#### [Journal of Environmental Management 181 \(2016\) 74](http://dx.doi.org/10.1016/j.jenvman.2016.05.067)-[79](http://dx.doi.org/10.1016/j.jenvman.2016.05.067)

Contents lists available at ScienceDirect

## Journal of Environmental Management

journal homepage: [www.elsevier.com/locate/jenvman](http://www.elsevier.com/locate/jenvman)



### 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





Michael E. Berndt <sup>a, \*</sup>, Wes Rutelonis <sup>b</sup>, Charles P. Regan <sup>c</sup>

<sup>a</sup> Minnesota Department of Natural Resources, 500 Lafayette Road, St. Paul, MN, 55155, USA

<sup>b</sup> University of Minnesota, Earth Sciences Department, 310 Pillsbury Drive SE, Minneapolis, MN, 55455, USA

<sup>c</sup> Minnesota Pollution Control Agency, 520 Lafayette Road, St. Paul, MN, 55155, USA

#### article info

Article history: Received 19 January 2016 Received in revised form 25 May 2016 Accepted 26 May 2016 Available online 17 June 2016

Keywords: Mining Sulfate Methylmercury Minnesota HSPF model

#### **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.

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license [\(http://creativecommons.org/licenses/by-nc-nd/4.0/](http://creativecommons.org/licenses/by-nc-nd/4.0/)).

#### 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

E-mail address: [mike.berndt@state.mn.us](mailto:mike.berndt@state.mn.us) (M.E. Berndt).

water chemistry. Such is the case for the St. Louis River in north-eastern Minnesota ([Fig. 1](#page-1-0)) 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.,](#page--1-0) [2013\)](#page--1-0).

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 anthropo-Expressionding author.<br>16 genic Hg emissions ([MPCA, 2009\)](#page--1-0). This should, in time, lead to a 65 \* Corresponding author.<br>16 genic Hg emissions (MPCA, 2009). This should, in time, lead to a 65

<http://dx.doi.org/10.1016/j.jenvman.2016.05.067>

0301-4797/© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license ([http://creativecommons.org/licenses/by-nc-nd/4.0/\)](http://creativecommons.org/licenses/by-nc-nd/4.0/).

<span id="page-1-0"></span>

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 [\(MPCA, 2014\)](#page--1-0). 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 [\(Benoit](#page--1-0) [et al., 1999; Gilmour et al., 1992\)](#page--1-0). 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 [\(Gabriel et al., 2014; Julian et al., 2015\)](#page--1-0). 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](#page--1-0)). 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 [\(Berndt](#page--1-0) [et al., 2014; Jeremiason et al., 2016; Johnson et al., in press\)](#page--1-0). 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\)](#page--1-0). 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\)](#page--1-0).

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;](#page--1-0) [Seibert et al., 2009; Winterdahl et al., 2011](#page--1-0)). 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.

Download English Version:

# <https://daneshyari.com/en/article/7479408>

Download Persian Version:

<https://daneshyari.com/article/7479408>

[Daneshyari.com](https://daneshyari.com)