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Research article

A comparison of results from a hydrologic transport model (HSPF) with distributions of sulfate and mercury in a mine-impacted watershed in northeastern Minnesota

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ABSTRACT

The St. Louis River watershed in northeast Minnesota hosts a major iron mining district that has operated continuously since the 1890s. Concern exists that chemical reduction of sulfate that is released from mines enhances the methylation of mercury in the watershed, leading to increased mercury concentrations in St. Louis River fish. This study tests this idea by simulating the behavior of chemical tracers using a hydrologic flow model (Hydrologic Simulation Program FORTRAN; HSPF) and comparing the results with measured chemistry from several key sites located both upstream and downstream from the mining region. It was found that peaks in measured methylmercury (MeHg), total mercury (THg), dissolved organic carbon (DOC), and dissolved iron (Fe) concentrations correspond to periods in time when modeled recharge was dominated by active groundwater throughout the watershed. This helps explain why the timing and size of the MeHg peaks was nearly the same at sites located just upstream and downstream from the mining region. Both the modeled percentages of mine water and the measured sulfate concentrations were low and computed transit times were short for sites downstream from the mining region at times when measured MeHg reached its peak. Taken together, the data and flow model imply that MeHg is released into groundwater that recharges the river through riparian sediments following periods of elevated summer rainfall. The measured sulfate concentrations at the upstream site reached minimum concentrations of approximately 1 mg/L just as MeHg reached its peak, suggesting that reduction of sulfate from non-point sources exerts an important influence on MeHg concentrations at this site. While mines are the dominant source of sulfate to sites downstream from them, it appears that the background sulfate which is present at only 1–6 mg/L, has the largest influence on MeHg concentrations. This is because point sourced sulfate is transported generally under oxidized conditions and is not flushed through riparian sediments in a gaining stream watershed system.

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1. Introduction

When a river is legally classified as *impaired* with respect to a constituent, the causes of the impairment need to be studied to determine what corrective steps may be needed to bring the river back to an unimpaired state. This can become a time consuming, high-stakes process, especially when considering changes to a watershed that contains streams and rivers of high scenic and recreational value and a major industry that impacts flow and

water chemistry. Such is the case for the St. Louis River in northeastern Minnesota (Fig. 1) which contains a richly forested land dotted with wetlands and lakes, but hosts world-class iron deposits that have been mined for more than a century and extensive, undeveloped, copper-nickel deposits that may be mined in the future. This river, like many others in Minnesota, is considered impaired with respect to mercury concentration in fish (Anderson et al., 2013).

The primary method Minnesota has chosen to address fish mercury impairments is to decrease mercury emissions in the state by 93 percent from 1990 levels and by active and aggressive participation in national and worldwide efforts to cut anthropogenic Hg emissions (MPCA, 2009). This should, in time, lead to a 65

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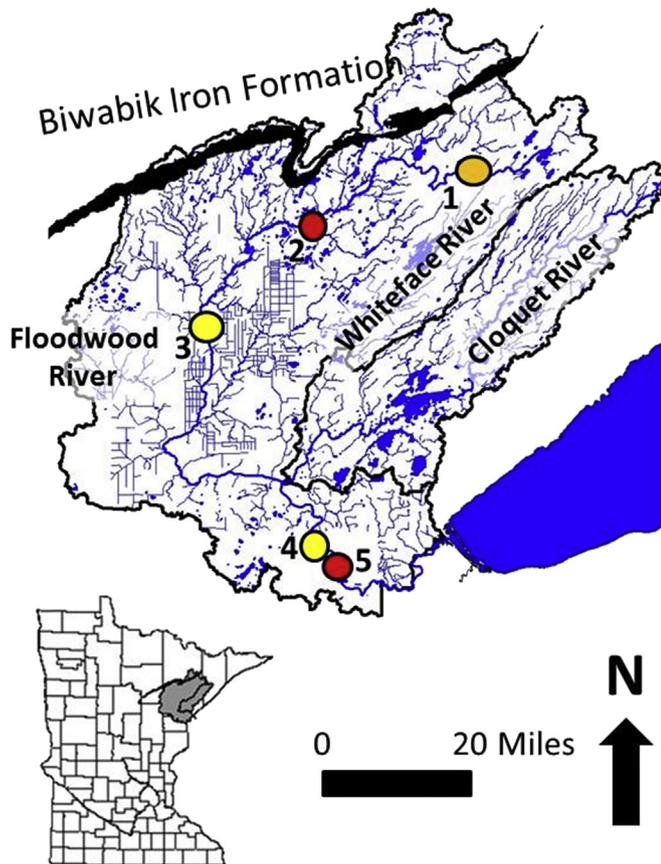


