

Technical Support Document for the St. Louis River Watershed and Estuary Mercury Total Maximum Daily Loads

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Final

PREPARED FOR

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ACRONYMS/ABBREVIATIONS

Acronyms/Abbreviations	Definition
µg/L	Micrograms per liter
ADCIRC	Advanced circulation model
AOC	Area of Concern
AUID	Assessment unit ID
BAF	Bioaccumulation factor
BASS	Bioaccumulation and aquatic system simulator
CBOD	Carbonaceous biochemical oxygen demand
dMeHg	Dissolved methylmercury
DMR	Discharge monitoring report
DOC	Dissolved organic carbon
EFDC	Environmental fluid dynamics code
FILET	Fillet without skin
FILSK	Fillet with skin
Hg	Mercury
Hg(0)	Elemental mercury
Hg(II)	Divalent mercury
HgS	Cinnabar (mercuric sulfide)
HSPF	Hydrologic Simulation Program - FORTRAN
IMPLND	Impervious land segment in HSPF
kg	Kilogram
m	Meter
m³/s (cms)	Cubic meters per second
MCES	Metropolitan Council of Environmental Services
MDN	Mercury deposition network
MeHg	Methylmercury
mg/L	Milligrams per liter
mg	Milligram
MGD	Million gallons per day
MNDNR	Minnesota Department of Natural Resources
MnDOT	Minnesota Department of Transportation
MOS	Margin of safety
MPCA	Minnesota Pollution Control Agency
MS4	Municipal separate storm sewer system
NA	Not applicable
NADP	National Atmospheric Deposition Program
ng/L	Nanograms per liter

Acronyms/Abbreviations	Definition
NOHV	Organism without head or viscera
NPDES	National Pollutant Discharge Elimination System
OC	Organic carbon
PERLND	Pervious land segment in HSPF
pg/L	Picogram per liter
PLUG	Dorsal muscle plug without skin
ppm	Parts per million
RCHRES	Reach segments in HSPF
RF	Reduction factor
SLR	St. Louis River
SLRW	St. Louis River Watershed
SO ₄ ²⁻	Sulfate
THg	Total mercury
TL	Trophic level
TMDL	Total maximum daily load
tMeHg	Total methylmercury
UMD	University of Minnesota-Duluth
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WARMF	Watershed analysis risk management framework
WASP	Water analysis simulation program
WHORG	Whole organism
WLA	Wasteload allocation
WRAPS	Watershed restoration and protection strategy
WWTP	Wastewater treatment plant
WY	Water year

1.0 INTRODUCTION

This technical assessment report was prepared to support the development of a Total Maximum Daily Load (TMDL) by the Minnesota Pollution Agency for mercury-related impairments of water quality in the St. Louis River Watershed (SLRW), including the tributary Cloquet River watershed and the St. Louis River Estuary and Duluth Harbor area. These are referred to collectively as the SLRW throughout this document.

Mercury is a naturally occurring element that cycles through the atmosphere, hydrosphere, and geosphere, existing in three major forms: elemental mercury, inorganic (ionic) mercury, and organic mercury (primarily methylmercury (MeHg), with chemical formula CH_3Hg). Elemental mercury is a potent neurotoxin in humans that can cause significant health effects. Elemental mercury converts to the ionic form Hg^{2+} or Hg(II) , which forms compounds and salts with other elements such as sulfur. Compounds of Hg(II) are collectively referred to as inorganic mercury. Inorganic mercury in waterbodies is rarely a direct threat to aquatic life, wildlife, and human health. However, bacterially mediated environmental processes that break down organic carbon under hypoxic or anoxic conditions in sediment and on suspended particulate matter can result in the formation of MeHg. MeHg is a highly toxic substance with a number of adverse health effects associated with its exposure in humans and animals. Neurotoxicity of MeHg is the greatest concern and high dose exposure can result in intellectual disability, cerebral palsy, deafness, blindness, and weakness of speech muscles (dysarthria) in utero and in sensory and motor impairment in adults (USEPA, 2001).

Low oxygen/high carbon environments such as the wetlands and peatlands in the St. Louis and Cloquet watersheds are likely areas of heightened mercury methylation. Chronic exposure to elevated MeHg levels in aquatic environments leads to ingestion by filter-feeding organisms, bioaccumulation in the food web, and ultimately to biomagnification of mercury in higher trophic level fish such as walleye, pike, and smallmouth bass. Worrisome human and wildlife exposure to mercury occurs primarily through repetitive consumption of contaminated fish and shellfish.

Minnesota issued statewide mercury TMDLs for the northeast and southwest regions in 2007 to address over 75 percent of the state's waterbodies listed as impaired on Minnesota's 2004 303(d) list for elevated mercury (Hg). The TMDLs (MPCA, 2007) applied a fish tissue target of 0.2 mg of total mercury (THg) per fish weight in kilograms (kg) to be achieved in top predator (trophic level [TL] 4) fish). The primary nonpoint source of mercury identified was atmospheric deposition and the TMDLs specified reductions of 51 percent of existing mercury loads for the southwest region and 65 percent for the northeast region.

The technical analysis in MPCA (2007) found that waters with fish tissue levels exceeding 0.572 mg-THg/kg would require greater reductions than necessitated by the northeast and southwest regional TMDLs. Waters meeting this condition include segments within the St. Louis and Cloquet 8-digit hydrologic unit codes. Minnesota is now seeking to develop TMDLs for waterbody segments that were not included in the original TMDL and listed as impaired for exceedances of fish tissue and water column mercury criteria in the St. Louis River and Cloquet River watersheds. This report describes the technical approach for establishing mercury loading capacities and quantifying mercury loads from point and nonpoint sources to support MPCA in the development of the mercury TMDLs for these impaired segments.

1.1 WATER QUALITY STANDARDS

Surface water quality is protected and regulated for fresh waters under standards approved by the United States Environmental Protection Agency (USEPA) and adopted by the state of Minnesota. Waters of the state are assigned designated use classifications, also called beneficial uses, which include aquatic life, wildlife, recreational, and drinking water uses as well as other uses. Definitions of the designated uses for fresh waters are found in the Minnesota Administrative Rules (7050.0140).

The designated uses of a water body or water segment determine the applicable surface water quality standards; these standards can include both numeric and narrative criteria that are used to identify impaired water segments. Moreover, water quality standards inform the development of loading capacity for a TMDL. Minnesota's water quality standards are described in Minnesota Rules chapters 7050 (Waters of the State) and 7052 (Lake Superior Basin Water Standards). Mercury standards applicable to the SLRW are listed in Table 1-1; the most stringent chronic water column standard defined by the state is 0.0013 µg/L (1.3 ng/L) total mercury. As discussed in Minnesota Rule 7052 (Lake Superior Basin water standards), water column metals standards are expressed in the total metal form but are implemented as the dissolved form. Pre-established, constituent specific factors are applied to convert from the total metal standard to the dissolved metal standard that is used for evaluation purposes. The acute and chronic conversion factors for mercury are 0.85 and 1.0, respectively.

Minnesota has also established an edible fish tissue criterion of 0.2 mg/kg based on the narrative water quality standard in Minnesota Rules 7050.0150, subp. 7, "Impairment of waters relating to fish for human consumption." As described in MPCA (2007), this numeric criterion is based on EPA's methylmercury criterion for fish tissue to protect human health (0.3 mg/kg; USEPA, 2010); however, the Minnesota fish tissue criterion is more stringent than EPA's because of higher fish consumption rates in the state relative to the national numbers used by EPA. The Minnesota and EPA fish tissue criteria are expressed as total mercury; however, the vast majority of mercury in edible fish tissue is in the form of methylmercury, so this is essentially a methylmercury standard. Because Minnesota has adopted water quality criteria for both total mercury in the water column and mercury in fish tissue, the most stringent of these requirements applies.

In addition to the state's water quality standards, there are five segments (AUID 04010201-503, -504, -505, -506, and -517) of the St. Louis River that are along the border of the Fond du Lac Reservation of the Fond du Lac Band of Lake Superior Chippewa ("Band") and these segments are also subject to the Band's chronic total mercury standard of 0.00077 µg/L in the water column (0.77 ng/L). The Band also uses the U.S. EPA's health criterion for fish tissue in their assessments (0.3 mg/kg methylmercury in fish tissue) instead of the 0.2 mg/kg criterion used by Minnesota.

MPCA is developing this TMDL for mercury impairments within the State of Minnesota. A substantial part of the St. Louis River Estuary lies within the State of Wisconsin. Wisconsin has the same applicable chronic total mercury standard as Minnesota (0.0013 µg/L of 1.3 ng/L) but has a slightly higher fish tissue criterion of 0.22 mg/kg versus 0.2 mg/kg for Minnesota.

Table 1-1. Mercury water quality standards and criteria applicable to the SLRW within Minnesota

Media	Form and Unit	Beneficial Use/Type	Numeric Target	Averaging Period
Minnesota				
Water column	Total mercury, µg/L	Aquatic life chronic standard	0.91	Four-day average
		Aquatic life maximum standard	1.7	One-day average
		Aquatic life final acute value	3.4	
		Human health chronic standard	0.00153	30-day average
		Wildlife chronic standard	0.0013	30-day average
		Applicable chronic standard	0.0013	30-day average
Fish tissue	Total mercury, mg/kg	Human health edible fish tissue criterion	0.2	standard length fish
Fond du Lac Band of Lake Superior Chippewa				
Water column	Total mercury, µg/L	Aquatic Life: Subsistence Fishing/Netting designated use	0.00077	"indefinite"
U.S. EPA (applicable to the Fond du Lac Reservation)				
Fish tissue	Methylmercury, mg/kg	Human health (used for the Fond du Lac's Aquatic Life: Subsistence Fishing/Netting designated use)	0.3	--

1.2 MERCURY IMPAIRED WATERBODIES

Mercury TMDLs are to be developed for 31 stream segments and 31 lakes in the SLRW (Table 1-2, Figure 1-1). Of the streams, 16 are listed for exceedances of the water column mercury standard and 23 are listed for exceedances of the fish tissue mercury standard. Five lakes are listed for elevated water column levels and 31 are listed for fish tissue levels in excess of the standard.

Table 1-2. Waterbody segments impaired for mercury to be addressed in the TMDL (2024 impaired waters list)

Waterbody	Segment Description	Use Class	Mercury Impairment		Assessment Unit ID (AUID)	Type
			Fish Tissue	Water Column		
St Louis River	Cloquet R to Pine R	2Bg	X	X	04010201-503	Stream
St Louis River	Stoney Bk to Cloquet R	2Bg	X		04010201-504	Stream
St Louis River	Artichoke R to Stoney Bk	2Bg	X		04010201-505	Stream
St Louis River	East Savanna R to Artichoke R	2Bg	X		04010201-506	Stream
St Louis River	Floodwood R to East Savanna R	2Bg	X		04010201-507	Stream
St Louis River	Whiteface R to Floodwood R	2Bg	X		04010201-508	Stream
St Louis River	West Two R to Swan R	2Bg	X		04010201-510	Stream
St Louis River	Embarrass R to East Two R	2Bg	X	X	04010201-511	Stream
St Louis River	Scanlon Dam to Thomson Reservoir	2Bg	X	X	04010201-515	Stream
St Louis River	Potlatch Dam to Scanlon Dam	2Bg	X		04010201-516	Stream
St Louis River	Pine R to Knife Dam	2Bg	X	X	04010201-517	Stream
St Louis River	Thomson Reservoir to Fond du Lac Dam	2Bg	X		04010201-523	Stream
St Louis River	Knife Dam to Potlatch Dam	2Bg	X		04010201-524	Stream
St Louis River	Swan R to Whiteface R	2Bg	X		04010201-525	Stream
St Louis River	Partridge R to Embarrass R	2Bg	X		04010201-526	Stream
West Two River	McQuade Lk outlet to St Louis R	2Bg		X	04010201-534	Stream
Partridge River	Headwaters to St Louis R	2Bg	X	X	04010201-552	Stream
St Louis River	East Two R to West Two R	2Bg	X		04010201-554	Stream
East Two River	Unnamed branch to St Louis R	2Bg		X	04010201-555	Stream
Swan River	Confluence of East and West Swan R to St Louis R	1B, 2Bdg		X	04010201-557	Stream
Floodwood River	Headwaters (Floodwood Lk 69-0884-00) to St Louis R	2Bg		X	04010201-560	Stream
Embarrass River	Headwaters to Embarrass Lk	2Bg		X	04010201-579	Stream
St Louis River	Headwaters (Seven Beaver Lk 69-0002-00) to T58 R13W S36, west line	2Bg	X		04010201-631	Stream
St Louis River	T58 R13W S35, east line to Partridge R	2Bg	X	X	04010201-644	Stream
Stony Creek	Unnamed creek to Unnamed creek	2Bg		X	04010201-963	Stream
Trimble Creek	-92.13 47.647 to Embarrass R	2Bg		X	04010201-A41	Stream

Waterbody	Segment Description	Use Class	Mercury Impairment		Assessment Unit ID (AUID)	Type
			Fish Tissue	Water Column		
Unnamed creek (Mud Lake Creek)	Wetland to Unnamed creek	2Bg		X	04010201-B50	Stream
Cloquet River	Us-kab-wan-ka R to St Louis R	2Bg	X	X	04010202-501	Stream
Cloquet River	Beaver R to Us-kab-wan-ka R	2Bg	X		04010202-502	Stream
Cloquet River	Island Lake Reservoir to Beaver R	2Bg	X		04010202-504	Stream
St Louis River	Fond du Lac dam to beginning of estuary	2Bg	X	X	04010201-B66	Stream
Thomson Reservoir	At Thomson	2B	X		09-0001-00	Lake
Cloquet	Finland	2B	X		38-0539-00	Lake
Sink	Two Harbors	2B	X		38-0540-00	Lake
White	4 miles SW of Rollins	2B	X		69-0030-00	Lake
Big Bear	Two Harbors	2B	X		69-0113-00	Lake
Alden	Duluth	2B	X		69-0131-00	Lake
Wolf	5.5 miles SW of Rollins	2B	X		69-0143-00	Lake
Otto	Brimson	2B	X		69-0144-00	Lake
Colby	At town of Hoyt Lakes	1B, 2Bd	X		69-0249-00	Lake
Island Lake Rsvr (W. Basin)	17 miles N of Duluth	2B	X		69-0372-01	Lake
Island Lake Rsvr (E. Basin)	16 miles N of Duluth	2B	X		69-0372-02	Lake
Whiteface Reservoir	9 MI miles N of Duluth	2B	X		69-0375-00	Lake
Upper Comstock	Whiteface	2B	X		69-0412-01	Lake
Lower Comstock	Markham	2B	X		69-0412-02	Lake
South Twin	Aurora	2B	X		69-0420-00	Lake
Loon	Aurora	2B	X		69-0426-00	Lake
Sabin	Biwabik	2B	X	X	69-0434-01	Lake
Wynne	Biwabik	2B	X	X	69-0434-02	Lake
Long	Eveleth	2B	X		69-0495-00	Lake
Embarrass	At Biwabik	2B	X		69-0496-00	Lake
Grand	16 miles N of Duluth	2B	X		69-0511-00	Lake

Waterbody	Segment Description	Use Class	Mercury Impairment		Assessment Unit ID (AUID)	Type
			Fish Tissue	Water Column		
Strand	3.5 miles SE of Cotton	2B	X		69-0529-00	Lake
Esquagama	4 miles S of Biwabik	2B	X		69-0565-00	Lake
Cedar Island (N. Portion)	0.8 miles S of Biwabik	2B	X		69-0568-01	Lake
Cedar Island (S. Portion)	1.6 miles S of Biwabik	2B	X		69-0568-02	Lake
Ely	At Gilbert	2B	X		69-0660-00	Lake
Elbow	1 mile NW of Iron Junction	2B	X		69-0717-00	Lake
Duluth/Superior Harbor	At Duluth	2B	X	X	69-1291-01	Lake
St. Louis Bay	None	2B	X	X	69-1291-02	Lake
Spirit Lake	At Duluth	2B	X		69-1291-03	Lake
Upper Estuary	None	2B	X	X	69-1291-04	Lake

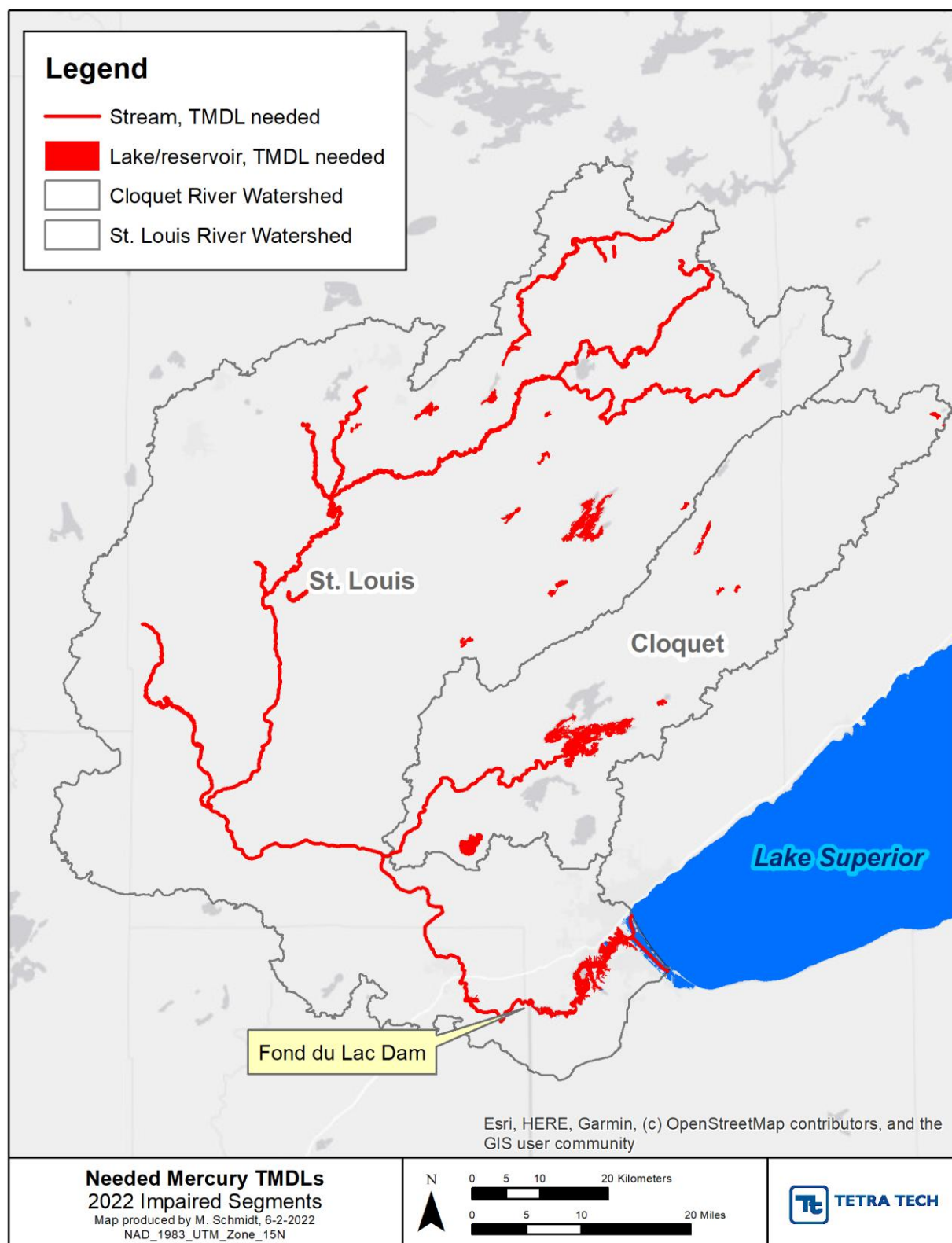


Figure 1-1. Stream and lake segments that need mercury TMDLs

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2.0 MERCURY IN THE SLRW

Both THg and MeHg are of concern for the mercury TMDLs. The greatest risk to human health comes from exposure due to dietary intake of MeHg from consumption of fish; however, most MeHg is created within the water column and sediment of the watershed, rather than being loaded externally. Strategies to address mercury in the system could focus on reduction of the mercury load, limits on processes that influence the creation of MeHg, avoiding land and water disturbances (e.g., peatland ditching, water level fluctuations in impoundments) or a combination of these factors.

The area of study is naturally divided into two sections, upstream and downstream of Fond du Lac Dam, which is the most downstream impoundment on the St. Louis River. Upstream of the dam, the watershed is dominated by wetlands, peatlands, and forest. Iron mining, taconite processing, and associated discharges are present, but there is limited urban development. Flow is essentially unidirectional, with many large reservoirs in the Cloquet watershed. Downstream of Fond du Lac Dam the St. Louis River enters the St. Louis River Estuary and Duluth Harbor. Flow patterns are more complex due to seiche effects from Lake Superior that cause tide-like effects and bi-directional flow. Contributions from the Nemadji River which, unlike the St. Louis and Cloquet, is a high sediment yielding system, enter the south end of Duluth Harbor. This area also contains parts of urban Duluth, MN and Superior, WI and has a long history of industrial development.

2.1 UPSTREAM OF FOND DU LAC DAM

2.1.1 Conceptual Understanding

The St. Louis River Watershed Mercury TMDL report will describe the conceptual model in more detail. The description here focuses on the components most related to the watershed and estuary models. See also the discussion of the watershed analysis technical approach in Section 3.1 for more information about the relationship of sulfate to mercury methylation.

The Minnesota statewide mercury TMDL found that the primary source of mercury to waterbodies of the state is atmospheric deposition, a portion of which is derived from regional or global emissions that originate outside of the state's boundaries that are not subject to local control. The TMDL set an overall goal of a 93 percent reduction in air emissions of mercury in Minnesota from 1990 baseline levels, of which a 76 percent reduction had been achieved by 2005 (MPCA 2007), and reductions across the state continue. While this is a significant achievement, the state is not on track to meet the reduction goal to be achieved by 2025, as prescribed in the implementation plan for the statewide TMDL (MPCA 2009). Furthermore, legacy sources of mercury, derived primarily from atmospheric deposition that was significant in North America throughout the 19th century and reached a peak at around 1970 (Beal et al., 2015), are stored in soils and sediments and continue to contribute mercury to waterbodies. While the rates of mercury loading from these sources will gradually decline as atmospheric deposition declines, it may require many decades to reach a new equilibrium due to large pools of legacy Hg accumulation in soils and sediments in the SLRW (and globally). Controlling mercury exposure to mitigate bioaccumulation in the food web needs to consider reductions in sources but also controlling transport and transformation processes.

The Mesabi Iron Range is a mining district of the Biwabik Iron Formation that crosses the northern St. Louis River watershed. Both underground mines and open-pit mines have been operated in this area. While these ore deposits do not have high levels of mercury, taconite processing in this area may contribute some mercury through discharging spent water, tailings, and stack emissions (Berndt, 2003). Mining discharges are regulated and monitored through the National Pollutant Discharge Elimination System (NPDES). Mercury concentrations in tailings basins have been lower or similar to concentrations in other surface waters (Berndt, 2003). Thus, atmospheric emission is the dominant pathway of mercury loading from mining activities according to Berndt. Berndt elaborates on this stating "Hg(II) in ore concentrate is converted to Hg(0) during the firing of pellets and

released to the atmosphere in stack emissions. Emission factors reflect primary distribution of mercury in the ore body and generally increase in a westward direction across the district from 1 to 17 kg Hg per million long tons of pellets. Atmospheric Hg emissions from taconite processing exceeded 100 kg/yr in the late 1960's and have ranged from between approximately 200 and 400 kg/yr ever since." MPCA is not aware of any local air deposition modeling undertaken for any of the Iron Range taconite facilities; however, the CMAQ modeling of dry atmospheric deposition of Hg discussed in Section 4.1.3.2 incorporates National Emission Inventory estimates of Hg emissions from taconite processing plants in the Iron Range and does estimate local deposition of Hg in the vicinity of these sources.

Sulfate (SO_4^{2-}), an oxidized form of sulfur, has long been associated with the production of MeHg – although the relationship between the two is complex (see discussion in Section 3.1). A primary source of sulfate in waterbodies is atmospheric deposition ("acid rain"). The main anthropogenic sources of atmospheric sulfate are sulfur oxides, which are primarily emitted to the atmosphere from sulfur-containing fuel combustion byproducts from both stationary and mobile sources. There are also natural sources of sulfates such as volcanic emissions. According to the National Atmospheric Deposition Program, the concentration of sulfate in precipitation in the SLRW was about 0.3 mg/L in 2020 (NADP, 2022). Sulfate is also a waste product associated with iron mining that has further elevated concentrations in parts of the SLRW (Myrbo et al., 2017). Hirshon et al. (2020) show that waters in the SLRW impacted by mining activities exhibit sulfate concentrations that are 5 to 80 times higher than waters not impacted by mining.

While limiting production of MeHg is critical to reducing fish tissue concentrations, so too is limiting transport of bioavailable mercury to waterbodies where aquatic organisms are exposed. According to Berndt and Bavin (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 evaluation of Hg transport involved understanding DOC [dissolved organic carbon] transport". Berndt and Bavin found that both THg and MeHg were found to have strong correlations with DOC in the SLRW (Figure 2-1). SO_4^{2-} and MeHg concentrations in the water column are not well correlated (Figure 2-2), and the timing of peak SO_4^{2-} and MeHg concentrations at sites along the St. Louis River do not correspond (Figure 2-3; personal communication, B. Monson, Minnesota Pollution Control Agency). MeHg concentration tends to peak in the late spring to early summer while SO_4^{2-} tends to peak in the late summer to fall, which may indicate that the MeHg was produced elsewhere (e.g., in wetlands) and transported to the monitoring sites where higher SO_4^{2-} loads are present from other sources such as mining discharges. This observation does not negate the influence of sulfate on the mercury cycle but rather helps explain the selected modeling approach relying on DOC to model mercury transport. Higher wetland density is associated with higher DOC concentrations in streams (Figure 2-4) and higher MeHg because MeHg readily binds to and is transported with DOC in the SLRW (Berndt and Bavin, 2012). This is consistent with the summary of Grigal (2002), while a global meta-analysis of the relationship between mercury and DOC found that an additional milligram (mg) of DOC in freshwater bodies increases Hg and MeHg concentrations by 0.25 nanograms (ng) and 0.029 ng, respectively (Lavoie et al., 2019). Grigal (2002) also demonstrated that the flux of both THg and MeHg had a strong positive correlation with percent wetland area in temperate and boreal watersheds throughout the world.

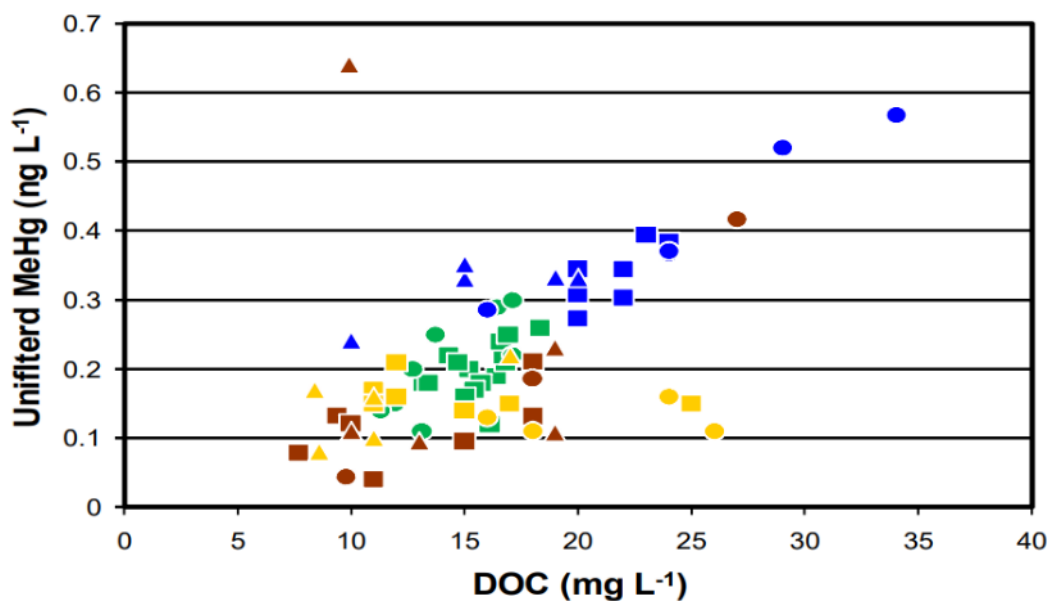


Figure 2-1. DOC and unfiltered MeHg concentration in the SLRW (Berndt and Bavin, 2009; Figure 21)

Note the colors reflect different sampling periods in 2007 and 2008. Triangles are for mine impacted tributaries, circles are for non-mine impacted tributaries, and squares are for the mainstem St. Louis River.

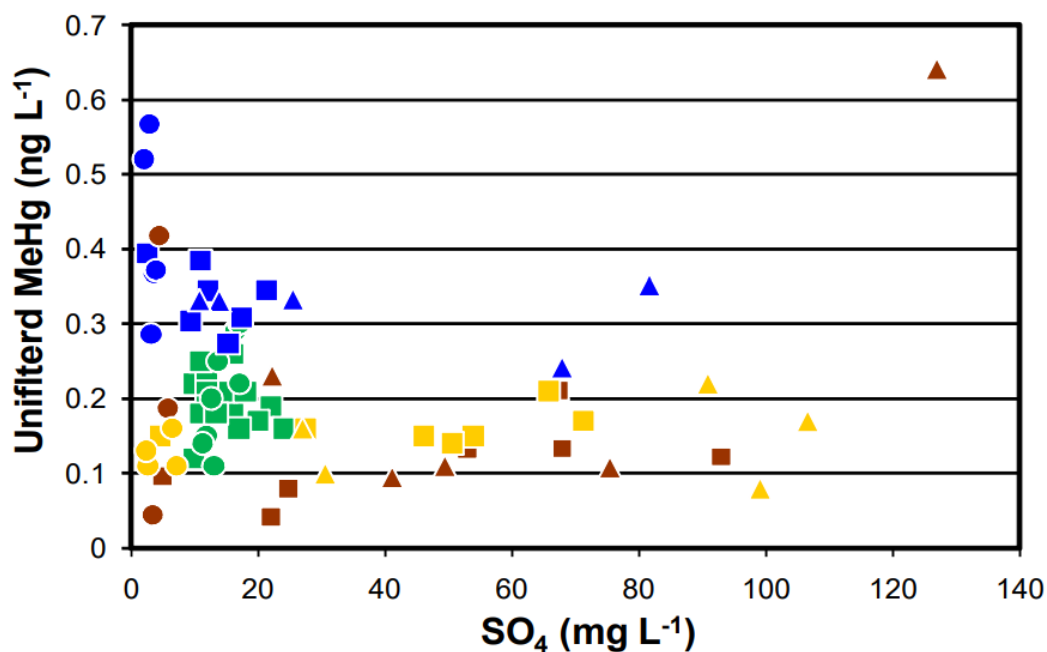


Figure 2-2. SO₄²⁻ and unfiltered MeHg concentration in the SLRW (Berndt and Bavin, 2009; Figure 22)

Note the colors reflect different sampling periods in 2007 and 2008. Triangles are for mine impacted tributaries, circles are for non-mine impacted tributaries, and squares are for the mainstem St. Louis River.

