3	0.1	0.5	0.1	0.1
Mn	0.3	0.1	0.1	0.1	0.1	0.05	0.01
Sr	0.03	0.1	0.1	0.1	0.1	0.1	0.1
Ba	<0.01	<0.01	0.02	0.02	0.02	0.02	0.01
Ca	8.6	26.6	30.2	32.7	31.5	24.6	24.2
Mg	6.4	13.1	31.1	41.2	32.5	19.9	16.9
Na	2.8	8.4	17.9	28.3	22.4	14.3	11.2
K	0.3	1.8	3.6	5.0	4.0	2.5	1.9
Anions							
F	0.1	0.1	0.2	0.3	0.2	0.2	0.2
Cl	0.6	8.3	11.6	21.1	18.5	10.7	8.8
Br	0.002	0.01	0.02	0.02	0.02	0.01	0.01
SO_4	4.9	24.7	67.9	93.0	67.4	53.0	22.0
$\delta^{34}S_{SO4}$		12.5	14.3	13.0	11.2	12.1	11.8
$\delta^{18}O_{SO4}$		7.1	2.9	2.6	2.1	3.6	6.2
Total Kjeld. N	0.6	0.3	0.4	0.5	0.7	0.7	0.5
NO_2-N	0.001	0.001	<0.002	0.001	0.002	0.002	0.001
NO_3-N	0.5	0.4	0.2	0.9	0.4	0.5	0.03
NH_3-N	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Total P	0.02	0.02	0.02	0.03	0.02	0.04	0.03
Phos-P	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Table 4. Values for selected parameters measured in samples collected from the St. Louis River in May 2008. DOC, cation, and anion concentrations are listed in mg/L.

Mile	*179*	*142*	*125*	*115*	*80*	*53*	*36*
Date	5/5/08	5/5/08	5/7/08	5/7/08	5/6/08	5/6/08	5/6/08
Time CDT	8:42	11:10	9:06	10:06	10:20	11:15	13:36
Temp. (C)	8.1	9.1	9.9	10.6	10	10.6	11.7
Cond (µS/cm)	31	90	110	130	125	100	100
pH	7.6	7.3	7.6	7.5	7.5	7.3	7.3
DOC	23.0	22.0	20.0	20.0	20.0	24.0	22.0
Cations							
Al	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Si	2.2	2.8	3.3	3.0	2.8	2.4	2.4
Fe	0.5	0.4	0.5	0.4	0.4	0.4	0.4
Mn	0.02	0.05	0.05	0.04	0.04	0.03	0.03
Sr	<0.02	0.03	0.04	0.04	0.04	0.03	0.03
Ba	<0.01	<0.01	0.01	0.01	0.01	0.01	0.01
Ca	3.2	6.1	8.9	9.7	10.5	9.7	9.4
Mg	2.2	4.6	6.6	8.3	4.5	5.7	5.1
Na	0.7	1.8	4.1	4.8	4.6	3.4	3.0
K	0.5	0.9	1.3	1.5	1.5	1.1	1.0
Anions							
F	0.04	0.05	0.07	0.08	0.07	0.07	0.07
Cl	0.04	1.6	2.9	4.5	4.7	3.5	3.4
Br	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SO_4	2.6	12.1	15.3	21.3	17.5	11.0	9.4
Total Kjeldahl N	1.1	0.8	0.9	0.9	0.6	0.8	1.0
NO_2-N	0.001	0.003	0.003	0.003	0.003	0.002	0.002
NO_3-N	0.1	0.2	0.4	0.5	0.7	0.5	0.5
NH_3-N	0.03	0.03	<0.2	0.05	0.03	0.02	0.02
Total P	0.05	0.07	0.05	0.05	0.03	0.06	0.03
Phosph-P	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Table 5. Values for selected parameters measured in samples collected from the St. Louis River in June 2008. DOC, cation, and anion concentrations are listed in mg/L.

Mile	*179*	*142*	*135*	*125*	*115*	*80*	*72*	*53*
Date	6/17/08	6/18/08	6/18/08	6/18/08	6/18/08	6/16/08	6/16/08	6/16/08
Time CDT	8:56	12:05	11:32	10:40	7:30	10:20	12:12	13:10
Temp. (C)	14.9	19.3	17.7	17.1	15.9	15.7	16.3	17.0
Cond (µS/cm)	36	110	110	115	150	150	135	125
pH	7.14	7.1	7.2	7.5	7.7	7.7	7.5	7.3
Flow(cfs)	313	663	1125	1270	1438	1979	2886	3298
Cations								
Al	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Si	0.8	1.2	2.3	2.3	2.3	2.3	2.3	2.3
Fe	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Mn	0.3	0.6	0.4	0.3	0.3	0.2	0.3	0.3
Sr	<0.02	0.04	0.04	0.04	0.05	0.04	0.04	0.04
Ba	<0.01	0.03	0.02	0.03	0.03	0.02	0.02	0.02
Ca	3.7	8.5	9.2	9.6	11.7	12.1	11.8	11.8
Mg	2.5	6.8	6.9	7.3	10.3	8.5	7.5	6.8
Na	0.8	2.5	3.7	4.0	5.9	5.0	4.3	3.8
K	0.8	2.5	3.7	4.0	5.9	5.0	4.3	3.8
Anions								
F	0.05	0.08	0.08	0.09	0.09	0.09	0.09	0.08
Cl	0.3	1.7	2.7	2.9	4.6	4.5	3.7	3.3
Br	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
SO_4	2.0	16.4	16.6	16.2	22.6	17.0	13.1	10.3
$\delta^{34}S_{SO4}$		8.6	7.9	8.2	8.9	8.2	8.4	8.0
$\delta^{18}O_{SO4}$		3.5	1.5	1.9	0.3	1.3	1.8	2.6
Total Kjeld.N	0.01	0.9	0.8	0.8	0.8	1.0	1.0	1.1
NO_2-N	<0.002	<0.002	<0.002	<0.002	0.002	0.002	0.003	0.003
NO_3-N	0.5	0.5	0.4	0.3	0.3	1.7	1.1	1.5
NH_3-N	0.01	0.03	0.03	0.03	0.03	0.03	0.04	0.03
Total P	0.03	0.03	0.03	0.03	0.04	0.05	0.06	0.06
Phosph-P	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.02	<0.002

Table 6. Values for selected parameters measured in samples collected from the St. Louis River in July 2008. DOC, cation, and anion concentrations are listed in mg/L.

Mile	*179*	*142*	*125*	*115*	*80*	*53*	*36*
Date	7/7/08	7/7/08	7/9/08	7/9/08	7/8/08	7/8/08	7/8/08
Time CDT	8:56	10:35	9:10	10:00	12:05	10:00	8;41
Temp. (C)	21.5	23.5	20.9	21.7	22.8	22.4	23.7
Cond (µS/cm)	50	275	280	310	280	200	165
pH	7.3	7.5	7.9	8.0	7.9	7.8	7.8
DOC	28.0	22.0	18.0	17.0	19.0	26.0	24.0
Cations							
Al	0.1	0.1	0.04	0.04	0.04	0.06	0.06
Si	0.6	2.8	3.0	2.7	2.9	2.9	2.9
Fe	0.8	0.9	0.7	0.6	0.7	1.0	1.0
Mn	0.03	0.08	0.05	0.04	0.04	0.1	0.1
Sr	<0.02	0.08	0.07	0.08	0.07	0.06	0.06
Ba	<0.01	0.01	0.02	0.02	0.02	0.02	0.02
Ca	4.7	15.9	15.8	17.7	19.1	17.1	17.0
Mg	3.2	22.6	18.8	21.2	17.0	12.0	11.8
Na	1.1	4.4	7.1	9.6	9.3	6.4	6.3
K	0.6	1.9	2.2	2.7	3.3	1.6	1.7
Anions							
F	0.07	0.1	0.1	0.1	0.1	0.1	0.1
Cl	0.3	2.6	4.2	6.7	7.7	5.0	4.3
Br	<0.005	<0.005	0.006	<0.005	0.009	0.005	<0.005
SO_4	2.2	70.0	50.4	52.7	34.8	19.5	13.3
Total Kjeldahl N	1.1	0.9	0.8	0.7	0.8	1.0	1.0
NO_2-N	0.002	0.002	0.002	0.001	0.001	0.001	0.003
NO_3-N	0.9	0.9	0.5	1.2	0.4	1.5	1.5
NH_3-N	0.03	0.04	0.03	0.04	0.03	0.03	0.04
Total P	0.04	0.03	0.03	0.04	0.03	0.03	0.03
Phosph-P	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Table 7. Values for selected parameters measured in samples collected from the St. Louis River in September/October 2008. DOC, cation, and anion concentrations are listed in mg/L.

Mile	*179*	*142*	*125*	*115*	*80*	*53*	*36*
Date	10/1/08	10/1/08	9/29/08	9/29/08	9/30/08	9/30/08	9/30/08
Time CDT	8:45	10:20	9:35	10:30	12:20	10:28	9:01
Temp. (C)	9.7	14.1	13.7	14.3	13.4	9.3	12.1
Cond (µS/cm)	65	210	325	410	320	340	255
pH	7.5	7.8	8.1	8.2	8.2	8.2	7.7
DOC	25.0	17.0	12.0	11.0	15.0	11.0	12.0
Cations							
Al	0.1	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Si	2.1	3.2	3.8	3.4	3.0	2.4	3.0
Fe	0.6	0.4	0.3	0.2	0.2	0.1	0.2
Mn	0.02	0.02	0.04	0.03	0.04	0.04	0.05
Sr	0.02	0.1	0.1	0.1	0.1	0.1	0.06
Ba	<0.01	<0.01	<0.01	0.02	0.02	0.02	0.01
Ca	5.0	20.5	24.5	26.1	26.0	27.0	21.6
Mg	4.0	15.0	23.9	30.3	22.8	23.3	16.4
Na	1.7	7.1	12.4	18.9	13.7	13.0	8.8
K	2.1	3.8	4.7	3.6	3.5	2.0	1.7
Anions							
F	0.06	0.2	0.2	0.3	0.2	0.2	0.1
Cl	0.5	3.8	7.0	13.6	11.2	10.5	8.2
Br	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
SO_4	4.7	53.9	65.7	71.9	50.5	46.1	27.5
Total Kjeldahl N	0.9	0.7	0.5	0.5	0.7	0.6	0.6
NO_2-N	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
NO_3-N	0.3	0.3	0.6	0.3	0.7	0.3	0.6
NH_3-N	0.03	0.02	<0.02	<0.02	0.3	<0.02	0.03
Total P	0.03	0.03	0.02	0.03	0.03	0.02	0.02
Phosph-P	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Table 8. Values for selected parameters measured in samples collected from selected tributaries of the St. Louis River in September 2007. DOC, cation, and anion concentrations are listed in mg/L.

Tributary	*Partridge River*	*Embarrass River*	*East Two Rivers*	*West Two Rivers*	*Swan River*	*Whiteface River*	*Floodwood River*	*Cloquet River*
Date	9/10/07	9/10/07	9/11/07	9/11/07	9/11/07	9/12/07	9/12/07	9/12/07
Time CDT	11:45	14:45	9:30	10:10	12:45	8:55	10:37	13:30
Temp. (C)	17.8	16.7	8.2	12.5	13.2	13.3	13.6	14.2
Cond (µS/cm)	260	295	900	410	325	175	200	135
pH	7.7	8.1	7.0	7.1	8.1	8.2	8.3	8.3
DOC	19.0	13.0	9.9	10.0	19.0	18.0	27.0	9.8
Cations								
Al	0.04	<0.03	<0.03	<0.03	0.07	<0.03	0.03	<0.03
Si	4.0	3.7	4.8	3.1	4.0	2.8	5.6	3.1
Fe	0.4	0.1	0.1	0.1	0.4	0.5	0.6	0.1
Mn	0.3	0.06	0.06	0.04	0.04	0.1	0.04	0.04
Sr	0.3	0.08	0.09	0.1	0.1	0.06	0.06	0.04
Ba	0.02	0.03	0.03	0.04	0.02	0.01	0.02	<0.01
Ca	31.0	20.2	30.7	30.9	30.7	17.2	30.9	17.4
Mg	15.2	20.0	63.7	30.4	16.3	12.1	10.8	7.3
Na	9.3	25.3	65.8	18.1	22.8	9.6	5.8	4.2
K	1.7	4.4	7.5	6.4	3.1	1.7	1.3	0.7
Anions								
F	0.2	0.1	0.3	0.2	0.2	0.1	0.3	0.1
Cl	6.6	10.9	78.4	11.8	27.0	7.3	6.3	4.7
Br	0.02	0.01	0.04	0.01	0.02	0.02	0.01	0.00
SO_4	75.5	41.2	127.0	49.5	22.3	5.8	4.5	3.4
$\delta^{34}S_{SO4}$ ‰	5.6	7.3	6.1	9.7	3.1	10.1		
$\delta^{18}O_{SO4}$ ‰	8.0	0.8	0.3	4.2	3.1	5.9		
Total Kjeldahl N	0.7	0.6	1.4	0.6	0.8	0.8	1.1	0.02
NO_2-N	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00
NO_3-N	0.5	0.2	0.9	0.4	0.2	0.3	0.3	0.1
NH_3-N	0.03	0.02	0.2	<0.02	0.02	0.03	0.03	0.02
Total P	0.02	0.02	0.2	0.05	0.08	0.05	0.06	0.02
Phos-P	0.01	<0.002	0.04	<0.002	<0.002	<0.002	0.01	<0.002

Table 9. Values for selected parameters measured in samples collected from selected tributaries of the St. Louis River in May 2008. DOC, cation, and anion concentrations are listed in mg/L.