Fig. 1. Location Map showing the St. Louis River watershed and major points of interest to this study. Site 1 is Mile 179 near Skibo, MN, where both flow and chemistry were monitored upstream from the mining region (Biwabik Iron Formation in black). Sites 3 and 4 refer to Miles 94 and 36, respectively, where chemistry was sampled progressively downstream from the mining region. Sites 2 and 5 refer to the Forbes and Scanlon flow monitoring stations.

percent decrease in the amount of mercury in fish throughout the state. However, several rivers, including the St. Louis River, are expected to remain impaired even if these reduction goals are achieved (MPCA, 2014). Thus, the state is interested in determining what other measures might be useful in bringing this and other rivers that will remain impaired into eventual compliance.

One possible management strategy under consideration for such rivers involves decreasing the amount of sulfate released from the mining industry. Sulfate reducing bacteria (SRB) have long been known to participate in mercury methylation processes (Benoit et al., 1999; Gilmour et al., 1992). Sulfate added to water from the agricultural industry is widely debated, for example, as a primary cause for elevated methylmercury levels in certain fish in the Florida Everglades region (Gabriel et al., 2014; Julian et al., 2015). Debate over a possible connection between mining-related sulfate and methylmercury has also ensued for the St. Louis River, and so the State of Minnesota has been urged by environmental and mining advocates alike to study this issue.

Sulfate in Minnesota's mining region is produced when small amounts of pyrite and other less abundant iron sulfide minerals are exposed to air during the mining of taconite iron ore. This sulfate is rinsed into surface and groundwaters when precipitation infiltrates the oxidized portions of rock stockpiles and tailings. The majority of the sulfate currently released from mine wastes in the St. Louis River watershed eventually reaches the bottoms of still active mine pits and is discharged with mine water into nearby surface streams

(Berndt and Bavin, 2012a,b). Additionally, some abandoned pits have become filled with high sulfate water (e.g., typically 100–1000 mg/L) that can overflow into nearby streams. The iron mining region, active since the 1890s, also contains other rock stockpiles and tailings piles that can promote oxidation of sulfide minerals that seep into the subsurface and emerge nearby, but this is a much smaller source than the sumps or pits that feed directly into streams in the St. Louis River's northern headwater regions.

Significant chemical and biological sampling efforts were made in this region in 2012 to identify linkages between sulfate release from the mining region and possible influence on MeHg production, transport, and bioaccumulation in the watershed (Berndt et al., 2014; Jeremiason et al., 2016; Johnson et al., in press). The watershed often experiences wet conditions in the spring and early summer that transitions to drier periods in late autumn and this also happened in 2012 (Fig. 2). Comparison of water chemistry for sites located both upstream and downstream from the mining region for this period indicated that sulfate was strongly correlated to magnesium, but not to dissolved organic carbon (DOC) or to methylmercury (MeHg), total mercury (THg), or dissolved iron (Fe) (Berndt et al., 2014). The latter components were, however, strongly correlated to each other. Although sulfate in reduced settings influenced mercury and methylmercury dynamics in sediments, the results suggested that the sulfate from mines may have had relatively little opportunity to interact with reduced sediments in a manner conducive for production and transport of MeHg. This study tests and expands this interpretation by comparing chemical results from the 2012 sampling study to seasonally varying differences in hydrologic flow components as modeled using an HSPF watershed model (Tetratech, 2015).

The HSPF model was selected for this study because it has the ability to provide an independent method to quantify and track the relative amounts of water delivered to the river specifically via surface runoff, interflow, and groundwater recharge. Recharge mechanisms that force hillslope flow paths through riparian zones have received recent attention for use in quantifying DOC, THg, and MeHg delivery to watersheds from similarly forested boreal catchments in Sweden (Bishop et al., 2004; Eklof et al., 2015; Seibert et al., 2009; Winterdahl et al., 2011). According to these models, groundwater that enters a river in its headwater regions attains much of its chemistry by reaction with riparian sediments, the last substrate with which it is in contact prior to becoming part of the surface water flowage. Thus, a comparison of measured chemistry to HSPF modeling results can help to determine the degree to which similar processes might help to account for the chemistry of water in mine-impacted portions of the St. Louis River.