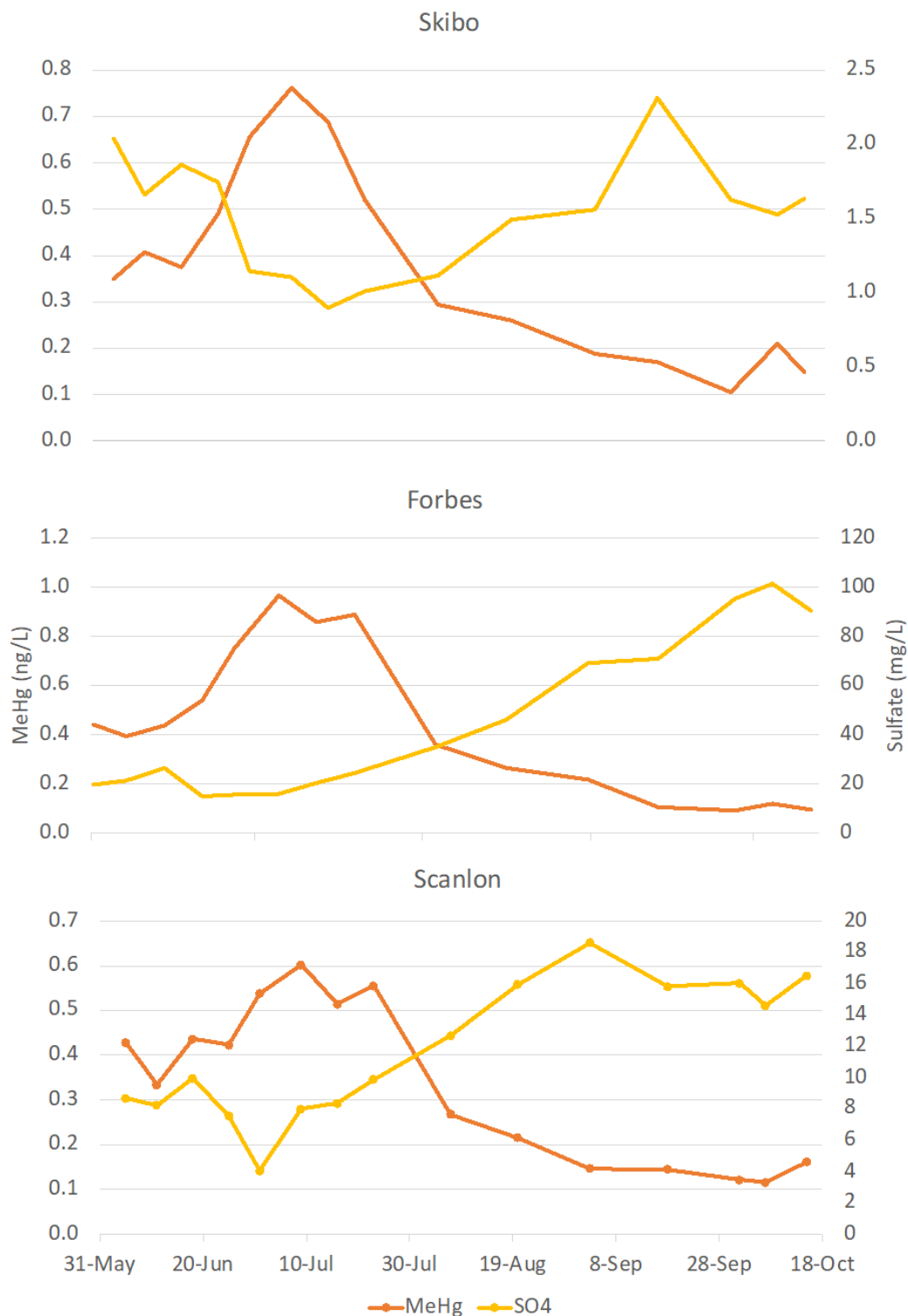


Figure 2-3. Time series of SO_4^{2-} and MeHg at St. Louis River near Skibo, Forbes, and Scanlon in 2013 (source: Results from 2013 mercury load study provided by B. Monson, Minnesota Pollution Control Agency)

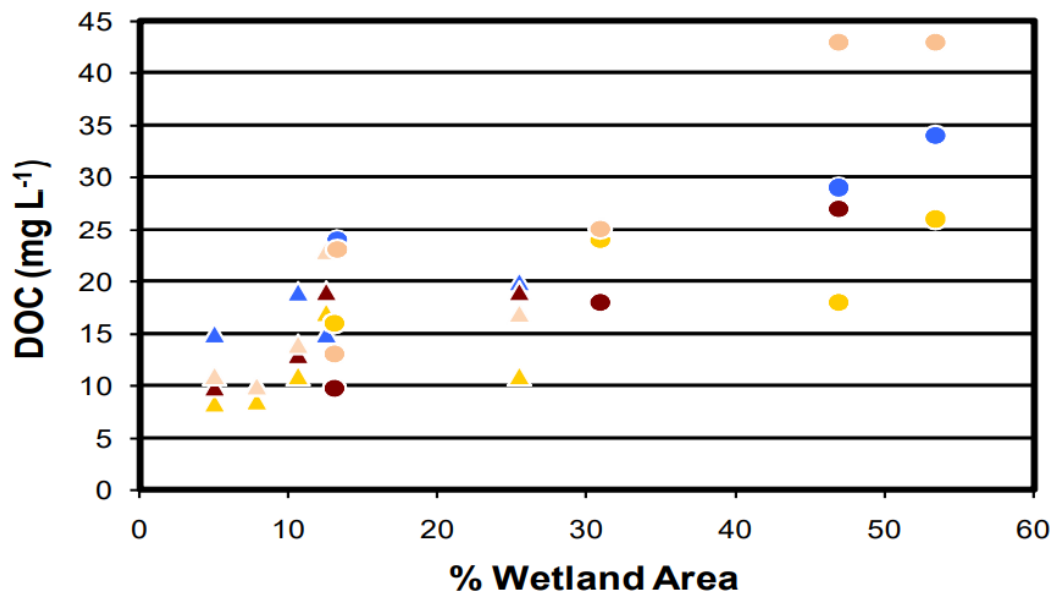


Figure 2-4. Wetland area and DOC concentration in the SLRW (Berndt and Bavin, 2009; Figure 18)

Note the colors reflect different sampling periods in 2007 and 2008. Triangles are for mine impacted tributaries and circles are for non-mine impacted tributaries.

2.1.2 Past Modeling Efforts

Preliminary modeling of mercury in the entire SLRW was undertaken in 2012-2013 (RTI 2013a, 2013b). This modeling effort generally concluded that there was a need for more data to develop and calibrate simulation tools.

Simulation of the watershed was accomplished by extending a previously developed WARMF model (Systech, 2006) that had been developed for Minnesota Power and the Electric Power Research Institute. The model achieved a fair representation of flow with average absolute errors ranging from 29 to 416%, but a poor representation of sediment and sulfate. The model apparently does not simulate the reservoirs in the system and represents wetlands and peatlands only through a generic representation of forested wetlands. The code also does not provide the capability to examine simulation results for individual land cover classes.

The WARMF modeling effort for mercury was severely constrained by limited data. As noted in the report, “Data gaps exist for numerous aspects of the watershed model. The existing instream mercury data was limited to a few points in time at multiple locations within the watershed.” Calibration to observed mercury data is in the right order of magnitude but provides limited insight into processes. “For all stations, the model simulated result for MeHg is consistent with data measurements but does not predict the magnitude of the seasonal variations. Given the limited number of samples (maximum of four measurements over a single year) these results appear reasonable... A weakness of the simulation that appears at all stations is the computer model under predicts particulate associated mercury concentration. Simulated dissolved mercury is generally lower than measured filtered mercury.” The modeling report also noted that the model simulates almost no mercury methylation because only well oxygenated streams were simulated and not wetlands where methylation is most likely to occur.

The WARMF modeling has not been extended since the 2013 preliminary effort. MPCA subsequently supported development of a detailed Hydrological Simulation Program – FORTTRAN [HSPF] model of the watershed that provides a more accurate simulation of flow, sediment, and nutrient fate and transport in the watershed (Tetra Tech 2016a, 2016b). The model was updated through water year 2021 (Tetra Tech, 2022a), but that version did

not represent mercury as a state parameter. A companion, finer resolution model covers the Duluth Urban area (Tetra Tech, 2022b).

2.2 ST. LOUIS RIVER ESTUARY AND DULUTH HARBOR

2.2.1 Conceptual Understanding

Below Fond du Lac Dam, the St. Louis River enters the St. Louis River Estuary and Duluth Harbor, where it is joined by the Nemadji River. The harbor is separated from Lake Superior by a narrow isthmus through which there are two connecting channels maintained for ship traffic – the Duluth Entrance and the Superior Entrance. The harbor area adjoins the City of Duluth, MN and the City of Superior, WI and has long been the site of significant industrial activity. Contaminated sediments, abandoned hazardous waste sites, landfills, industrial discharges, and other pollutant sources have been documented throughout estuary/harbor area. The estuary portion of the river was included in the 1987 designation of the St. Louis River Area of Concern (AOC), one of 43 such areas in the Great Lakes region identified by the U.S. and Canadian governments, which show signs of significant environmental harm from local causes. A Remedial Action Plan was started in 1989 as part of a collaborative effort to address environmental concerns in the St. Louis River AOC.

Flow patterns in the AOC are complex due to the interaction of river flows with the Lake Superior seiche, a tide-like periodic water level variation. The seiche has a 7.9-hour period and a counter-clockwise rotation along the lake shoreline. Fresh water inflows from the St. Louis River exhibit seasonal variation, with an average flow of 2,387 cfs with a reported minimum of 88 cfs and a maximum of 43,800 cfs. The harbor is maintained for shipping, which requires periodic dredging due to sedimentation within the system. The combination of dredging and energetic flows results in bottom sediments that are poorly sorted with a high degree of variability over small scales.

Starting in 1995, MPCA (1999) undertook a major study of toxics in the harbor area, including mercury. In this study, THg concentrations in water ranged from 0.32 to 11 ng/L with a mean and standard deviation of 2.1 ± 1.5 (n = 80). The study estimated that the harbor loaded about 5.5 kg/yr of THg to Lake Superior, but that the load from upstream was greater than that amount, resulting in net accumulation of THg in harbor sediments. Sediment sampling reported by RTI (2016) found that surficial sediment in the harbor had an average THg concentration of 132 ng/g with MeHg concentrations at about 1 percent of THg. THg concentrations tended to be slightly lower in deeper sediments. These contaminated sediments may provide a continuing source of mercury to the water column; however, their distribution is highly heterogenous and has been altered over time by various dredging and remediation activities along with occasional extreme freshwater flows.

Recently, USGS undertook a study of mercury sources and cycling in the St. Louis River estuary using mercury isotopes (Janssen et al., 2021). A major objective of the study was to determine the extent to which legacy mercury contamination within estuary sediments is contributing to fish tissue mercury burdens, “Hg stable isotope values revealed that legacy contamination of Hg was widespread and heterogeneously distributed in sediments...even in areas lacking industrial Hg sources. Similar isotope values were found in benthic invertebrates, riparian spiders, and prey fish...confirming legacy Hg reaches the...food web.” Comparison to Bad River estuary, a similar but undeveloped “reference system” in northern Wisconsin, confirmed the importance of industrial sources to fish tissue concentration in the St. Louis estuary. The study also showed that mercury in higher trophic level game fish in the estuary was derived both from the estuary and from open waters of Lake Superior as a result of migration in and out of the harbor. Within the main part of the harbor about half of the mercury in surficial sediments was attributable to industrial sources with the remainder due to watershed and precipitation sources in that order; upstream of the harbor, watershed sources contributed more than 50 percent of the total.

2.2.2 Past Modeling

Preliminary modeling of mercury in the St. Louis Estuary is reported in RTI (2013b). This effort comprised three models: an Environmental Fluid Dynamics Code (EFDC; Hamrick, 1996) model of hydrodynamics, a Water Analysis Simulation Program (WASP; code documented in Wool et al., 2020) model of sediment and mercury transport, and a Bioaccumulation and Aquatic System Simulator (BASS; Barber, 2001) model of food chain mercury bioaccumulation. The 2013 EFDC model appears to provide a reasonable representation of water level, seiche effects, and exchanges with Lake Superior.

The RTI EFDC, WASP, and BASS models are not tightly linked. Hydrodynamic simulation within the WASP model does not directly use the EFDC model as input. Rather, the WASP model is a simplified aggregation of the modeling domain to a coarser scale that uses the net flow option to route inflows through the system. The EFDC output is used to inform WASP relative to the split of flows between the two harbor entrances and as a basis for calculating macrodispersion coefficients that attempt to account for seiche-induced mixing between segments. The BASS model is also not tightly linked to WASP due to data limitations and uncertainty about the feeding range of top predator fish.

Both the WASP and BASS modeling efforts were hampered by data gaps that precluded rigorous calibration. For the WASP model, RTI (2013b) notes “The lack of comprehensive and recent site-specific water column mercury data prevents a rigorous calibration and validation of the WASP model for the SLR estuary. The calibration plan has therefore been devised to make use of the older 1999 Harbor Toxics Loading Study, which reported data collected in 1998 at 4 locations in the SLR estuary...” The authors then note that the existing WARMF watershed model for the 1990s was calibrated to suspect mercury data and was recalibrated based on 2004-2011 observations. “The WASP model was then calibrated so that the average total mercury concentrations and spatial trends of the 1998 mercury data were reproduced.” The report concludes with a statement that additional data collection was needed “to provide a better understanding of the controlling processes and provide additional data to constrain and improve the reliability of the EFDC and WASP models.”

Similar to WASP, the BASS model was also not rigorously calibrated due to a shortage of data. RTI (2013c) notes “The primary data gap ... is the quantity and quality of observed fish data. Specifically, fish tissue Hg data are lacking for all study reaches and size classes of the endpoint fish species of interest (e.g., walleye and northern pike), as well as the lower trophic-level fish modeled for inclusion in the model as dietary items.” Also, “The BASS model, in its current state, is a preliminary tool that can be used to explore mercury management issues in the SLR watershed” and “shows promise of being capable of supporting a more detailed analysis, especially if additional data are collected for calibration.”

Hydrodynamic modeling of the estuary and harbor has subsequently been advanced by the development and rigorous calibration of a refined EFDC model by USGS (Smith et al., 2020). This revised hydrodynamic model was used in the development of the estuary modeling described in Section 4.4.

2.3 MONITORING DATA SUMMARY

2.3.1 Water Column Mercury Data

The available observation datasets upstream from Fond du Lac Dam for THg and MeHg and related parameters were primarily assembled by Bruce Monson (MPCA) and provided to Tetra Tech in a series of data transmittals that are listed in Table 2-1. These samples were collected for various purposes including total metals monitoring, stressor identification, and lake and river monitoring during different field campaigns. For instance, RTI water quality samples were collected during a field campaign from May to October 2015 in the St. Louis River/Estuary, Nemadji River, and Thomson Reservoir/Scanlon Dam. The measurements generally included dissolved organic carbon concentration, as well as filtered and unfiltered concentrations of THg and MeHg. Figure 2-5 maps locations of available THg and MeHg data within the SLRW upstream of Fond du Lac Dam. Additional information on data in the St. Louis River Estuary, including sediment data, is provided in Section 4.4.

Table 2-1. Sources of water column Hg/MeHg data

Investigator	Sample Dates	Summary & Citation (if applicable)
Balogh, Steve (MCES) ^a	April-Sept. 2002	Steve Balogh (MCES) was contracted by MPCA to collect water samples throughout the state of MN in 2002.
Berndt, Michael (MN DNR)	2007-2010, 2012	MNDNR conducted studies on the impact of sulfate mining on Hg and MeHg in the upper St. Louis River (SLR); reports available at https://www.dnr.state.mn.us/lands_minerals/dnr_so4_research.html ; documented in Berndt and Bavin (2009, 2011) and Berndt et al. (2014).
Berndt, Michael (MN DNR)	June-October 2013	Mercury load monitoring study; MPCA contracted with MNDNR to collect water samples throughout the SLRW.
Brigham, Mark, and Sarah Janssen (USGS)	2019-2021	USGS-provided peatland load monitoring study data from NWIS database
Janssen, Sarah (USGS)	August 2017	USGS fingerprinting study of the St. Louis Estuary, documented in Janssen et al. (2021); data tables provided by Sarah Janssen, USGS
Johnson, Nathan (UMD)	May-Oct 2014, Sept. 2015	Study of mercury bioavailability in the St. Louis Estuary, report to MPCA. Data tables provided by Nathan Johnson, UMD; documented in Johnson et al. (2016)
Monson, Bruce (MPCA)	January-June 2019	Partial results of peatland load monitoring study data from MPCA sites on the Water Quality Portal (waterqualitydata.us)
Monson, Bruce (MPCA) and Nathan Johnson (UMD)	June 2016	Mercury in Rivers study; data from food web task led by Kris Rohlfus (UW-LaCrosse). The mercury research group at the University of Wisconsin-La Crosse was tasked with evaluating the extent of total Hg (THg) and methylmercury (MeHg) contamination in the lower food webs of five Minnesota rivers including the St. Louis.
MPCA	2009-2021	Query of MPCA's EQulS database
RTI International	May-October 2015	RTI International was lead PI through a contract with EPA Region 5 to collect water and sediment data from the St. Louis Estuary. Document in RTI (2016).
Ruzycki, E.M. (UMD)	2004-2006	Mercury data from four Duluth streams. See Ruzycki et al. (2011)
Schuldt, Nancy (Fond du Lac Band)	July-October 2005	Data from 2005 cooperative study, documented in Lindgren et al., 2006.

Investigator	Sample Dates	Summary & Citation (if applicable)
Schuldt, Nancy (Fond du Lac Band)	2011-2015	Water chemistry data for the headwater reservoir study.
Tuominen, Tim (WLSSD) ^a	October 2003	Data submitted to MPCA for non-regulatory study of Hg and MeHg
White, Amber (UMD)	2014-2017 (primarily sediment)	University of Minnesota - Duluth study of methylmercury in St. Louis Estuary, documented in White (2022) and White et al. (2022); data tables provided by Nathan Johnson (UMD).

a. Data are from before model period and were not used in calibration.

Dr. Jennifer Brentrup (MPCA) checked and reviewed all the water column data and produced a final authoritative data set under the name wq_data_v16_Tt.csv.

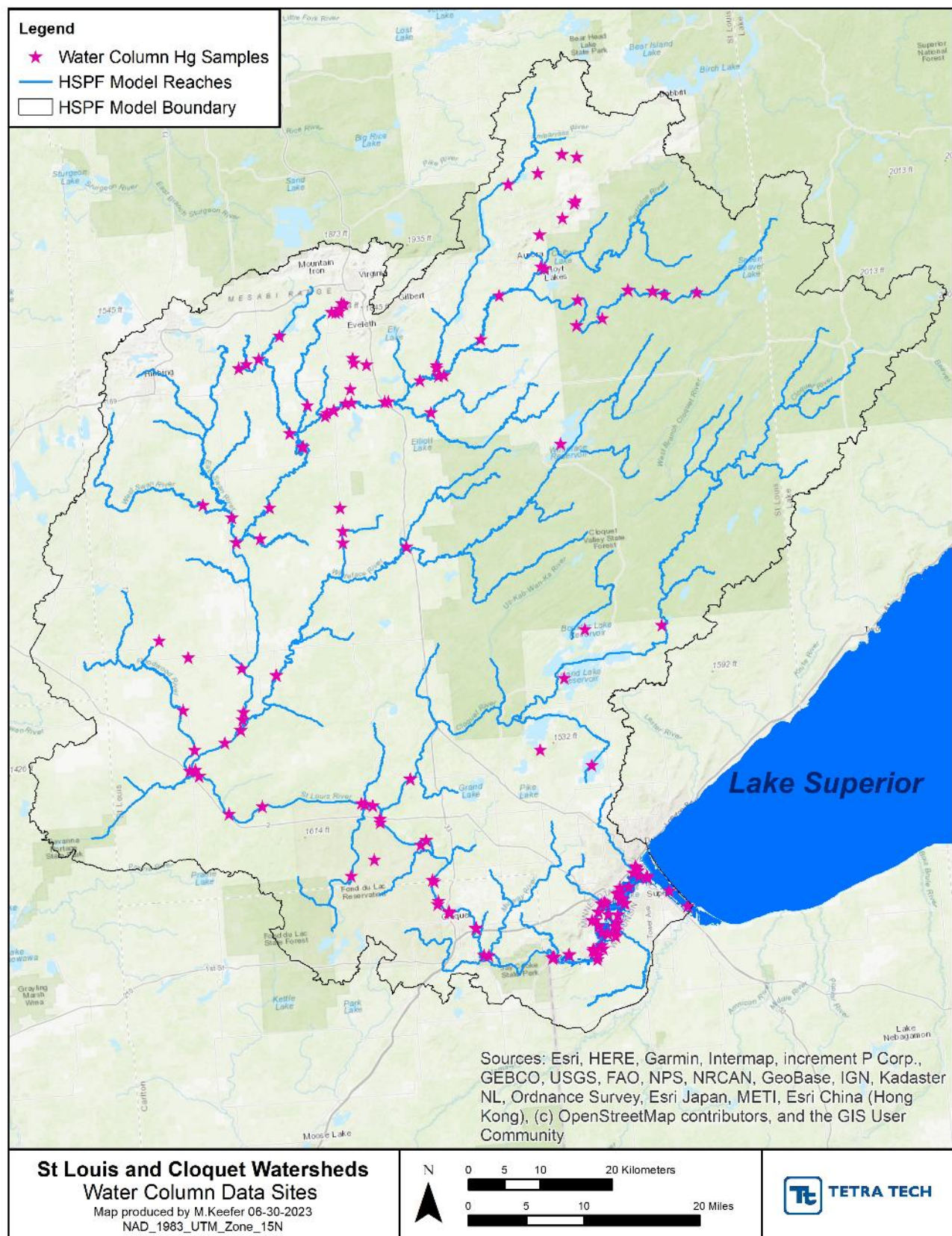


Figure 2-5. Mercury and methylmercury monitoring locations in the SLRW

2.3.2 Fish Tissue Mercury Data

Fish tissue mercury samples collected by MPCA, Minnesota Department of Natural Resources, Wisconsin, USEPA, Fond du Lac Band, and other agencies and research efforts were used to evaluate mercury in fish. Because atmospheric deposition of Hg declined sharply from its peak around 1970, fish samples from 2000 through 2019 were used in the modeling study. The species with the most records include walleye, northern pike, and channel catfish. Sample anatomies included dorsal muscle plug without skin (PLUG), whole organism (WHORG), fillet with skin (FILSK), fillet without skin (FILET), organism without head or viscera (NOHV), and dorsal muscle plug using biopsy sampler or scalpel without skin (BIOPSY). The majority of samples are nearly equally split between FILET and FILSK. As there did not appear to be a significant difference in Hg concentrations for a given species and location between samples obtained as FILET, FILSK, and BIOPSY, these three sample types, all of which sample edible muscle tissue of the fish, were combined for the bioaccumulation analysis discussed in Section 6.0.

The median recorded fish tissue Hg level from the 2000-2019 samples of the higher trophic level species (northern pike, walleye, and channel catfish) is 0.335 mg/kg. The 21st percentile of the fish tissue data approximates the fish tissue criterion of 0.2 mg/kg, meaning that about 79 percent of fish tissue samples collected from the St. Louis River and Estuary exceed the water quality standard. Sources of fish tissue Hg data within the St. Louis River and Estuary are summarized in Table 2-2.

Table 2-2. Sources of fish tissue Hg data

Source	Provider	Sampling Medium(s)	Sample Dates
Great Lakes Toxicology and Ecology Division (GLTED)	Bruce Monson (MPCA)	Fish tissue Hg and fish length	2017
Minnesota Department of Natural Resources and USEPA data compiled by MPCA ^a	Bruce Monson (MPCA)	Fish tissue Hg and fish length	2000-2019 ^a
Wisconsin	Bruce Monson (MPCA)	Fish tissue Hg and fish length	2001, 2006, 2009, 2012-2013
Lakes+Streams Data	Bruce Monson (MPCA)	Fish tissue Hg and fish length	1991-2019

a. MPCA provided Tetra Tech with pre-compiled data that included samples collected by MNDNR as well as from a USEPA 2013 study of the SLRE. MPCA also provided an earlier compilation that included fish tissue data going back to 1970 but directed Tetra Tech to use the 2000-2019 version for model development and calibration purposes.

2.3.3 Organic Carbon Data

Available dissolved organic carbon (DOC) and total organic carbon (TOC) data records were previously calibrated for the St. Louis/Cloquet HSPF model update (Tetra Tech, 2022a), but additional records were made available to Tetra Tech in September 2022 during the mercury model development, and these additional records were used to improve the calibration. Various sources of DOC and TOC data within the St. Louis and Cloquet River HSPF model boundary are summarized in Table 2-3. Upon reviewing the available data for water column organic carbon and mercury, the most suitable sites were selected for instream DOC/TOC and Hg/MeHg calibration efforts, which are discussed further in Section 4.3. Figure 2-6 shows the monitoring locations used for DOC, TOC, THg, and MeHg calibration.

Table 2-3. Sources of DOC/TOC data

Source	Provider	Sampling Medium(s)	Sample Dates	Summary & Citation (if applicable)
Lindgren Report	Bruce Monson (MPCA)	Water column DOC	July-October 2005	Data from 2005 cooperative study, documented in Lindgren et al. (2006)
Major Watershed Pollutant Load Monitoring Network	Chuck Regan (MPCA)	Water column DOC/TOC	2011-2016	The Watershed Pollutant Load Monitoring Network (WPLMN) is a long-term MPCA monitoring program designed to collect data on water quality and flow to measure pollutant load information from Minnesota's river and streams.
Mercury Rivers and Lakes	Chuck Regan (MPCA)	Water column DOC/TOC	2005, 2013, 2015	MPCA monitoring program to collect water quality data to develop river-specific mercury TMDLs
Minnesota Milestone Site River Monitoring Program	Chuck Regan (MPCA)	Water column TOC	2007-2010	Precursor monitoring program to WPLMN (see above)
RTI 2015	Bruce Monson (MPCA)	Water column DOC	May-October 2015	RTI International (2016) was lead PI through a contract with EPA Region 5 to collect water and sediment data, along with a sediment mobility study subcontracted to the UW-Madison
SLR Mercury Load Monitoring Study	Bruce Monson (MPCA)	Water column DOC	June-October 2013	Mercury load monitoring study; MPCA contracted with MNDNR to collect water samples throughout the SLRW.
Total Metal Monitoring	Chuck Regan (MPCA)	Water column DOC/TOC	2011, 2014, 2017	MPCA monitoring program designed to collect water samples three times per year at 83 pourpoint stations on a three-year cycle. The two stations monitored in the SLRW are the gage station at Scanlon on the St. Louis River and the Cloquet River gage station. Samples were collected in 2011, 2014, 2017, and 2021.

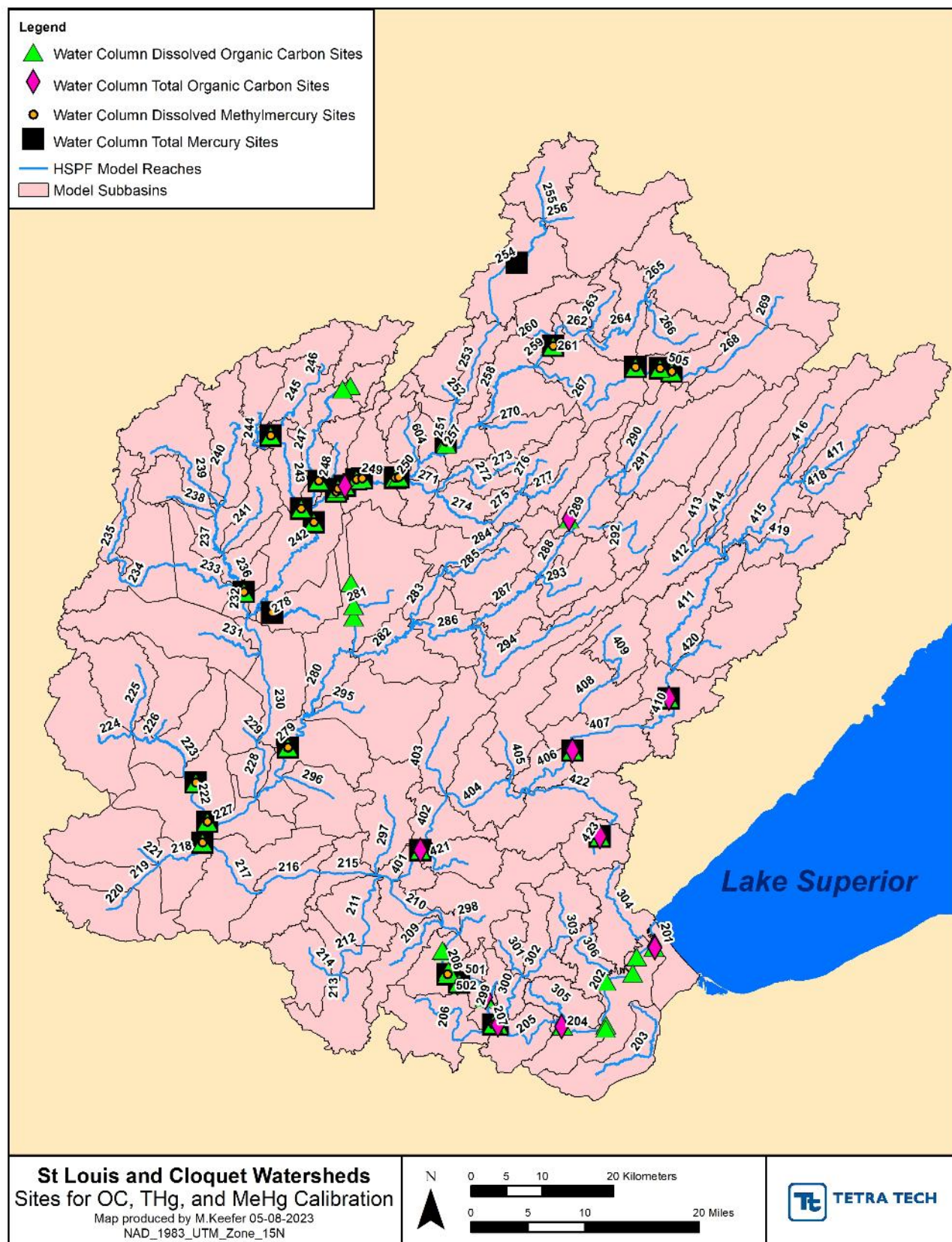


Figure 2-6. Location of monitoring sites used for OC, THg, and MeHg calibration

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3.0 TECHNICAL APPROACH

The technical approach to support the mercury TMDL builds on past efforts to the extent possible. The approach is naturally divided into two sections, one representing sources, fate, and transport of mercury within the watershed and its lake and stream network, and the other representing mercury cycling, fate, and transport within Duluth Harbor and the St. Louis River Estuary.