Tributary	*Partridge River*	*Embarrass River*	*Mud Hen Creek*	*East Two Rivers*	*West Two Rivers*	*Swan River*	*Stony Creek*	*Whiteface River*	*Floodwood River*	*Cloquet River*
Date	5/5/08	5/5/08	5/5/08	5/7/08	5/7/08	5/7/08	5/7/08	5/6/08	5/6/08	5/6/08
Time (CDT)	9:32	12:16	13:10	8:30	7:49	12:25	11:39	8:05	10:21	12:35
Temp. (C)	9.0	7.1	10.3	9.1	9.1	11.2	12.5	10.5	11.3	10.2
Cond (µS/cm)	70	160	75	650	400	145	80	70	85	90
pH	7.2	7.2	7.1	8.3	8.0	7.4	7.2	7.6	7.2	7.4
DOC	15.0	19.0	24.0	15.0	10.0	20.0	34.0	24.0	29.0	16.0
Cations										
Al	0.1	0.05	0.1	0.05	0.04	0.08	0.2	0.1	0.1	0.06
Si	3.1	4.7	1.9	0.7	2.5	1.7	0.6	2.1	0.8	3.0
Fe	0.4	0.6	0.4	0.2	0.2	0.4	0.6	0.5	0.4	0.3
Mn	0.02	0.09	0.02	0.08	0.07	0.06	0.03	0.03	0.02	0.03
Sr	0.04	0.05	<0.02	0.07	0.08	0.04	0.03	<0.02	<0.02	0.02
Ba	<0.01	0.03	<0.01	0.02	0.02	0.02	0.01	<0.01	0.01	<0.01
Ca	6.1	13.2	6.3	23.2	21.8	13.6	10.9	7.1	11.6	9.7
Mg	3.7	9.6	3.2	36.7	28.7	7.8	3.8	3.3	3.7	4.0
Na	1.6	6.9	1.5	36.2	13.1	5.2	1.2	1.7	2.2	2.3
K	<0.3	1.1	<0.3	4.2	4.5	1.3	0.9	0.7	<0.3	<0.3
Anions										
F	0.06	0.1	0.1	0.1	0.1	0.1	0.05	0.07	0.04	0.07
Cl	1.6	4.8	2.1	42.7	11.8	7.1	0.7	2.0	2.9	3.6
Br	<0.005	0.02	<0.005	0.03	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
SO_4	14.0	25.6	3.7	81.7	67.9	10.9	2.9	4.0	2.1	3.2
Total Kjeldahl N	0.8	0.8	0.6	0.9	1.3	1.1	0.9	0.5	1.4	1.3
NO_2-N	0.002	0.004	0.001	0.003	0.02	0.002	0.001	0.002	<0.002	0.001
NO_3-N	0.3	0.3	0.06	0.5	1.1	0.5	0.2	1.3	0.3	0.2
NH_3-N	<0.02	0.03	0.06	0.03	0.1	0.03	0.03	0.04	<0.2	0.03
Total P	0.04	0.08	0.03	0.07	0.05	0.03	0.06	0.02	0.1	0.05
Phosph -P	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Table 10. Values for selected parameters measured in samples collected from a more extended set of tributaries of the St. Louis River in June 2008. DOC, cation, and anion concentrations are listed in mg/L.

Tributary	*Partridge River*	*Embarrass River*	*Mud Hen Creek*	*Long Lake Creek*	*Elbow Creek*	*East Two Rivers*	*West Two Rivers*	*Swan River*	*Stony Creek*	*Whiteface River*	*Floodwood River*	*Cloquet River*
Date	6/17/08	6/18/08	6/18/08	6/18/08	6/18/08	6/18/08	6/18/08	6/16/08	6/16/08	6/16/08	6/16/08	6/16/08
Time CDT	7:52	11.52	-	10:00	9:15	8:45	8:10	7:32	8:15	9:27	11:08	14:11
Temp. (C)	17.7	17.9	17.7	15	15.8	15.5	16.9	15.1	16..0	16.2	16.0	16.8
Cond (µS/cm)	110	130	85	320	650	650	380	170	105	90	110	85
pH	7.3	7.3	7.2	8.0	7.9	8.0	8.1	7.7	7.3	7.3	7.3	7.4
Flow (cfs)_	350	462	145	12	17.1	29.3	110	491	49.5	907	412	1770
Cations												
Al	0.1	<0.03	0.1	0.06	<0.03	<0.03	<0.03	0.09	0.2	0.1	0.1	0.05
Si	2.4	2.9	1.7	3.8	1.8	1.6	1.2	2.4	2.1	2.3	1.8	3.5
Fe	0.5	0.3	0.7	0.4	0.2	0.3	0.3	0.5	0.8	0.7	0.6	0.3
Mn	0.05	0.03	0.07	0.09	0.2	0.1	0.1	0.05	0.08	0.05	0.06	0.03
Sr	0.07	0.04	0.03	0.09	0.1	0.8	0.9	0.4	0.4	0.03	0.03	<0.03
Ba	<0.01	0.02	0.01	0.01	0.02	0.02	0.03	0.02	0.01	0.01	0.02	<0.01
Ca	9.6	9.8	9.6	26.9	38.0	26.1	24.3	15.1	13.4	10.0	15.2	9.0
Mg	5.6	7.2	4.6	23.8	49.5	44.2	30.0	7.4	4.6	4.5	4.7	3.7
Na	3.3	6.0	2.6	11.7	20.8	42.2	14.4	5.4	1.4	2.6	2.4	2.1
K	0.9	1.5	0.7	2.3	3.5	3.2	5.0	0.8	0.7	0.6	<0.3	0.3
Anions												
F	0.1	0.1	0.1	-	-	-	-	0.1	0.1	0.1	0.1	0.1
Cl	2.0	4.0	1.8	14.5	25.1	46.2	11.0	6.3	0.3	1.9	2.3	2.2
Br	<0.005	0.02	<0.005	<0.005	<0.005	0.04	0.02	<0.005	<0.005	<0.005	<0.005	<0.005
SO_4	17.1	18.3	2.3	52.5	155.1	96.9	68.9	7.4	0.7	3.3	0.8	3.1
$\delta^{34}S_{SO4}$ ‰	8.9	8.0		16.6	15.1	6.1	6.9	4.3		10.7		6.8
$\delta^{18}O_{SO4}$ ‰	7.0	-0.8		5.3	0.8	-0.9	-1.7	1.8		6.7		5.4
Total Kjeldahl N	0.8	0.6	1.0	0.7	0.7	1.1	0.8	1.3	1.6	1.3	1.7	0.6
NO_2-N	<0.002	0.002	0.002	0.003	<0.002	0.009	0.02	0.003	0.004	0.003	0.005	0.003
NO_3-N	0.4	0.3	0.5	0.4	0.3	0.8	0.8	1.8	0.4	1.5	1.2	0.4
NH_3-N	0.04	0.03	0.03	0.03	0.03	0.07	0.05	0.04	0.06	0.04	0.1	0.02
Total P	0.02	0.02	0.06	0.04	0.05	0.1	0.05	0.07	0.08	0.05	0.1	0.03
Phosph -P	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Table 11. Values for selected parameters measured in samples collected from tributaries of the St. Louis River in July 2008. DOC, cation, and anion concentrations are listed in mg/L.

Tributary	*Partridge River*	*Embarrass River*	*Mud Hen Creek*	*East Two Rivers*	*West Two Rivers*	*Swan River*	*Stony Creek*	*Whiteface River*	*Floodwood River*	*Cloquet River*
Date	7/7/08	7/7/08	7/7/08	7/9/08	7/9/08	7/9/08	7/9/08	7/8/08	7/8/08	7/8/08
Time CDT	9:25	11:40	12:15	8:30	8:00	11:15	10:50	12:37	11:00	9:25
Temp. (C)	24.3	23.6	25.3	17.8	17.9	21.0	19.7	22.6	21.8	21.1
Cond (µS/cm)	550	160	160	750	500	370	80	120	155	105
pH	7.8	7.7	7.4	8.4	8.1	7.9	6.9	7.6	7.4	7.9
DOC	23.0	14.0	23.0	11.0	10.0	17.0	43.0	25.0	43.0	13.0
Cations										
Al	0.09	<0.03	0.04	<0.03	<0.03	0.03	0.3	0.06	0.09	0.03
Si	3.0	2.8	2.1	0.3	0.5	3.3	1.6	2.8	3.3	3.4
Fe	0.9	0.4	1.2	0.07	0.2	0.6	1.3	1.2	2.5	0.3
Mn	0.3	0.03	0.1	0.1	0.08	0.05	0.3	0.05	0.4	0.02
Sr	0.1	0.04	0.06	0.09	0.1	0.09	0.03	0.04	0.04	0.03
Ba	0.01	0.02	0.01	0.02	0.02	0.02	0.01	<0.01	0.02	<0.01
Ca	23.7	11.3	16.8	29.2	27.3	31.6	11.6	11.8	22.0	11.6
Mg	54.3	9.0	8.1	56.3	32.7	20.5	3.8	5.6	6.6	4.8
Na	7.1	7.0	4.5	52.0	15.9	13.5	0.8	2.8	2.5	2.0
K	2.9	1.1	<0.3	7.2	5.5	2.6	0.9	1.0	<0.3	<0.3
Anions										
F	0.1	0.1	0.1	0.2	0.1	0.2	0.05	0.1	0.07	0.09
Cl	3.7	4.5	4.2	57.1	11.1	16.2	0.2	1.7	2.8	2.7
Br	0.005	<0.005	<0.005	0.03	0.02	0.02	<0.005	<0.005	0.006	<0.005
SO_4	188.9	21.2	2.2	118.1	70.59	24.4	0.3	2.8	1.0	3.3
Total Kjeld N	0.9	0.8	1.0	1.0	0.07	1.0	1.5	1.0	1.7	0.6
NO_2-N	0.003	0.001	<0.002	0.001	0.002	0.006	0.001	0.003	0.004	0.001
NO_3-N	1.2	0.8	0.2	0.1	1.3	2.2	0.2	0.3	0.2	0.3
NH_3-N	0.04	0.2	0.03	0.04	0.03	0.3	0.5	0.04	0.1	0.02
Total P	0.03	0.03	0.06	0.2	0.04	0.06	0.1	0.05	0.1	0.03
Phos -P	<0.002	<0.002	<0.002	0.1	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Table 12. Values for selected parameters measured in samples collected from selected tributaries of the St. Louis River in September/October 2008. DOC, cation, and anion concentrations are listed in mg/L.

Tributary	*Partridge River*	*Embarrass River*	*East Two Rivers*	*West Two Rivers*	*Swan River*	*Stony Creek*	*Whiteface River*	*Floodwood River*	*Cloquet River*
Date	10/1/08	10/1/08	9/29/08	9/29/08	9/29/08	9/29/08	9/30/08	9/30/08	9/30/08
Time CDT	9:30	11:00	9:05	8:25	12:15	11:15	12:50	11:30	9:52
Temp. (C)	14.6	12.4	13.2	12.6	13.9	13.4	13.4	13.1	11.2
Cond (µS/cm)	320	235	750	480	290	150	135	255	125
pH	7.5	7.8	8.3	8.3	7.8	7.5	7.8	7.7	7.9
DOC	17.0	11.0	8.4	8.6	11.0	26.0	24.0	18.0	16.0
Cations									
Al	0.04	<0.03	<0.03	<0.03	<0.03	<0.03	0.05	<0.03	<0.03
Si	3.7	3.3	2.6	3.0	3.7	1.2	2.7	3.7	3.9
Fe	0.5	0.2	0.04	0.07	0.2	0.3	0.6	0.5	0.3
Mn	0.1	0.04	0.04	0.08	0.04	0.05	0.04	0.05	0.03
Sr	0.2	0.06	0.1	0.1	0.08	0.05	0.04	0.07	0.03
Ba	0.02	0.02	0.02	0.04	0.02	0.01	0.01	0.02	<0.01
Ca	28.7	16.8	30.8	32.8	29.9	19.3	13.6	31.7	13.8
Mg	21.5	15.1	56.6	39.6	18.7	7.0	7.0	11.5	5.9
Na	9.7	13.2	48.6	21.1	12.7	2.3	5.4	11.1	3.5
K	2.2	2.4	8.5	7.2	3.3	1.6	1.8	1.1	0.3
Anions									
F	0.2	0.1	0.2	0.2	0.1	0.06	0.2	0.1	0.09
Cl	4.7	5.9	49.2	15.6	16.1	0.6	5.1	11.0	5.8
Br	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
SO_4	90.9	30.6	106.6	99.1	27.0	2.7	6.5	7.1	2.5
Total Kjeld. N	0.8	0.5	0.8	0.6	0.7	1.2	1.1	0.8	1.1
NO_2-N	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.004	<0.002	<0.002
NO_3-N	0.3	0.5	0.9	0.6	0.8	1.0	0.9	0.5	0.8
NH_3-N	0.03	0.02	0.03	0.02	0.03	0.03	0.03	0.04	0.03
Total P	0.02	0.01	0.2	0.04	0.07	0.07	0.04	0.05	0.02
Phos -P	<0.002	<0.002	0.07	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Table 13. Concentrations of mercury species and values for selected parameters measured in (or calculated for) samples collected from the St. Louis River in September 2007. DOC, cation, and anion concentrations are listed in mg/L. Concentrations for mercury species are listed in units of ng/L.

Mile	*179*	*142*	*125*	*98*	*80*	*53*	*36*
Date	9/10/07	9/10/07	9/11/07	9/11/07	9/12/07	9/12/07	9/12/07
Time CDT	10:36	13:35	8:25	13:15	9:50	12:53	14:15
Temp. (C)	14.9	16.8	12.8	14.5	14.2	17	16.8
Cond (µS/cm)	95	225	380	550	430	275	260
pH	7.6	8.1	8.3	8.4	8.2	8.3	8.3
DOC	15.0	7.7	9.4	10.0	18.0	18.0	11.0
SO_4	4.9	24.7	67.9	93.0	67.4	53.0	22.0
Fe	0.3	0.3	0.3	0.1	0.5	0.1	0.1
Cl	0.6	8.3	11.6	21.1	18.5	10.7	8.8
Unfiltered							
THg	2.1	0.9	1.5	1.5	2.5	3.0	1.1
MeHg	0.10	0.08	0.13	0.12	0.21	0.13	0.05
AHg(II)	0.9	0.08	0.1	0.1	0.2	0.1	0.05
SHg	1.0	0.4	0.8	0.7	1.2	2.1	0.6

Table 14. Concentrations of mercury species and values for selected parameters measured in (or calculated for) samples collected from the St. Louis River in May 2008. DOC, cation, and anion concentrations are listed in mg/L. Concentrations for mercury species are listed in units of ng/L.

Mile	*179*	*142*	*125*	*115*	*80*	*53*	*36*
Date	5/5/08	5/5/08	5/7/08	5/7/08	5/6/08	5/6/08	5/6/08
Time CDT	8:42	11:10	9:06	10:06	10:20	11:15	13:36
Temp. (C)	8.1	9.1	9.9	10.6	10	10.6	11.7
Cond (µS/cm)	31	90	110	130	125	100	100
pH	7.6	7.3	7.6	7.5	7.5	7.3	7.3
DOC	23.0	22.0	20.0	20.0	20.0	24.0	22.0
SO_4	2.6	12.1	15.3	21.3	17.5	11.0	9.4
Fe	0.5	0.4	0.5	0.4	0.4	0.4	0.4
Cl	0.04	1.6	2.9	4.5	4.7	3.5	3.4
Unfiltered							
THg	12.3	10.4	8.9	10.0	9.4	10.4	9.4
MeHg	0.39	0.32	0.27	0.34	0.31	0.38	0.30
AHg(II)	7.9	4.7	4.2	5.1	3.2	3.9	3.6
SHg	4.0	5.3	4.4	4.6	5.9	6.2	5.6
Filtered							
THg	10.4	8.0	6.9	6.8	7.2	7.3	6.4
MeHg	0.42	0.38	0.31	0.27	0.33	0.31	0.30
AHg(II)	6.3	4.4	3.8	4.2	3.2	3.6	3.3
SHg	3.7	3.2	2.7	2.3	3.7	3.4	2.8
Particulate							
THg	1.9	2.4	2.0	3.2	2.2	3.1	3.0
MeHg	-0.03	-0.06	-0.04	0.07	-0.02	0.07	0.0
AHg(II)	1.6	0.3	0.4	0.9	0.02	0.3	0.2
SHg	0.3	2.1	1.697	2.3	2.2	2.7	2.8

Table 15. Concentrations of mercury species and values for selected parameters measured in samples collected from the St. Louis River in July 2008. DOC, cation, and anion concentrations are listed in mg/L. Concentrations for mercury species are listed in units of ng/L.