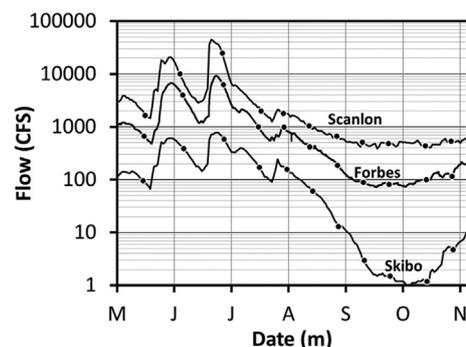


Fig. 2. Measured flow volumes in the St. Louis River during the study period (lines). Solid dots refer to dates when chemical samples were collected at Miles 36, 94, and 179.

2. Methods

HSPF modeling tools provide a well-established means to numerically characterize water recharge and routing in a watershed (Bicknell et al., 2001; Ouyang et al., 2012; Rolle et al., 2012). This model is part of the United States Environment Protection Agency's US-EPA's Better Assessment Science Integrating point and Nonpoint Sources (BASINS) software package (US-EPA, 2013). To the extent possible, HSPF models take into account all available climatological information, land use, topography, and surficial geology. Records from point sources, dams, and gaging stations located along the river or its tributaries are also considered directly in the final hydrologic calibration. The state of Minnesota has invested heavily in the development of HSPF watershed models as a means to improve its understanding of nutrient, sediment, and contaminant loading to rivers and lakes throughout the state. In 2015, a calibrated HSPF model became available for the St. Louis River watershed, with hydrologic calibration extending through the end of 2012 (Tetrattech, 2015).

Flow measurements from 11 gaged stations located throughout the watershed were used in the calibration. This included sites at Scanlon (2005–2012 data set, $R^2 = 0.9293$ for monthly average flows), Forbes (2010–2012; $R^2 = 0.8561$), and Skibo (2011–2012, $R^2 = 0.8756$) (Fig. 1). Part of the calibration involved distributing non-point recharge to rivers along three primary flow paths that depend on land characteristics and the intensity and duration of storm events. The HSPF model was used to calculate the percentages of water at each of our sampling locations derived from different recharge sources. Five simulated tracers were defined (n with concentration C_n) each unique to water source types. These tracers were then introduced independently to each water source type as they entered the surface water flow environment as follows:

1. $C_{SR} = 1.0$ mg/L added only to water that enters the surface waters as surface runoff,
2. $C_{IF} = 1.0$ mg/L added only to water that enters the surface waters as interflow,
3. $C_{AG} = 1.0$ mg/L added only to water that enters the surface waters as active groundwater,
4. $C_{P1} = 1.0$ mg/L added only to water that enters the surface waters from mining point sources.
5. $C_{P2} = 1.0$ mg/L added only to water that enters the surface waters from non-mining point sources.

Direct precipitation onto open water was also modeled with a tracer, but its percentage was generally small compared to the others and its contribution is ignored here. The other tracer concentrations were used as proxies for the relative amounts of water derived as a function of time from individual source types.

A second calculation was also conducted for groundwater that involved additional input of a decaying tracer, $^*C_{AG}$, also at 1 mg/L concentration to all water entering the watershed as groundwater. This tracer was allowed to decay by a small fraction, k , each day. An indication of actual and relative transit time for dissolved components entering the stream from groundwater could then be computed using $^*C_{AG}/C_{AG}$ ratios as follows:

$$\text{Transit time (days)} = -\ln(^*C_{AG}/C_{AG})/k \quad (1)$$

where k is a decay rate in units of days^{-1} (e.g., $dC_{AG}/dt = -kC_{AG}$). In reality, some molecules in a watershed could take years to move from source region to sampling site while other molecules sourced nearby can make the transit in seconds. Thus, transit times defined in this way are not singular or statistically defined values

(McDonnell et al., 2010). The transit time in this application is operationally defined by Equation (1). It is used more appropriately in a semiquantitative sense to systematically compare the time that the majority of molecules transported in a stream have spent in the water column since entering the river.