3.1 WATERSHED ANALYSIS

The statewide TMDLs identify atmospheric deposition as the primary source of mercury in the state and call for reductions in local mercury emissions to the atmosphere. Peatlands and other wetlands in the SLRW are likely areas of heightened methylation due to the low oxygen conditions and presence of sulfate and iron reducing bacteria. However, the main exposure pathway for fish and other aquatic species is within streams and lakes.

The relationship between MeHg and THg concentrations is a key issue in mercury TMDLs that are based on attaining fish tissue criteria. It has frequently been observed that fish THg concentrations are not strongly correlated with sediment or water column THg, but instead depend on the processes that control the creation (methylation) and demethylation of MeHg, resulting in a stronger correlation between fish tissue concentrations and ambient MeHg concentrations in sediment than to THg concentrations in the water column (Eagles-Smith et al., 2016; Alpers et al., 2016). It has proven difficult to use process-based models to predict mercury methylation and demethylation rates in the environment. Methylation is a bacteria-mediated process that occurs under low oxygen conditions as a byproduct of a wide variety of microbially mediated processes from heterotrophic sulfate and iron reduction to fermentation and methanogenesis that all lead to the breakdown of natural organic carbon matter and conversion of inorganic Hg to MeHg. Rates of methylation depend on several variables including: redox conditions, microbial populations, temperature, availability of inorganic Hg, and the carbon and sulfur cycles. While sulfate availability is an important factor in mercury methylation, Berndt and Bavin (2012; note Fig. 4 in that paper) found a poor correlation between sulfate and MeHg in streams of the SLRW. This is likely observed because sulfate concentrations have a dichotomous (“hump-shaped”) relationship with MeHg concentrations in most aquatic ecosystems (Peterson et al., 2023) and at low concentrations can limit methylation, while at high sulfate conditions the accumulation of sulfide can restrict the bioavailability of inorganic Hg for methylation. Additionally, with the advent and rapidly expanding use of metagenomics to directly assess the specific genetic capability of methylating microbes, a number of research groups have shown that sulfate reducers play an indirect role in methylation rather than the previously assumed direct role (Jones et al., 2019; Peterson et al., 2023). Importantly, the Jones et al., (2019) study was conducted on sulfated-contaminated aquatic ecosystems within the SLRW.

Attempts to simulate mercury methylation at the watershed scale with process-based models have generally been unsatisfactory as predictors of MeHg concentrations (e.g., Knightes et al., 2014, Knightes et al., 2016). It appears that empirical relationships of MeHg to THg based on monitoring from specific waterbodies is generally a more useful approach than process-based simulation. For example, USGS developed an empirical-statistical approach to predict MeHg concentrations as a function of water temperature, antecedent flow, and the prior history of water table elevation (all of which influence the rates of methylation in riparian groundwater) in an Adirondack stream (Burns et al., 2014).

A recent review of the state of process-based mercury modeling (Zhu et al., 2019) emphasizes “the insufficient quantity of adequate measurements and the unsatisfactory accuracy of mercury models”. In particular, current models do not accurately capture the complex relationships between mercury methylation and the sulfur cycle: where sulfate is in short supply, increasing the supply tends to increase methylation, but only up to a point. As sulfate concentrations increase (generally about 20 mg/L), bacterial sulfate reduction yields excess sulfide in

porewater, which depresses methylation rates because high concentration of sulfide result in the formation of large, polymerized crystalline HgS particles that are not bioavailable due to size and charge constraints (Poulin et al., 2019). Indeed, the relationship between sulfate and MeHg in the SLRW exhibit this same trend (Figure 2-2).

Past research in the SLRW has found strong relationships between DOC and Hg and MeHg concentrations (Berndt and Bavin, 2009; Berndt and Bavin, 2012). Wetland and peat bog areas provide high loads of DOC and are also areas where MeHg production is likely. The relationship is due to the linked processes of when, where, and how MeHg is produced in the environment. It is the result of microbial breakdown of the peat (organic matter more generally) and once produced the MeHg partitions to the dissolved organic matter where it is very stable and very mobile due to the inherent properties of the dissolved organic matter. Dissolved organic matter also forms strong complexes with oxidized mercury (Hg(II)), which enhances its transport (Skylberg, 2008; Haitzer et al., 2002; Gu et al., 2011). Thus, modeling DOC can serve as an indicator for modeling landscape transport and delivery mechanisms of both MeHg and THg from nonpoint sources in the rural, wetland-dominated portions of the watershed (Figure 3-1).

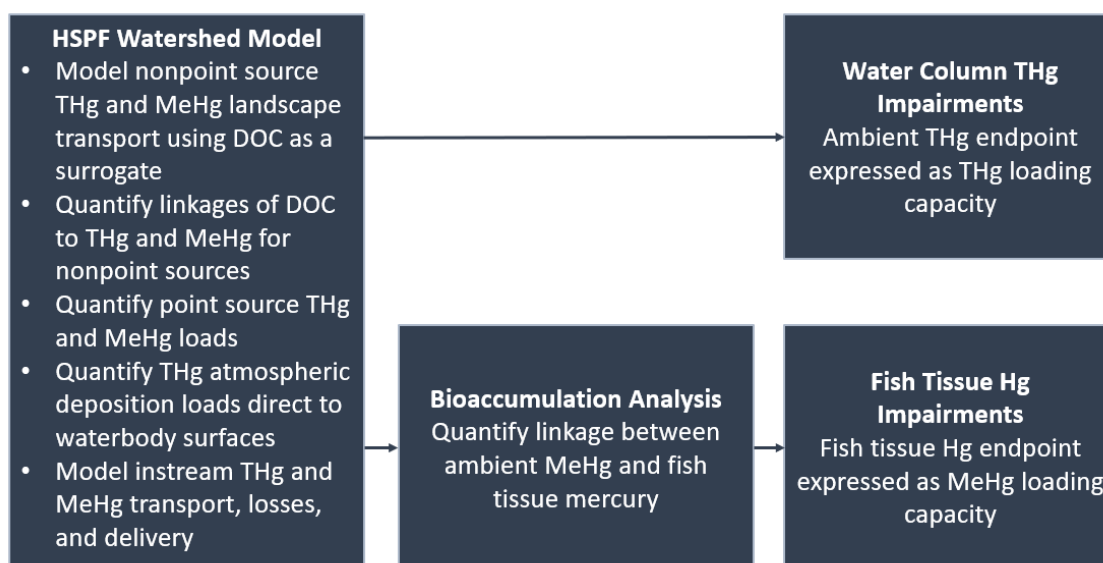


Figure 3-1. Conceptual schematic of the technical approach

There is a strong relationship between DOC and MeHg/THg concentrations in the watershed that is the result of the fundamental tie between carbon breakdown, DOM evolution, and MeHg production (Berndt and Bavin, 2009; Berndt and Bavin, 2012; Poulin et al., 2019). Using DOC to model Hg transport assumes that in general THg concentrations in soils are similar across the watershed because the primary originating source is the same – atmospheric deposition. This is consistent with the distribution of mercury in surface soils (depth 0 to 5 cm) in this vicinity that have concentrations within a narrow range from 0.03 to 0.07 mg/kg (dry weight) compared to the conterminous United States range of <0.01 to 3.55 mg-Hg/kg (Smith et al., 2014).

The association of MeHg production and mercury transport with DOC leads to a natural seasonal cycle as is conceptually represented for a forest area in Figure 3-2. During low water levels of the Fall and Winter, the upland areas accumulate particulate organic matter and atmospherically deposited Hg. During the Spring flood, water inundates the land surface, dissolving organic carbon, setting off the mercury methylation process, and associating dissolved mercury with DOC. As water levels recede in the early summer, the water recedes, and DOC and its associated mercury loads are transported into the stream network.

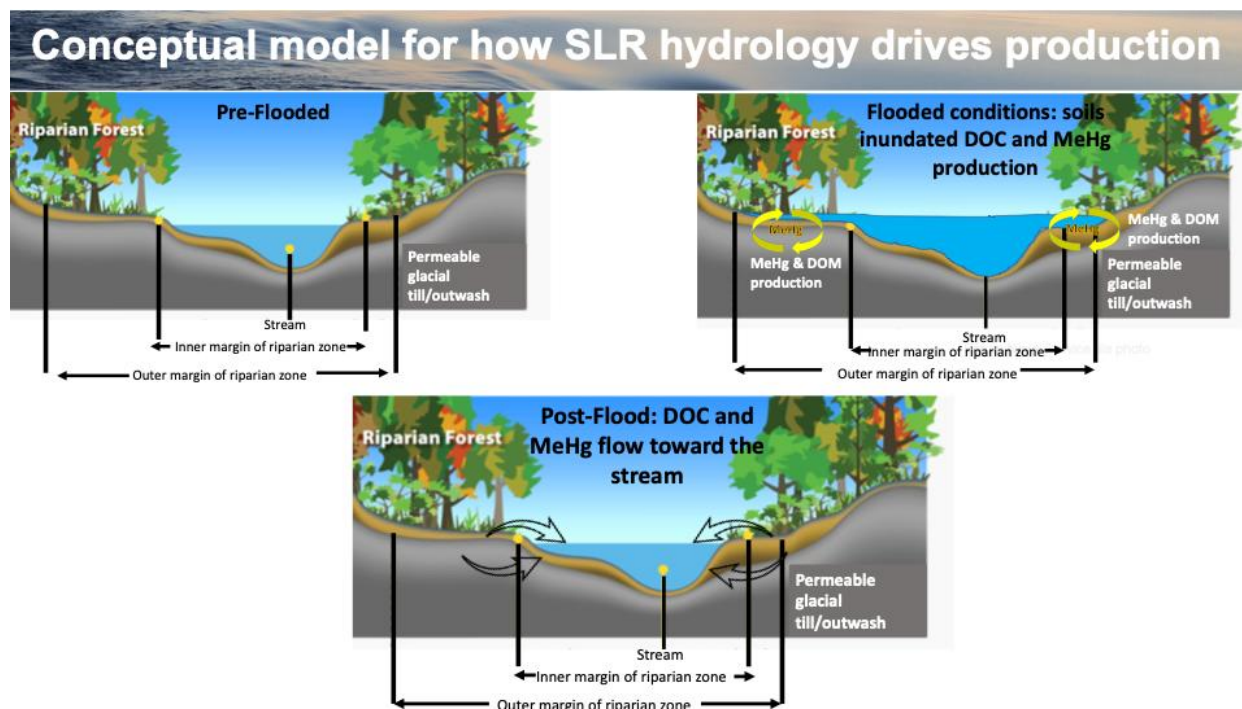


Figure 3-2. Seasonal cycles of DOC and Hg transport to the stream network

Figure Credit: Dr. David P. Krabbenhoft, USGS

Mercury readily partitions to DOC, leading to similar transport mechanisms for the two constituents. Thus, DOC serves as a relative indicator of Hg delivery from pervious nonpoint sources. The HSPF model is useful for this TMDL analysis because it 1) can be directly used to quantify sources of DOC in the watershed, 2) it eliminates the need for empirical upland delivery ratios for Hg and instead provides relevant process-based and calibrated outputs, and 3) provides multi-decadal, hourly surface and subsurface flows and loads for point and nonpoint sources for modeled constituents.

HSPF can simulate total organic carbon, dead refractory organic carbon, and total inorganic carbon, as well as the carbon contained within living phytoplankton. HSPF does not split total organic carbon into truly dissolved, colloidal, and particulate portions. Therefore, Tetra Tech (2022a) calibrated the HSPF model for organic carbon with the assumption that dead refractory organic carbon and the organic carbon contained within phytoplankton approximate particulate organic carbon whereas the labile organic carbon that is reported by HSPF as a stoichiometric fraction of carbonaceous biochemical oxygen demand [CBOD] approximates the apparent dissolved (truly dissolved and colloidal) organic carbon fraction.

Total organic matter loading is simulated on pervious lands (PERLNDs) and impervious surfaces (IMPLNDs) in HSPF and partitioned at the water's edge into refractory and labile organic carbon and other components. The upland simulation includes transport of organic matter by overland flow, the buildup/washoff of particulate organic matter in conjunction with soil erosion, and the transport of dissolved organic matter in shallow lateral interflow and resurfacing groundwater. Instream organic carbon monitoring records (total and dissolved) collected in the watershed are used for model calibration as described in Tetra Tech (2022a) and updated in Section 4.1.3.2 of this document.

For impervious surface areas that are directly connected to the waterbody network, delivery of mercury to streams simulated by the HSPF IMPLND module is largely due to direct runoff of mercury in wet atmospheric deposition coupled with washoff of mercury derived from dry atmospheric deposition or anthropogenic sources such as spills, mercury switches, or fluorescent light bulbs. These sources and their transport to streams are not

associated with DOC, so DOC cannot be used to predict the Hg load from impervious surfaces. Minimal MeHg loading is expected in impervious surface runoff. Therefore, loading in runoff from impervious surfaces is simulated directly as THg based on wet deposition concentrations in precipitation coupled with buildup of THg that occurs during dry weather conditions as the net balance of dry deposition rates, re-emission to the atmosphere, and anthropogenic sources (see Eckley and Branfireun, 2008; Eckley et al., 2016).

In summary, the HSPF models of the St. Louis, Cloquet, and Duluth Urban Area watersheds were extended to simulate landscape processes with DOC as a predictor mercury transport, and to include DOC, THg and dissolved MeHg (dMeHg) as instream water quality parameters (Figure 3-3). DOC from the upland and wetland areas is translated to THg and dMeHg within the HSPF model and DOC, THg, and dMeHg are calibrated using available monitoring data collected throughout the study area. Spatial or source-specific linkages are explored to account for differences in sulfate availability given its correlation with methylation.

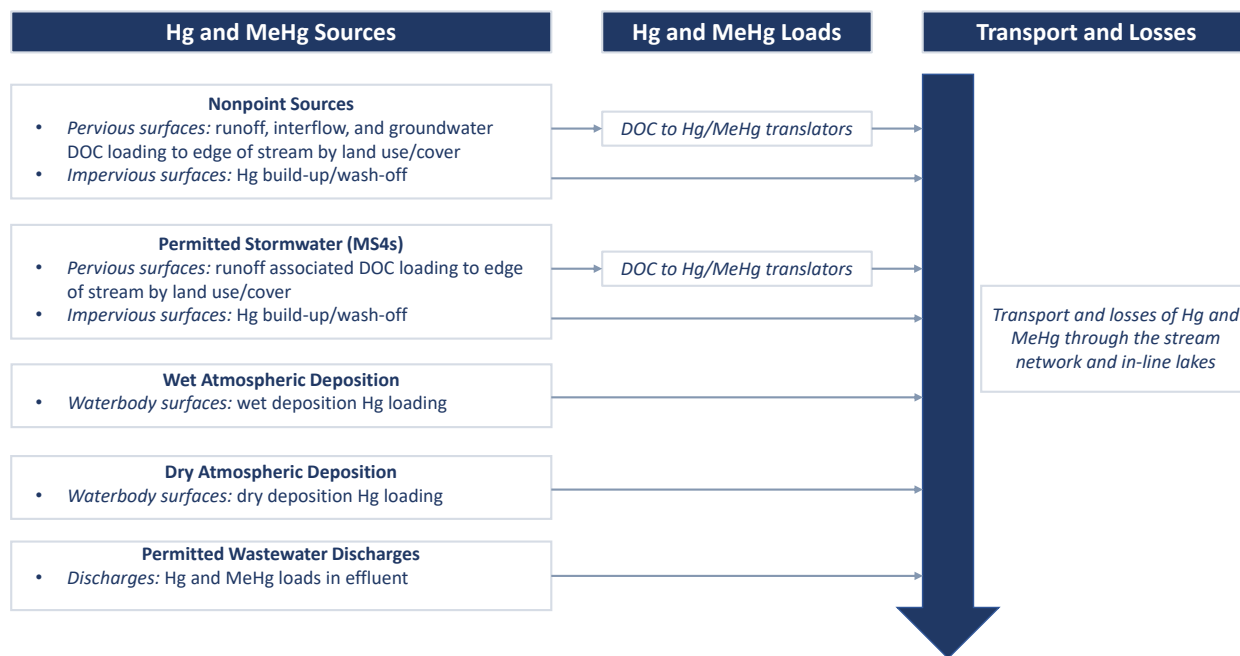


Figure 3-3. Accounting for DOC/Hg source categories in the HSPF model

For the waterbody segments listed for exceedances of ambient THg, the calibrated HSPF modeling results can be directly applied to determine TMDL loading capacities expressed as THg loads. For waterbody segments listed for elevated fish tissue mercury, the HSPF dMeHg results are paired with a statistical analysis that links dMeHg exposure concentrations to bioaccumulation in fish tissue. This linkage is used to establish target dMeHg concentrations and loading capacities.

In this approach, HSPF does not fully replicate the complex kinetics and transformations of mercury in water. Rather, it is used for mass balance purposes to approximate instream THg and dMeHg advective transport, losses (e.g., demethylation and long-term burial), and delivery to waterbodies listed as impaired using the observed relationship to DOC. The approach does not directly represent specific reactions such as methylation in riverine and lake environments and activities that influence these reactions (e.g., springtime flooding of the overbank areas, and fluctuating reservoir levels). However, the approach is useful and efficient because it 1) comprehensively accounts for instream dynamics that impact chronic water column mercury levels and bioaccumulation in the food web, 2) is a defensible and feasible option for developing TMDLs for 50+ mercury impaired segments within the relatively short time frame of the project, 3) leverages the recently updated watershed-scale HSPF models, 4) uses available data as evidence for attributing mercury loading to point and

nonpoint sources in the watershed to support allocations and implementation planning efforts, and 5) provides the opportunity to define loading capacities for two end-points of interest – THg (water column impairments) and dMeHg (fish tissue impairments) - to support TMDL development. THg TMDLs will be developed for water column impairments, and MeHg TMDLs will be developed for fish tissue impairments.

3.2 HARBOR AND ESTUARY ANALYSIS

The original scope for this project focused on mercury impairments upstream of Fond du Lac Dam. MPCA subsequently obtained additional, limited funding for analysis of the mercury impairments in the harbor and estuary. Given the limited funding it was not feasible to develop a new or highly complex mercury model of the harbor and estuary. Instead, the approach taken was to update and recalibrate the existing WASP model (RTI, 2013b) using information from the more recent USGS EFDC modeling (Smith et al., 2020) and incorporating additional monitoring data that were not available for the 2012-2013 WASP modeling.

The development of the linked modeling system for the harbor and estuary is described in Section 4.4.

3.3 BIOACCUMULATION OF MERCURY IN FISH

The bioaccumulation component of the technical assessment seeks to link ambient MeHg exposure concentrations with fish tissue mercury levels. As with methylation, process-based models of bioaccumulation of MeHg are available but are complex and have high data requirements. Fish targeted for human consumption are primarily larger fish at higher trophic levels that accumulate most of their body burden through consumption of smaller fish. As such, there tends to be a progressive accumulation of MeHg tissue concentrations at each step of the food chain. Direct uptake of MeHg from the water column occurs primarily in plankton and algae. A process-based simulation of MeHg bioaccumulation requires understanding the population structure and bioenergetics of all trophic levels, the rates at which different species are able to clear mercury from their systems, and, most importantly, a description of the dietary composition of each species, which often varies with age, size, and physical location. Such data are not available in detail for the majority of the SLRW. Without such data, simpler empirical approaches, which implicitly incorporate the food web complexities through the specification of bioaccumulation factors (BAFs), have proved more robust.

As part of the development of the national dMeHg criterion, USEPA (2001, Appendix A) undertook a thorough re-evaluation of past work on developing MeHg BAFs. Three different methods were used. These are, in order of USEPA preference: (1) the direct method, based on the ratio of the chemical concentration in tissue and water; (2) the indirect method, where a BAF is derived by multiplying a bioconcentration factor (BCF) by a food chain multiplier, and (3) a modified direct approach based on the ratio of concentration in tissue and water, but where the water dMeHg concentration was estimated based on chemical translator relationships to other forms of mercury. Tables A-1 through A-9 in USEPA (2001) summarize the various types of BAF estimates, including separation by lentic versus lotic systems. The indirect results were discarded due to uncertainties regarding specific food chain pathways in many data sets and lentic and lotic results were combined because there was not a statistically significant difference between the two. Table A-9 in USEPA (2001) gives the final recommendations for national dMeHg BAFs, summarized as the median of the distribution but also providing the 95th percentile value. (The median is an unbiased estimate of the geometric mean if the underlying data are drawn from a lognormal distribution.)

USEPA (2010) revisited the issue of MeHg BAFs and “cautions water quality managers that methylmercury bioaccumulation is generally viewed as a site-specific process and that BAFs can vary greatly across ecosystems, leading to significant risk of being either under-protective or over-protective when the national BAF numbers are used.” For this reason, USEPA (2010) instead indicated a preference for site-specific BAFs. In the current study, BAFs are calculated as the ratio between the geometric mean fish tissue concentration (adjusted to a standardized length) and the geometric mean of the water column MeHg exposure concentration. We use the ratio of geometric means (an aggregate approach) instead of a summary measure of the ratio between

concentrations in individual fish samples and contemporaneous water column concentrations to calculate a site-specific BAF because bioaccumulation of mercury is a long-term chronic process that depends on the past history of MeHg exposure that may differ from the contemporaneous exposure concentration at the time fish are sampled.

For the statewide Hg TMDL, MPCA (2007) used a “generalized” BAF approach based on the geometric mean of a set of BAFs calculated from fish tissue mercury concentrations and THg concentrations in 14 lakes representing three geographic areas of Minnesota (Table 6 in MPCA, 2007) to translate the fish tissue target to a corresponding water column THg concentration. This approach has considerable uncertainty because the tissue concentration depends more on MeHg exposure than THg; however, accurate estimates of MeHg BAFs were not widely available statewide because MeHg is reported less frequently than THg and, when available, often includes a large number of censored results below the method reporting limit. The water column THg concentration derived from the BAF was not used directly in the statewide mercury TMDL calculation but rather was used to demonstrate that the target derived from the BAFs is more stringent than the statewide and Lake Superior Basin water quality standards. (Note that in the SLRW mercury TMDL technical approach discussed in Section 6.0, the BAF approach and the reduction factor approach are equivalent; however, the specifics of the approaches differ in this site-specific study compared to the statewide TMDL.)

For this SLRW TMDL, BAFs are calculated using MeHg not THg. The approach involves using fish tissue mercury concentration data and MeHg water column data collected in the project area to estimate the relationship between ambient MeHg, fish length (i.e., a surrogate for age and accumulation timespan), and tissue Hg concentrations (which are predominantly MeHg) for the target endpoint species. It is primarily dMeHg that enters the food chain; however, BAFs can be calculated on the basis of either dMeHg or total MeHg (tMeHg), as described in Section 6.0. Setting a target based on dMeHg is preferable because dMeHg is more closely tied to bioaccumulation. On the other hand, estimates based on tMeHg are also useful because tMeHg measurements are likely to have greater precision than dMeHg observations that are often near the practical quantitation limit. In addition, the solubility of MeHg is complex: MeHg is a cation, and its solubility is dependent in part on the concentrations of various anions. Also, in the SLRW tMeHg is strongly associated with dissolved organic carbon (DOC), but a significant fraction of the OC measured as DOC is likely fine colloidal material that can pass through a filter and thus will be tabulated as part of the dissolved fraction when it is actually sorbed. For the SLRW located upstream of the estuary, BAFs were calculated with dMeHg data, and the water column targets are expressed as dMeHg concentrations. For the estuary, BAFs were calculated with tMeHg data, and the water column targets are expressed as tMeHg concentrations. This is because HSPF modeled dMeHg while WASP modeled tMeHg.

For the SLRW TMDLs, a regression of observed fish tissue mercury concentrations vs fish length for three species of commonly eaten fish (northern pike, walleye, and channel catfish) in the watershed and estuary is established. Fish tissue mercury concentration data are length standardized using the standard size applied in mercury studies for adult northern pike (55 cm), walleye (40 cm), and channel catfish (48 cm) (MPCA 2007, B. Monson pers. comm). BAFs for different waterbody types are calculated from the length-standardized fish tissue concentrations and ambient water column MeHg concentration. Here, the 50th percentile length-standardized fish tissue concentration for each species and the geometric mean of the water column MeHg data were used in the BAF calculation. The waterbody specific BAFs are then used to estimate the MeHg target concentration to attain the 0.2 mg/kg fish tissue criterion. Food webs across the watershed may differ. Therefore, different environment-specific (e.g., waterbody type) relationships and BAFs are used to account for these differences. For the TMDL calculations upstream of the estuary, one BAF for each target species is calculated for the reservoir/lake impairments and one BAF is calculated for the river/stream impairments. In the estuary, separate BAFs are calculated for each target species. See Section 6.0 for more detailed information on the BAF calculations.

4.0 MERCURY MODEL DEVELOPMENT FOR THE SLRW EXCLUSIVE OF THE ST. LOUIS RIVER ESTUARY AND DULUTH HARBOR

The HSPF simulation model of the St. Louis and Cloquet River watersheds was used to simulate mercury sources and transport to support TMDL development. HSPF is a watershed scale, process-based model for simulating hydrology and water quality. HSPF is capable of producing accurate daily streamflow and pollutant concentration predictions, allowing detailed calibration to instream observations. HSPF provides dynamic simulation of upland and instream processes at a level of detail and complexity suitable for addressing the project objectives. HSPF can be used to address water quality impairments associated with combined point and nonpoint sources and has historically been used for TMDL development. For example, HSPF served as the foundation of the mercury mass balance model developed for the recent Willamette River Basin mercury TMDL (final TMDL issued by EPA on Feb. 4, 2021), was used to model THg transport for TMDLs in the Shenandoah Valley, Virginia (Eggleston, 2009), and has been applied in the development of TMDLs for other water quality impairments (e.g., elevated nutrients and low dissolved oxygen) in Minnesota and across the country. HSPF is supported by USEPA with open-source code. MPCA has long allocated funds towards the development of HSPF models for the purposes of supporting TMDLs, watershed restoration and protection strategies (WRAPS), and other initiatives across the state that can be leveraged to support the SLRW mercury TMDLs.

Two HSPF models, one of which covers the entire extent of the St. Louis River and Cloquet River watersheds, and the other of which is a finer-scale model of the Duluth Urban Area were used (Figure 4-1). Both models were developed by Tetra Tech over the last decade and were updated by Tetra Tech for MPCA (Tetra Tech 2022a, 2022b) to cover the more recent time period in support of the mercury TMDLs. Recent data related to land use/cover, hydraulics, permitted point source discharges, atmospheric deposition of nutrients, reservoir dam releases, and weather (Figure 4-2) have been incorporated to update the models and extend the simulation periods through Water Year 2021 (WY 2021). The St. Louis and Cloquet watershed model was further refined using the National Wetland Inventory to differentiate intact and ditched peatlands from herbaceous and shrub wetlands and both models were re-calibrated for hydrology (i.e., streamflow, snow, evapotranspiration), sediment, nutrients, dissolved oxygen, algae, and organic carbon (Tetra Tech, 2022a, 2022b). Only the portion of the Duluth Urban Area model that drains to the St. Louis River Estuary and Duluth Harbor are used in this study (see Section 5.2.1). Additional work to develop the mercury simulations following the approach laid out in Section 3.0 and the conceptual model shown in Figure 4-3 is described below.