Mile	*179*	*142*	*125*	*115*	*80*	*53*	*36*
Date	7/7/08	7/7/08	7/9/08	7/9/08	7/8/08	7/8/08	7/8/08
Time	8:56	10:35	9:10	10:00	12:05	10:00	8:41
Temp. (C)	21.5	23.5	20.9	21.7	22.8	22.4	23.7
Cond (µS/cm)	50	275	280	310	280	200	165
PH	7.3	7.5	7.9	8.0	7.9	7.8	7.8
DOC	28.0	22.0	18.0	17.0	19.0	26.0	24.0
SO_4	2.2	70.0	50.4	52.7	34.8	19.5	13.3
Fe	0.8	0.9	0.7	0.6	0.7	1.0	1.0
Cl	0.3	2.6	4.2	6.7	7.7	5.0	4.3
Unfiltered							
THg		*6.1*				*6.4*	*5.6*
MeHg		*0.65*				*0.64*	*0.51*
AHg(II)		*4.0*				*3.0*	*3.5*
DMM		*<0.1*				*<0.1*	*0.1*
Filtered							
THg	*8.4*	*4.8*					
MeHg	*0.48*	*0.58*					
AHg(II)	*5.3*	*2.3*					
DMM	*<0.1*	*<0.1*					

DMM is Dimethyl mercury that was detected in samples following storage in ice-coolers with DMM-contaminated ice packs, which is the reason Hg values for most samples are rejected from this table. See Appendix 1 for complete data set.

Table 16. Concentrations of mercury species and values for selected parameters measured in (or calculated for) samples collected from the St. Louis River in September/October 2008. DOC, cation, and anion concentrations are listed in mg/L. Concentrations for mercury species are listed in units of ng/L.

Mile	*179*	*142*	*125*	*115*	*80*	*53*	*36*
Date	10/1/08	10/1/08	9/29/08	9/29/08	9/30/08	9/30/08	9/30/08
Time	8:45	10:20	9:35	10:30	12:20	10:28	9:01
Temp. (C)	9.7	14.1	13.7	14.3	13.4	9.3	12.1
Cond (µS/cm)	65	210	325	410	320	340	255
PH	7.5	7.8	8.1	8.2	8.2	8.2	7.7
DOC	25.0	17.0	12.0	11.0	15.0	11.0	12.0
SO_4	4.7	53.9	65.7	71.9	50.5	46.1	27.5
Fe	0.6	0.4	0.3	0.2	0.2	0.1	0.2
Cl	0.5	3.8	7.0	13.6	11.2	10.5	8.2
Unfiltered							
THg	5.5	2.7	2.0	2.1	2.5	2.0	2.3
MeHg	0.15	0.15	0.21	0.17	0.14	0.15	0.16
AHg(II)	2.6	1.8	1.5	1.9	1.1	1.0	1.4
SHg	2.8	1.5	0.3	0.1	1.2	0.9	0.7
Filtered							
THg	4.5	2.1	1.9	1.5	2.0	1.5	2.0
MeHg	0.16	0.18	0.21	0.12	0.15	0.11	0.15
AHg(II)	2.7	1.0	1.5	0.9	1.2	0.7	1.1
SHg	1.6	0.9	0.1	0.6	0.6	0.7	0.8
Particulate							
THg	1.1	0.6	0.1	0.6	0.5	0.5	0.3
MeHg	-0.01	-0.03	0.00	0.05	-0.01	0.04	0.01
AHg(II)	-0.09	-0.07	-0.01	1.01	-0.087	0.2	0.3
SHg	1.2	0.7	0.1	-0.5	0.6	0.2	-0.05

Table 17. Concentrations of mercury species and values for selected parameters measured in (or calculated for) samples collected from tributaries of the St. Louis River in September 2007. DOC, cation, and anion concentrations are listed in mg/L. Concentrations for mercury species are listed in units of ng/L.

Tributary	*Partridge River*	*Embarrass River*	*East Two Rivers*	*West Two Rivers*	*Swan River*	*Whiteface River*	*Floodwood River*	*Cloquet River*
Date	9/10/07	9/10/07	9/11/07	9/11/07	9/11/07	9/12/07	9/12/07	9/12/07
Time	11:45	14:45	9:30	10:10	12:45	8:55	10:37	13:30
Temp. (C)	17.8	16.7	8.2	12.5	13.2	13.3	13.6	14.2
Cond (µS/cm)	260	295	900	410	325	175	200	135
pH	7.7	8.1	7.0	7.1	8.1	8.2	8.3	8.3
DOC	19.0	13.0	9.9	10.0	19.0	18.0	27.0	9.8
SO_4	75.5	41.2	127.0	49.5	22.3	5.8	4.5	3.4
Fe	0.4	0.1	0.1	0.1	0.4	0.5	0.6	0.1
Cl	6.6	10.9	78.4	11.8	27.0	7.3	6.3	4.7
Unfiltered								
THg	2.3	2.2	3.9	1.7	4.6	2.6	3.0	1.0
MeHg	0.11	0.10	0.64	0.11	0.23	0.19	0.41	0.04
AHg(II)	0.9	0.5	2.1	0.6	2.0	1.0	1.0	0.4
SHg	1.3	1.5	1.1	1.0	2.4	1.5	1.7	0.6

Table 18. Concentrations of mercury species and values for selected parameters measured in (or calculated for) samples collected from tributaries of the St. Louis River in May 2008. DOC, cation, and anion concentrations are listed in mg/L. Concentrations for mercury species are listed in units of ng/L.

Tributary	*Partridge River*	*Embarrass River*	*Mud Hen Creek*	*East Two Rivers*	*West Two Rivers*	*Swan River*	*Stony Creek*	*Whiteface River*	*Floodwood River*	*Cloquet River*
Date	5/5/08	5/5/08	5/5/08	5/7/08	5/7/08	5/7/08	5/7/08	5/6/08	5/6/08	5/6/08
Time	9:32	12:16	13:10	8:30	7:49	12:25	11:39	8:05	10:21	12:35
Temp. (C)	9.0	7.1	10.3	9.1	9.1	11.2	12.5	10.5	11.3	10.2
Cond (μS/cm)	70	160	75	650	400	145	80	70	85	90
pH	7.2	7.2	7.1	8.3	8.0	7.4	7.2	7.6	7.2	7.4
DOC	15.0	19.0	24.0	15.0	10.0	20.0	34.0	24.0	29.0	16.0
SO_4	14.0	25.6	3.7	81.7	67.9	10.9	2.9	4.0	2.1	3.2
Fe	0.4	0.6	0.4	0.2	0.2	0.4	0.6	0.5	0.4	0.3
Cl	1.6	4.8	2.1	42.7	11.8	7.1	0.7	2.0	2.9	3.6
Unfiltered										
THg	9.5	4.8	8.4	4.9	4.5	10.4	9.0	9.6	7.5	6.1
MeHg	0.33	0.33	0.37	0.35	0.24	0.33	0.57	0.37	0.52	0.29
AHg	5.4	1.4	3.8	2.8	2.1	4.6	4.1	4.0	3.0	1.8
SHg	3.7	3.1	4.2	1.8	2.1	5.5	4.4	5.2	3.9	3.9
Filtered										
THg	8.5	4.2	8.3	4.0	2.5	6.2	7.8	7.2	6.6	6.7
MeHg	0.31	0.33	0.17	0.21	0.23	0.32	0.58	0.38	0.46	0.23
AHg	6.3	1.2	3.7	2.2	1.8	3.3	3.4	4.2	2.9	1.8
SHg	1.9	2.7	4.4	1.5	0.5	2.6	3.8	2.7	3.2	4.7
Particulate										
THg	1.0	0.6	0.1	0.9	2.0	2.6	1.2	2.4	0.9	-0.6
MeHg	0.02	0.00	0.20	0.14	0.01	0.01	-0.01	-0.01	0.06	0.06
AHg	-0.9	0.2	0.2	0.5	0.3	1.3	0.6	-0.1	0.1	0.1
SHg	1.8	0.4	-0.2	0.3	1.6	2.9	0.6	2.6	0.7	-0.7

Table 19. Concentrations of mercury species and values for selected parameters measured in samples collected from tributaries of the St. Louis River in July 2008. DOC, cation, and anion concentrations are listed in mg/L. Concentrations for mercury species are listed in units of ng/L.

Tributary	*Partridge River*	*Embarrass River*	*Mud Hen Creek*	*East Two Rivers*	*West Two Rivers*	*Swan River*	*Stony Creek*	*Whiteface River*	*Floodwood River*	*Cloquet River*
Date	7/7/08	7/7/08	7/7/08	7/9/08	7/9/08	7/9/08	7/9/08	7/8/08	7/8/08	7/8/08
Time	9:25	11:40	12:15	8:30	8:00	11:15	10:50	12:37	11:00	9:25
Temp. (C)	24.3	23.6	25.3	17.8	17.9	21.0	19.7	22.6	21.8	21.1
Cond (µS/cm)	550	160	160	750	500	370	80	120	155	105
PH	7.8	7.7	7.4	8.4	8.1	7.9	6.9	7.6	7.4	7.9
DOC	23.0	14.0	23.0	11.0	10.0	17.0	43.0	25.0	43.0	13.0
SO_4	188.9	21.2	2.2	118.1	70.59	24.4	0.3	2.8	1.0	3.3
Fe	0.9	0.4	1.2	0.07	0.2	0.6	1.3	1.2	2.5	0.3
Cl	3.7	4.5	4.2	57.1	11.1	16.2	0.2	1.7	2.8	2.7
Unfiltered										
THg		*5.8*						*5.1*		
MeHg		*0.2*						*0.7*		
AHg		*2.8*						*2.9*		
#DMM		*<0.1*						*0.1*		
Filtered										
THg		*4.4*	*4.0*							*3.3*
MeHg		*0.2*	*0.6*							*0.2*
AHg		*2.5*	*2.2*							*0.3*
#DMM		*<0.1*	*<0.1*							*<0.1*

DMM is Dimethyl mercury that was detected in samples following storage in ice-coolers with DMM-contaminated ice packs, which is the reason most samples are rejected from this table. See Appendix 1 for complete data set.

Table 20 Concentrations of mercury species and values for selected parameters measured in (or calculated for) samples collected from tributaries of the St. Louis River in September/October 2008. Concentrations for mercury species are listed in units of ng/L.

Tributary	*Partridge River*	*Embarrass River*	*East Two Rivers*	*West Two Rivers*	*Swan River*	*Stony Creek*	*Whiteface River*	*Floodwood River*	*Cloquet River*
Date	10/1/08	10/1/08	9/29/08	9/29/08	9/29/08	9/29/08	9/30/08	9/30/08	9/30/08
Time	9:30	11:00	9:05	8:25	12:15	11:15	12:50	11:30	9:52
Temp. (C)	14.6	12.4	13.2	12.6	13.9	13.4	13.4	13.1	11.2
Cond (µS/cm)	320	235	750	480	290	150	135	255	125
PH	7.5	7.8	8.3	8.3	7.8	7.5	7.8	7.7	7.9
DOC	17.0	11.0	8.4	8.6	11.0	26.0	24.0	18.0	16.0
SO_4	90.9	30.6	106.6	99.1	27.0	2.7	6.5	7.1	2.5
Fe	0.5	0.2	0.04	0.07	0.2	0.3	0.6	0.5	0.3
Cl	4.7	5.9	49.2	15.6	16.1	0.6	5.1	11.0	5.8
Unfiltered									
THg	2.2	1.5	1.9	1.7	3.5	3.0	4.5	2.4	2.5
MeHg	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.1
AHg	0.8	0.6	0.4	0.9	2.4	1.0	2.2	1.2	1.2
SHg	1.2	0.8	1.4	0.7	1.0	1.9	2.1	1.1	1.2
Filtered									
THg	2.0	1.3	1.0	0.9	2.0	2.0	3.6	2.4	2.0
MeHg	0.2	0.1	0.1	0.04	0.2	0.1	0.1	0.7	0.1
AHg	0.7	0.6	0.5	0.8	2.1	1.5	1.5	1.0	1.3
SHg	1.1	0.6	0.5	0.03	-0.4	0.4	2.0	1.3	0.6
Particulate									
THg	0.2	0.2	0.9	0.8	1.6	1.0	0.8	-0.01	0.4
MeHg	0.02	0.01	0.05	0.04	0.03	0.02	0.02	0.04	0.02
AHg	0.06	0.0	-0.09	0.1	0.3	-0.5	0.7	0.2	-0.2
SHg	0.1	0.2	0.9	0.7	1.3	1.5	0.1	-0.2	0.6

10. Figures

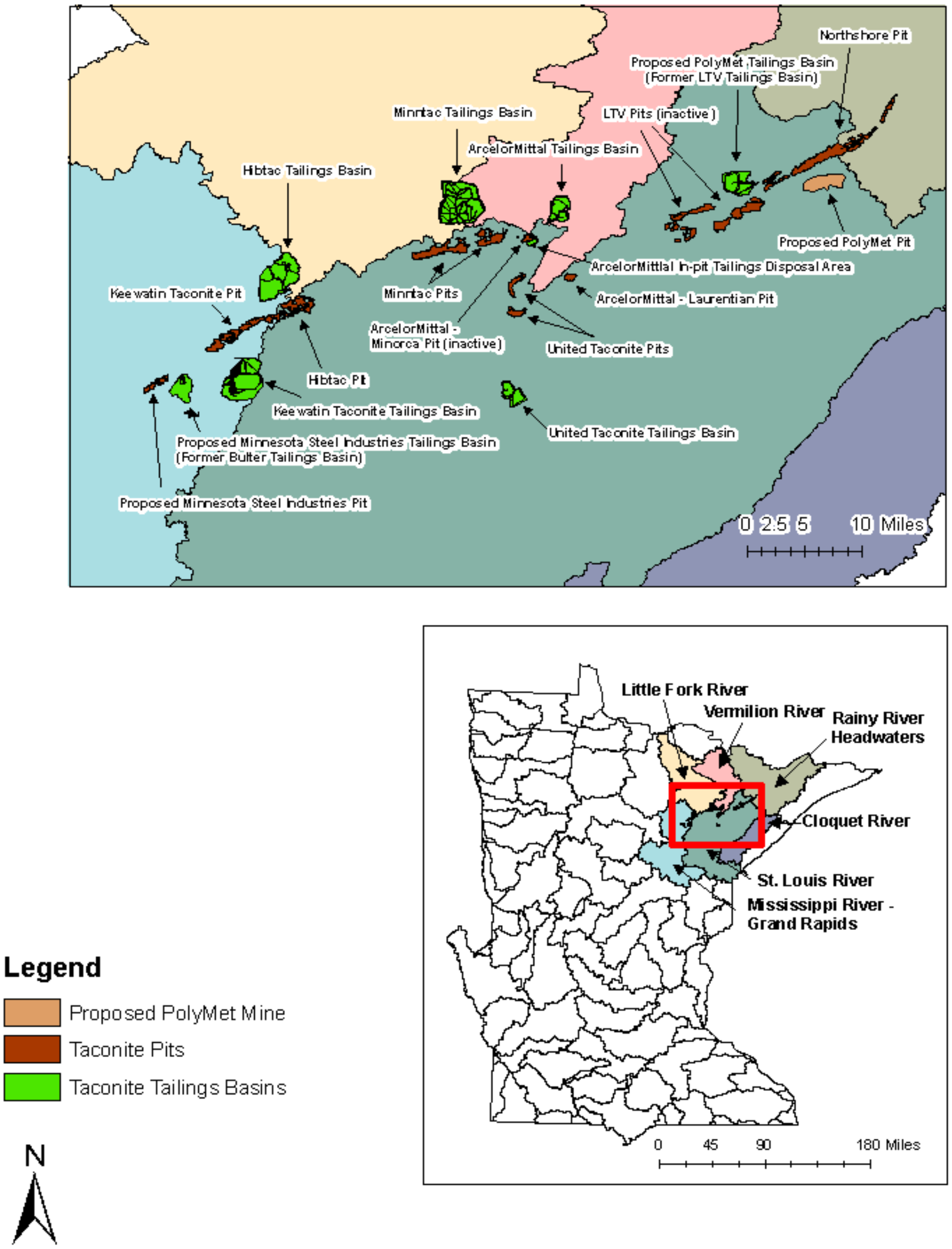


Figure 1. Taconite pit and tailings basin locations (top panel) and watersheds affected by mining (bottom panel) in NE Minnesota. The red box in the lower right panel outlines the area shown in the top panel. The location of the proposed Polymet mining pit and tailings basin is also shown.