3. Results

Simulated C_{SR} , C_{IF} , C_{AG} , C_{P1} , and C_{P2} concentrations varied by site and by season (Fig. 3). Relative tracer concentrations at all three sites summed very closely to unity in all cases, so the concentration of a particular constituent represents the fraction of water that originated from the tracer's designated source type. C_{AG} values close to 1.0 throughout the region indicate that active groundwater was the overwhelmingly dominant source of water input during most periods from April through July. Overland surface runoff and interflow waters were common immediately following large rain events, but these were flushed quickly downstream by more persistent, longer lasting recharge from active groundwater flow. The simulated tracer concentrations suggest that groundwater also dominated through the winter and dry autumn months at Mile 179, where no significant point sources were present upstream. Modeled mining point sources accounted for over 40 percent of the flow at Mile 94 during winter and at the height of the autumn dry period. Point sources accounted for less than 20 percent of flow in winter at Mile 36 but reached approximately 30 percent in the autumn, 20 percent of which was from the mining industry.

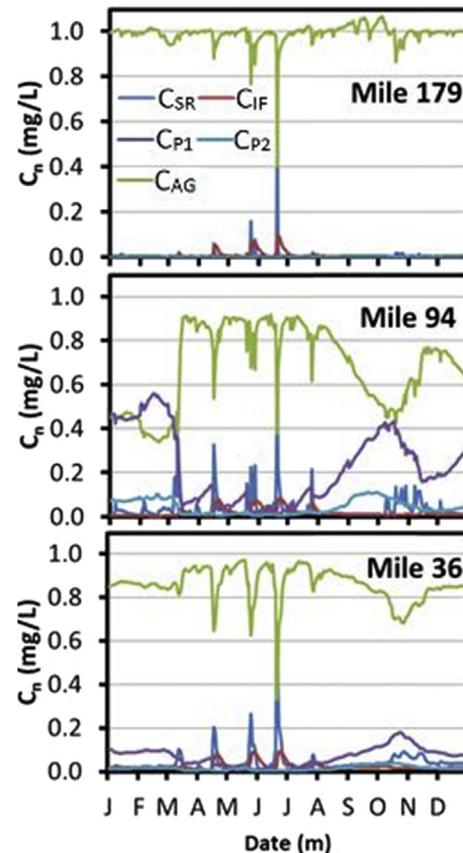


Fig. 3. Computed source type tracer concentrations (C_n) for the three sites sampled in 2012. The model indicates that May through July were dominated by discharge from active groundwater sources (C_{AG}). Mining (C_{P1}) and other (C_{P2}) point sources became progressively more important from August through October downstream from the mining region (Miles 94 and 36) as flow rates declined throughout the watershed.

Sulfate, DOC, THg, MeHg, and Fe concentrations measured at the three sites can be compared with computed mining point source tracer concentrations (Fig. 4) to provide insight on the potential for mine waters to impact these constituents. Dissolved sulfate measured in the water column increased when modeled mine tracer concentrations also increased at Mile 94, but the arrival of the measured sulfate peak at Mile 36 was somewhat delayed compared to that predicted by the minewater tracer. The source of this offset is part of an ongoing investigation to improve the HSPF model's accuracy.

Measured DOC, THg, MeHg, and Fe concentrations declined rapidly as the modeled mine water fraction increased. However, the fraction of mine water present in the watershed at the sampling sites was far too small to explain the declines by simple dilution. While there were peaks for DOC, THg, MeHg, and Fe at all sites, a second large peak in measured concentrations at Mile 179 occurred in August for DOC, THg, Fe, but not MeHg. This later peak followed a relatively small precipitation event near the end of July. The second peak in measured concentrations at Mile 179 was more pronounced for DOC and Fe than for THg and not observed at the downstream sites.