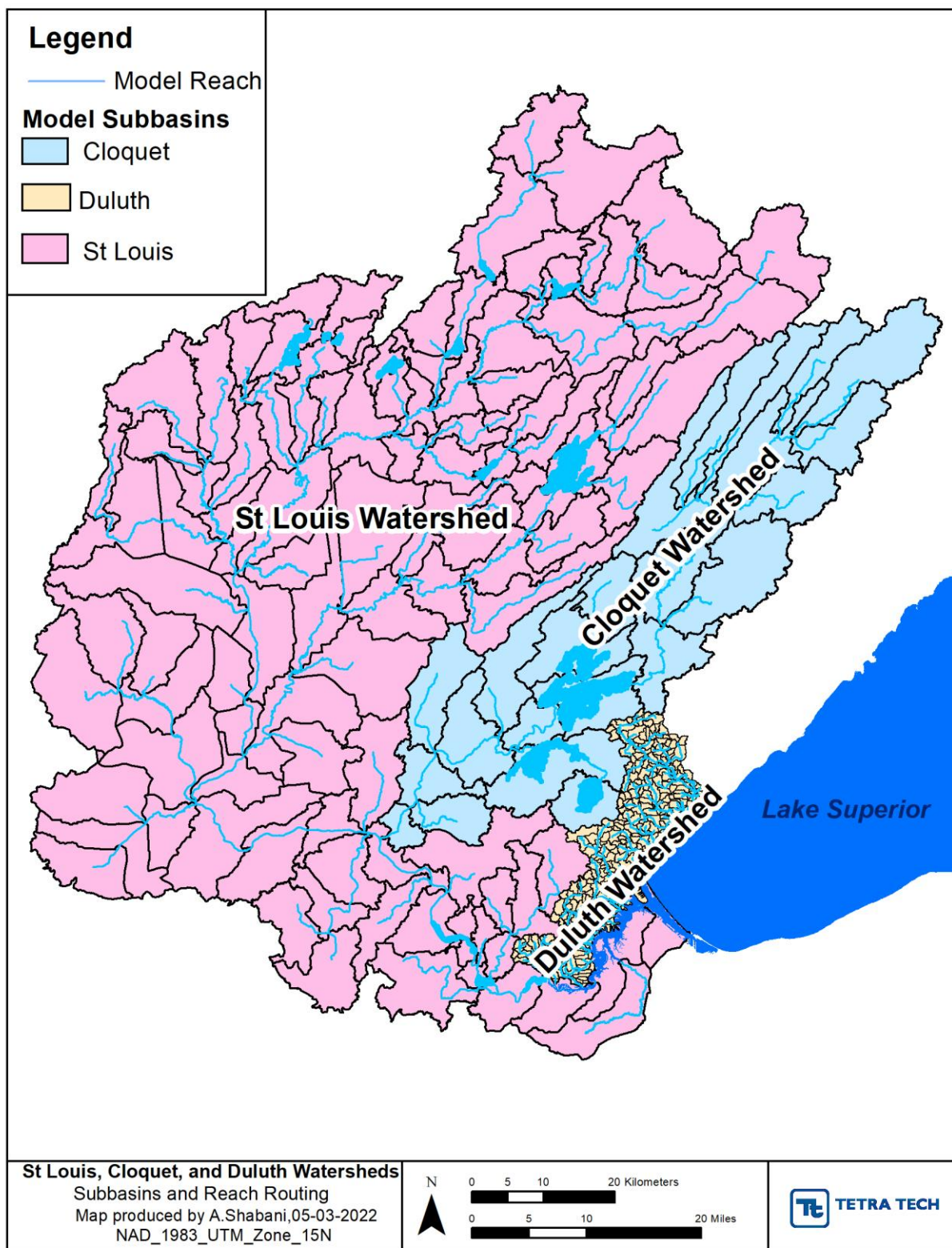


Figure 4-1. Subbasins and reaches for the St. Louis and Cloquet HSPF model and Duluth urban area HSPF models

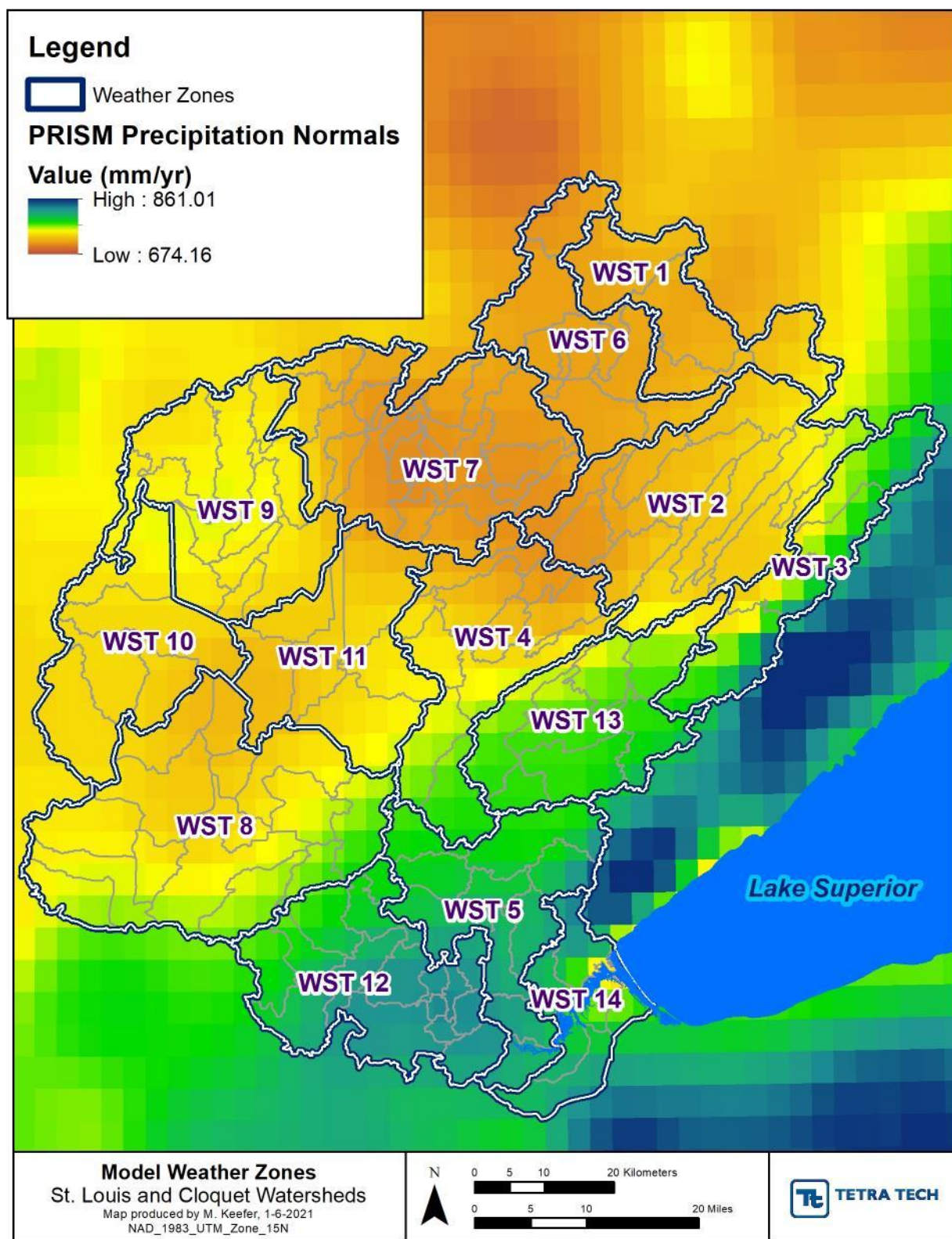


Figure 4-2. Model weather zones

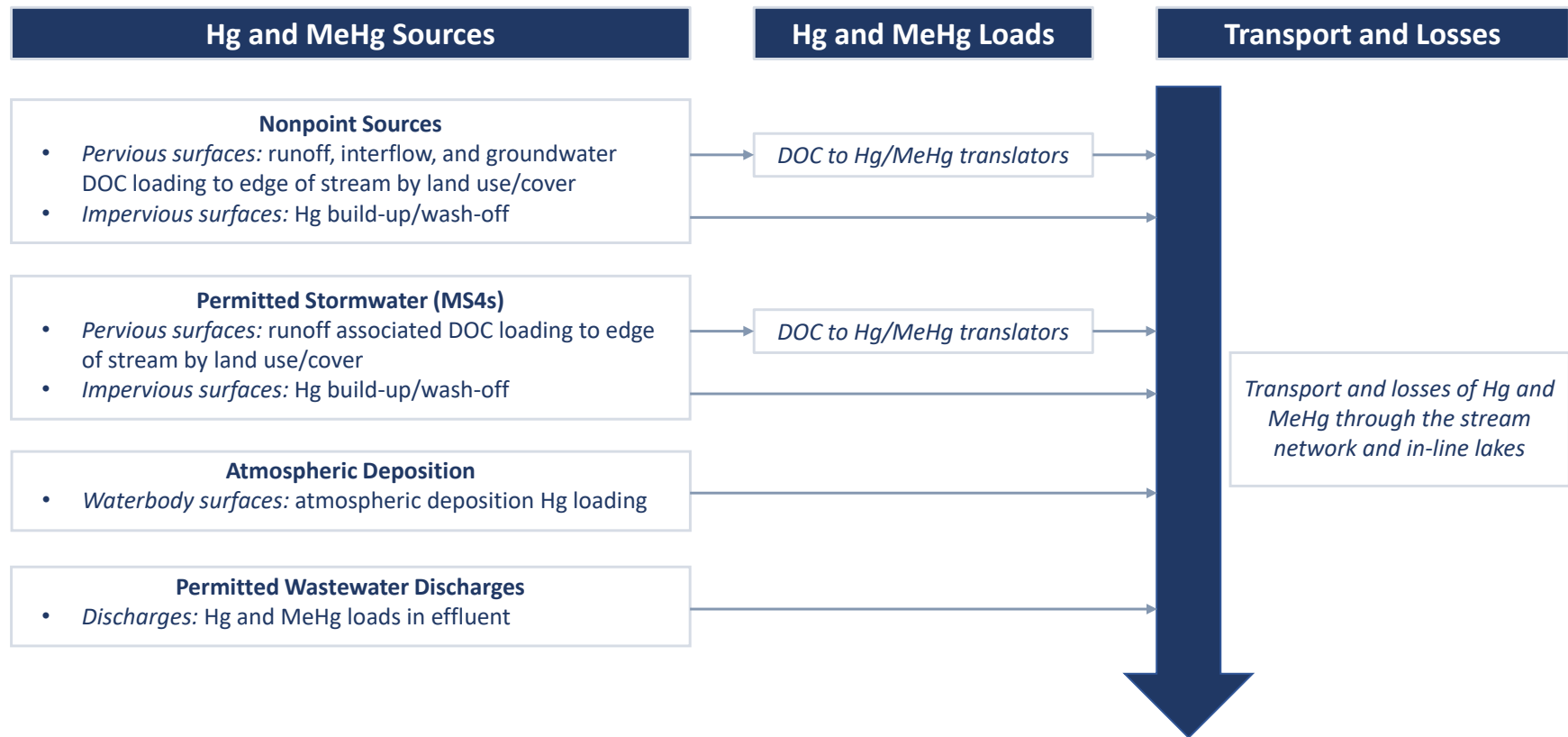


Figure 4-3. Conceptual schematic of mercury sources and modeling

4.1 MERCURY SOURCES

4.1.1 Nonpoint Sources

Anthropogenic and natural emissions of mercury to the atmosphere are deposited to the landscape and direct to waterbody surfaces. Atmospheric deposition is the predominant source of new mercury loads to Minnesota waterbodies. Humans have emitted Hg into the atmosphere since ancient times as a result of mining, smelting, and burning of fossil fuels and mercury currently stored in soils and sediments reflects the net effects of a long history of atmospheric deposition. The statewide mercury TMDL (MPCA, 2007) attributed 10 percent of U.S. emissions to Minnesota sources based on estimates completed in the early 2000s; however, this estimate was based on limited data, and we are not aware of revised estimates to date. The contribution of local vs. regional and global mercury emissions to Minnesota waterbodies is not currently known. Ferrous metal mining and processing operations are currently the largest source of atmospheric emissions of mercury within Minnesota, accounting for an estimated 622.5 lbs of emissions for 2022, or 47 percent of the statewide total (MPCA, 2023).¹

While reductions in mercury air emissions within Minnesota are important, reductions in global mercury emissions may also be needed to delist the mercury impairments within the St. Louis and Cloquet River watersheds because atmospheric mercury also originates outside of Minnesota and substantial amounts of anthropogenically derived mercury attributable to historic atmospheric deposition are present within the soils and sediments of the watershed. Therefore, this modeling approach focuses on the mechanisms that transport MeHg and THg from sources in the watershed to streams, lakes, and reservoirs from nonpoint sources in the watershed using DOC to simulate mercury transport (Section 3.1).

Direct atmospheric deposition to waterbodies that are explicitly represented in the watershed model and atmospheric deposition onto impervious surfaces is simulated separately and is not associated with DOC. Sources of atmospheric deposition rates are described in Section 4.1.3.

Unit-area nonpoint loads of THg and MeHg are determined by applying the mercury-to-DOC ratios to the upland simulation of organic matter export and depend on the runoff and particulate matter erosion and transport characteristics of each land use type (coupled with a buildup-washoff simulation of mercury from impervious surface areas that does not depend on DOC, as described in Section 3.1). The resulting unit-area loading rates (averaged across the watershed) are summarized in Table 4-1. The spatial distribution of land use and land cover is shown in Figure 4-4. Development of the land use/land cover specifications is described in Tetra Tech (2022a and 2022b).

¹ TMDLs formally distinguish pollutant discharges that are permitted by an NPDES permit from pollutant sources that are not permitted by an NPDES permit. Therefore, permitted discharges are discussed separately from nonpermitted sources. Because point source air emissions are not considered a permitted point source in the TMDL realm, air emissions are treated as a nonpoint, nonpermitted source of mercury in TMDLs.

Table 4-1. Annual unit area loading rates of mercury from pervious and impervious land areas

Land Area	THg Load (mg/ha/yr) ³	dMeHg Load (mg/ha/yr)
Forest	21.73	1.40
Shrub	9.02	0.55
Water (as a land use) ¹	0.62	0.04
Pasture	30.08	1.85
Cropland	18.38	1.20
Wetland	13.39	1.60
Barren	28.83	1.70
Peatlands	13.52	1.69
Drained Peatlands	26.47	2.65
Developed, Pervious ³	21.86	1.34
Developed, Impervious ²	184.23	~0

Notes: 1. Water (as a land use) represents small ponds that are not simulated as reaches in the model.
 2. "Developed, Impervious" land includes road surfaces.
 3. Unit area loading rates for pervious land depend in part on the relative rate of particulate matter export, which is why average unit-area loading rates are higher from pasture and barren land than from forest.

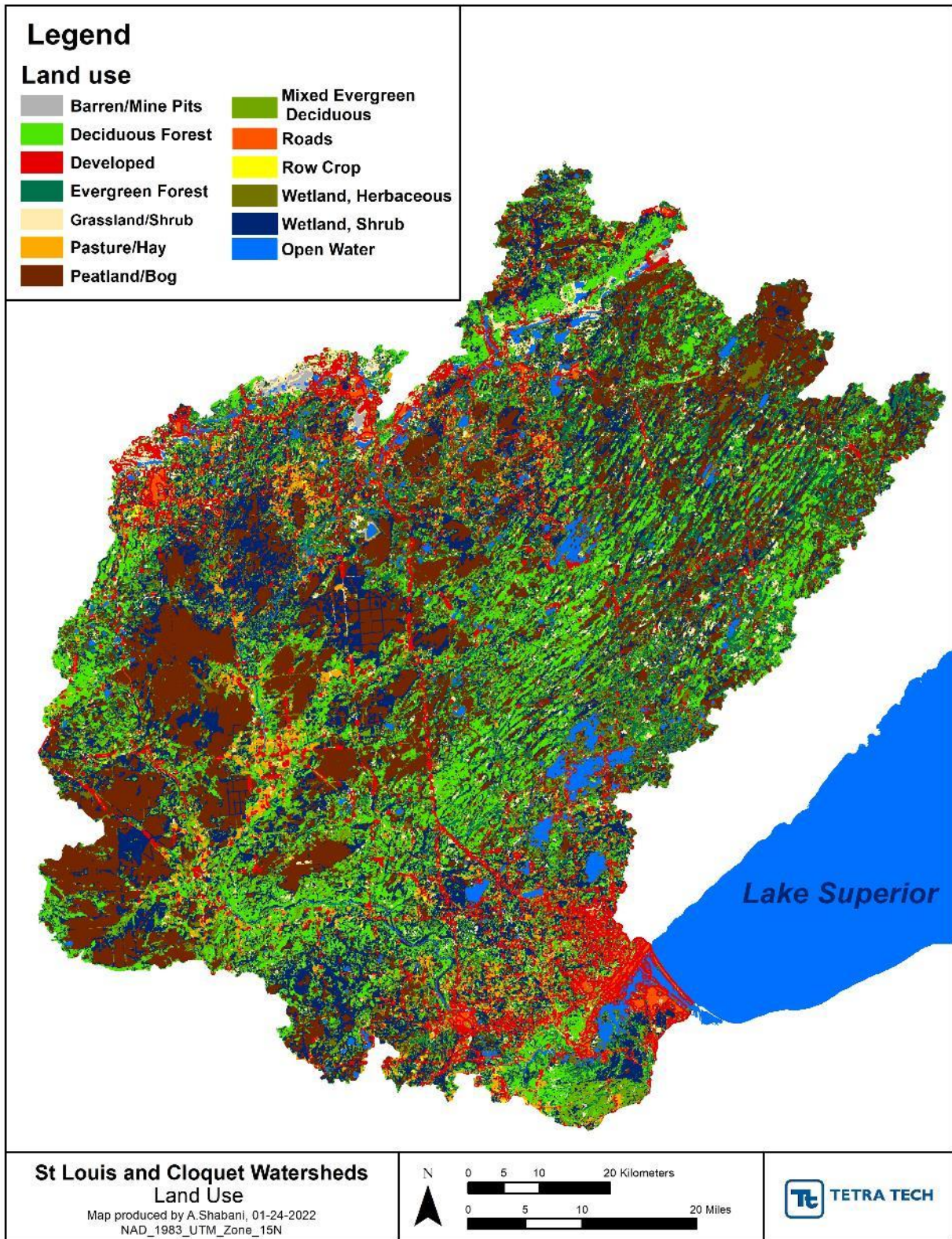


Figure 4-4. Model land use/cover in the St. Louis and Cloquet HSPF model

4.1.1.1 Drained Peatlands

Judging from the Minnesota Statewide Altered Watercourses Project (<https://gisdata.mn.gov/dataset/water-altered-watercourse>) coverage, significant areas of peatlands in the SLRW have been ditched for drainage. These ditched peatlands appear to be concentrated in the central and southwestern portions of the SLRW, corresponding with HSPF model weather zones 8, 11, and 12 (Figure 4-2). Research indicates that undrained peatlands tend to be carbon sinks and ditching of peatlands makes them carbon sources to receiving water bodies (Planas-Clarke et al., 2020; Krause et al., 2021). Accordingly, the calibrated model uses alternative hydrology and DOC parameters for peatlands within weather zones that have relatively dense ditching (weather zones 8, 11, and 12) or moderate ditching (weather zones 5, 9, and 10) of peatlands.

Regarding the effect of drained peatlands on peatland hydrology, studies suggest that drainage affects peatlands by establishing a new, lower equilibrium for the groundwater table. Most studies find that peatland drainage causes decreased GWT (groundwater table) depth, increased runoff, and increased subsidence (e.g., Young et al. 2017, Manninen 1998). Overall, past drained peatland hydrology studies show that GWT depth decreases with ditch cleaning and draining. Peatland drainage also tends to cause greater discharge to surface waters. A survey of the literature on mean annual runoff shows an increase from catchments after draining peatlands of 7 to 52 percent (Enetjärn 2018). In a long-term study on a bog (Seuna 1981), significant changes in spring high flow events (+31 percent), summer high flow (+131 percent), and both summer and winter minimal flow (+several hundred percent) occurred for a monitored drained bog compared to an undrained and calibrated control bog. In every study reviewed by Enetjärn (2018), subsidence, which is dependent on peat depth and ditch depth, occurred from 2 to 22 cm as a consequence of a lowered GWT.

Drained peatlands are simulated with higher runoff rates and higher DOC loading rates, which in turn produces higher estimates of THg and MeHg loads.

4.1.1.2 Sulfate Impacted Wetlands

Mercury methylation has long been associated with the activity of sulfate-reducing bacteria under low oxygen conditions where sulfate is used as an electron acceptor for the digestion of organic carbon (e.g., Jeremiason et al., 2006, working in the Marcell Experimental Forest). Peterson et al. (2023) show that in the Florida Everglades sulfate-reducing bacteria exert important controls on redox conditions, overall microbial activity, and the bioavailability of inorganic mercury to methylators in organic matter rich soils and sediments. However, the sulfate-reducing bacteria may not actually methylate mercury, which instead may be accomplished by a variety of other microbes.

Coleman-Wasik et al. (2021) recently showed for experimentally managed SLRW wetlands that water-level fluctuations alone can strongly affect sulfate, DOM, and MeHg levels. Johnson et al. (2016) studied two wetlands in the St. Louis River watershed, one with high sulfate loads derived from the Mesabi Iron Range and one with much lower sulfate loads and confirmed that MeHg concentrations and methylation rate potentials were statistically similar in these wetlands. Johnson et al. concluded that “chronically impacted” [by sulfate-containing mine discharges] “wetlands do not appear to continually accumulate or produce MeHg at rates different from wetlands unimpacted by mining.” Work in other sulfate-impacted freshwater systems such as the Florida Everglades (where sulfate is applied as an agricultural fertilizer; Gilmour et al., 1998) and in Saskatchewan’s Prairie Pothole Region (where sulfate is naturally high; Hoggarth et al., 2015) suggest a “Goldilocks zone” wherein inputs of sulfate are associated with increased Hg methylation up to a point until the accumulation of sulfide due to sulfate reduction eventually inhibits Hg methylation. Peterson et al. (2023) show this effect is due to reduced bioavailability of inorganic mercury complexes at high sulfide levels and likely reduced metabolic activity of methylators in high sulfate systems. Thus, for the SLRW it appears that while sulfate reduction activity exacerbates the potential for mercury methylation up to a point, sulfate concentrations are not currently thought to be the

primary rate-limiting factor on the creation of MeHg, providing one potential explanation for the lack of strong correlation between sulfate and MeHg concentrations.

During the calibration of the mercury transport model to observed MeHg concentrations throughout the SLRW it did appear that there was some increased MeHg production in wetlands in drainage areas influenced by higher sulfate loads associated with mining and ore processing discharges. We addressed this observation during calibration by adjusting the ratio of MeHg to DOC for wetlands and peatlands in high sulfate areas. Increasing the MeHg-DOC ratio for wetlands and peatlands in areas with higher sulfate loads coupled with adjustment of instream decay rates produced a better fit to observed instream data. Optimal results in terms of minimizing the average absolute difference between simulated and observed concentrations and loads were obtained with an increase of 50% in the MeHg-DOC ratio; however, the effect at the monitoring stations is the product of the MeHg-DOC ratio and the rate of MeHg decay in the intervening stream segments, so care should be taken in interpreting this number.

4.1.2 Permitted Discharges

Municipal and industrial facilities that produce wastewater are regulated by MPCA. A National Pollutant Discharge Elimination System (NPDES) permit is required for facilities that discharge to surface waters in the state. The HSPF watershed model simulates wastewater discharges to surface waters as these contribute non-negligible sources of nutrients and other pollutants to waterbodies. NPDES permits and Discharge Monitoring Records (DMRs) are publicly available and were provided by MPCA.

Facilities were inventoried within the SLRW. Those within the watershed boundary include 17 domestic facilities, five of which are major facilities, and 31 industrial facilities (Figure 4-5). After evaluation of the permits, the following general steps were used to transform the raw data into daily time series that are used in the model. First, blank reported values and non-discharge days were filtered out of the datasets. If data were missing from a facility during a time period that the facility was believed to be discharging, and thus contributing a mercury load, the time series was gap filled using the following procedures: First, the data were assessed to determine which facilities have daily mercury concentration data from which daily mercury loading could be calculated. Various mercury monitoring metrics are reported by each facility and thus, the best available data had to be identified and selected. Monthly average mercury concentrations were prioritized over single values or monthly maximum reported values. The load time series are formed from the monitoring data by multiplying reported flow times THg concentration and converting to the lb/day units required by HSPF. If there are data reported for a month that data value is used; if there are no data for a given month the median of all other observations for that calendar month is used. If no data are reported for a given calendar month, the overall median is used. For facilities that did not have reported mercury concentration data, an average concentration representative of facilities of similar size and type was used as a multiplier on flow to populate the daily mercury loading time series. QA/QC checks were conducted throughout the data processing procedure.

The domestic and industrial permitted discharges that are explicitly included in the HSPF model are further discussed in Section 4.1.2.1 and Section 4.1.2.2, respectively.

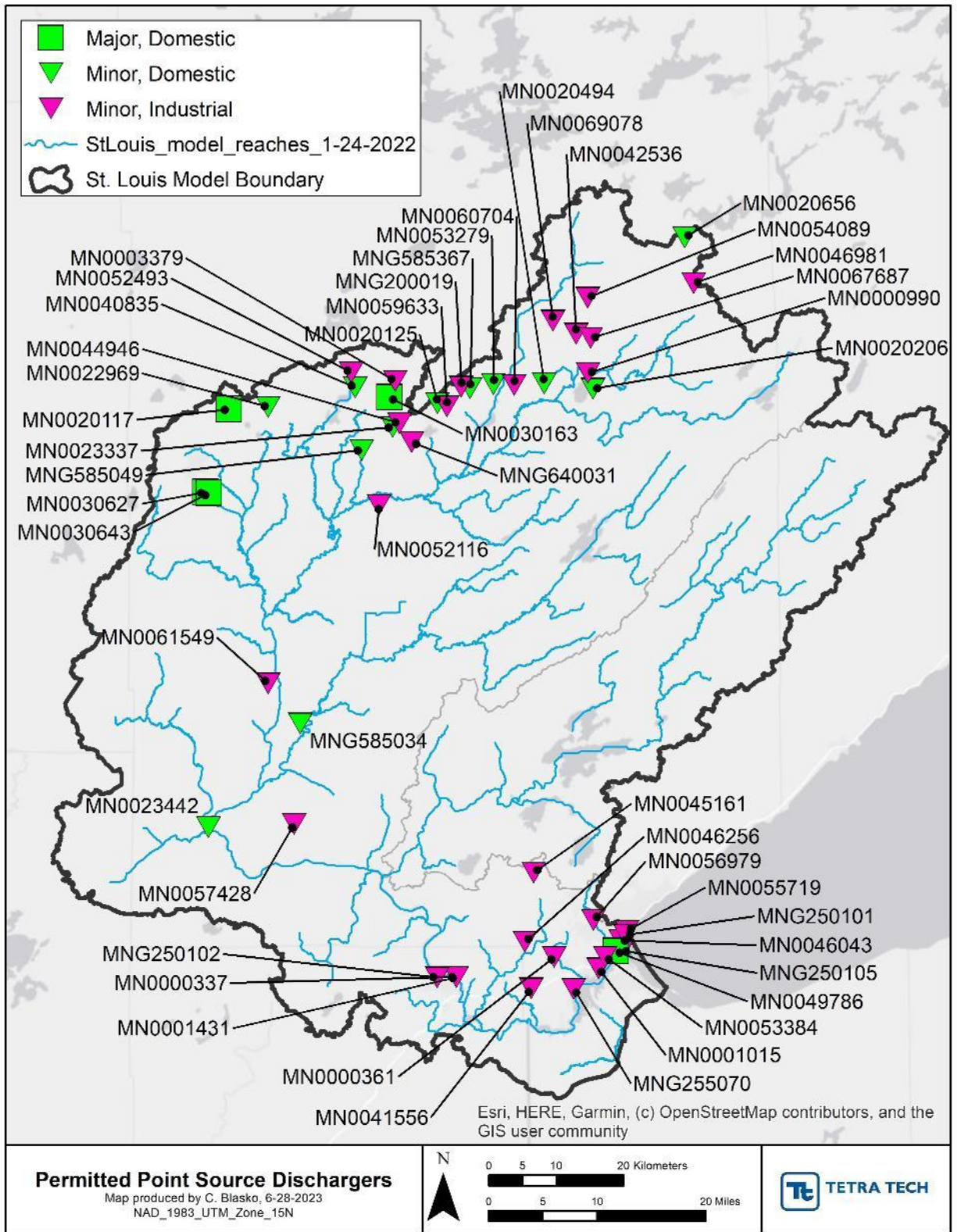


Figure 4-5. Permitted dischargers

4.1.2.1 Domestic Wastewater Discharges

Domestic wastewater treatment plants (WWTPs) primarily process and treat domestic sewage. Discharge monitoring records from 17 WWTPs that discharge to the watershed were characterized in the model (Table 4-2). Major WWTPs provided flow and THg concentration data that were used to compute representative THg loads. MeHg data were not available for point source discharges and MPCA assumed that MeHg was 2 percent of THg based on the upper bound of the ranges reported by Balogh and Nollet (2008), Liu et al. (2018), and Gbondo-Tugbawa et al. (2010). Mercury loading time series for minor WWTPs were calculated using their daily flow records and a constant mercury concentration value representative of the size and type of facility. The Western Lake Superior Sanitary District (WLSSD) is the largest WWTP in the model. WLSSD collects sanitary discharges from most of the greater Duluth-Cloquet area and treats up to 13,760 MG per year on average (Table 4-3). For this reason, this facility has the largest THg load among domestic permitted dischargers despite its average THg concentration falling within the range of other similar facilities.

Table 4-2. Permitted domestic wastewater discharges

Facility	Permit ID	Class	City/Township	County
Aurora WWTP	MN0020494	Minor	White Township	St. Louis
Babbitt WWTP	MN0020656	Minor	City of Babbitt	St. Louis
Biwabik WWTP	MN0053279	Minor	Biwabik Township	St. Louis
Buhl Kinney WWTP (terminated)	MN0022969	Minor	Great Scott Township	St. Louis
Central Iron Range Sanitary Sewer District WWTP	MN0020117	Major	City of Chisholm	St. Louis
Eveleth WWTP	MN0023337	Minor	City of Eveleth	St. Louis
Floodwood WWTP	MN0023442	Minor	City of Floodwood	St. Louis
Gilbert WWTP	MN0020125	Minor	City of Gilbert	St. Louis
Hibbing N (terminated)	MN0030627	Major	City of Hibbing	St. Louis
Hibbing WWTP South Plant	MN0030643	Major	City of Hibbing	St. Louis
Hoyt Lakes Mining Area WWTP	MN0020206	Minor	City of Hoyt Lakes	St. Louis
Iron Junction WWTP	MNG585049	Minor	Clinton Township	St. Louis
McKinley WWTP	MNG585367	Minor	City of McKinley	St. Louis
Meadowlands WWTP	MNG585034	Minor	Meadowlands Township	St. Louis
Mountain Iron WWTP	MN0040835	Minor	City of Mountain Iron	St. Louis
Virginia WWTP	MN0030163	Major	City of Virginia	St. Louis
WLSSD WWTP	MN0049786	Major	City of Duluth	St. Louis

Note: Table shows discharges active during the modeling period (1/1/1993-9/30/2021).

Table 4-3. Annual average effluent flow, THg concentration, and estimated THg load for permitted domestic wastewater discharges

Facility	Permit ID	Average Flow (MG/yr)	Average THg (µg/L)	Load (lb-THg/yr)
Aurora WWTP	MN0020494	116.5	1.33E-03	1.29E-03
Babbitt WWTP	MN0020656	72.0	1.86E-03	1.12E-03
Biwabik WWTP	MN0053279	249.8	2.40E-03	7.42E-03
Buhl Kinney WWTP (terminated)	MN0022969	30.8	3.00E-03 *	7.72E-04
Central Iron Range Sanitary Sewer District WWTP	MN0020117	304.6	9.95E-04	2.58E-03
Eveleth WWTP	MN0023337	214.8	1.32E-03 *	2.36E-03
Floodwood WWTP	MN0023442	93.3	3.00E-03 *	2.34E-03
Gilbert WWTP	MN0020125	102.2	2.64E-03	2.24E-03
Hibbing N (terminated)	MN0030627	144.8	3.00E-03 *	3.63E-03
Hibbing WWTP South Plant	MN0030643	779.7	3.77E-03	2.44E-02
Hoyt Lakes Mining Area WWTP	MN0020206	96.3	3.97E-03	3.12E-03
Iron Junction WWTP	MNG585049	7.8	3.00E-03 *	1.94E-04
McKinley WWTP	MNG585367	11.9	3.00E-03 *	2.98E-04
Meadowlands WWTP	MNG585034	18.6	3.00E-03 *	4.67E-04
Mountain Iron WWTP	MN0040835	153.9	1.20E-03	1.56E-03
Virginia WWTP	MN0030163	684.7	1.43E-03 *	9.25E-03
WLSSD WWTP	MN0049786	13,760.2	2.51E-03	2.90E-01

Notes: Table shows averages of available data for the modeling period (1/1/1993-9/30/2021). * Facility where THg concentration data were not available, average from facilities of similar type and size was used.