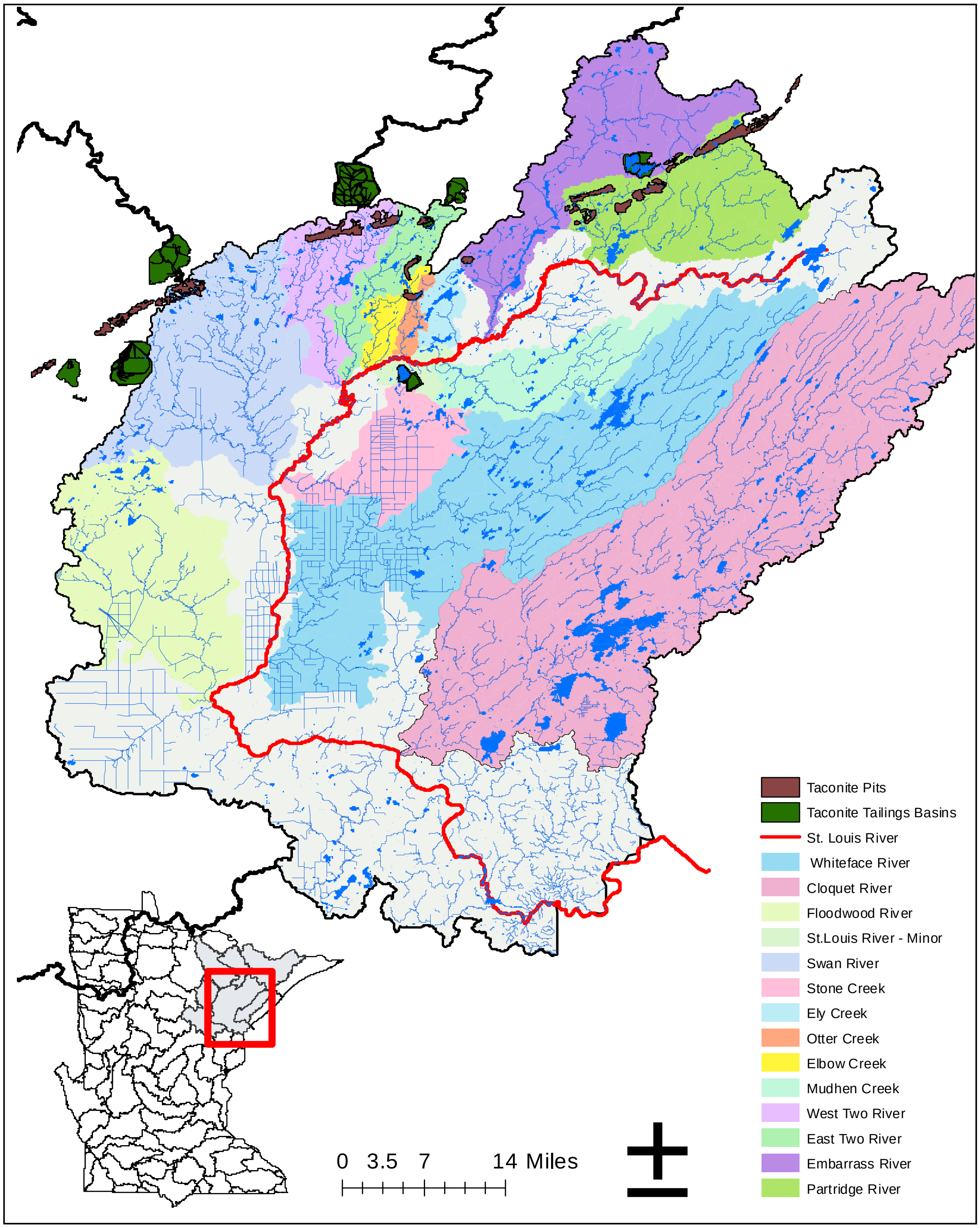


Figure 2. Major watersheds within the St. Louis River basin. Sampling during this study included most of the major tributaries shown and the St. Louis River.

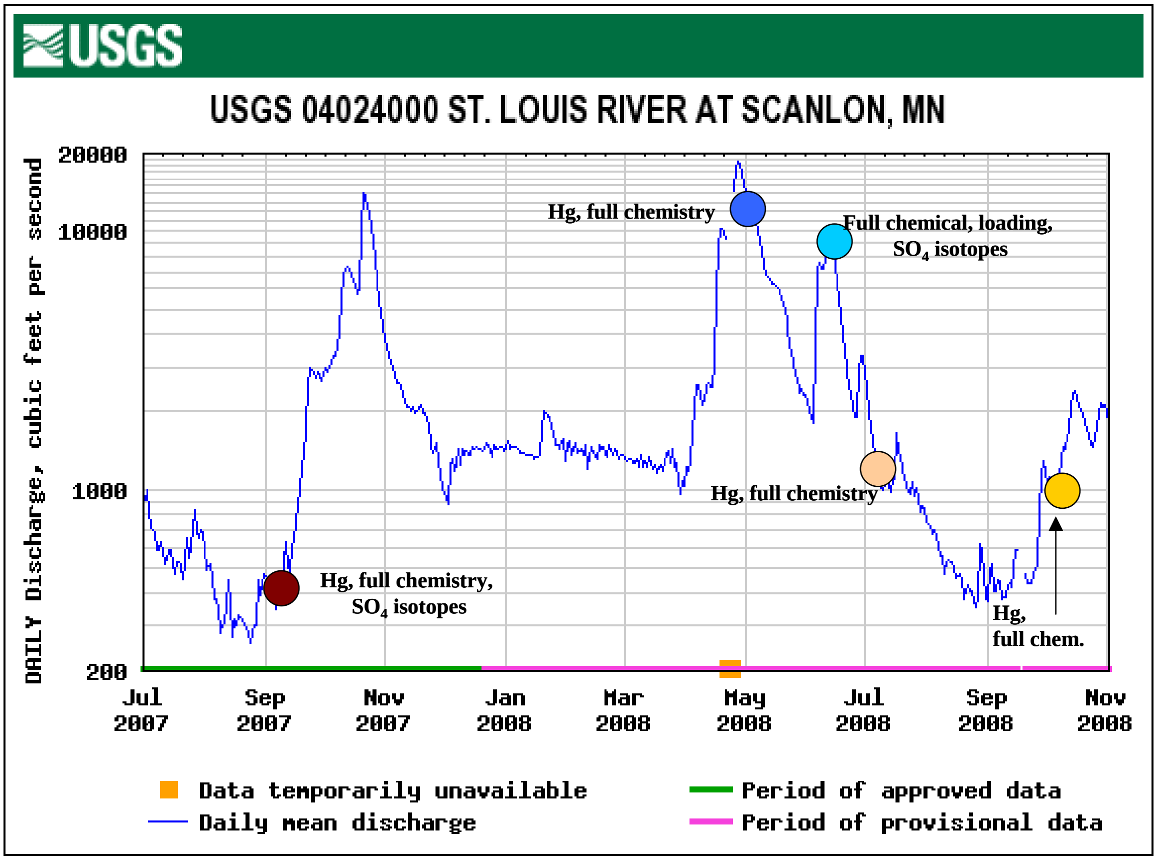


Figure 3. Sampling dates and flow rates (at the Scanlon Dam near Cloquet). Hg speciation samples were collected in September 2007, and in May, July, and October of 2008. Sulfate isotope samples were collected in September 2007 and June 2008. A primary objective of this study was to collect samples under a wide variety of flow conditions.

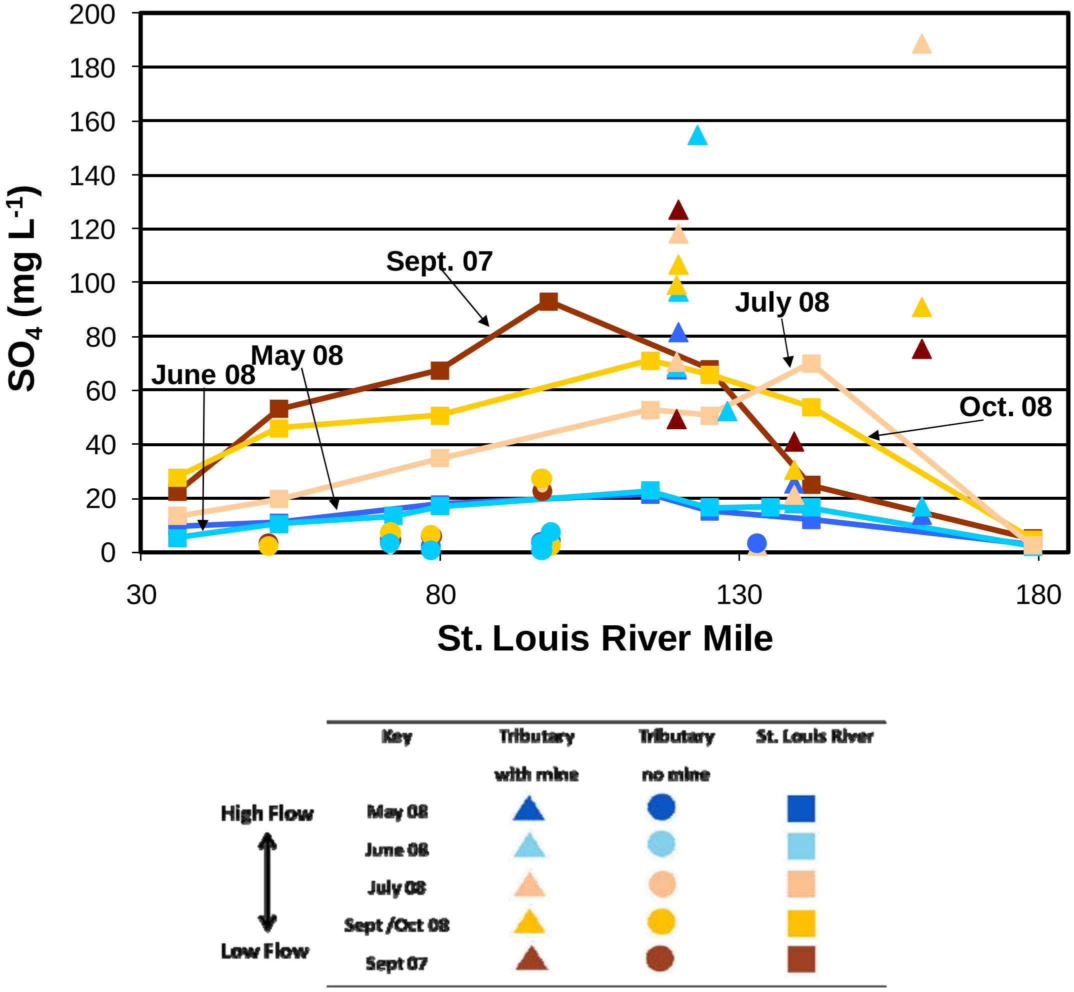


Figure 4. Sulfate concentrations for the St. Louis River and its tributaries as a function of St. Louis River mile (See Table 1 for sampling locations as function of river mile). The blue colors represent samples collected under relatively high flow conditions, while tan, brown and orange represent samples collected under moderate to low flow conditions.

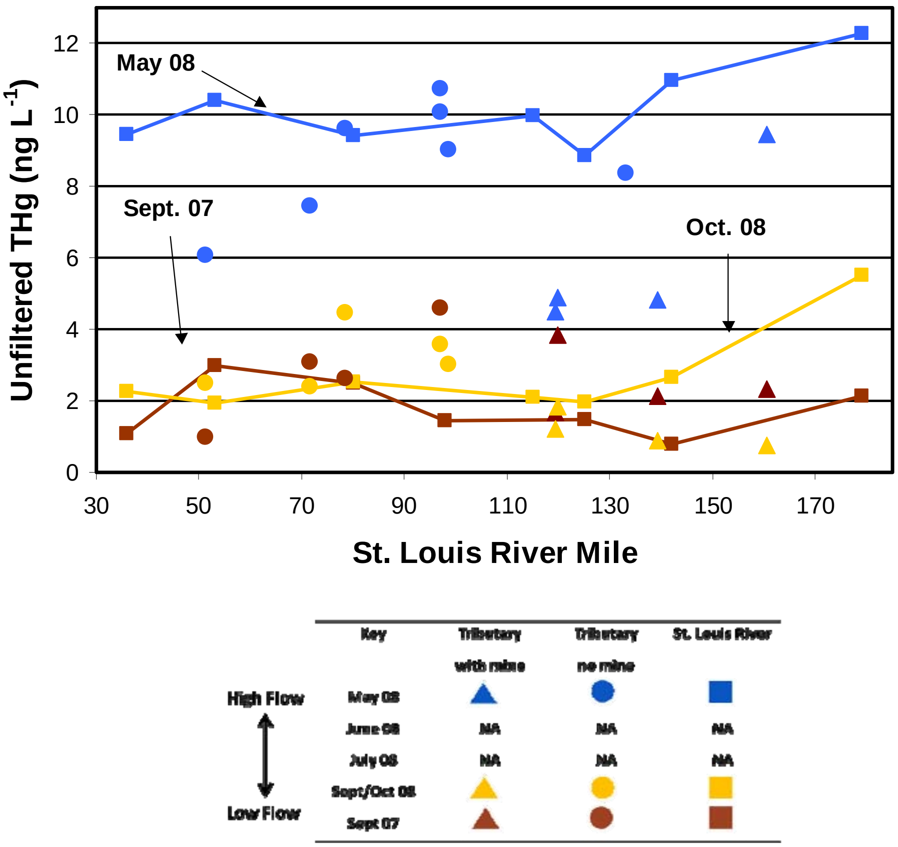


Figure 5. THg concentrations for unfiltered samples collected from the St. Louis River and tributaries during this study. Key is the same as in Figure 4. THg concentrations were highest under relatively wet conditions (blue colors) while SO_4 concentrations which are shown in Figure 4 were highest under dry conditions (yellow to red colors).