Calculated transit times for groundwater-derived components were generally 10 days or less at all sites from April through July (Fig. 5) but increased significantly, especially at Miles 36 and 94 in the fall and winter months. Transit times were never greater than 8 days at Mile 179, where there must be limited in stream storage between sources and the sampling site. The short computed transit

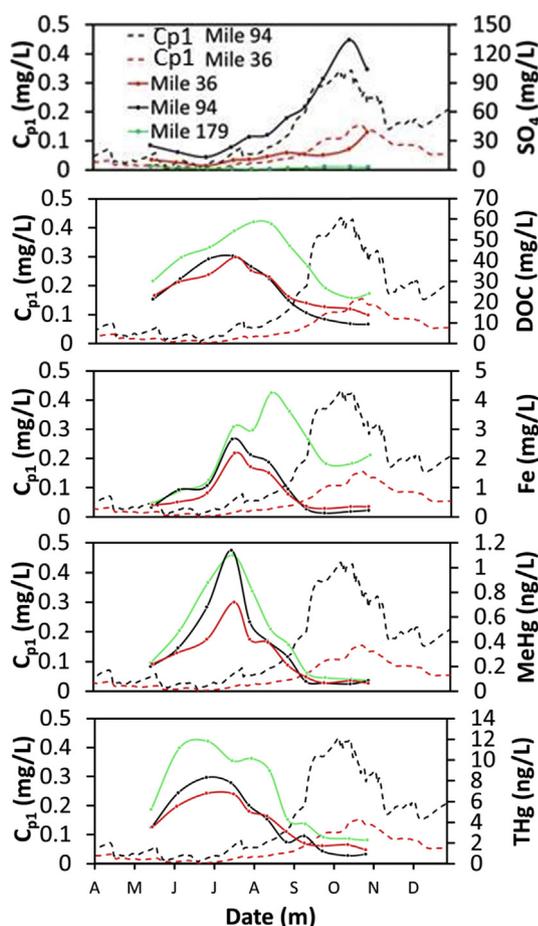


Fig. 4. Relationship between modeled mine water tracer concentration (C_{p1} , dashed lines) and dissolved concentrations of a variety of dissolved constituents (Sulfate, DOC, THg, MeHg, and Fe; solid lines) at Miles 36, 94, and 179.

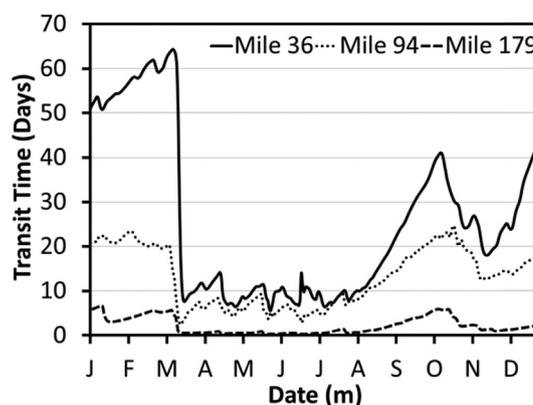


Fig. 5. Calculated transit times at the three sampling sites for components that enter the watershed from active groundwater sources. Transit times become short when flow rates become elevated.

times at Mile 179 suggest that water column demethylation processes were likely not important and, thus, the lack of high MeHg in the autumn is indicative of processes occurring in the source regions. Computed transit times for Mile 94 and Mile 36 increased, respectively, to approximately 25 and 40 days by early October suggesting there was greater opportunity for instream reactions such as DOC photodegradation and mercury demethylation during these periods.

4. Discussion

Landscapes and climate create complicated variables that result in many possible dynamically changing flow paths and mixtures of water in a river. Water from precipitation is added to streams via surface runoff or may be progressively delayed as it flows through and reacts with sediments along interflow and groundwater flow paths. Owing to this complexity, contextual information needed to interpret the chemistry of water draining a large river system can probably best be provided by computer watershed models like HSPF. The model developed here used simulated tracers to provide a mechanism to independently distinguish and track the source and fate of water entering the St. Louis River watershed for a year characterized by periodic sampling at sites located upstream and downstream from the mining region.

Active groundwater tracer concentrations calculated for each of the sampling points approached unity during periods when elevated methylmercury concentrations were found, signifying the importance of groundwater recharge in the MeHg generating process in this river. Although three major rain events early in the growing season led to pronounced but briefly elevated simulated tracer concentrations for interflow and surface water runoff, these components were diluted and washed quickly downstream by groundwater recharge when elevated MeHg concentrations were found in the river (Figs. 3 and 4).