4.1.2.2 Industrial and Commercial Wastewater Discharges

Mercury loads associated with industrial and commercial process wastewater are also characterized in the model. Discharge monitoring records from 31 facilities that discharge to the watershed are summarized in Table 4-4. As with domestic wastewater, MeHg was not monitored but assumed to be 2 percent of THg. Daily mercury concentration data was not available for all industrial/commercial facilities. When daily concentration data was available, mercury loading was calculated at a daily timestep as a multiplier on flow. For facilities that did not report mercury concentration data, a constant mercury concentration value representative of the size and type of facility was used to calculate daily mercury loading time series.

Industrial and commercial dischargers include facilities of various kinds including, but not limited to, mining operations, power plants, manufacturing facilities, shopping malls, aquariums, and water treatment plants. Details on incorporating mining operations in the model is discussed in detail below. The largest annual flows come from Minnesota Powers' Laskin Energy Center and Hibbard Renewable Energy Center with average flows of 37,155.2 MG/yr and 6,659.6 MG/yr respectively (Table 4-4). These large annual flows result in these facilities having the greatest THg load among all commercial and industrial permitted dischargers despite their average THg concentration falling within the range of other similar

facilities. Most of the flow from these facilities is non-contact cooling water that reflects the THg content of the source water.

NPDES/SDS permits for taconite mining and processing operations in the St. Louis River watershed regulate the discharge of process water from tailings basins, stormwater management, the dewatering of mine pits, and mine pit closure. In general, industrial process waters are reused, and discharges from tailings basins are only permitted to the extent that annual precipitation in a facility's drainage area exceeds the annual evaporation from the tailings basin (40 CFR §440.12(c)). Mine dewatering discharges can, however, be much larger and are often discharged to streams. The dewatering discharges as well as permitted tailings basin seeps and other tailings basin direct discharges (where there are data) are included in the model. For instance, for the United Taconite permit, the HSPF model EXT SOURCES block contains the following entry:

*** MN0052116 United Taconite

WDM3 6034 THG ENGL 0.01467 SAME RCHRES 249 INFLOW IDQAL 2

The second line uses the daily time series 6034 (THg load in lb/day) to route THg to reach 249 (combining all three of the discharging outfalls covered by the permit). The factor 0.01467 converts from lb/day to lb/hr units required by HSPF.

Table 4-4. Permitted industrial discharges

Facility	Permit ID	DMR Average Flow (MG/yr)	Average THg (µg/L)	Load (lb-THg/yr)
Aitkin Agri-Peat Inc - Floodwood Operation	MN0057428	309.4	3.63E-03	9.54E-03
Cleveland-Cliffs Minorca Mine	MN0059633	1,062.4	1.09E-03	1.07E-02
Cliffs Erie - Hoyt Lakes Mining Area	MN0042536	715.5	6.30E-04	3.60E-03
Duluth Steam Plant 1	MN0055719	2,556.6	1.40E-03 *	2.99E-02
Dyno Nobel	MN0060704	0.3	9.12E-03 *	2.34E-05
Eveleth WTP	MNG640031	30.4	7.34E-03 *	1.86E-03
Georgia Pacific Wood (terminated)	MN0046043	251.4	1.30E-02 *	2.73E-02
Gerdau Ameristeel	MNG250105	281.9	1.40E-03 *	3.29E-03
Great Lakes Aquarium	MNG250101	106.1	7.34E-03 *	6.50E-03
ISD 704 (terminated)	MN0045161	0.1	7.34E-03 *	8.88E-06
Jarden Home Brands (terminated)	MN0000337	5.3	1.30E-02 *	5.74E-04
McKinley WTP (terminated)	MNG200019	1.7	7.34E-03 *	1.02E-04
Mesabi Mining Area	MN0069078	432.5	5.08E-04	2.10E-03
Mesabi Nugget Delaware LLC	MN0067687	421.0	6.11E-04	1.98E-03
Miller Hill Mall (terminated)	MN0056979	42.9	7.34E-03 *	2.63E-03
Minnesota Power - Hibbard Renewable Energy Center	MN0001015	6,659.6	1.40E-03 *	7.78E-02
Minnesota Power - Laskin Energy Center	MN0000990	37,155.2	2.22E-03	7.07E-01

Facility	Permit ID	DMR Average Flow (MG/yr)	Average THg (µg/L)	Load (lb-THg/yr)
Minnesota Power Inc - Arrowhead HVDC	MN0046256	0.5	1.40E-03 *	6.12E-06
Northshore Mining Co - Peter Mitchell	MN0046981	871.8	6.24E-04	4.53E-03
Poly Met Mining, Inc. - Tailings Basin Area	MN0054089	71.9	1.09E-03	6.33E-04
Primary Products Ingredients Americas	MNG255070	175.1	3.78E-03 *	5.52E-03
Sappi Cloquet	MN0001431	49.7	1.30E-02 *	5.39E-03
Superior Refining Company	MN0041556	14.0	9.12E-03 *	1.06E-03
United Taconite LLC - Fairlane Plant	MN0052116	1.0	5.20E-04	4.37E-06
United Taconite LLC - Thunderbird Mine	MN0044946	989.7	9.12E-03 *	7.53E-02
US Steel - Minntac Mining Area	MN0052493	2,888.8	9.19E-04	2.26E-02
USG Interiors LLC – Cloquet, MN	MNG250102	169.3	1.30E-02 *	1.84E-02
Virginia Department of Public Utilities	MN0003379	6,058.7	1.40E-03 *	7.08E-02
Waupaca North Woods	MN0061549	29.5	9.12E-03 ^a	2.24E-03
Wisconsin Central Limited – Duluth Ore Dock	MN0053384	0.004	9.12E-03 ^a	3.07E-07
Wisconsin Central Limited - Proctor Yard	MN0000361	85.8	5.73E-03	2.32E-03

Note: Table shows discharges active during the modeling period (1/1/1993-9/30/2021). Note that the mining permit DMRs often include mine dewatering discharges that are highly variable over time. * Facility THg concentration data were not available, average from facilities of similar type and size was used.

4.1.2.3 Municipal Separate Storm Sewer Systems (MS4s)

Stormwater discharges from NPDES permitted municipal separate storm sewer systems (MS4s) are included in the HSPF model. To comprehensively account for THg and dMeHg in urban stormwater, loads from currently permitted MS4s were estimated.

There are 11 currently permitted MS4s entirely or partially within the watershed including cities, townships, St. Louis County, MnDOT and Lake Superior College–Duluth.

Historically in Minnesota, cities and townships exclusively regulated under Minn. R. 7090.1010, subp. 1(B)(1)², were required to manage stormwater in compliance with the general permit for small MS4s in the “entire” jurisdiction. Legislation passed in 2019, and subsequently amended in 2021, changed the regulated area for those MS4s. The 2019 legislation reduced the land area in which stormwater must be managed within the affected permittees’ jurisdiction to only urban areas with a population of at least 50,000, as defined by the most recent decennial census, and other “platted areas” as defined by

² Any MS4s partially in urbanized area with populations up to 4,999 or between 5,000-9,999 and not discharging to a special water.

Minnesota Statute 462.352, subp. 132³. Within the SLRW, 3 of the 11 regulated MS4s are affected by this legislation (Table 4-5). If any part of the regulated area of a permitted MS4 is in the TMDL watershed, the portion within the watershed is considered a permitted MS4 subject to the St. Louis River Hg TMDL.

Table 4-5. MS4 permitted dischargers

MS4 Permittee	MS4 Regulated area
Cloquet City	Regulated throughout entire jurisdiction
Duluth City	Regulated throughout entire jurisdiction
Hermantown City	Regulated throughout entire jurisdiction
Hibbing City	Regulated throughout entire jurisdiction
Lake Superior College – Duluth	Regulated throughout entire jurisdiction
Midway Township	Regulated in urban areas with a population of at least 50,000 and other platted areas
MnDOT	State owned/operated transportation corridors in urban areas with a population of at least 50,000
Proctor City	Regulated in urban areas with a population of at least 50,000 and other platted areas
Rice Lake City	Regulated in urban areas with a population of at least 50,000 and other platted areas
St Louis County	County owned/operated transportation corridors in urban areas with a population of at least 50,000
Thomson Township	Regulated throughout entire jurisdiction

MS4 jurisdictional areas were defined spatially using a coverage provided by MPCA (MS4 Boundaries in Minnesota: <https://gisdata.mn.gov/dataset/util-ms4-boundaries>) (Figure 4-6). For cities and townships only regulated in urban areas with a population of at least 50,000 and in other platted areas, the following data sources were used to determine regulated areas within the jurisdictional boundaries: 1) the 2010 Census-defined urban areas with a population of at least 50,000; and 2) platted areas provided by MPCA (October 2022).

State-owned and county-owned roads within the 2010 Census defined urban areas with a population of at least 50,000 were identified from a MnDOT route centerlines coverage. Right of way widths used were

³ Minn. Stat. 462.352, subd. 13: "Plat" means the drawing or map of a subdivision prepared for filing of record pursuant to chapter 505 and containing all elements and requirements set forth in applicable local regulations adopted pursuant to section 462.358 and chapter 505.

consistent with the 2018 St. Louis River Watershed Total Maximum Daily Load Report (MPCA 2018). MnDOT responsible areas were delineated by buffering the state-owned roads (ROUTE_SYSTEM = 01 (Interstate), 02 (U.S.), or 03 (State)) by a surface width of 180 feet, which covers right-of-way lanes and shoulders, such that the full buffer width equaled the total surface width. County responsible transportation corridors within the urbanized areas were delineated by buffering the county-owned roads (ROUTE_SYSTEM = 04 (CSAH) or 07 (County)) by a surface width of 70 feet such that the full buffer width equaled the total surface width. Where the MnDOT MS4 area intersects city/township or county MS4s, the regulated area is attributed to the MnDOT MS4.

In addition to municipalities and townships, county roads, and MnDOT-owned roads, certain publicly owned entities such as universities, prisons, and hospitals with average daily user populations of 1,000 or more within decennial census defined urban areas with a population of at least 50,000 are regulated as “non-traditional” MS4s. Within the St. Louis River watershed, Lake Superior College – Duluth is regulated as a non-traditional MS4.

Hg loads in urban stormwater are believed to derive primarily from atmospheric deposition to impervious and pervious surfaces that route to the storm sewer network with overland flow, but Hg associated with shallow interflow and groundwater on pervious lands in regulated areas also contributes to urban stormwater loads. Hg loads from impervious and pervious surfaces outside of the MS4 regulated areas are represented under the surface runoff, interflow, and groundwater categories. Low, medium, and high density developed land cover classes (based on NLCD 2019) within the regulated areas of the MS4 boundaries described above were used to approximate the contribution to regulated storm sewer conveyance systems. THg and dMeHg from other land uses (e.g., forested, wetlands, etc.) within permitted MS4 boundaries are attributed to the respective non-MS4 source category.

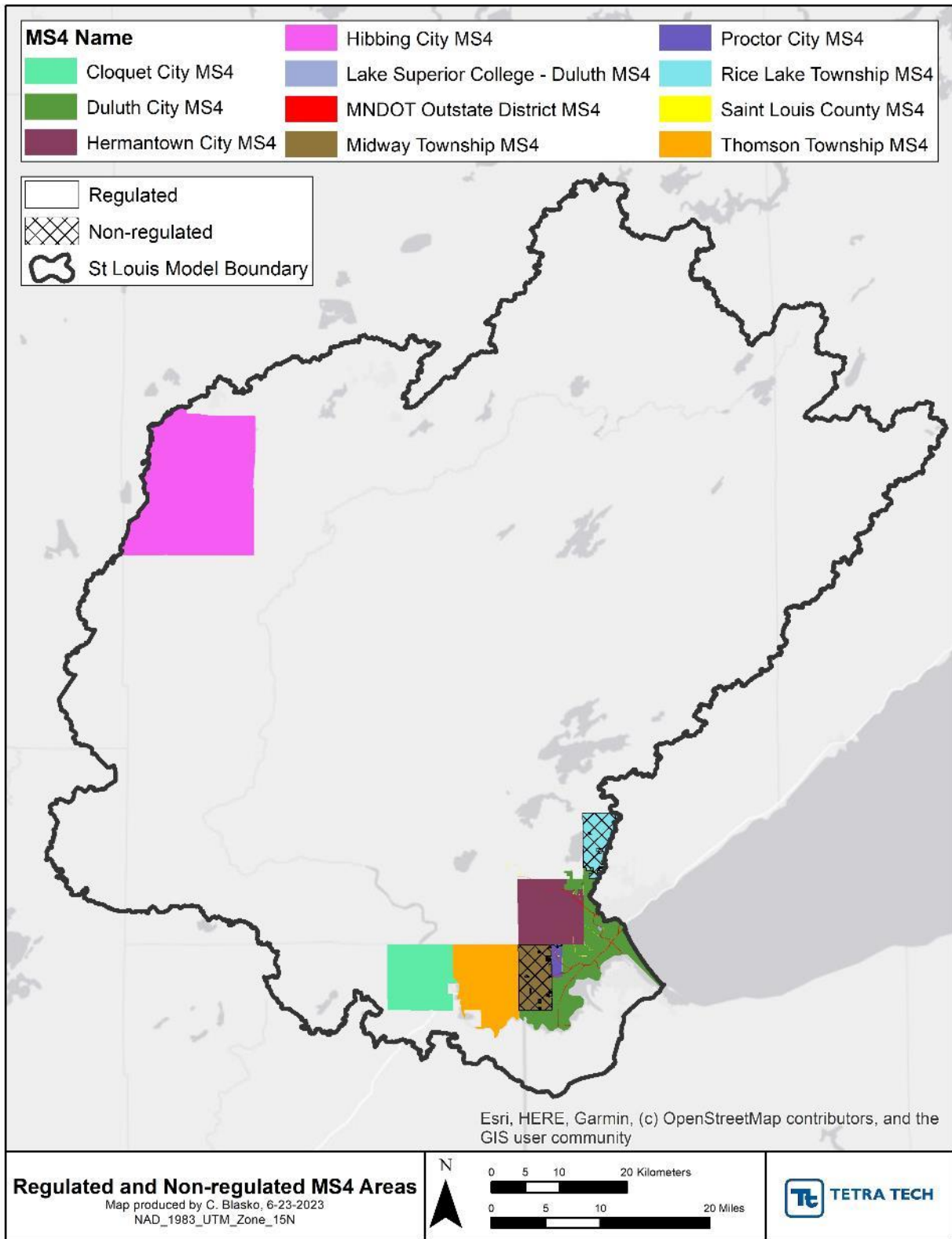


Figure 4-6. Regulated and non-regulated MS4 areas in the SLRW

4.1.3 Atmospheric Deposition of Mercury

In the model, total atmospheric deposition (wet and dry) of mercury to the pervious portions of the landscape and associated loading to the stream network, is implicitly represented within the modeled transport approach based on organic carbon and its relationship to Hg and MeHg. Dry and wet deposition to water surfaces that are simulated as model reaches is represented as a direct load to the reaches.

In contrast to pervious land surfaces, mercury load from impervious surfaces is not necessarily associated with the transport of organic carbon, nor is direct atmospheric deposition of mercury to water surfaces, so the organic carbon–mercury approach is not appropriate for this portion of the load. Rather, wet and dry deposition of THg to impervious surfaces is represented as a buildup/washoff process that allows deposited THg to be transported when runoff occurs. The model also incorporates an accumulation limit, which implies and accounts for removal of THg from the land surface due to re-emission to the atmosphere.

4.1.3.1 Wet Atmospheric Deposition

The Fond du Lac Tribal Air Program operates outdoor air monitors located at the Cloquet Forestry Center in collaboration with the Minnesota Pollution Control Agency. Weekly monitoring of wet atmospheric deposition of mercury is available beginning in December of 1996. However, the weekly recorded Fond du Lac data did not cover the entire model simulation period and was therefore gap filled and extrapolated to produce a daily time series for model input. If a month had one or more weekly recorded concentration(s), the average concentration was applied to that entire month's daily time series. For months that did not have any data, the average concentration of that corresponding month across all years was used.

Data from the National Atmospheric Deposition Program's (NADP) Mercury Deposition Network (MDN) were used to validate the Fond du Lac Tribal Air Program data. The MDN has rigorous standard operating procedures for all monitoring sites⁴. For example, automated Aerochem (ACM) collectors limit loss of dissolved mercury by reducing sample exposure to the open atmosphere. Additionally, microbial action and conversion/loss of Hg(0) is prevented by pre-loading sample bottles with hydrochloric acid. Finally, THg is measured using the Trace Element Clean Laboratory (TECL) on a Tekran 2600 following USPEA Method 1631 Revision E. NADP MDN sites closest to the study area are the Marcell Experimental Forest (Site ID: MN16) west of Hibbing, Minnesota that has been in operation since February 1996 and Brule River (Site ID: WI08) east of Superior, Wisconsin that has been in operation since March 1996. Figure 4-7 shows that non-gap filled wet atmospheric deposition mercury concentration is comparable across all data sources from 2004 through 2021. Spikes in concentration over 50 ng/L occur relatively frequently at the Fond du Lac station prior to 2004. However, the NADP MDN MN16 station has a similar spike in February 2001 of 375 ng/L that was quality checked and deemed valid data by NADP MDN. Considering the rigorous standard operating procedures of the NADP MDN the spikes in concentration recorded by the Fond du Lac station are within reason. Because the Fond du Lac station is within the study area and has more weekly recorded data than NADP, it was used for the model input time series.

⁴ More information about the NADP MDN standard operating procedures can be found on their website: <https://nadp.slh.wisc.edu/networks/mercury-deposition-network/>

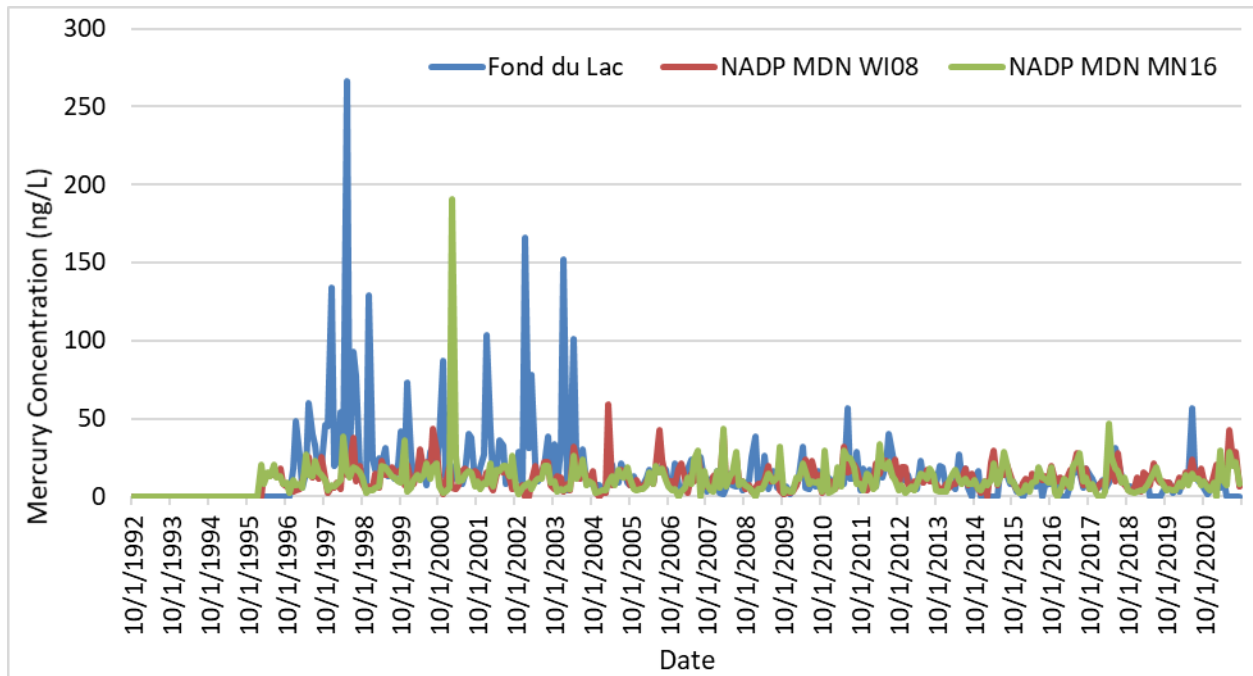


Figure 4-7. Monthly average observed wet deposition total mercury concentration by data source

For water years 2006-2021, estimated wet deposition of THg to the SLR watershed averaged 94 kg/yr, with a range from 90 to 100 kg/yr. This estimate refers to the entire watershed and much of the total loading is retained in upland soils. Wet deposition loading of THg was substantially higher prior to the institution of controls on mercury emissions in the 2000s.

Some wet atmospheric deposition of MeHg in precipitation does occur; however, few measurements are available. MeHg data was collected by the Fond du Lac Air Program in 2003 where they calculated a mean annual MeHg deposition rate of 63.3 ng/m² (Hedin, 2021). When compared to the mean annual THg deposition of 6 ug/m², the MeHg deposition is a small fraction (1.05%) of THg deposition. Hall et al. (2005) measured wet deposition of THg and MeHg at five sites in the Great Lakes region between May 1997 and December 2003. At the three sites nearest the SLRW (Brule River, WI; Eagle Harbor, MI, and Isle Royale, MI) the fraction of MeHg was less than 6 percent of THg. Other monitoring studies generally show that MeHg concentrations in wet deposition are a small fraction of THg deposition (e.g., Conaway et al., 2010; Gerson et al., 2017). Gerson et al. (2017) in a detailed study of atmospheric mercury fluxes in New York's Adirondack mountains found that MeHg concentrations in precipitation were consistently less than 1% of THg concentrations. Risch et al. (2017) report the median ratio of MeHg to THg in eastern U.S. forests was 2.0 percent and ranged from 1.0 to 3.1 percent. Similarly, RTI (2013b) concluded that the atmospheric deposition of MeHg in the SLRW was "near zero." NADP evaluated MeHg concentration in precipitation for the period of 1996-2015; a majority of the samples were less than the method detection limit and those detected were less than 2 percent of total mercury in precipitation (David Gay, pers. Comm. to MPCA). Given these low fractions, wet deposition of MeHg was not explicitly simulated.

4.1.3.2 Dry Atmospheric Deposition

Data from the National Atmospheric Deposition Program's (NADP) Mercury Deposition Network (MDN) report wet deposition of mercury but not dry deposition. Dry deposition of Hg is not often directly measured in Minnesota and indeed is difficult to measure due to complex patterns of deposition and re-emission. However, the Fond du Lac Band has collected dry mercury deposition data within the watershed as described by Hedin (2021):

“In addition to the wet deposition site, in 2012 the FDL Air Program began collecting dry deposition mercury data on three sites on the Reservation where they placed six to seven bins that caught leaf litter from deciduous and coniferous trees. The leaves were ground and processed for mercury concentrations. The dry deposition study was conducted because of a gap in data in the mass balance of mercury for Fond du Lac and there was an assumption it was bound up in leaf litter.” Total mercury concentrations found in leaf litter from the FDL Air Program’s dry atmospheric Hg deposition data collection range 14.6 ng/g dry weight to 41.3 ng/g dry weight at three sites with site means of 36.0 (Ditchbank), 30.7 (Cloquet Forestry Center), and 25.2 ng/g (S. Burnett Rd.). Rates of litterfall are not reported by Hedin et al. so these concentrations cannot be directly converted to mass loading rates.

For the entire SLRW, dry deposition of Hg to impervious surfaces and water as an average annual rate (lb/ac/day, as required by HSPF) was estimated based on EPA’s Community Multiscale Air Quality (CMAQ; <https://www.cmascenter.org/cmaq/>) model run for 2009 conditions at a 40-km spatial resolution as described in Domagalski et al. (2016). The SLRW intersects 13 different CMAQ cells (Figure 4-8). These were summarized into nine zones for the watershed model, with simulated THg dry deposition rates ranging from 1.3 to 18.1 $\mu\text{g}/\text{m}^2/\text{yr}$. Note that the CMAQ model run incorporates emissions from the 2008 National Emissions Inventory (<https://www.epa.gov/air-emissions-inventories/2008-national-emissions-inventory-nei-data>). This includes emissions reported from within and near the St. Louis watershed, including the taconite processing facilities in the Iron Range so fluxes associated with these facilities are included in the estimates.

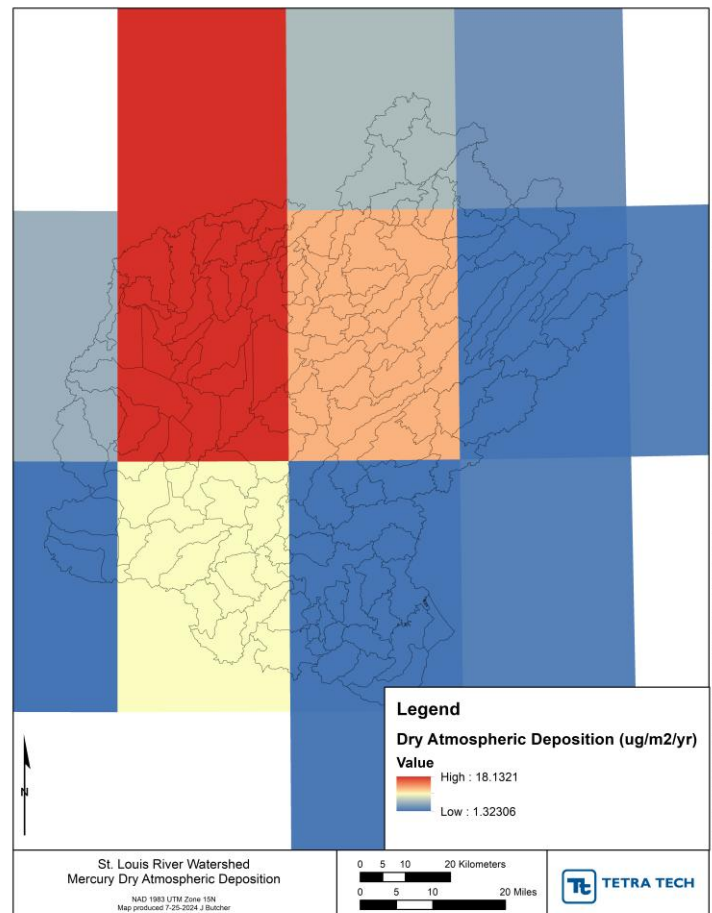


Figure 4-8. Geographic distribution of THg dry atmospheric deposition loading rates predicted by the CMAQ model for 2008 – 2009 conditions

Dry deposition loads of THg to the SLRW based on the CMAQ model runs averaged 73 kg/yr (44 percent of the total atmospheric deposition loading rate for water years 2006 - 2021), with a range from 13 to 178 kg/yr, with higher loading rates near the Iron Range and lower loading rates along the Lake Superior shore (Figure 4-8).

Risch et al. (2017) report estimates of mercury dry deposition at or near NADP sites, of which the two closest to the SLRW are Marcell, MN (MN16) and Bad River, WI (WI95). For Marcell, concentrations of THg in leaf litter ranged from 21 to 29 ng/g, while at Bad River they ranged from 24 to 32 ng/g, generally consistent with the Fond du Lac monitoring. Risch et al. reported litterfall rates of 123 – 163 g/m²/yr and 253 – 271 g/m²/yr at Marcell and Bad River, respectively, resulting in THg dry deposition rates of 3.5 – 4.1 and 6.2 – 8.8 µg/m²/yr. Other estimates of litterfall rates in northern forests are in a similar range (e.g., Yang et al., 2017). These litterfall rates suggest that Fond du Lac monitoring (with a median around 30 ng/g) represent deposition rates for THg of about 4 to 8 µg/m²/yr. This estimate is applicable to forested areas only, with lower estimates expected for open water and cleared land. The CMAQ model estimate of dry atmospheric deposition of THg at the Fond du Lac reservation for 2009 conditions is 6.96 µg/m²/yr, consistent with the estimate from Fond du Lac monitoring. Dry deposition remains a source of uncertainty; however, direct dry deposition to water is a small fraction of the total mercury mass balance (Section 4.3.2.2).

4.1.4 Methylmercury Generation in Reservoirs and Lakes

Sediment in lakes that stratify and have low dissolved oxygen at the sediment-water interface can also be a significant locus for mercury methylation. This can have important consequences for local fish exposure and tissue concentrations in such lakes, but effects on downstream MeHg loads may be muted because low shade and high residence time for lake surfaces can cause high rates of photo-demethylation. Relatively little information is available on MeHg/THg balances in lakes of the SLRW.

Bailey et al. (2014) evaluated the MeHg balance in two sulfate-impacted small lakes near the Iron Range in the St. Louis watershed – Lake Manganika and Lake McQuade. Analysis of the hypolimnions of Lake Manganika and Lake McQuade showed likely net MeHg production in lake bottom waters and surface sediment, particularly in the summer. Despite MeHg production, a limited amount of MeHg was exported from the lakes due to stratification isolating the hypolimnion.

MeHg flux from sediments to the water column were generally positive, although with seasonal variations. MeHg concentrations in outflows were much lower than the high bottom water MeHg concentrations (e.g., <0.1 ng/L compared to 3.3 ng/L for Lake Manganika). Inlet, surface, and outlet concentrations of MeHg were similar for Lake McQuade, with high MeHg in anoxic bottom water being relatively contained.

Bailey et al. conclude: “Despite production of MeHg in bottom waters and sediment porewaters, there is little evidence of MeHg export out of the lakes into the downstream water systems while lakes are stably stratified, likely due to limited exchange across the limnetic surface. At McQuade, export of MeHg appears to be highest during a brief period from after lake turnover, when mixing brought MeHg from the hypolimnion to the surface, until net demethylation had diminished MeHg concentrations in the water column.”

Hines and Brezonik (2007) evaluated storages and cycling of THg, MeHg, and Hg(0) in Spring Lake, a small bog lake in the Marcell Experimental Forest near the SLRW. They found that internal MeHg production was the major source of MeHg in the lake, while photo-demethylation was the dominant loss process. Photo-demethylation removed three times the lake mass of MeHg than was created so the lake was a net sink of MeHg to the downstream watershed. In-lake cycling of inorganic Hg(II) to MeHg and then to gaseous Hg(0) via abiotic photo-demethylation could cause a net reduction in THg load, as is represented in mechanistic models such as WASP (Wool et al., 2020), although the science on this appears to be unresolved (see discussion in Barkay and Gu, 2021).