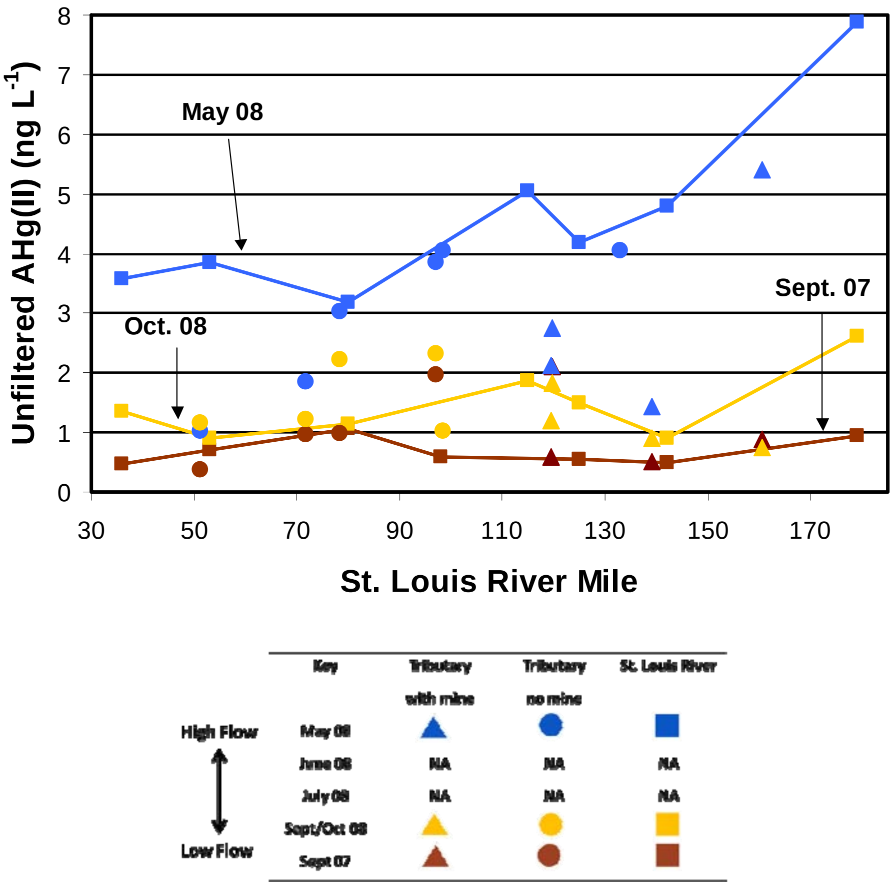


Figure 6. AHg concentrations for unfiltered samples collected from the St. Louis River and its tributaries during this study.

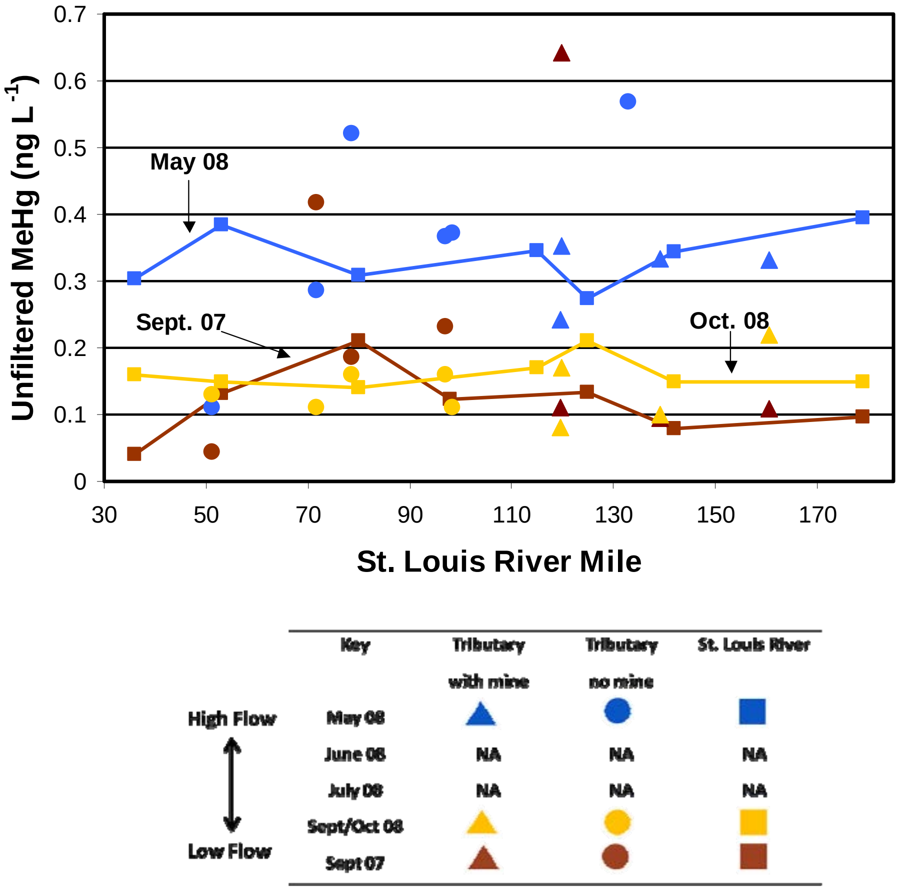


Figure 7. MeHg concentrations for unfiltered samples collected from the St. Louis River and its tributaries during this study.

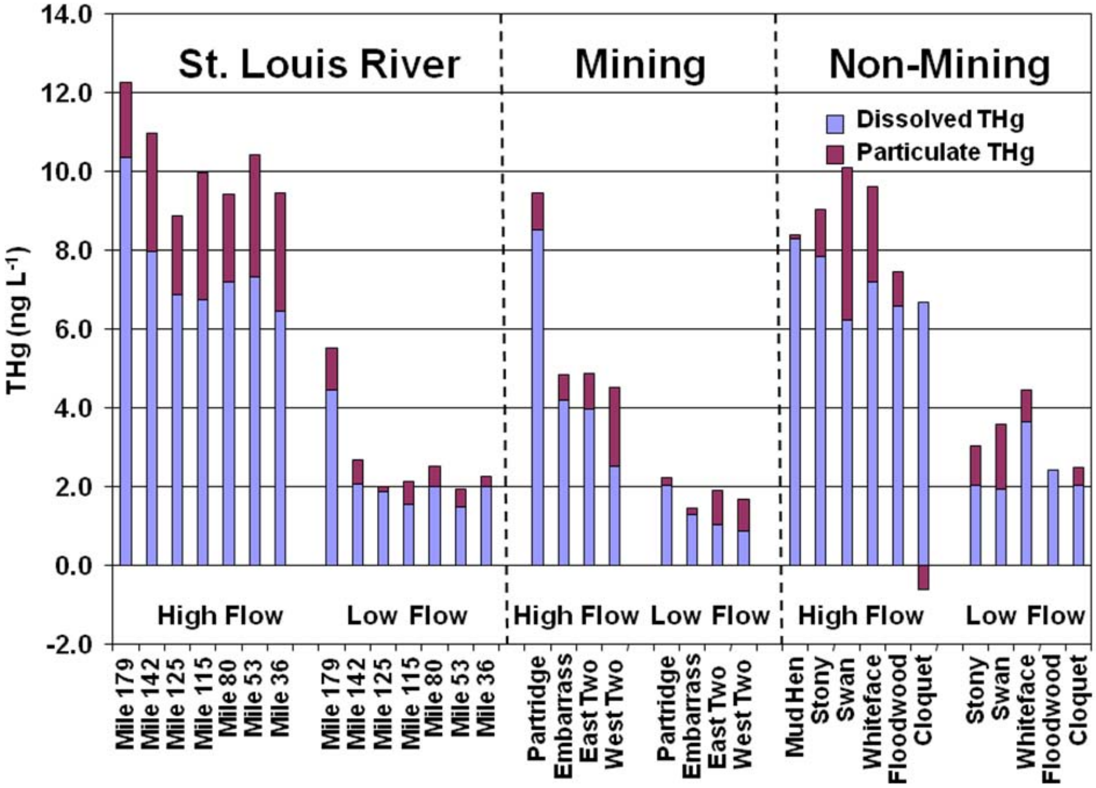


Figure 8. Dissolved and particulate THg concentrations for samples collected from the St. Louis River and its tributaries during May and September/October 2008. The negative value for particulate THg indicates the filtered sample had slightly higher THg concentration than the unfiltered sample.

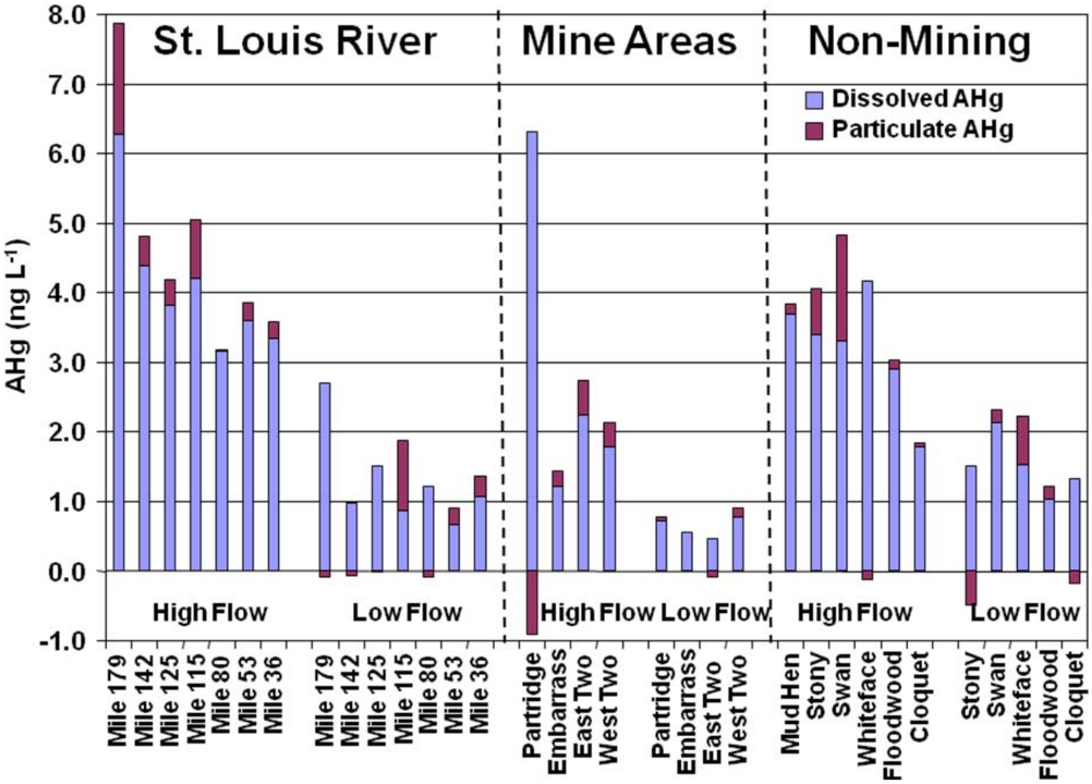


Figure 9. Dissolved and particulate AHg concentrations in samples collected from the St. Louis River and its tributaries during May and September/October 2008. Slightly negative values for particulated AHg represents cases where the filtered samples had slightly higher AHg concentrations than the unfiltered samples.

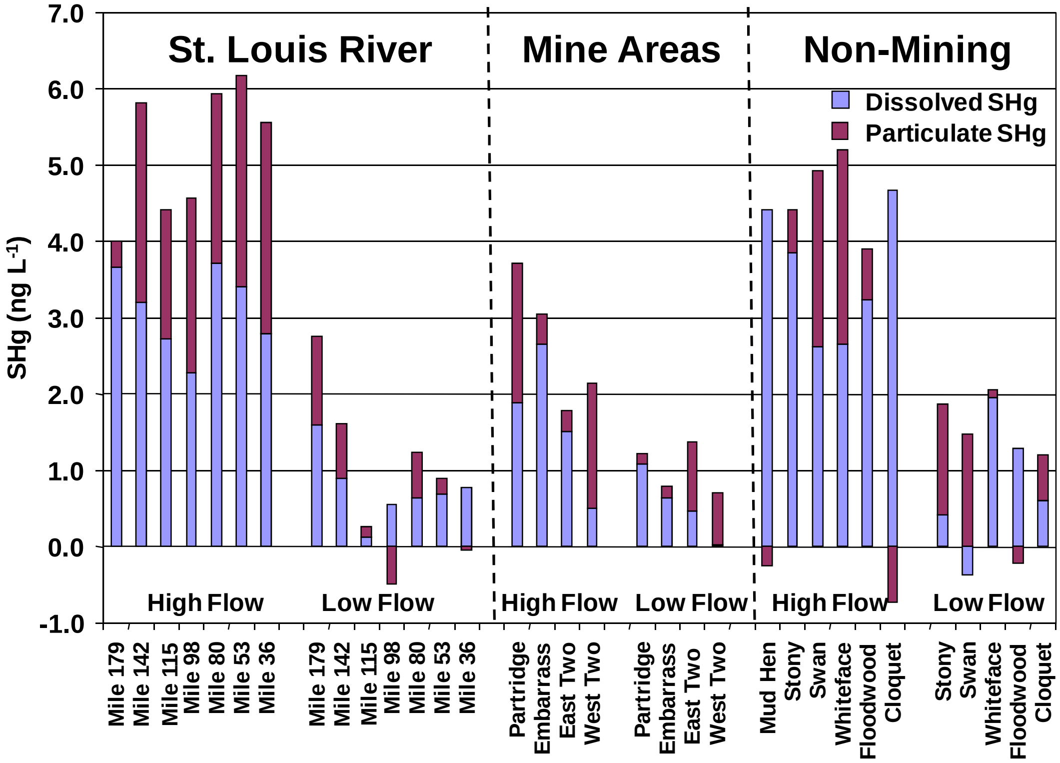


Fig. 10. Dissolved and particulate SHg concentrations calculated for samples collected from the St. Louis River and its tributaries during May and September/October 2008. Slightly negative values represent cases where the filtered samples have slightly higher SHg concentrations than the unfiltered samples.