It has long been known that riparian sediments can exert an important influence on the chemistry of stream waters recharged by groundwater (Bishop et al., 2004; Brigham et al., 2009; Vidon et al., 2010). Stream waters in several heavily studied forested boreal watersheds in Sweden, with composition similar to the St. Louis River, are thought to take their chemistry directly from riparian pore waters that obtained their chemistry during reaction with riparian sediments (Eklöf et al., 2015; Seibert et al., 2009; Winterdahl et al., 2011). Under conditions of high flow the stream chemistry more closely mimics pore water chemistry that evolves in upper riparian soils. Conversely, stream chemistry under lower flow conditions mimics that of pore fluids that evolve in deeper

sediments underlying the riparian soils. The Riparian Profile Flow-Concentration Model (RIM) describes changes in stream chemistry by integrating groundwater flux and concentration profiles for water moving laterally across riparian soils and sediments (Seibert et al., 2009). Based on the above theory, we hypothesize that stream chemistry reflects riparian pore fluid processes during periods of high groundwater input in our region, and use measured stream chemistry (Fig. 6) to infer processes occurring in riparian sediments upstream from the Mile 179 site. This HSPF model indicates water sampled at this site was almost totally from groundwater and had relatively short flow path from stream recharge to the sampling site (Fig. 6).

Sulfate concentration was initially above 5 mg/L when methylmercury and DOC concentrations were low, indicating that constituents in groundwater passing into the stream were not being rapidly metabolized and DOC was not being as actively produced as later in the season. By late July, the growing season was near its peak and sulfate concentrations dropped to approximately 1 mg/L while dissolved MeHg concentration reached its peak. As the summer continued, sulfate continued to remain close to 1 mg/L while iron began to climb to values eventually reaching 4 mg/L. This suggests that iron and sulfate reduction were both occurring within the pore fluid environment in the groundwater source region during these periods. The fact that MeHg concentrations were in decline as iron concentrations began to increase implies that iron reduction may not be the primary process associated with MeHg production and transport during the late summer months. Near the end of August, sulfate levels again began to climb, eventually to approximately 3 mg/L, just as MeHg reached stable low values (e.g., approximately 0.1 ng/L) and iron concentrations declined to approximately 2 mg/L. The gain in sulfate and loss of iron signals the slowing of both iron and sulfate reduction processes and corresponds to a decrease in DOC from almost 60 mg/L to values near 25 mg/L. Water levels in the watershed had declined greatly by this time, meaning that most water entering the streams may have been occurring through long-lasting springs and seeps, involving less contact with labile organic matter or at colder temperatures. For this part of the watershed, however, the attainment of minimum sulfate concentrations coincided with the methylmercury maximum, suggesting a strong role for sulfate reduction in the process that methylates mercury. It is reasonable to expect a similar reaction sequence in the nonmining portions of the mining watersheds where water filters through the landscape and riparian soils.

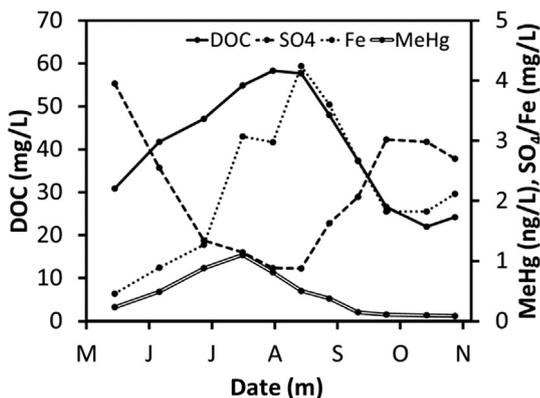


Fig. 6. Dissolved DOC, sulfate, Fe, and MeHg at Mile 179 in 2012. The MeHg peak occurred and Fe concentration quickly increased when sulfate dipped to approximately 1 mg/L. This suggests that DOC, MeHg, and Fe are generated by reactions involving sulfate and iron reduction as groundwater passes through riparian sediments on its way to recharging the river.