During model calibration it did not appear necessary to simulate additional mercury loads from bottom sediments in large or small lakes to the remainder of the watershed, consistent with the studies cited above. Notably, the model predictions for both THg and MeHg have a positive average error for observations at Cloquet River near Burnett, downstream of the major hydropower reservoirs on the Cloquet, suggesting the model is not missing a major source of Hg from these reservoirs. In addition, comparison to observations in the upper estuary suggest that there may also be net reduction of MeHg load in the mainstem St. Louis River series of reservoirs as a result of demethylation. Representation of MeHg net concentrations based on relationships to DOC provided reasonable results and data are not sufficient to resolve finer details. There is very limited data on mercury cycling in the lakes and reservoirs of the SLRW; however, based on the available data we suggest that methylation in reservoirs is likely not a major net source of MeHg load in the watershed as a whole but may have important effects on exposure concentrations in individual lakes that may require further site-specific investigation. One potential caveat is that within-year fluctuations in water level – which are typical for hydropower reservoirs – can enhance replenishment of atmospheric sulfate and labile organic carbon in temporarily exposed areas, which could be important in determining the rate of methylation under hypoxic conditions when the water level recovers (Willacker et al., 2016; Eckley et al., 2015). This was addressed by calculating a separate BAF for the lake/reservoir fish impairments upstream of the estuary (See Section 6.0 for more detailed information).

4.2 ORGANIC CARBON CALIBRATION

In the St. Louis HSPF model for mercury, dissolved organic carbon (DOC) is used to model upland transport of mercury. Available organic carbon records were used to calibrate DOC and total organic carbon (TOC). DOC and TOC were previously calibrated for the St. Louis/Cloquet HSPF model update (Tetra Tech, 2022a), but additional records were made available to Tetra Tech in September 2022 during the mercury model development, and these additional records were used to improve the calibration. Only more recent data (2005 – 2021) were used in the final organic carbon calibration. The RQUAL module of HSPF simulates dead refractory organic carbon and total inorganic carbon, while total organic carbon is reported as the dead refractory organic carbon plus the organic carbon contained in phytoplankton and in carbonaceous BOD. (The model uses BOD as the state variable for labile organic carbon with user-specified stoichiometric ratios relating carbon and nutrient concentrations to potential oxygen demand.) HSPF does not simulate separate dissolved and particulate fractions of organic carbon. Therefore, the model was calibrated such that phytoplankton-associated organic carbon is assumed to be particulate organic carbon while the organic carbon in BOD and dead refractory organic carbon were considered as the dissolved portion (Tetra Tech, 2022a).

Various authors have demonstrated that wetlands and peatlands are major sources of organic carbon in northern forest areas and that just 10% of wetland land cover can explain as much as 50% of DOC concentrations throughout the watershed (Laudon et al., 2011; Andersson, 2009; Cracknell, 2017).

The model was calibrated for TOC and DOC by adjusting parameters controlling organic carbon concentrations in each land use/land cover class and nutrient-algae interactions in streams and lakes. Simultaneous calibration to multiple monitoring stations with different mixes of land uses helps ensure a robust representation.

Within the SLRW, the model estimates that 62 percent of the organic carbon load is derived from wetlands and peatlands. These land covers also have the highest organic carbon loading rates, as shown in Figure 4-9.

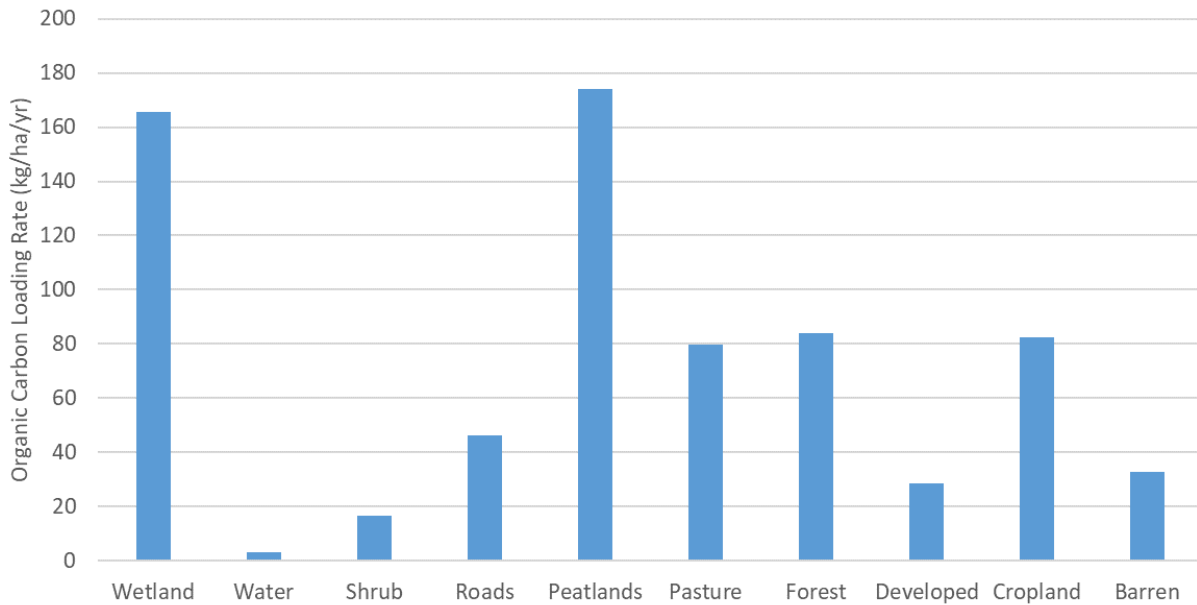


Figure 4-9. Simulated organic carbon loading rates by land cover

Table 4-6 and Table 4-7 show the comparison between simulated and observed concentrations of TOC and DOC, respectively. The model reasonably simulates TOC and DOC concentrations for the calibrated streams. The simulated TOC concentrations had median relative errors within $\pm 16\%$ and average errors within $\pm 20\%$, except for Cloquet River at Burnett. Additionally, the model simulated DOC concentrations with a median relative error within $\pm 19\%$ for all streams (and average errors within $\pm 22\%$), consistent with the “Very Good” or “Good” ratings in Table 4-8. While average DOC is sometimes greater than average TOC for a given station, this is due to the larger sample size for DOC, with many samples reporting only TOC or only DOC, not paired results.

Table 4-6. Comparison of observed and simulated TOC concentration (mg/L), WY 2005-2021

Site	Model reach	Sample count	Observed median concentration (average concentration)	Simulated median concentration (average concentration)	Relative error on median concentration (average concentration)
St. Louis River near Superior Bay	202	5	13 (18)	14 (14)	-11% (-26%)
St. Louis River near Highway 23	204	5	20 (20)	18 (17)	-3% (-15%)
Thomson Reservoir	207	15	23 (22)	19 (20)	-11% (-10%)
St. Louis River at Forbes	249	5	14 (17)	14 (17)	-2% (-4%)
Whiteface Reservoir	289	16	19 (19)	19 (19)	-10% (-4%)
Island Lake Reservoir	407	15	17 (17)	14 (14)	-12% (-19%)
Alden Lake	410	15	19 (18)	21 (20)	8% (12%)
Wild Rice Lake Reservoir	423	15	13 (12)	12 (11)	-5% (-8%)
St. Louis River at Scanlon	502	23	23 (23)	22 (22)	-6% (-1%)
Cloquet River at Burnett	402+421	22	14 (13)	20 (21)	46% (56%)

Table 4-7. Comparison of observed and simulated DOC concentration (mg/L), WY 2005-2021

Site	Model reach	Sample count	Observed median concentration (average concentration)	Simulated median concentration (average concentration)	Relative error on median concentration (average concentration)
1. St. Louis River near Superior Bay	202	17	18 (20)	16 (16)	-21% (-21%)
2. St. Louis River near Highway 23	204	16	20 (22)	20 (21)	-2% (-3%)
3. Thomson Reservoir	207	21	22 (21)	20 (20)	-10% (-3%)
4. St. Louis river near Hwy 33	208	36	23 (24)	20 (20)	-16% (-18%)
5. Floodwood River	222	33	31 (31)	31 (33)	-5% (4%)
6. Swan River	232	31	21 (21)	24 (24)	19% (17%)
7. West Two River	243	36	13 (13)	10 (11)	-13% (-14%)
8. East Two River	247	38	10 (10)	11 (10)	-4% (2%)
9. St. Louis River at Forbes	249	60	16 (18)	18 (17)	-10% (-9%)
10. Embarrass River	251	21	15 (15)	16 (14)	-4% (-4%)
11. Whiteface River	279	27	28 (29)	28 (30)	-7% (4%)
12. County Ditch	281	15	45 (46)	40 (43)	-11% (-7%)
13. Whiteface Reservoir	289	15	19 (19)	19 (18)	-5% (-3%)
14. Island Lake Reservoir	407	15	15 (16)	14 (14)	-5% (-12%)
15. Alden Lake	410	15	19 (17)	21 (20)	14% (18%)
16. Wild Rice Lake Reservoir	423	15	11 (11)	12 (11)	7% (1%)
17. St. Louis River at Scanlon	502	38	19 (20)	20 (23)	10% (16%)
18. St. Louis River near Seven Beaver Lake	505	35	31 (33)	30 (29)	-9% (-12%)
19. Partridge River	260+261	20	24 (26)	24 (23)	-11% (-12%)
20. Cloquet River at Burnett	402+421	50	14 (14)	18 (20)	33% (41%)

4.3 INSTREAM MERCURY CALIBRATION

TMDLs will be developed for segments listed as impaired for elevated ambient THg and/or elevated fish tissue mercury concentrations, which are primarily due to MeHg. Fish tissue concentrations reflect bioaccumulation from lower trophic levels and are often weakly correlated with water column THg due to complexities that drive mercury methylation by bacteria such as temperature and oxygen, sulfate, and iron availability. Therefore, the models are calibrated for THg and MeHg using instream monitoring records.

As described in Section 3.0, the DOC simulation on the upland pervious land covers drives the mercury simulation in model reaches through the HSPF Mass Link block that is used to connect upland segments to model reaches. Separate DOC relationships are established for THg and MeHg.

Transport of THg and MeHg through the reach network, including lakes, reservoirs, and streams, is simulated subject to transit losses described by a first-order decay function that accounts for a variety of loss mechanisms including re-emission of gaseous mercury and net settling loss of insoluble precipitates such as cinnabar (HgS).

Duda et al. (2012) provides general performance targets for water quality constituents in HSPF simulations that are useful for a qualitative evaluation of the performance of the model to predict THg and MeHg concentrations (Table 4-8). Average annual relative errors are calculated from observed and simulated daily concentrations at a monitoring location. Evaluation of water quality simulations presents a challenge because water quality is not monitored continuously. Rather, grab samples represent conditions at a specific location at a point in time and may not be representative of average conditions across a broader waterbody and timeframe. Therefore, the qualitative ratings are applicable to sites with a minimum of 20 observations to reduce the impact of high leverage outliers.

Table 4-8. General performance targets for HSPF water quality simulation, relative error on daily values (Duda et al., 2012)

Variable	Very Good	Good	Fair	Poor
THg or MeHg	≤ 15%	15 – 25%	25 – 35%	> 35%

4.3.1 Sensitivity Analysis for the Watershed Mercury Model

Certain components of the watershed mercury model, such as mercury loading from point sources, are relatively well constrained by monitoring data. Further, as is summarized in Section 4.3.2.2, permitted point sources contribute only a small percentage of the total load, so the model has low sensitivity to uncertainty in specifying these sources.

The primary component of the loads of both THg and MeHg is nonpoint source runoff that transports mercury from soils, vegetative matter, and rainfall, most of which is ultimately derived from ongoing and historic atmospheric deposition. These nonpoint sources of mercury are simulated indirectly based on the linked processes of dissolved organic carbon and THg and MeHg transport. The mercury loading estimates produced by the model are subject to the uncertainty in simulating organic carbon and the uncertainty in the relationship between organic carbon concentrations and THg/MeHg concentrations in runoff from different land use types.

Fortunately, there are relatively numerous instream measurements of THg and MeHg that allow empirical calibration of the model to reproduce observed concentrations. The calibration process yields direct

measures of the precision of the simulation. This information, however, is available primarily at the scale of larger watersheds and provides relatively less evidence to constrain the estimates of loads from individual land uses within the contributing area.

Watershed model predictions of mercury loads and concentrations are most sensitive to the ratios used to model THg and MeHg loads from DOC loads. Changes in these values result in linear changes in simulated mercury loads. Model results are also highly sensitive to uncertainties in the simulation of DOC. Fortunately, the net results of these two components are relatively well constrained by instream monitoring data.

As will be seen in the following sections, the model is able to reproduce average THg and MeHg concentrations at most (but not all) monitoring sites within about 25 percent. It further appears that on the order of one-third of the total variability in THg is due to the DOC calibration with the remainder presumably due to uncertainties inherent in the relationship between DOC to THg and MeHg.

Model predictions for mercury are also sensitive to the specification of the first-order decay rate for losses during transit. This is particularly important for MeHg, which can be converted in the water column into gaseous elemental mercury via photo-demethylation, which can then be volatilized into the atmosphere. Calibrated exponential decay rates for MeHg are highly variable across the watershed and range from 0.01 to 0.40 per day with most reaches around 0.08 per day. Although decay is expressed as an exponential with the form $(1 - \exp(-K \cdot T))$ where K is the decay rate per unit time and T is the time duration, the response is nearly linear to a value of K of 0.08 is equivalent to a mass loss of 7.7 percent per day of travel.

The mercury simulations have some, but relatively much lower sensitivity to the following:

- Errors in flow, though these errors are well constrained
- Errors in temperature simulation, as decay has a temperature adjustment
- Other aspects not considered in the HSPF model, such as
 - a. Detailed simulation of the Hg cycle within lakes and reservoirs
 - b. Hg methylation in riparian sediments that do not involve the introduction of new DOC into the watershed system

4.3.2 Calibration to Observed Mercury

Data availability and timespan varies widely between different monitoring stations. The model runs from January 1993 to September 2021, although the period before October 1995 was used for model spin up to allow hydrologic and water quality to reach dynamic equilibrium with boundary condition inputs. THg and MeHg simulations in the watershed model were calibrated to data collected between 2008 and 2021 to include recent information consistent in time with the updated model land use from a broad range of stations.

Data were checked for quality assurance. Physically impossible values (e.g., negative concentrations) were screened – none were found. Zero values for concentration were also screened – none were found. Nondetect (censored) data were replaced with one-half the reported censoring level. In total, 30 out of 1,627 (1.84%) and 30 out of 1,265 (2.37%) of the water samples were identified as nondetects for mercury (Hg) and methylmercury (MeHg), respectively. It is well established that calculating statistics with replacement of censored data with one-half the detection limit can yield suboptimal or biased estimates and a variety of sophisticated methods are available to address this problem (Helsel, 2005; Bolks et al., 2014); however, because the count of censored data was small, the use of one-half the detection limit is not expected to introduce significant bias in this study.

The St. Louis and Cloquet HSPF model provides mercury simulations for both HUC8s down to Fond du Lac Dam, which is the boundary between the free-flowing river and the estuary. The SLRE has bi-

directional flow due to the Lake Superior seiche that is not suitable for simulation with HSPF, so that part of the system is simulated separately with more sophisticated hydrodynamic models as described in Section 4.4.

4.3.2.1 St. Louis and Cloquet Watershed Instream Mercury Calibration

At the edge of the stream, linkage relationships were applied as ratios to model instream mercury from the DOC simulation on the upland pervious land covers; this was done through the HSPF Mass Link blocks that are used to connect PERLNDs and IMPLNDs to model reaches (RCHRES). Separate DOC ratios were established for THg and MeHg. Initial values were estimated from paired data, but these were significantly modified during calibration. The calibration-informed ratios for upland sources applied in the St. Louis and Cloquet River watersheds model are summarized in Table 4-9 and Table 4-10 for total mercury and dissolved methylmercury, respectively. Linkage ratios are for labile organic carbon (which HSPF tracks as the carbonaceous biochemical oxygen demand or CBOD equivalent) and for dead refractory carbon. Both are specified as fractions of the total organic matter yield from upland areas through both surface and subsurface pathways.

Comparisons between model predictions and sample observations are made to evaluate the ability of the model to represent mercury and methylmercury conditions in the St. Louis and Cloquet watershed. Table 4-11 and Table 4-12 list the average and median errors relative to observed concentrations. Key stations that have 20 or more observations are denoted in bold.

Figure 4-10 shows that observed and predicted concentrations at these stations generally match well.

The observed average concentrations of THg and MeHg at stream calibration locations were within the ranges of 1.3 to 6.2 ng/L and 0.13 to 0.60 ng/L, respectively. The model's average simulated concentrations ranged from 1.2 to 6.7 ng/L for THg and 0.14 to 0.50 µg/L for MeHg. Overall, the model adequately simulated the concentrations of THg and MeHg for the watershed, with the relative average error on concentrations being less than 35% for THg and MeHg for all reaches.

The simulated THg average concentration at the 18 monitored sites is greater than the chronic water quality criterion of 0.0013 µg/L (1.3 ng/L) at all sites except for Wild Rice Lake Reservoir (reach 423). The percentage of concentrations greater than the criterion is near 100 percent at many sites (Table 4-13), indicating that large reductions will be needed.

For St. Louis River near Hoyt Lakes, the model tends to under-predict THg at flows above about 50 cfs; however, the majority of samples at this station are from the summer of 2013, so it is difficult to draw firm conclusions about whether the error represents a systematic bias or is due to the specific conditions present in 2013. At the next downstream station, St. Louis River at Forbes, the model on average over-predicts THg and a compromise is needed to fit the data at both stations simultaneously. For St. Louis River at Scanlon, the model tends to over-predict dMeHg, although the data set is small (10 samples), and the average error is mostly attributable to two outliers. A similar over-prediction is not seen for the observations upstream at St. Louis River near Cloquet and there are only a few samples available between Scanlon and Fond du Lac Dam. One possibility is that there is a substantial loss of dMeHg due to photo-demethylation in the series of impoundments between Cloquet and Fond du Lac Dam (see further discussion in Section 5.2.1).

Figure 4-11 and Figure 4-12 show time series for the THg and dMeHg simulation for St. Louis River at Forbes, which is one of the more data rich sites. Simulated and observed data are in general agreement. Typical of other stations, data collection has been sporadic. Small amounts of THg observations are

available across the calibration period, although there is a gap from 2014 to 2018. The MeHg observations are not always paired with the THg observations and consist of intensive data collection in 2012 and 2013 with a limited number of observations from 2009 and after 2013.

Across all sites, the weighted (by sample size) average error on concentration for THg is 5% and for dMeHg -1%; the average absolute error for THg is 32% and for dMeHg 31%. Because the DOC linkage ratios were adjusted during calibration based on performance of the Hg models the uncertainty associated with the linkage ratios cannot be analyzed directly. However, the weighted average absolute error for the DOC simulations is approximately 10% from which we can infer that the assumption of fixed linkage ratios increases the uncertainty in THg and MeHg by approximately a factor of 3, although other factors such as loss rates during transit also affect this estimate.

Table 4-9. THg to DOC linkage ratios for the St. Louis and Cloquet watersheds HSPF model

Source Category	Flow Type	Pervious Land Covers (Other)	Mine-Impacted Wetlands and Barren Lands	Peatlands/ Wetlands	Higher Sulfate Peatlands/ Wetlands
Carbon from BOD via Organic Matter	Surface Flow	1.14E-07	1.14E-07	9.11E-08	9.11E-08
	Interflow	1.43E-07	1.43E-07	1.15E-07	1.15E-07
	Groundwater Flow	6.51E-09	6.51E-09	5.2E-09	5.20E-09
Dead Refractory Carbon via Organic Matter	Surface Flow	1.18E-06	1.18E-06	9.42E-07	9.42E-07
	Interflow	1.85E-06	1.85E-06	1.48E-06	1.48E-06
	Groundwater Flow	6.73E-08	6.73E-08	5.38E-08	5.38E-08
Carbon Sources Combined	Surface Flow	1.29E-06	1.29E-06	1.03E-06	1.03E-06
	Interflow	1.99E-06	1.99E-06	1.60E-06	1.60E-06
	Groundwater Flow	7.38E-08	NA*	5.91E-08	5.91E-08

Note: * In some mine-impacted areas groundwater flow from wetlands and barren land is assumed to be cut off due to interception by pumped mine pits.

Table 4-10. dMeHg to DOC linkage ratios for the St. Louis and Cloquet watersheds HSPF model

Source Category	Flow Type	Pervious Land Covers (Other)	Mine-Impacted Wetlands and Barren Lands	Peatlands/ Wetlands	Higher Sulfate Peatlands/ Wetlands
Carbon from BOD via Organic Matter	Surface Flow	6.60E-09	6.60E-09	7.92E-09	1.19E-08
	Interflow	8.44E-09	8.44E-09	1.01E-08	1.52E-08
	Groundwater Flow	5.28E-10	5.28E-10	6.33E-10	9.5E-10
Dead Refractory Carbon via Organic Matter	Surface Flow	6.82E-08	6.82E-08	8.19E-08	1.23E-07
	Interflow	1.09E-07	1.09E-07	1.31E-07	1.97E-07
	Groundwater Flow	5.46E-09	5.46E-09	6.55E-09	9.83E-09
Carbon Sources Combined	Surface Flow	7.48E-08	7.48E-08	8.98E-08	1.35E-07
	Interflow	1.18E-07	1.18E-07	1.41E-07	2.12E-07
	Groundwater Flow	5.99E-09	NA*	7.19E-09	1.08E-08

Note: * In some mine-impacted areas groundwater flow from wetlands and barren land is assumed to be cut off due to interception by pumped mine pits.

Table 4-11. THg calibration summary (water year 2005 - 2021)

Station ID(s)	Description	HSPF Reach	Sample Count	Average Concentration (ng/L)		Relative Error on Concentration	
				Observed	Simulated	Average	Median
SLR 2 *	Thomson Reservoir	207	20	3.81	3.54	-7.0%	-7.9%
S003-973 *	St. Louis River near Cloquet	208	25	4.18	4.07	-2.7%	-4.0%
S005-755 *	Floodwood River at CR-835	222	33	3.84	5.16	34.5%	12.8%
S005-770 *	Swan River at CR-750	232	20	5.57	5.53	-0.6%	-0.9%
S004-601 *	West Two Rivers at CR-661 (Fraser Rd)	243	21	2.01	2.40	19.8%	2.6%
S007-615 *	East Two Rivers at Town Line Rd	247	22	3.04	3.19	4.8%	-38.4%
S000-119 *	St. Louis River at Forbes	249	39	3.63	4.18	15.4%	14.5%
S005-751 *	Embarrass River	251	20	2.58	1.72	-33.5%	-32.6%
S001-472 *	Cobb River at 250 th St	254	21	2.43	2.19	-10.0%	-8.6%
S005-752	Partridge River	260+261	19	5.22	4.27	-18.2%	-33.7%
S007-052	Stony Creek at CSAH-83	278	9	6.19	5.71	-7.7%	-24.3%
S005-763 *	Whiteface River	279	28	5.17	4.80	-7.2%	-12.4%
S005-147 *	Cloquet River near Burnett	402+421	46	2.96	3.77	27.4%	9.7%
69-0372-01-201	Island Lake Reservoir	407	14	3.46	3.16	-8.6%	-0.7%
69-0131-00-201	Alden Lake	410	13	3.89	4.17	7.1%	-6.1%
69-0371-00-100	Wild Rice Lake Reservoir	423	13	1.34	1.17	-12.2%	-1.0%
S005-089 *	St. Louis River at Scanlon	502	34	4.41	5.49	24.5%	4.8%
S000-631 *	St. Louis River near Hoyt Lakes	505	23	6.02	4.74	-21.3%	-50.5%

Note: * Stations with 20 or more samples are indicated in boldface.

Table 4-12. dMeHg calibration summary (water year 2005 - 2021)

Station ID(s)	Description	HSPF Reach	Count	Average Concentration (ng/L)		Relative Error on Concentration	
				Observed	Simulated	Average	Median
SLR 2	Thomson Reservoir	207	6	0.227	0.190	-16.35%	-13.96%
S003-973 *	St. Louis River near Cloquet	208	33	0.281	0.273	-2.86%	8.12%
S005-755	Floodwood River at CR-835	222	19	0.274	0.329	19.90%	-7.88%
S005-770 *	Swan River at CR-750	232	29	0.321	0.314	-2.16%	-6.02%
S004-601 *	West Two Rivers at CR-661 (Fraser Rd)	243	33	0.185	0.168	-9.39%	-18.13%
S007-615 *	East Two Rivers at Town Line Rd	247	36	0.113	0.143	27.42%	9.09%
S000-119 *	St. Louis River at Forbes	249	42	0.382	0.331	-13.35%	-4.26%
S005-751	Embarrass River	251	19	0.211	0.198	-6.26%	-9.28%
S005-752	Partridge River	260+261	19	0.529	0.380	-28.29%	-5.14%
S007-052	Stony Creek at CSAH-83	278	8	0.601	0.497	-17.28%	-34.41%
S005-763	Whiteface River	279	15	0.427	0.313	-26.73%	-14.78%
S005-147 *	Cloquet River near Burnett	402+421	20	0.168	0.185	10.23%	-7.16%
S005-089	St. Louis River at Scanlon	502	10	0.198	0.255	29.28%	15.04%
S000-631 *	St. Louis River near Hoyt Lakes	505	31	0.359	0.373	3.91%	21.63%

Note: * Stations with 20 or more samples are indicated in boldface.

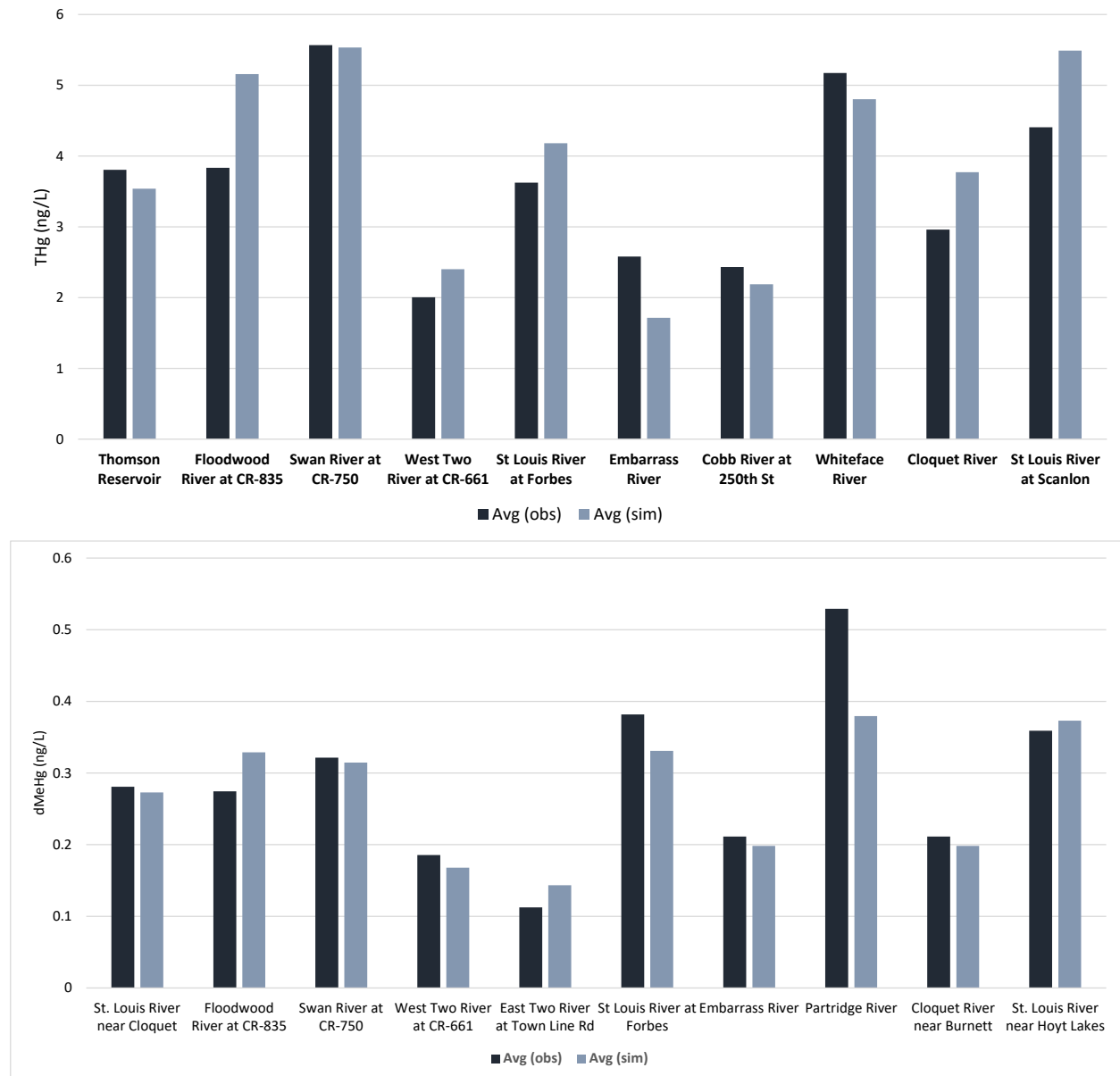


Figure 4-10. Comparison of observed and simulated average THg and MeHg concentrations at stations with at least 20 observations

Table 4-13. Percentage of simulated daily THg concentrations greater than the chronic criterion of 0.0013 µg/L at water quality monitoring stations (model period water year 2008–2021)

Monitoring site	Model Reach	Percent > 1.3 ng/L
Thomson Reservoir	R207	94.60%
St Louis River near Cloquet	R208	100.00%
Floodwood R at CR-835	R222	100.00%
Swan R at CR-750	R232	100.00%
West Two R at CR-661 (Fraser Rd)	R243	64.00%
East Two R At Town Line Rd	R247	89.68%
St Louis River at Forbes	R249	92.11%
Embarrass River	R251	80.59%
Cobb R at 250th Street	R254	81.91%
Partridge River	R260+R261	100.00%
Stony Ck at CSAH-83	R278	100.00%
Whiteface River	R279	100.00%
Cloquet River	R402+R421	94.39%
Island Lake Reservoir	R407	99.36%
Alden Lake	R410	90.48%
Wild Rice Lake Reservoir	R423	41.06%
St. Louis R at Scanlon ^A	R502	86.98%
St. Louis R nr Hoyt Lakes	R505	100.00%

^a Station is located immediately downstream of the St. Louis River reaches that border Fond du Lac Reservation, where the water quality standard is 0.77 ng/L THg.