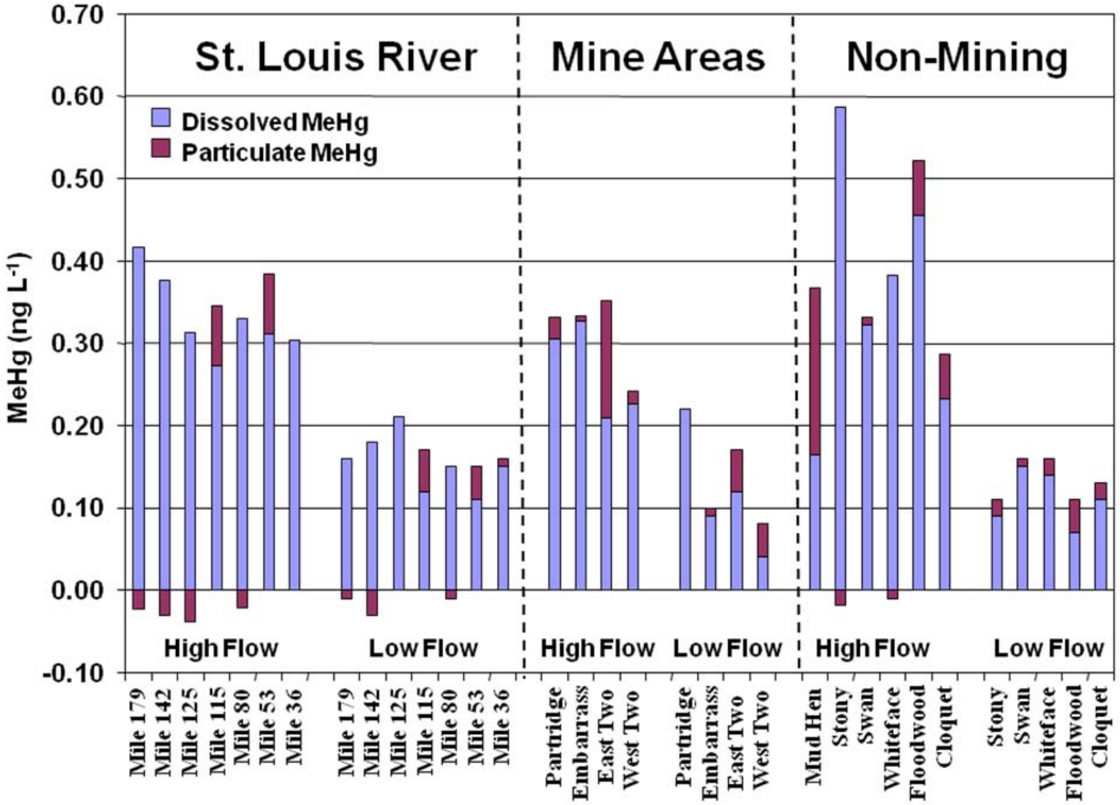


Figure 11. Dissolved and particulate MeHg concentrations for samples collected from the St. Louis River and its tributaries during May and September/October 2008. Negative values for particulate MeHg indicates samples where the MeHg concentration measured in filtered samples was slightly higher than that in unfiltered samples.

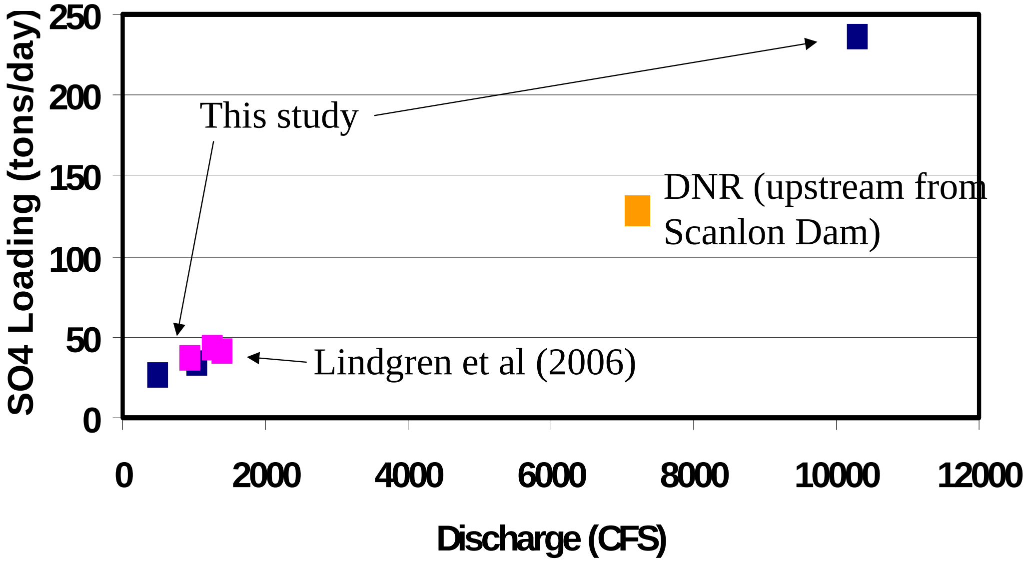


Figure 12. Loading rates for SO_4 estimated for the St. Louis River at the Scanlon Dam (Mile 33). Loads were estimated using measured concentrations for samples collected within a few miles upstream of the Scanlon Dam and multiplying these values by the flow rate reported on the same day at the Scanlon Dam. Pink squares represent loading values calculated using SO_4 data from Lindgren et al. (2006). The blue squares represent loading values calculated using SO_4 data from this study. The orange square represents loading data for the June 2008, which was determined independently from the Scanlon Dam measurements, as measured at Brookston, Minnesota (Mile 53) and also adding in loading values for the Cloquet River. Even though SO_4 concentrations decrease considerably during periods of high flow, SO_4 loading increased greatly due to increasing discharge.

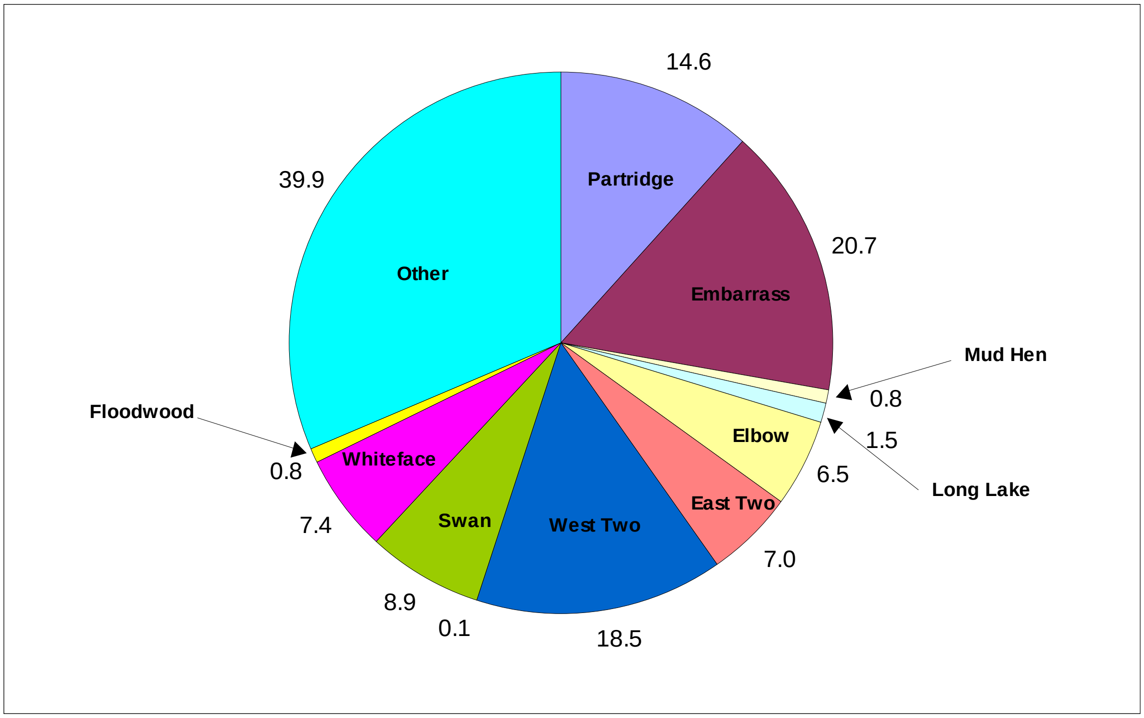


Fig. 13. Pie chart diagram showing sulfate contributions (metric tons/day) to the St. Louis River upstream of the Cloquet River during a relatively high flow period in June 2008. Loading values for each tributary were calculated using flow measurements and concentrations presented in Table 10. The total loading for this chart is 126.5 metric tons/day. This value was calculated using flow measurement and sulfate concentration measured during the same time period at the St. Louis River at Mile 53 which is just upstream of its confluence with the Cloquet River.

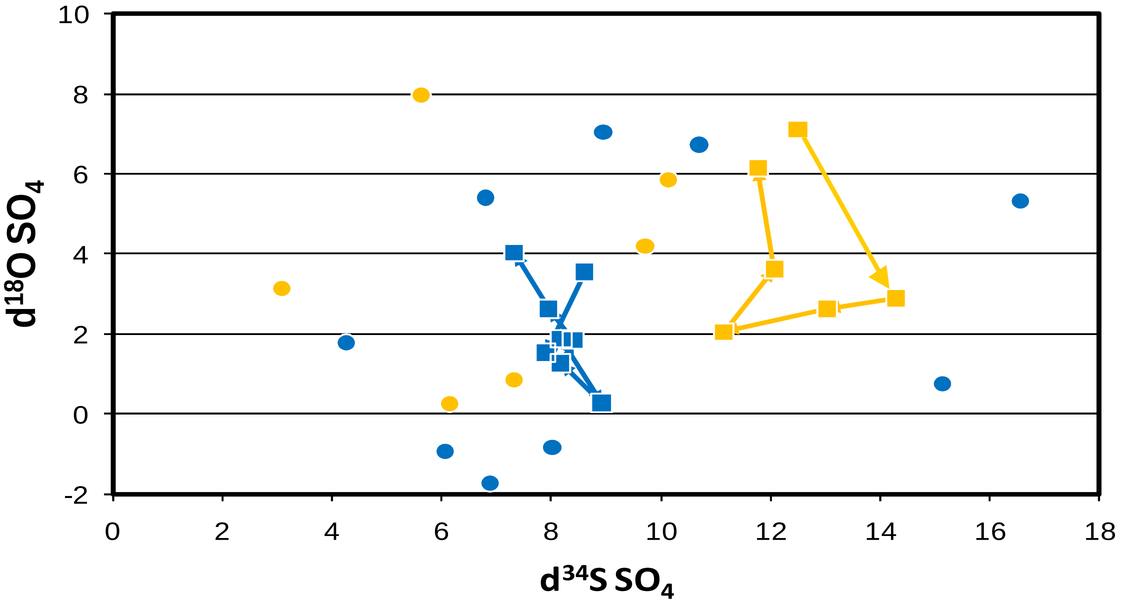


Figure 14. Sulfate isotope values for water in the St. Louis River and its tributaries. The yellow symbols reflect St. Louis River (connected squares) and tributary (circles) samples collected under dry conditions in September 2007. The blue symbols represent St. Louis River (connected squares) and an extended set of tributary samples (circles) collected under wet conditions in June 2008. The very high $\delta^{34}S_{SO4}$ values (15 and greater) were found for Elbow and Long Lake Creeks, which were not sampled during the September sampling trip. The shift to lower $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values for SO_4 in the St. Louis River under wet conditions (compared to dry conditions) indicates a major change occurred in the relative loading from individual SO_4 sources. It is suspected that the high $\delta^{34}S_{SO4}$ source represented by the Elbow Creek samples was a very significant contributor of sulfate to the St. Louis River during the dry period. However this component was dominated by the other lower $\delta^{34}S_{SO4}$ sources under wet conditions in June.

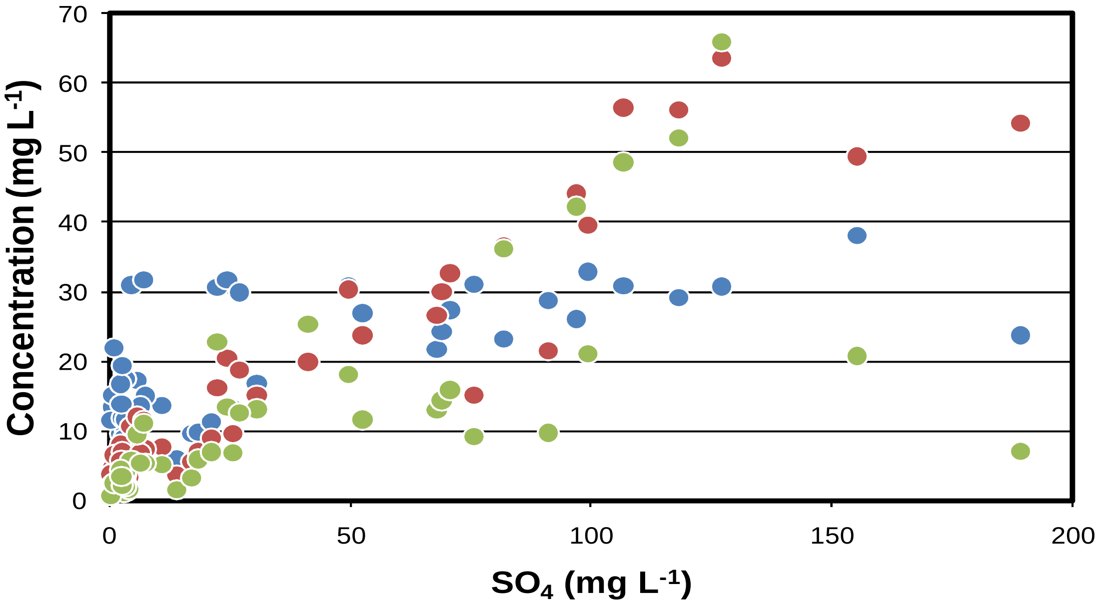


Figure 15. Ca (blue), Mg (red), and Na (green) concentrations as a function of sulfate for samples collected from tributaries in this study. Each SO_4 value corresponds to the Ca, Mg, and Na points lying in a vertical array directly above it. In most natural waters, from areas where there is little or no sulfide oxidation taking place, or where acid generated from oxidation is titrated by calcium carbonate, the trend is for Ca>Mg>Na. In this case, samples having Mg>Ca suggest instances where sulfate was derived by sulfide oxidation in stockpiles and open pits from the Biwabik Iron Formation which hosts Mg-rich carbonates (magnesian-siderite and ankerite). For many of these samples, Mg>Ca>Na. Samples with high Na were collected from tributaries where NaCl or NaOH apparently are used extensively in the watershed (See Figure 16).