The climate impacting the different parts of the watershed appears to be similar based on the similarity of hydrographs for different parts of the river (Fig. 2). The geography and geology of the regions is variable and some differences in chemistry can be expected even without the presence of any mine influences. There are also more lakes and reservoirs that can enhance the importance of in-lake reactions for water collected at Miles 36 and 94, as compared to Mile 179. Despite these differences, the MeHg peaks occurred at the same time in all parts of the watershed, specifically when HSPF modeling suggests there was a very small fraction of mine water flowing in the river at the sampling sites. There was also an extended Fe and DOC peak in the area upstream from Mile 179 compared to at the sites downstream (Fig. 4). Flows at Mile 179 during the late summer become exceedingly small compared to earlier in the summer (Fig. 2). It is possible that a similar high-Fe peak was delivered to the other parts of the watershed, too, but in volumes so small that they were masked by iron-poor water already stored in the watershed. Modeled transit times for components of groundwater recharge increased during this time much more at Mile 36 and Mile 94 than at Mile 179 (Fig. 5), supporting this interpretation.

Two factors make it difficult for sulfate from the mines to impact MeHg in the rivers. First, the sulfate from mines is introduced largely as point sources at the ends of a relatively few tributaries and, thus, is limited geographically from interacting with riparian sediments in the great majority of the region. Second, even in the streams it flows through, it may be hydrologically excluded from reacting with riparian sediments that have the reduced conditions needed to promote methylation. The St. Louis River watershed receives, on average, approximately 8 inches more precipitation than is evaporated or transpired, and thus stream segments along the flow path mostly gain water from the surrounding landscape. The hydraulic gradient, is therefore, well poised to produce and transport chemicals like DOC and MeHg to the river, but water derived from mines is not well poised hydrologically to interact with riparian sediments where DOC and MeHg are likely to be produced.

This does not mean that sulfate introduced as point sources from mines or municipalities will never impact zones of active mercury methylation, but it does imply that instances may be rare in a mining region that receives more rainfall than can evaporate or transpire from the landscape. For example, a wetland rich area may become flooded with mine water containing sulfate during periods of increased pumping rate or from formation of temporary dams (e.g., beavers). Riverine sulfate may also react with materials in its streambed through diffusional exchange and hyporheic flow. Several studies have been conducted in the St. Louis River's mining region to evaluate stream and lake bed processes (Bailey et al., 2014a, 2014b; Berndt and Bavin, 2011). In general, MeHg production was found to be suppressed in sediments when overlying sulfate levels were high, owing likely to the binding of Hg with dissolved sulfide (Johnson et al., in press). This is consistent with findings from other studies which indicate that sulfate availability can lead to reduced sulfur species that can bind with Hg(II), reducing bioavailability (Benoit et al., 1999). A hypereutrophic lake (Lake Manganika) that receives mine water and municipal waste water has also been studied during several seasons. In the first season, when only the outflow for the lake was studied, large amounts of MeHg were found and it was proposed that the lake was producing MeHg in its water column or sediments and mixing on a relatively frequent basis (Berndt and Bavin, 2011). Subsequent years with intensified efforts found that the lake remained stratified during the summer months and while dissolved MeHg concentrations were elevated in the hypolimnion, they remained low in the epilimnion and Lake's outlet (Bailey et al., 2014b).

Instances like these should still be avoided or controlled to limit

potential local impacts to MeHg inventories in local streams. However, the great majority of the mining sulfate added to streams apparently has little measureable impact on stream chemistry because opportunities are rare for the sulfate added as a point source to flow onto landscapes, through reduced soils, and back out into openly flowing waters. Elevated MeHg levels at sites located upstream and downstream from the mining region appear linked in time to periods of high summer groundwater recharge and not to periods of elevated minewater influence. Thus, it appears that limiting sulfate from point discharges would be an ineffective strategy for lowering MeHg levels in the St. Louis River.

5. Conclusions

Comparison of measured chemical trends to an HSPF source tracer model for the St. Louis River suggests that MeHg production and transport is associated primarily with the reduction of nonpoint sourced sulfate in groundwater that recharges the river through riparian sediments throughout the watershed. While abundant point sourced sulfate is delivered to the watershed from mines, this type of sulfate is typically delivered to the river in a manner that is isolated geographically and hydrologically from impacting the river's primary MeHg production and transport process. Thus, controlling mine derived sulfate would likely serve as an ineffective means for decreasing MeHg levels in the St. Louis River.

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