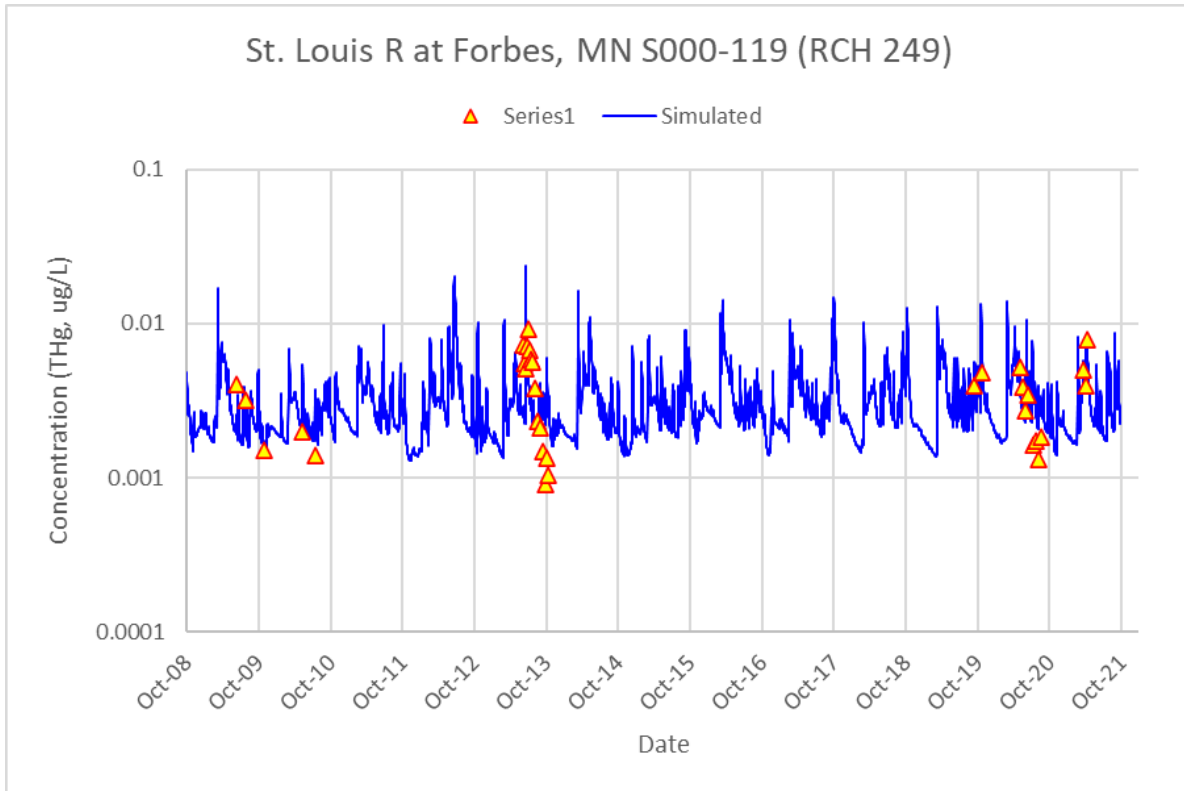


Figure 4-11. THg time series for St. Louis River at Forbes

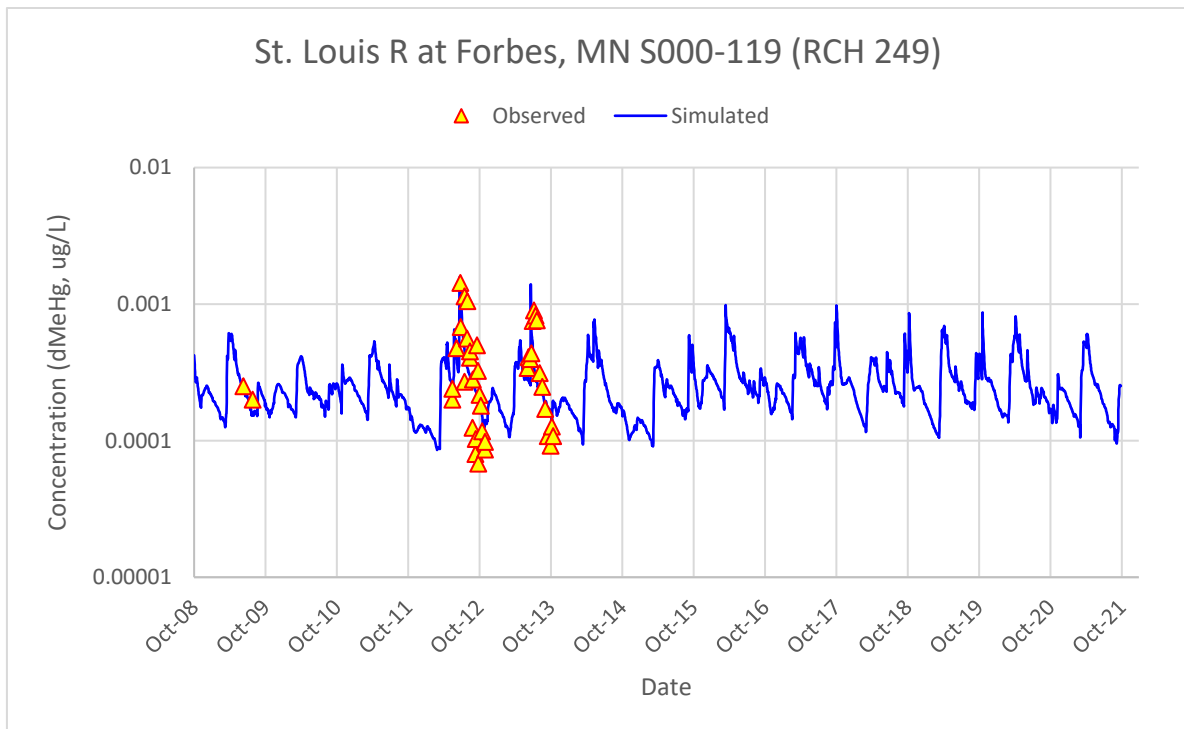


Figure 4-12. dMeHg time series for St. Louis River at Forbes

4.3.2.2 Duluth Urban Watershed Instream Mercury Calibration

The many small tributaries on the northwest side of the St. Louis River Estuary downstream of Fond du Lac Dam are simulated with the detailed Duluth Urban Watershed HSPF model (Tetra Tech, 2022b). As in the St. Louis and Cloquet HSPF model, the direct link between dissolved organic carbon (DOC) and mercury is used to represent upland transport of mercury.

The Duluth Urban Watershed model is rigorously calibrated for hydrology and conventional pollutants; however, very few data are available for mercury calibration. Parameters for the THg and MeHg simulation are therefore primarily based on the calibration of the St. Louis and Cloquet model. The calibration was refined by comparing simulated THg and MeHg concentrations and loads against limited observations for five Duluth streams: East Branch Amity Creek, Chester Creek, Kingsbury Creek, Tischer Creek, and Lester River – of which only Kingsbury Creek drains to the St. Louis River estuary. These data were collected in 2003-2006 in research sponsored by the Minnesota Sea Grant College Program and documented in Ruzyski et al. (2011; data table relayed by Bruce Monson, MPCA). The model refinements for the urban area involved adjusting the DOC to THg and DOC to MeHg linkage ratios and multipliers for surface flow, interflow, and groundwater flow to better reflect observed THg and MeHg concentrations and loads during different flow regimes.

Table 4-14 and Table 4-15 show the DOC to THg and MeHg linkage ratios used in the Duluth model. The linkage ratios for most land uses are the same as those used for the general St. Louis and Cloquet Watersheds HSPF model (Table 4-9 and Table 4-10) except that the ratios for peatlands/wetlands were adjusted higher during calibration for the Duluth model. Results of simulated THg and MeHg concentrations for the Duluth urban watershed sites are presented in Figure 4-13 and Figure 4-14. Statistical metrics summarizing the model performance are presented in Table 4-16 and Table 4-17.

The model was able to simulate THg concentrations with an average relative error of less than $\pm 35\%$ for all streams, except for Lester River at the northern end of Duluth; however, the statistics for Lester River are highly uncertain as the model performance is evaluated based on only three observations. The HSPF simulation predicted MeHg concentrations with an average relative error of less than $\pm 21.6\%$ for all streams, except for East Branch Amity, which showed an average relative error of 83.3%. However, note that there were only four available MeHg measurements for East Branch Amity Creek, with three taken during low flow (< 3 cfs) and one during a storm event (56.45 cfs). As a result, the ability to rigorously evaluate the model's calibration performance during high flow conditions is limited, and the calibration metrics may unfairly overestimate bias in the model output for this stream. A similar issue exists for Chester Creek, where a THg sample taken during high flow (47.6 cfs) significantly impacted the simulation error. Thus, using relative error on median concentration and load may be a better measure for comparing the model's performance against the observation.

Results for the Duluth urban simulations are consistent with results for urban stormwater collected at 51 sites across the U.S. (which included one in Minneapolis but none from Duluth) and reported by Masoner et al. (2019). Masoner et al. report THg concentrations from 4 to 180 ng/L with a median of 26 ng/L while simulated results for the four calibration watersheds under higher flow conditions (operationally defined here as simulated flow above the 90th percentile) have an average of 7.2 and a median of 5.3 ng/L THg. These concentrations are within the range but near the low end of Masoner's results but would be expected to be lower because Masoner et al. were sampling urban storm drains whereas the model has a mix of pervious and impervious land in the drainage area. The model results are closer to Masoner et al. for MeHg. Masoner et al. report a range of MeHg concentrations from <0.04 to 1.0 ng/L with a median of 0.19 ng/L, while model results for higher flow conditions had an average of 0.204 and a median of 0.181 ng/L MeHg.

Table 4-14. THg to DOC linkage ratios for the Duluth Urban Watershed HSPF model

Source Category	Flow Type	Pervious Land Covers (Other)	Peatlands/Wetlands
Carbon from BOD via Organic Matter	Surface Flow	1.14E-07	2.62E-07
	Interflow	1.43E-07	2.16E-07
	Groundwater Flow	6.51E-09	3.61E-08
Dead Refractory Carbon via Organic Matter	Surface Flow	1.18E-06	8.13E-07
	Interflow	1.85E-06	8.41E-07
	Groundwater Flow	6.73E-08	1.12E-07
Carbon Sources Combined	Surface Flow	4.46E-07	1.07E-06
	Interflow	4.53E-07	1.06E-06
	Groundwater Flow	6.15E-08	1.48E-07

Table 4-15. dMeHg to DOC linkage ratios for the Duluth Urban Watershed HSPF model

Source Category	Flow Type	Pervious Land Covers (Other)	Peatlands/Wetlands
Carbon from BOD via Organic Matter	Surface Flow	6.60E-09	8.87E-09
	Interflow	8.44E-09	8.87E-09
	Groundwater Flow	5.28E-10	4.44E-09
Dead Refractory Carbon via Organic Matter	Surface Flow	6.82E-08	2.76E-08
	Interflow	1.09E-07	3.45E-08
	Groundwater Flow	5.46E-09	1.38E-08
Carbon Sources Combined	Surface Flow	7.56E-09	3.65E-08
	Interflow	9.29E-09	4.34E-08
	Groundwater Flow	3.78E-09	1.82E-08

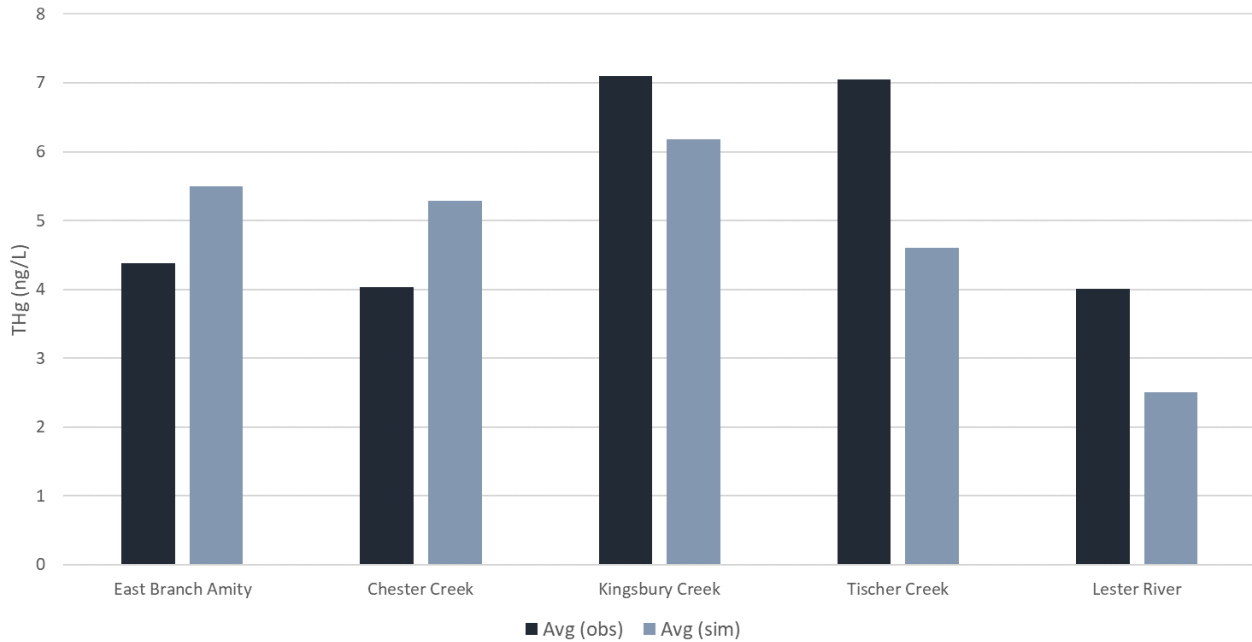


Figure 4-13. THg simulated concentrations versus observations for five model reaches in Duluth Urban watershed

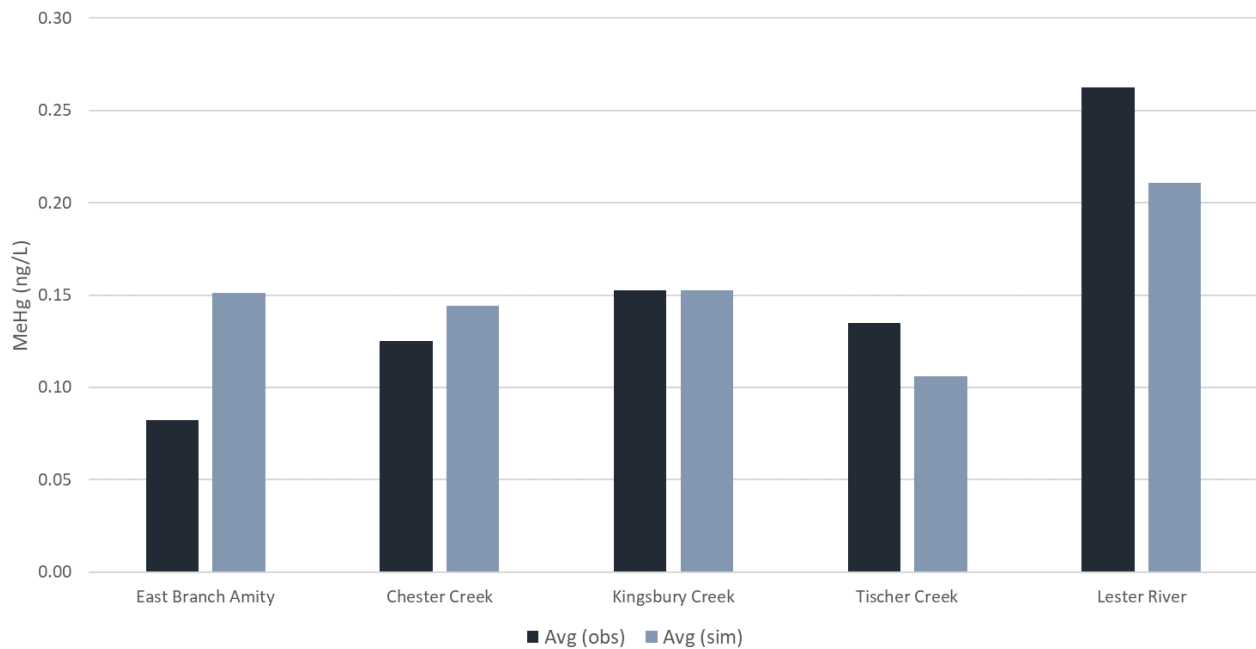


Figure 4-14. MeHg simulated concentrations versus observations for five model reaches in Duluth Urban Watershed

Table 4-16. THg calibration summary statistics for Duluth Urban Watershed model

Description	Count	HSPF Reach	Average Concentration (ng/L)		Relative Error on Concentration (%)	
			Observed	Simulated	Average	Median
East Branch Amity	9	454	4.38	5.50	25.6%	-10.4%
Chester Creek	9	386	4.03	5.29	31.1%	9.0%
Kingsbury Creek	10	272	7.10	6.19	-12.9%	-23.0%
Tischer Creek	10	407	7.05	4.60	-34.7%	-17.6%
Lester River	3	483	4.01	2.51	-37.5%	-10.6%

Note: Data collection documented in Ruzyski et al., 2011, which does not provide station identifiers.

Table 4-17. MeHg calibration summary statistics for Duluth Urban Watershed

Description	Count	HSPF Reach	Average Concentration (ng/L)		Relative Error on Concentration (%)	
			Observed	Simulated	Average	Median
East Branch Amity	4	454	0.083	0.151	83.3%	43.0%
Chester Creek	4	386	0.125	0.144	15.3%	30.4%
Kingsbury Creek	4	272	0.153	0.153	0.2%	17.1%
Tischer Creek	4	407	0.135	0.106	-21.6%	-19.8%
Lester River	3	483	0.262	0.211	-19.7%	-7.2%

Note: Data collection documented in Ruzyski et al., 2011, which does not provide station identifiers.

4.4 MERCURY SOURCE ASSESSMENT

Following the HSPF model calibration, existing at-source THg and MeHg loads were tabulated for nonpoint and permitted wastewater sources. This tabulation is for water years 2012-2021 to match the time period used for the TMDL calculations by MPCA. Based on model calibration statistics, uncertainty in the total load estimates is on the order of $\pm 25\%$ due primarily to the uncertainty in nonpoint load estimates. Point source loads are known more precisely for larger facilities that have reliable mercury monitoring but constitute only a small portion of the total load amounts.

The modeling evaluates loads for nonpoint sources by land use/cover, permitted stormwater entities (MS4s), wet atmospheric deposition, and permitted wastewater dischargers. To better understand THg/MeHg sources and to support the assignment of load allocations and wasteload allocations, THg and MeHg loads were tabulated for subset drainage areas or source assessment zones within the broader watershed. These zones are aggregated up from the model subbasins to approximately the HUC10 scale. A benefit of this approach is that it provides finer scale loading information compared to evaluating source contributions only at the watershed-scale. The source assessment zones are (refer to Figure 4-15):

- St. Louis River upstream of confluence with Partridge River
- Partridge River
- Embarrass River
- St. Louis River between confluences with Partridge River and East Two River
- East Two River
- West Two River
- Stony Creek
- Swan River
- Whiteface River
- St. Louis River between confluences with East Two River and Floodwood
- Floodwood River
- Cloquet River above Island Reservoir
- Cloquet River below Island Reservoir
- St. Louis River between confluence with Floodwood to Fond du Lac dam
- St. Louis River below Fond du Lac Dam. This zone includes four impaired segments covering the St. Louis River Estuary and Duluth Superior Harbor, as well as assessment unit 04010201-B66, which is defined as a stream segment from Fond du Lac Dam to the beginning of the estuary. (Note that a full discussion of upland loads within this zone is included in Section 5.2.1).

Nonpoint source loads of THg by land cover type are summarized in Figure 4-16. Forest is the greatest overall source of THg load because it occupies the majority of the watershed; however, the loading rates are highest for peatlands and wetlands. Spatially, the total loading rates are highest in the northwest zones with many drained peatlands and in the Duluth urban area downstream of Fond du Lac Dam. Loads are elevated in the urban area due to direct runoff of atmospheric deposition from impervious surfaces. The point source loads are only about 1 percent of the THg load over the entire watershed and less than 1 percent of the dMeHg load.

Nonpoint source loading of MeHg by land cover type and loading rates by zone are shown in Figure 4-17. MeHg loads are more strongly associated with drained peatlands than THg loads. The MeHg loading rates are lowest for the Duluth urban area because there are fewer wetlands and atmospheric deposition is not a significant source of MeHg.

Total loads and loading rates by land cover and zone are summarized in Table 4-18 and Table 4-19. The zone totals in these tables include only the areas upstream of Fond du Lac Dam and the mass balance for the complex sources and sinks in the St. Louis River Estuary are presented in Section 5.5.

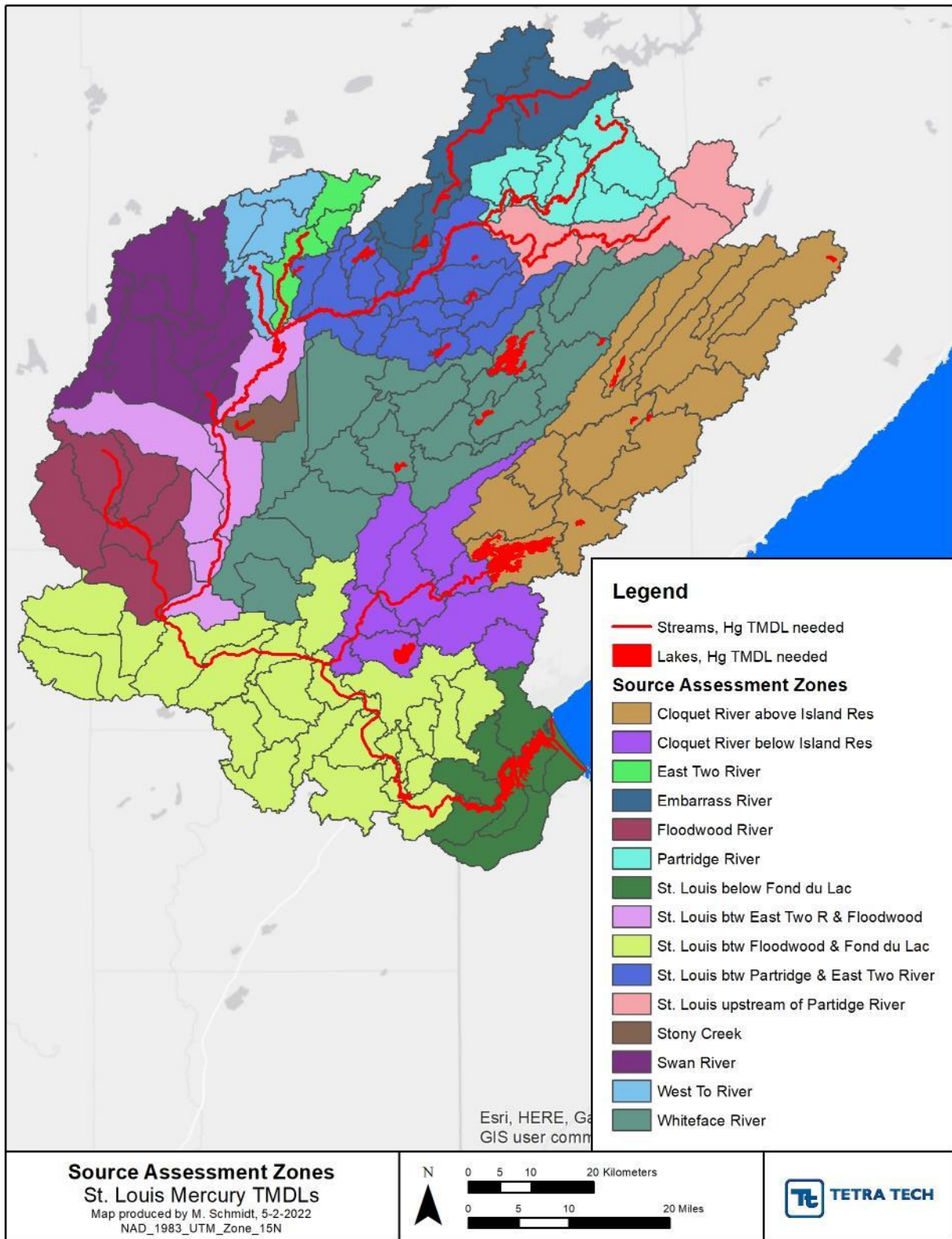


Figure 4-15. Source assessment zones for the Hg TMDLs

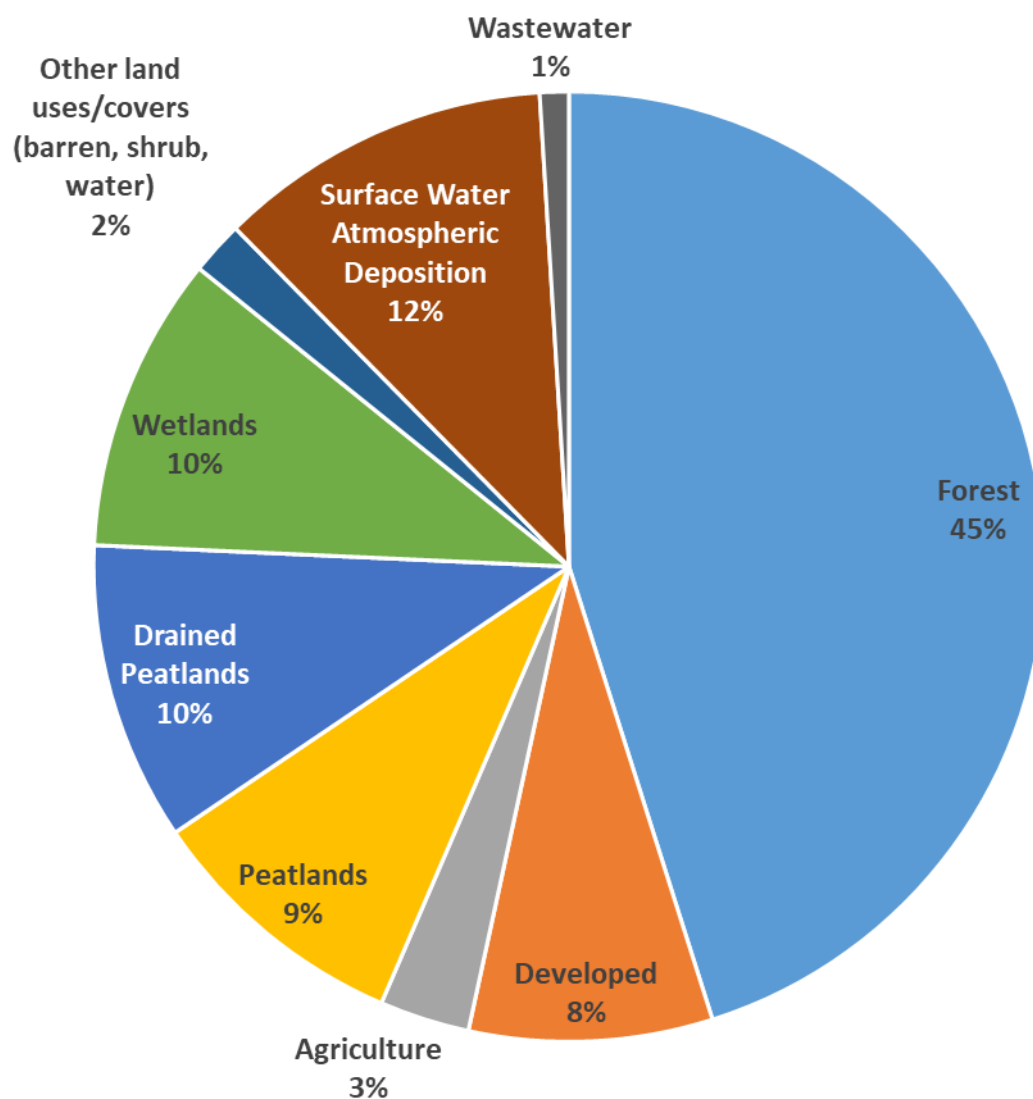


Figure 4-16. Sources of THg Load to the SLRW

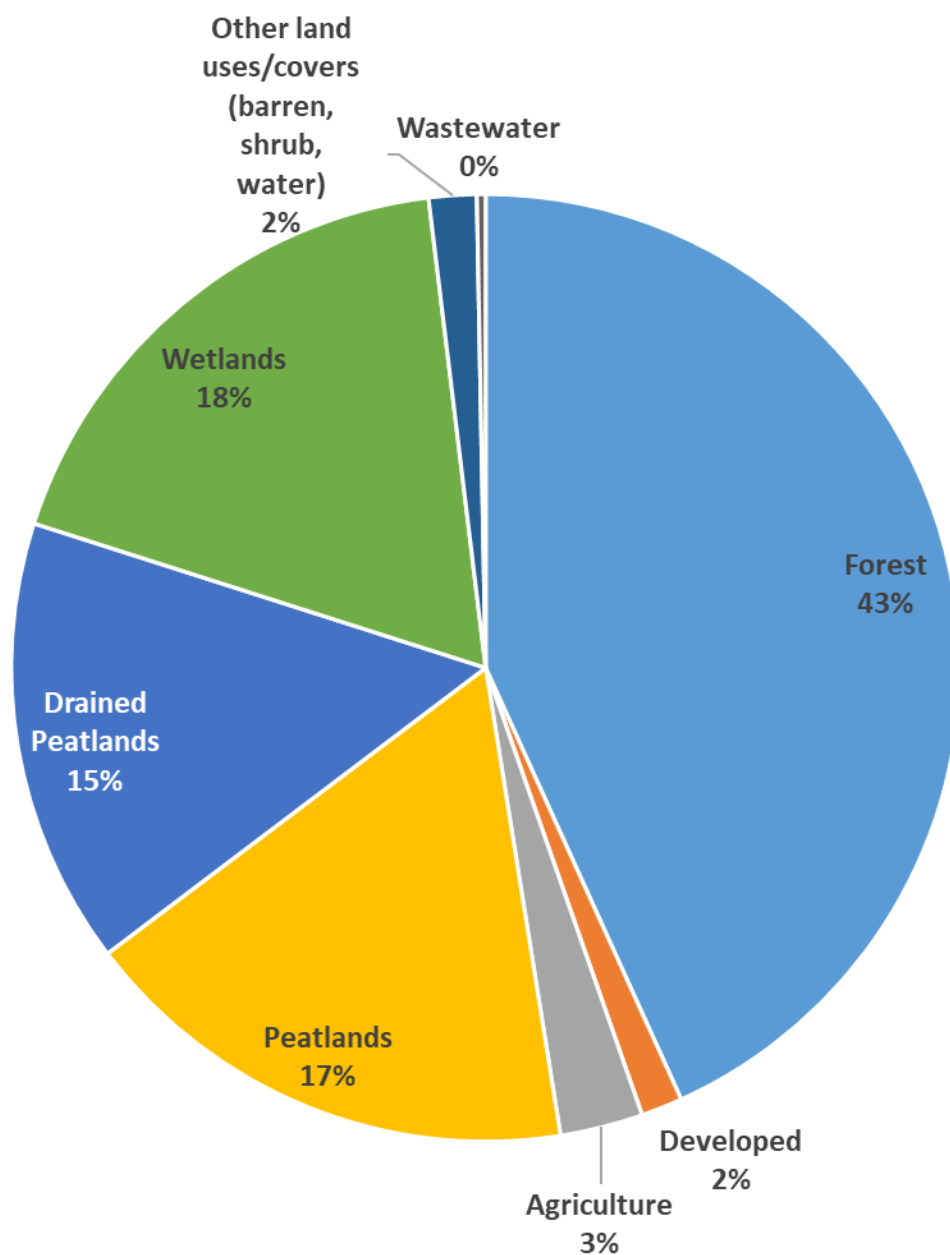


Figure 4-17. Sources of MeHg Load to the SLRW

Table 4-18. THg and MeHg loads and loading rates by land cover and source type ^a

Land Cover	Area (Hectares)	THg (g/yr)	MeHg (g/yr)	THg (mg/ha/yr)	MeHg (mg/ha/yr)
Forest	445,868	10,024.2	640.9	22.48	1.44
Developed/ Roads	26,390	1,839.9	21.0	69.72	0.79
Cropland/ Pasture	22,311	679.4	41.9	30.45	1.88
Peatlands	152,098	2,017.7	255.1	13.27	1.68
Drained Peatlands	80,174	2,261.0	225.8	28.20	2.82
Wetlands	168,853	2,240.2	268.9	13.27	1.59
Other (barren, shrub, water)	66,438	402.9	24.1	6.06	0.36
Wet atm. deposition to model reaches	14,886	1,736.8	0.0	116.68	0.00
Dry atm. deposition to model reaches		794.3	0.0	53.36	0.00
Point Sources, Industrial	NA	79.9	1.6	NA	NA
Point Sources, Domestic	NA	140.0	2.8	NA	NA
Total	977,017	22,216.4	1,482.1	NA	NA

Notes: NA = Not Applicable. The HSPF model estimates of area, Hg load, and Hg loading rate by land cover and source type includes the area and loads generated within the St. Louis River watershed below Fond du Lac Dam zone and discharging to the estuary for completeness. For a full discussion of loads to the estuary refer to Section 5.2.1.