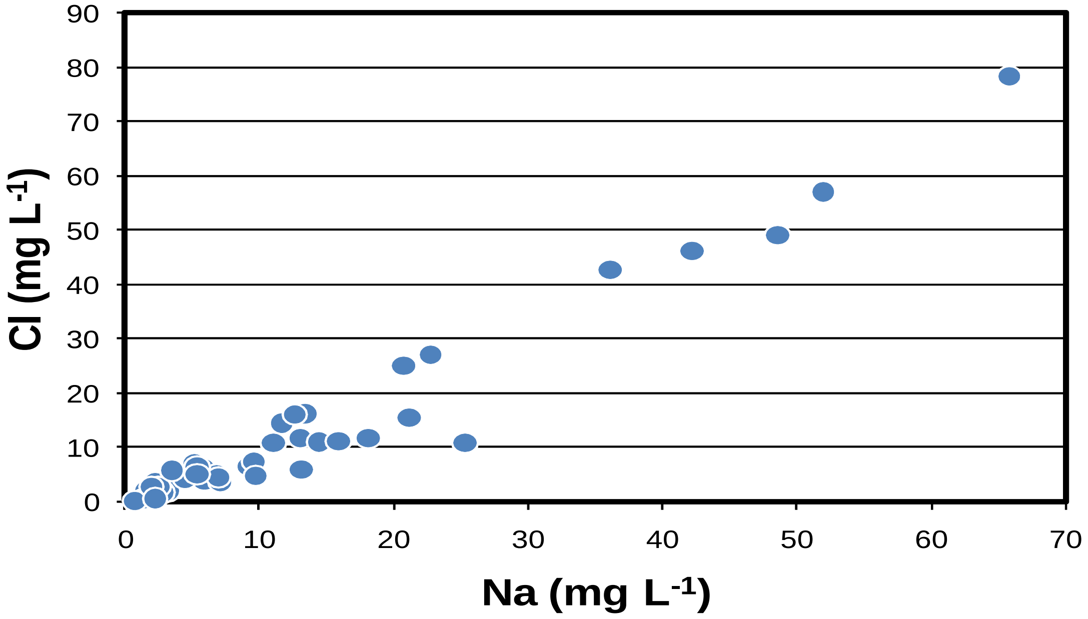


Figure 16. Na versus Cl concentration for tributaries of the St. Louis River. The highest Na and Cl concentrations were found in samples collected from the East Two and Swan Rivers under relatively dry conditions. Both of these rivers have relatively large cities in their watersheds. The samples containing increased Na without a corresponding increase in Cl (around 10 mg/L Cl) are from the Embarrass and West Two River watersheds and are believed to have arisen from long term use of NaOH as a softening agent during mineral processing in the watershed. This association suggests that some tailings basin water may also be contributing to the SO_4 load in these watersheds.

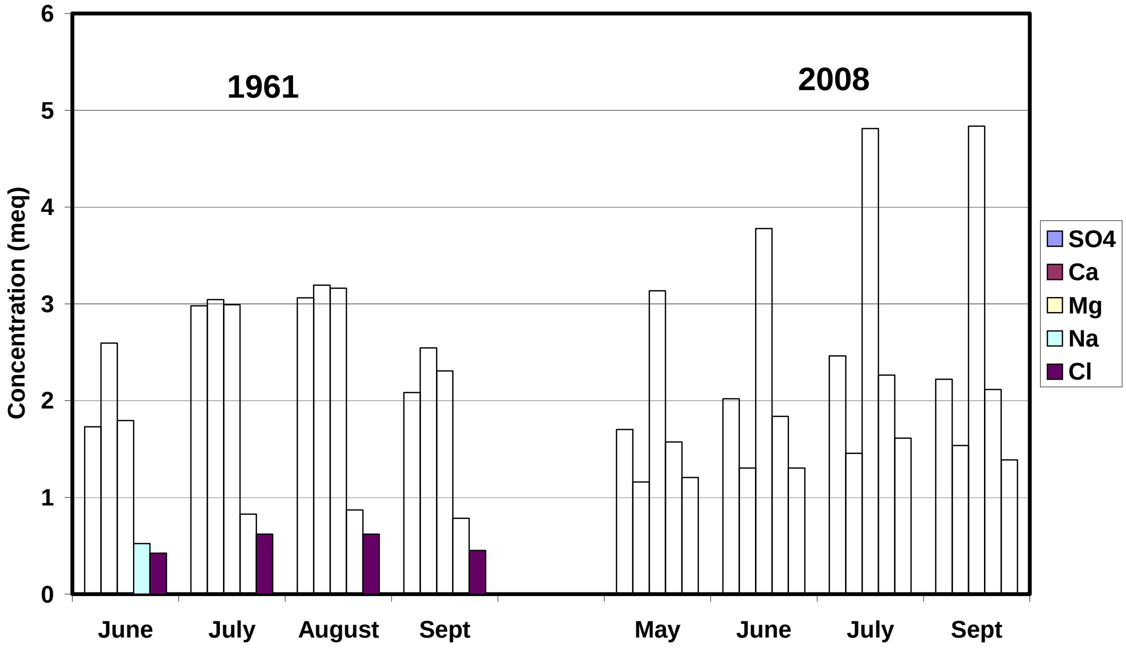


Figure 17. Major element chemistry for East Two Rivers in 1961 (from Maderak, 1963) and 2008 (this study). The SO_4 concentration in 1961 was close to that of Ca and Mg (when compared on a meq basis). SO_4 concentrations were slightly lower in 2008 than in 1961, but Ca has decreased and Mg increased compared to SO_4. This same change in major cation ratios, which is seen in other tributaries on the Iron Range, is thought to represent a change in sulfate source materials from 1961 to 2008. The proportion of Na to Cl, meanwhile, has remained approximately the same for this river, but the total concentrations of Na and Cl have increased, perhaps reflecting a watershed-wide increase in the use of NaCl has occurred in the last 50 years.

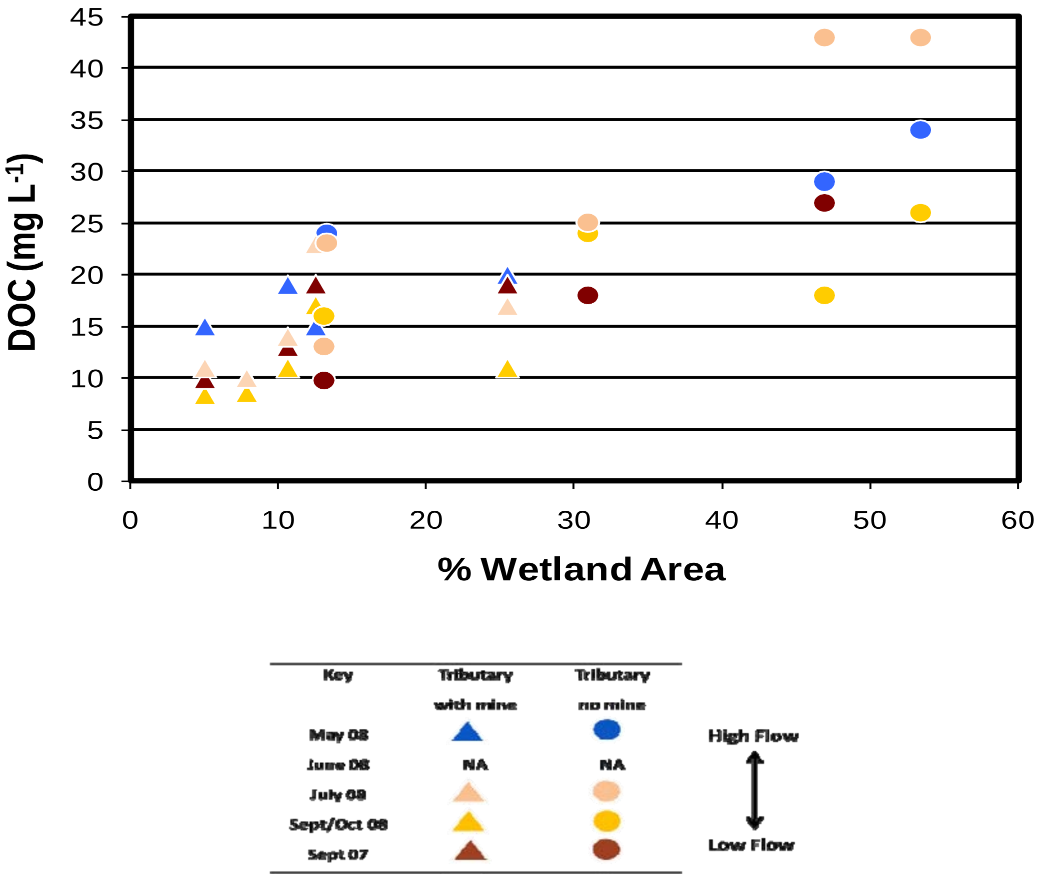


Figure 18. Relationship between % wetland area and DOC concentration for tributaries of the St. Louis River. Each series of points directly above a specific value for wetland percentage represents the seasonal variation for a single watershed. If the tan symbol is found above the blue, it signals that the stream may be prone to high wetland input following flooding events, a phenomenon that has been shown previously to produce elevated MeHg in streams. When the blue symbol plots above the tan symbol, it may indicate areas that are less prone to the flooding/drainage cycle that leads to high MeHg events in rivers.

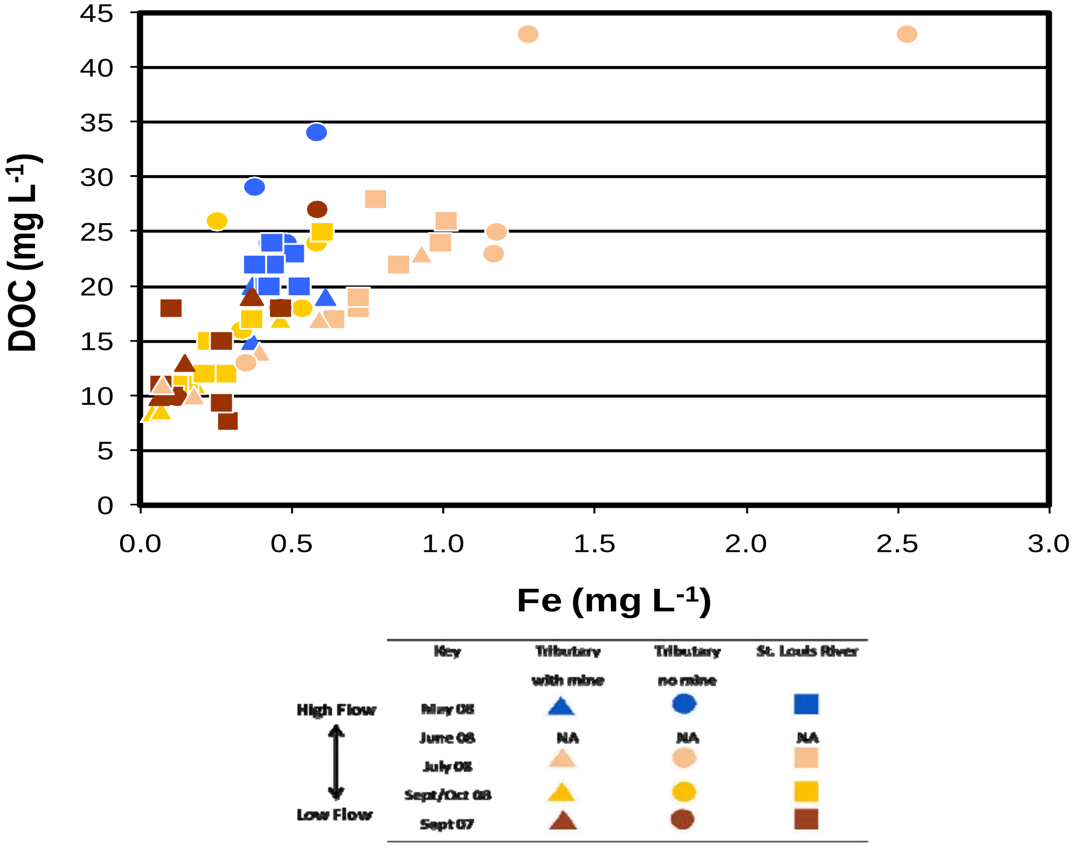
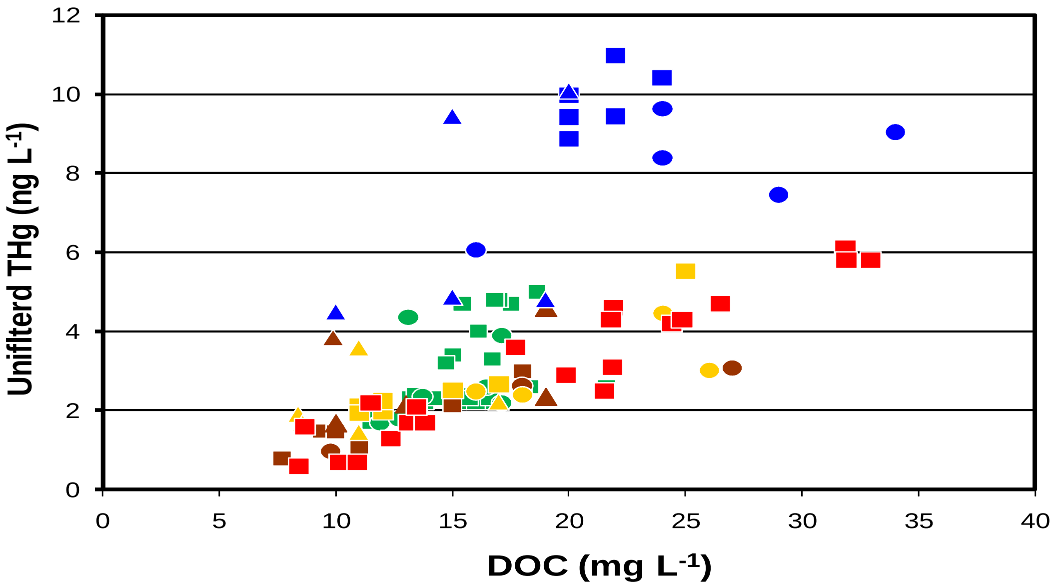


Figure 19. DOC versus dissolved Fe concentration for samples collected from the St. Louis River and its tributaries during this study. The data indicate that waters containing high Fe and DOC from wetlands invaded many of the tributaries and the St. Louis River under declining flow conditions in July 08.



	Key	Tributary with mine	Tributary no mine	St. Louis River	Source
High Flow	May 08	▲	🔵	🟦	This Paper
↕	June 08	NA	NA	NA	"
	July 08	NA	NA	NA	"
	Sept /Oct 08	▲	🟡	🟨	"
Low Flow	Sept 07	▲	🟤	🟫	"
	Summer 2005	NA	NA	🟥	Lindgren et al 2006
	Summer 2003,2004	NA	🟢	🟩	Tuominem Pers. Comm.

Figure 20. THg and DOC concentrations for unfiltered samples collected from the St. Louis River and its tributaries. This figure also includes THg and DOC data reported by Lindgren et al. (2006) for St. Louis River samples collected in the summer of 2005 (red, moderate to low flow conditions) and unpublished THg and DOC data collected from the summer of 2003 and 2004 for the Western Lake Superior Sanitary District (Tim Tuominen, personal communication). The latter data set are represented by green squares for the St. Louis River samples and green circles for tributaries.

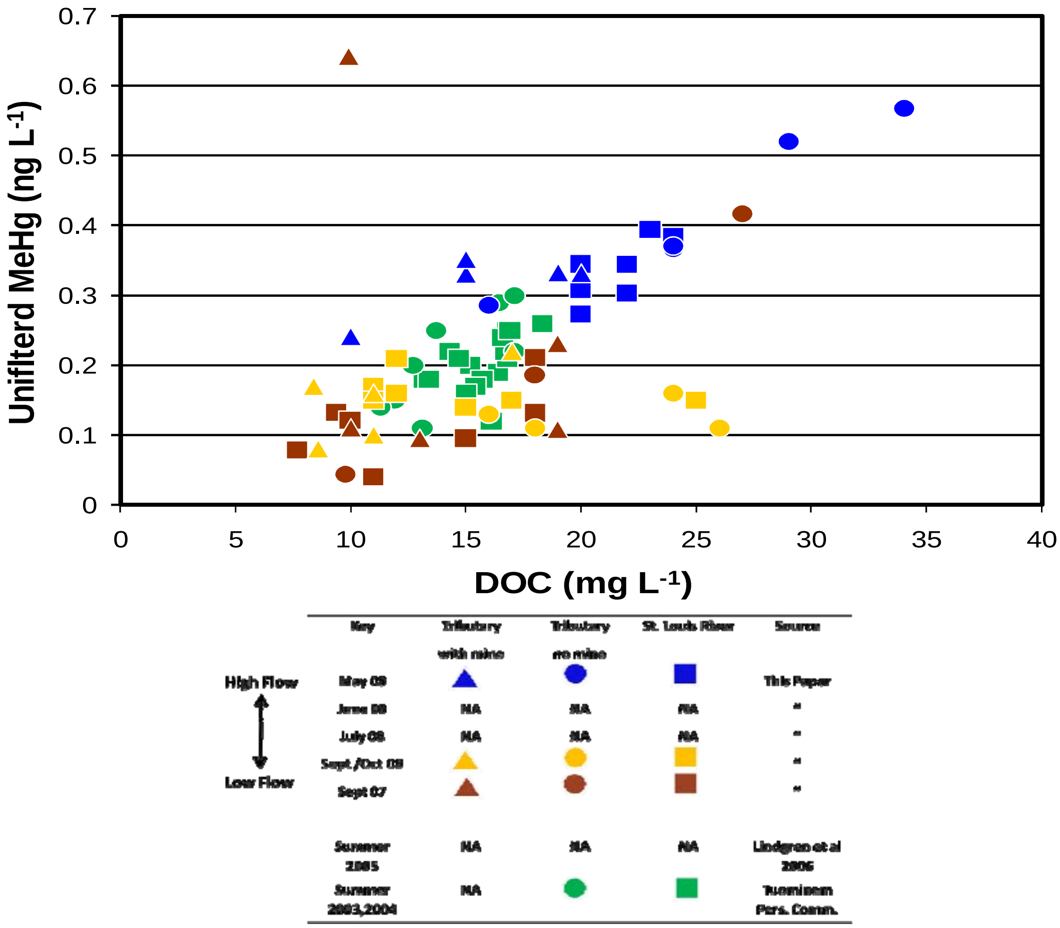
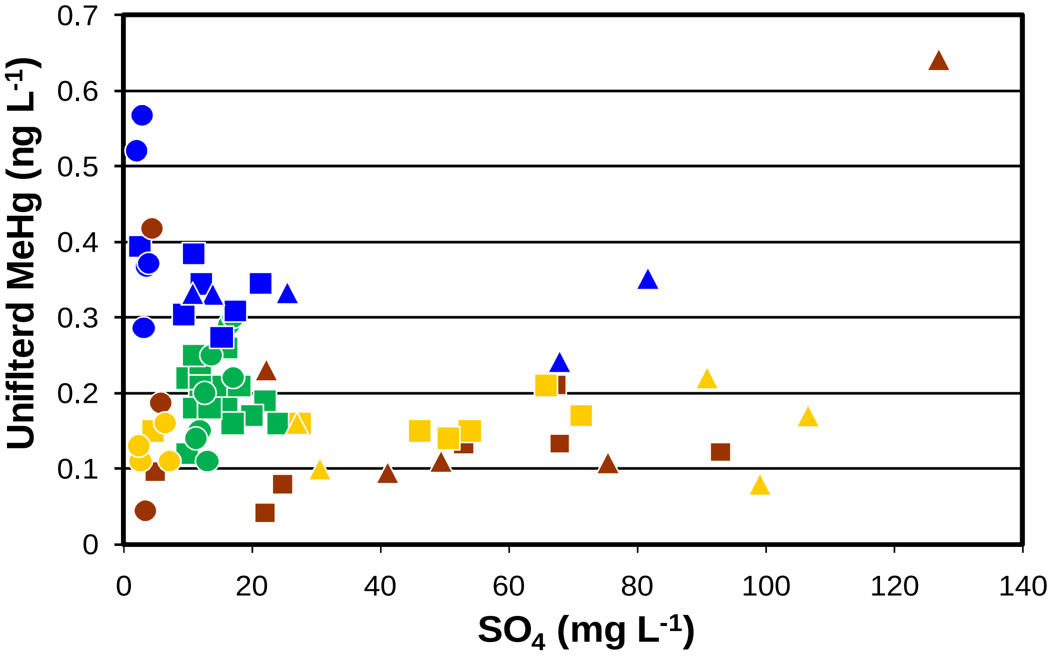
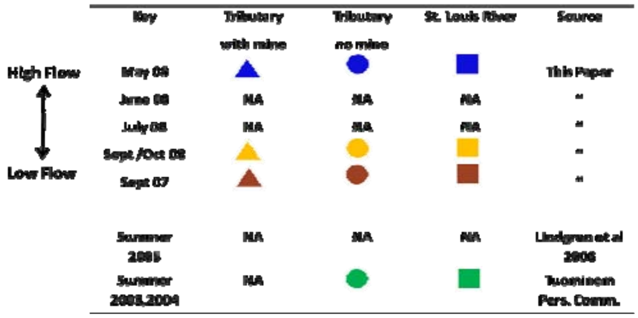


Figure 21. Relationship between unfiltered MeHg and DOC concentrations in the St. Louis River and its tributaries. Western Lake Superior Sanitary District samples from 2003 and 2004 (Tim Tuominen, personal communication) are shown using green squares for the St. Louis River and green circles for tributaries.





	Key	Tributary with mine	Tributary no mine	St. Louis River	Source
High Flow	May 08	▲	🔵	🟦	This Paper
↕	June 08	NA	NA	NA	"
	July 08	NA	NA	NA	"
	Sept /Oct 08	▲	🟡	🟨	"
Low Flow	Sept 07	▲	🟤	🟫	"
	Summer 2005	NA	NA	NA	Lindgren et al 2006
	Summer 2003,2004	NA	🟢	🟩	Tuominem Pers. Comm.

Figure 22. Unfiltered MeHg and SO_4 concentrations in the St. Louis River and its tributaries.

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12. Appendix 1: DMM in July 2008 samples

Sampling, shipment, and delivery of Hg samples was all normally synchronized between the field sampling crew and the receiving laboratory to permit all samples to be processed at the analytical facility in Seattle within 48 hours of sample collection. However, an internal contract issue emerged within the DNR in early July 2008, specifically at a time when water levels from a peak were decreasing within the St. Louis River. The timing for collection of this sample was considered critical owing to the manner in which MeHg had been observed to behave in other river systems. A decision was reached to collect the samples and ship them to the laboratory as the contract issues were being resolved.

Those samples were processed following a one week delay, a period thought to be within the normal holding time for these types of samples except possibly for AHg where no holding time has been established. When the analyses were conducted, the samples from July 2008 were reported to have very high THg and MeHg concentrations even though the blank samples that were analyzed were still all within acceptable ranges. Importantly, duplicate samples from the same site had measured concentrations that varied considerably during this period.

Dr. Lian Liang, who had conducted the primary analysis, performed an exhaustive internal study to determine why the duplicate samples from July did not agree with each other and why some of the samples from this batch had very high THg and MeHg concentrations. It was found that samples containing the highest MeHg concentrations contained an extremely volatile mercury species dimethyl mercury (DMM or $Hg(CH_3)_2$). There was initially great concern over these samples, because DMM is a highly toxic and dangerous chemical. Dr. Liang eventually traced the DMM source to ice packs that were stored in her laboratory for many years in a freezer next to a frozen DMM standard.

Exposure of our July samples to DMM began with the unfortunate occurrence of a power outage at the analytical facility between the time the samples were received and processed at the laboratory. A set of ice packs was needed to keep the July samples cool. The gradual thawing of the ice packs released the DMM, which was then able to penetrate the plastic wrapping and the Teflon-lined caps of many of the bottles holding the samples. The blanks sent to the laboratory did not receive the DMM contamination because they were not stored in the same cooler with the ice packs.

Reported Hg data for the July samples are shown in Tables A-1 and A-2 including the values for DMM. Sites from the St. Louis River for which samples appeared minimally impacted by the DMM include the filtered sample from Miles 179 and 142, and the unfiltered samples from miles 142, 53, and 36. Filtered and unfiltered samples for the Embarrass River had no detectable DMM nor did filtered samples for Mud Hen Creek or the Cloquet River. The unfiltered sample from the Whiteface River also appeared to be minimally affected by DMM contamination. THg and MeHg numbers for even these samples, however, must be regarded as maximum values because DMM was found to slowly convert to MeHg within sample bottles (Liang, personal communication) and the effect, if any, on AHg is unknown. It is clear that these sites must be sampled under similar conditions to verify any conclusions based on Hg and MeHg analysis from any of the July samples. Nevertheless, values for samples with minimal or undetectable

DMM contamination were included in this report acknowledging that the true values might have been slightly less than the reported values.

In addition the July samples, further consideration was given to the possibility of DMM contamination in other samples from the present study. Inquiry with Dr. Liang’s lab revealed that the DMM in the ice packs could not have affected the analysis of any other samples shipped earlier and later in the study. First, the other blanks and samples were processed immediately upon arrival to the laboratory and they were never stored apart from each other or close to the freezer containing the frozen DMM standard. Second, the contaminated ice packs were never taken out of the freezer and stored near the samples. The ice packs were not needed because no other power outages occurred. Finally, all of the numerous blanks, samples, and duplicates for the other sample periods showed no evidence for the presence of DMM or of any other contaminant.

This contamination pathway had never before been described for a laboratory setting and so it was an unforeseeable occurrence and not the result of any negligent or irresponsible act on the part of the analytical facility. Indeed, the laboratory worked diligently to uncover the DMM source when the problem occurred and immediately reported the problem to the state once the problem was found. Furthermore, it is worth mentioning that analytical laboratory acted quite responsibly by not charging the state of Minnesota for analysis of the July samples.

Table A-1. Concentrations of mercury species reported for samples collected from the St. Louis River in July 2008.

Mile	*179*	*142*	*125*	*115*	*80*	*53*	*36*
Date	7/7/08	7/7/08	7/9/08	7/9/08	7/8/08	7/8/08	7/8/08
Unfiltered							
THg	*14.2*	*6.1*	*7.7*	*3.4*	*5.4*	*6.4*	*5.6*
MeHg	*1.7*	*0.65*	*0.8*	*0.5*	*0.8*	*0.64*	*0.51*
AHg(II)	*4.4*	*4.0*	*2.5*	*2.8*	*3.3*	*3.0*	*3.5*
DMM	*3.6*	*<0.1*	*3.0*	*0.2*	*0.9*	*<0.1*	*0.1*
Filtered							
THg	*8.4*	*4.8*	*4.6*	*13.8*	*16.6*	*5.2*	*24.9*
MeHg	*0.48*	*0.58*	*0.3*	*2.0*	*2.4*	*0.6*	*6.4*
AHg(II)	*5.3*	*2.3*	*0.3*	*0.1*	*0.2*	*2.5*	*2.1*
DMM	*<0.1*	*<0.1*	*0.6*	*4.1*	*7.2*	*0.5*	*11.2*

DMM is Dimethyl mercury that was detected in samples following storage in ice-coolers with DMM-contaminated ice packs. Because DMM can convert to other mercury species during storage, none of the mercury analysis in this table can be used with full confidence. However, those containing low levels of DMM were likely exposed to less contamination than those with high DMM. The MeHg and THg concentrations in those cases can be used as upper limits to the actual values. The St. Louis River will be sampled under similar conditions to this in July 2009.

Table A-2. Concentrations of mercury species reported for samples collected from tributaries of the St. Louis River in July 2008.

Tributary	*Partridge River*	*Embarrass River*	*Mud Hen Creek*	*East Two Rivers*	*West Two Rivers*	*Swan River*	*Stony Creek*	*Whiteface River*	*Floodwood River*	*Cloquet River*
Date	7/7/08	7/7/08	7/7/08	7/9/08	7/9/08	7/9/08	7/9/08	7/8/08	7/8/08	7/8/08
Unfiltered										
THg	*9.5*	*5.8*	*4.8*	*7.1*	*92.1*	*9.0*	*6.2*	*5.1*	*7.8*	*10.4*
MeHg	*1.4*	*0.2*	*0.7*	*0.5*	*6.4*	*0.9*	*0.6*	*0.7*	*1.3*	*0.8*
AHg	*4.0*	*2.8*	*2.4*	*2.0*	*1.8*	*2.5*	*2.7*	*2.9*	*1.0*	*2.1*
#DMM	*0.4*	*<0.1*	*2.2*	*4.9*	*69.8*	*2.9*	*0.6*	*0.1*	*0.5*	*4.4*
Filtered										
THg	*6.2*	*4.4*	*4.0*	*2.0*	*10.0*	*13.3*		*6.3*	*7.7*	*3.3*
MeHg	*1.1*	*0.2*	*0.6*	*0.3*	*2.0*	*1.3*		*1.3*	*0.9*	*0.2*
AHg	*3.6*	*2.5*	*2.2*	*1.0*	*1.0*	*0.4*		*3.4*	*0.6*	*0.3*
#DMM	*0.8*	*<0.1*	*<0.1*	*0.7*	*3.5*	*8.5*		*1.0*	*0.5*	*<0.1*

DMM is Dimethyl mercury that was detected in samples following storage in ice-coolers with DMM-contaminated ice packs. Because DMM can convert to other mercury species during storage, none of the mercury analysis in this table can be used with full confidence. However, those containing low levels of DMM were likely exposed to less contamination than those with high DMM. The MeHg and THg concentrations in those cases can be used as upper limits to the actual values. The St. Louis River will be sampled under similar conditions to this in July 2009.