Table 4-19. THg and MeHg loads by zone

Zone	THg Sum (g/yr)	MeHg Sum (g/yr)
St. Louis River upstream of Partridge River	545.38	47.72
Partridge River	662.43	57.62
Embarrass River	756.07	60.87
St. Louis River between Partridge and East Two River	1,157.74	88.52
East Two River	332.82	15.03
West Two River	555.50	30.53
Stony Creek	169.49	13.91
Swan River	1,541.95	93.62
Whiteface River	3,979.30	287.51
St. Louis River between East Two River and Floodwood	1,193.92	88.55
Floodwood River	964.81	82.92
Cloquet River above Island Reservoir	3,402.61	205.21
Cloquet River below Island Reservoir	1,652.72	97.71
St. Louis River between Floodwood and Fond du Lac Dam	3,719.72	262.15
St. Louis River below Fond du Lac Dam ^a	See note	See note
Total (excluding St. Louis River below Fond du Lac Dam)	20,634.47	1,431.88

- a. The HSPF model estimate of upland mercury loads generated below Fond du Lac Dam and discharging to the estuary are omitted from this table. For a full discussion of loads to the estuary refer to Section 5.2.1.

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5.0 MERCURY MODEL DEVELOPMENT FOR THE ST. LOUIS ESTUARY AND HARBOR

As noted above, the mercury model for the estuary and harbor is based primarily on two existing models, the USGS EFDC hydrodynamic model (Smith et al., 2020) and the preliminary WASP water quality model developed by RTI (2013b).

For the USGS EFDC model, the primary calibration and validation runs are for the ice-free periods of 2016-17, for which water surface elevations and currents at the Lake Superior boundary were available from a detailed Advanced Circulation (ADCIRC) model of western Lake Superior (Hayter et al., 2015). The EFDC model contains 11,326 grid cells with four vertical layers and extends out into Lake Superior for 7.5 km to give the model enough stability to transition from the relatively shallow depths of the estuary to the deeper depths in the open lake (Figure 5-1).

In addition to the 2016 and 2017 simulations described in the report, Smith et al. also completed simulations for 2012 and 2019, although the lake boundary conditions for these years had to be based on interpolated buoy observations and completed the development of model forcing time series for the entire 2008 to 2019 period. All model files were provided by USGS via ScienceBase (<https://doi.org/10.5066/P990OUS6> and <https://doi.org/10.5066/P9U1XXG0>).

The RTI (2013b) WASP model has flows derived from the RTI EFDC model and covers the same extent as the USGS EFDC model for the harbor and estuary, with some truncation of the area within Lake Superior. WASP aggregates the study area as 26 major water column and underlying sediment segment sets extending from Fond du Lac Dam out into the lake (Figure 5-2).

Most of the water column areas are represented with multiple layers including water column sub-segments (1 deep on the shallow edges, 2 deep in the middle of the channel as shown in Figure 5-3), yielding a total of 73 water column sub-segments. The channel vs. edge areas were delineated at approximately the 1 m depth contour. In Tetra Tech's rebuild of the WASP model, each water column segment or set of segments has an underlying surface sediment layer. The surface sediment layers are in turn underlain by seven grouped subsurface sediment layers for a total of 134 model segments.

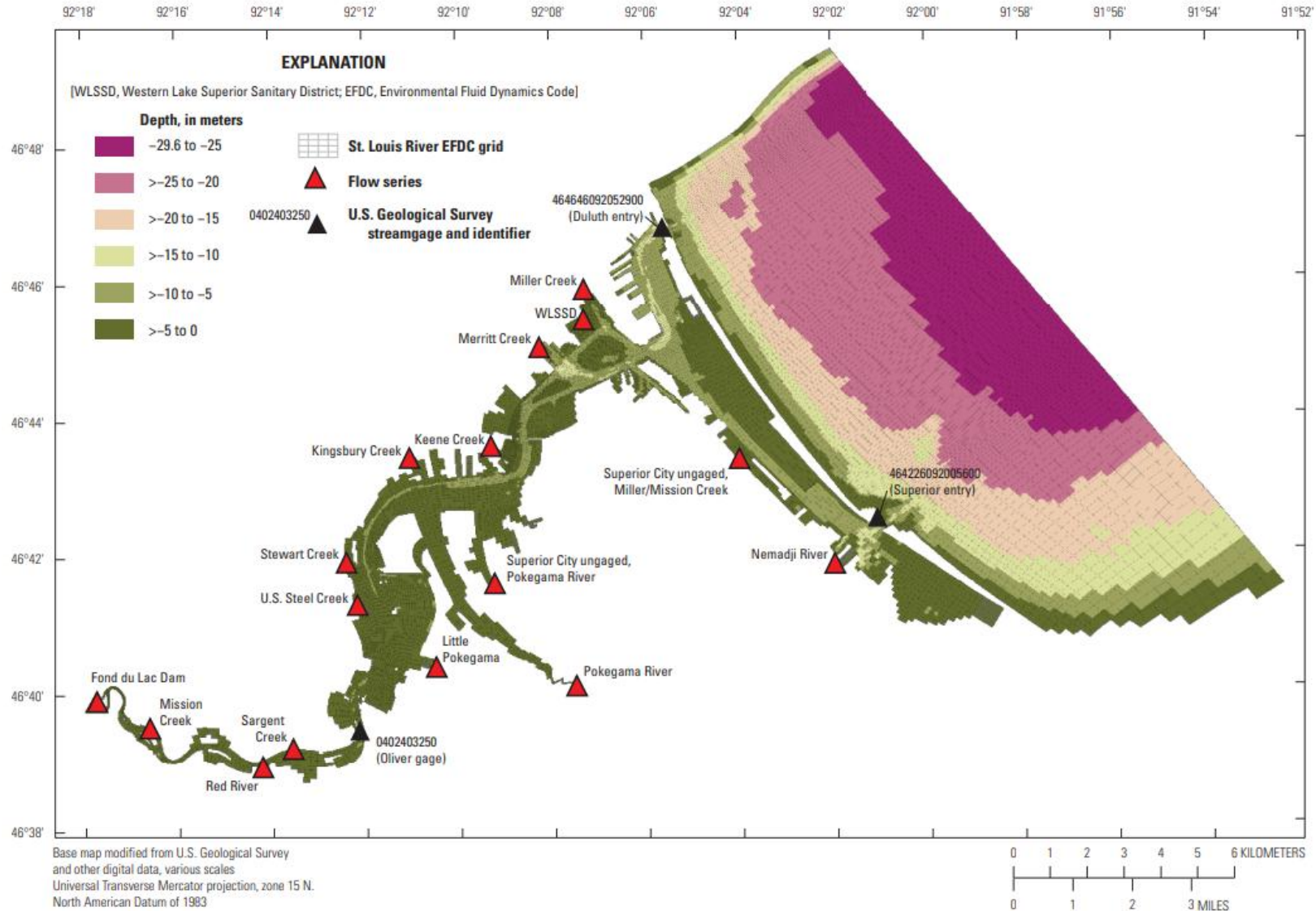


Figure 5-1. USGS EFDC model of St. Louis River Estuary/Duluth Harbor (from Smith et al., 2020)

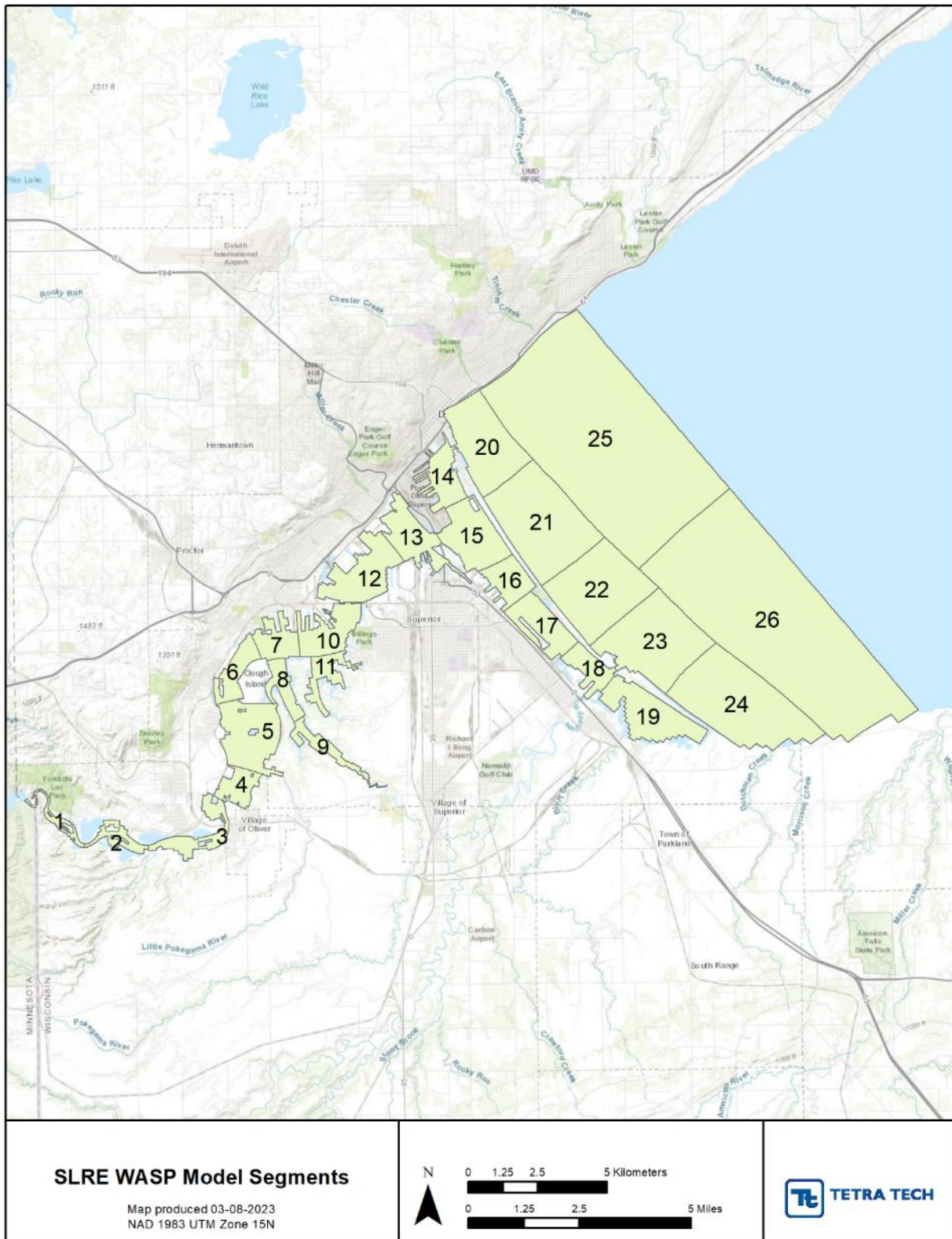


Figure 5-2. Existing WASP model segmentation for the St. Louis River/Duluth Harbor mercury model (from RTI, 2013b)

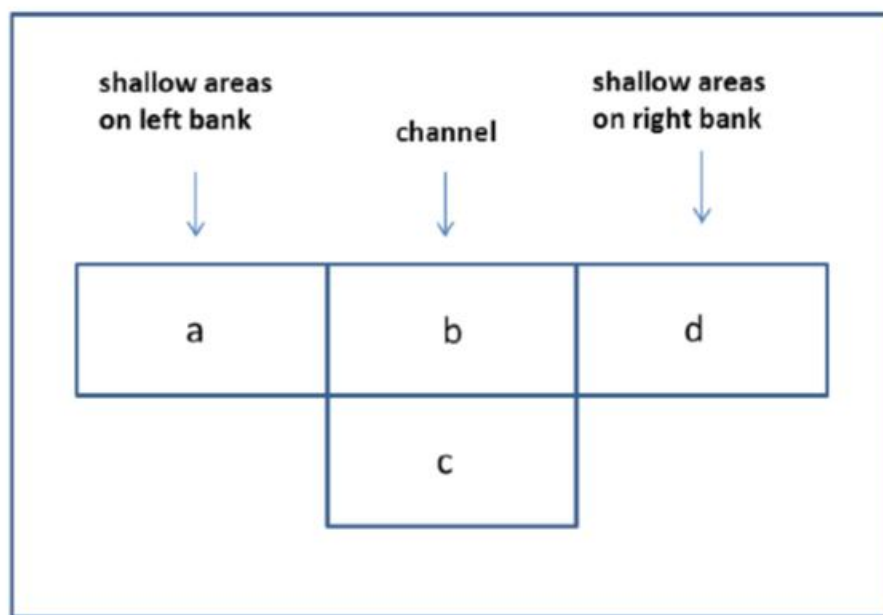


Figure 5-3. Definition of WASP model sub-segments, looking downstream (from RTI, 2013b)

The WASP model is implemented on a net flow basis and does not use a detailed hydrodynamic file. Instead, flow series are routed from their entrance point (e.g., Fond du Lac Dam) through the WASP network and out to the model boundary in Lake Superior. This simplified approach is sufficient for long-term analysis of mercury cycling in the estuary/harbor.

The RTI WASP model routes two flow series, one representing the St. Louis River inflow and one the Nemadji River, which together account for more than 90 percent of the inflows. The RTI report suggests there is also a net flow series for the Pokegama River (WASP segment 8), but this is not included in the model files and the Pokegama is connected to the mainstem only through diffusive exchanges. In contrast, the USGS EFDC model specifies 17 distinct inflow points, including the Western Lake Superior Sanitary District (WLSSD) wastewater discharge (Figure 5-1). While the inflow at these points is small relative to the flow in the St. Louis River, the contributing drainages are still potential sources of mercury loading that should be included in the model. This is accomplished by including these sources as mercury loads rather than as inflow boundary conditions. Daily load series are generated by the HSPF model described in Section 4.0.

The net flow approach is not capable of representing the effects of seiche and other water level oscillations in the harbor and its entrances. Instead, the net mixing caused by these processes is represented through macrodispersion coefficients. The macrodispersion coefficients can be estimated by simulating die tracer experiments with the USGS EFDC model.

Elemental mercury ($\text{Hg}(0)$), divalent ionic mercury ($\text{Hg}(\text{II})$), and methylmercury (MeHg) are state variables in the WASP model. Inorganic and organic solids are also state variables and mercury sorption/desorption, deposition, and scour are all represented. Sediment bed and water column mercury are linked through pore water exchange functions in addition to scour and deposition. Wet atmospheric deposition of mercury to the water surface is represented as a load series on rainy days; dry deposition is simulated via the net volatilization process.

The RTI (2013b) WASP model was built in WASP version 7.5. The WASP mercury module, introduced in WASP 7, has a full process description of mercury transformation and kinetics (Ambrose et al., 2005;

Knights, 2010; Knights et al., 2014; Wool et al., 2020). Various improvements to toxicant simulation in general and to the mercury routines were incorporated in WASP 8 (Wool et al., 2020). Tim Wool, the model developer, recommended use of the WASP 8.32 official release for mercury simulations, so the older WASP 7.5 model was updated to 8.32⁵.

In addition to updating the model version, the technical approach includes updating the model to simulate conditions for water years 2011-2021 to take advantage of more recent data collection and to overlap with the USGS EFDC simulations. The WASP model will then be used to estimate allowable total mercury and MeHg loads to the estuary/harbor consistent with MPCA's water column criteria for total mercury and fish tissue mercury using a bioaccumulation factor approach. Development of the WASP model is described in Section 4.4 and bioaccumulation is covered in Section 6.0.

5.1 EXTRACTING INFORMATION FROM USGS EFDC MODEL RUNS

Results from the USGS EFDC model of the estuary and harbor (Smith et al., 2020) are used to inform flow routing in the WASP model and to develop estuarine macrodispersion coefficients that approximate seiche-induced mixing. The models were supplied by USGS and re-run by Tetra Tech, confirming that their performance matches the published documentation.

5.1.1 Flow Routing

The existing WASP model (RTI, 2013b) uses the Net Flow Routing option, in which each boundary inflow series is routed through the model network without a detailed simulation of hydraulics. A complicating factor for this approach is that upstream flows from the St. Louis River split in the lower harbor area (in WASP segment 15; see Figure 5-2) and can reach Lake Superior via either the Duluth or Superior entrances. The fraction of discharge leading to each of these exits must be specified to the model as a constant.

The RTI team built a simplified, medium resolution EFDC hydrodynamic model to evaluate flow patterns through the St. Louis Estuary (since superseded by the more detailed EFDC model developed by USGS [Smith et al., 2020]). The RTI EFDC model was previously used “to simulate three 1-month periods using typical seiching patterns and high, medium, and low river flow conditions” and analysis of the net flow results suggested that approximately 30 percent of the upstream flow exited via the Duluth channel and 70 percent via the Superior channel.

The actual division of flow between these channels varies over time depending on conditions in the river and Lake Superior – but the WASP Net Flow approach requires a constant ratio. We therefore reanalyzed the flow patterns using the USGS EFDC model. That model is developed for non-winter (April – November) conditions. The most rigorously calibrated models (documented in Smith et al., 2020) are for 2016 and 2017, which is the period that had the best freshwater gaging combined with lake boundary conditions from a detailed Advanced Circulation (ADCIRC) model of western Lake Superior near Duluth (Hayter et al., 2015).

In addition to the 2016 and 2017 models, USGS also developed models for 2012 and 2019, which were obtained directly from Dr. Smith (personal communication from Erik A. Smith, USGS to Jonathan Butcher,

⁵ EPA released WASP 8.4 in March 2022; however, that version appears to engender stability problems when the presence of bottom sediment sections is combined with the net flow transport option. The model developer, Tim Wool, indicated that the mercury routines had not changed since WASP 8.32, which is fully tested and stable, and recommended use of the 8.32 release for this project (personal communication to Jonathan Butcher, Tetra Tech, 1/29/22).

Tetra Tech, Sept. 13, 2022). The boundary time series provided with the 2012 model also include 2015, which was a key year for mercury monitoring in the harbor/estuary, so Tetra Tech built a 2015 EFDC model as well. Dr. Smith did note that, other than for 2016 and 2017, USGS used buoy data for the Lake Superior boundary condition instead of an external model such as ADCIRC, so the estimates of lake boundary conditions are not as detailed or accurate as those for 2016-2017.

The harbor entrance channels are two cells wide in the EFDC model. Flows between the harbor and Lake Superior were estimated near the center of each channel, using EFDC cells (34,323) and (35,323) for the Duluth entrance and (118,319) and (119,319) for the Superior entrance and calculating discharge as the product of velocity times depth times width. In all years tested, approximately 40 – 45 percent of the total flow volume leaving the harbor (positive U velocity) exits through the Duluth channel; however, in some years the model also simulates a much larger volume of water flowing from Lake Superior into the harbor via the Duluth entrance resulting in low net outflow of upstream water (Figure 5-4). This is likely due to elevation, wind, and current conditions that result in a simulated buildup of water to the north in Lake Superior. Note in 2012 that the model simulates a negative net outflow via the Duluth entrance, indicating that some water entering via this route ends up exiting through the Superior entrance – a phenomenon that needs to be accounted for in the macrodispersion coefficients. We therefore estimate the fraction of upstream flow that passes through each harbor exit as a function only of the outflows and assume that flow from the Nemadji River passes only through the Superior exit. Results of the analysis are shown in Table 5-1.

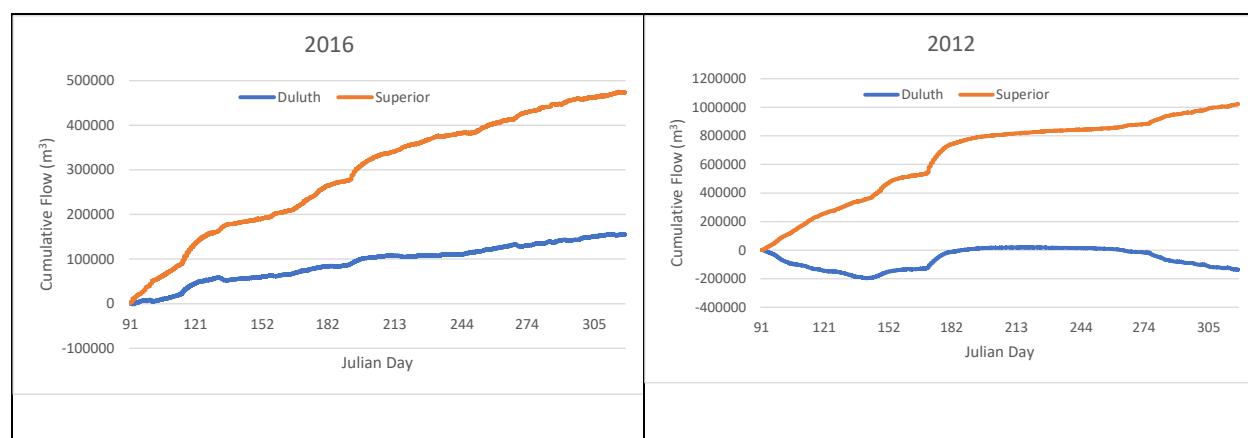


Figure 5-4. Cumulative Simulated Flows via Duluth and Superior Entrances

Table 5-1. Estimated fraction of St. Louis River flows exiting via the Duluth and Superior entrance channels

	2012	2015	2016	2017	2019
Duluth	-4.08%	2.14%	39.72%	29.27%	26.14%
Superior	104.08%	97.86%	60.28%	70.73%	73.86%

The results in Table 5-1 are approximations of total flow based on instantaneous model output at a 1-hour time step. In addition, the results for 2016 and 2017 are believed to be based on a more accurate simulation of conditions in Lake Superior. The results for those years are close to the 30%/70% split obtained by RTI (2013b) in their EFDC simulations based on three one-month periods from the earlier (2004-2011) EFDC model. In Table 5-1 the results for 2019 represent the median of the five years tested. As the WASP Net Flow approach requires a single estimate for the split, these values are used in

the model, with flow that enters WASP cell 15 being partitioned 26.14% to cell 14 and 73.86% to WASP cell 16.

5.2 SETUP OF THE WASP MODEL

As noted in Section 5.1.1, the WASP simulation is set up using the Net Flow option that describes how the boundary flows are routed through the WASP segments to the Lake Superior boundary. The model is not directly linked to the output of the EFDC hydrodynamic model because that model is only available for certain years and not for the winter period within the years that are represented. The lack of a detailed hydraulic simulation also means that a process-based simulation of sediment scour and deposition in WASP is not feasible. (Turning those parameters on also results in approximately doubled run times of about 6 hours per run and often causes the model to crash.) In addition, suspended sediment data for calibration within the harbor/estuary are sparse. As a result, the WASP model as set up here uses WASP's descriptive sediment transport option (Ambrose et al., 2017) in which average sediment deposition rates from water column to surface sediment (m/d as a function of particle size) and net surface sediment resuspension rates from surface sediment to the water column (m/d) are specified directly as constants and adjusted during calibration (Table 5-3). This simplified approach means that the effects of harbor dredging and propwash cannot be directly represented on a physical basis.

In addition to sediment deposition and resuspension, the WASP model also incorporates porewater flux between the sediment and water column.

5.2.1 Inflows and Loads

5.2.1.1 Flows

Only two flow series are fully routed through the WASP model – flow from the St. Louis River at Scanlon Dam (USGS 0424000, St. Louis River near Scanlon, MN [located downstream of Scanlon Dam]) and flow from the Nemadji River (USGS 04024430, Nemadji River near South Superior, WI). The upstream boundary of the WASP model is actually at Fond du Lac Dam (HSPF reach 205), which is two HSPF model segments downstream of Scanlon Dam but is not gaged. There is only a small additional drainage area between Scanlon Dam and Fond du Lac Dam, so the gage at Scanlon is considered a reasonable proxy for flows entering the estuary; however, Thomson Reservoir lies between the two sites and likely alters the timing of flows at Fond du Lac Dam.

USGS provides complete flow series for both the Scanlon Dam and Nemadji River inputs (although some winter records are estimated during frozen conditions), and the gaged flows were used in the WASP model rather than simulated flows. Flows from smaller tributaries direct to the SLRE are a small fraction of the total flow entering the harbor/estuary (less than 5 percent) and are not included in the WASP flow routing (as was also the case in the RTI WASP model) because they have a small impact on advective transport and incorporating them via net flow routing series would unnecessarily complicate the model. The mercury load from these tributaries is of potentially greater significance. Therefore, these tributary loads (from the watershed model) are represented as mass loads entering the model at the segments corresponding to each tributary, as described in the next section.

5.2.1.2 Solids and Mercury Loads

For the St. Louis River and Nemadji inflows, boundary concentrations are needed for solids (sand, inorganic fine sediment, and organic matter, as mg/L), dissolved organic carbon (DOC, as ng/L), and mercury species (Hg(II), Hg(0), and MeHg, as ng/L). WASP multiplies these concentrations times flow to determine the influent load. Concentrations in the St. Louis River leaving Scanlon Dam are obtained from the SLRW HSPF model. The SLRW HSPF model is calibrated to total suspended solids (TSS) and represents TSS in sand, silt, and clay fractions, which implicitly incorporate organic solids. HSPF also

simulates total organic carbon without separating the dissolved and particulate fractions but does distinguish between the refractory and labile fractions. The following logic is applied to translate from HSPF state variables to WASP state variables:

- Sand concentrations for WASP inflows are equal to SAND as simulated by HSPF.
- Organic solids for WASP are assumed to be equal to the total refractory carbon concentration predicted by HSPF divided by the ratio of carbon to biomass of 0.57, consistent with the stoichiometry used in HSPF.
- Dissolved organic carbon for WASP is set equal to the total organic carbon concentration predicted by HSPF minus the carbon equivalent of organic solids.
- Inorganic fine sediment for WASP is set equal to the sum of silt and clay predicted by HSPF minus the estimated organic solids concentration.
- MeHg concentration for WASP inflows is taken from MeHg predicted by HSPF after conversion from mg/L to ng/L. Note that HSPF predicts dMeHg while WASP requires tMeHg as an input.
- Hg(0) for WASP inflows is assumed to be zero.
- Hg(II) concentration for WASP inflows is equal to THg predicted by HSPF less MeHg with conversion from mg/L to ng/L.

The WASP model setup does not include flow from minor tributary urban creeks on the north bank of the St. Louis River (Mission, Sargent, U.S. Steel, Stewart, Kingsbury, Keene, Merritt and Miller creeks) along with the Red River, Pokegama River, Little Pokegama, and other surface runoff (including stormwater flow from Superior, WI) on the south bank of the St. Louis River. However, mercury loads from these areas must be accounted for. These loads are represented as point sources of mercury (MeHg and Hg(II)) for which WASP requires units of kg/d. The mercury loads for the north bank tributaries are specified individually from the Duluth Urban Area HSPF model, while estimates for the south bank tributaries are taken from the coarser scale St. Louis River watershed HSPF model. In both cases the loads are summarized to WASP as daily timeseries calculated from the hourly HSPF model output.

Flow and loads from the Nemadji River are estimated separately as described in Section 5.2.3.

5.2.2 Point Sources

There is one major wastewater discharge to Duluth Harbor: Western Lake Superior Sanitary District (WLSSD; MN0049786), which discharges to the Harbor just west of Miller Creek (refer to Figure 5-1). The outfall is in cell (22, 282) of the USGS EFDC model and falls within WASP segment 13, sub-segment 13a.

Discharge monitoring report data for WLSSD was downloaded from the Minnesota Wastewater Browser and includes daily flow and monthly THg concentration monitoring, from which daily THg load series were constructed. These average 4.29×10^{-4} kg/day (which are the units required by WASP for loads). MeHg monitoring is not available for WLSSD but was assumed to be 2% of THg based on data from other WWTPs.

Permitted MS4 discharges are included in the loads described in Section 4.1.2.

5.2.3 Representation of Nemadji River

For the periods simulated by EFDC, the Nemadji River provides about 14 percent of the total inflow to the harbor and estuary. This presents a challenge because the Nemadji watershed is largely in Wisconsin and an updated HSPF model has not been developed. Unlike the St. Louis watershed, the Nemadji watershed is largely composed of highly erodible lacustrine sediment that provides high sediment yields.

Water column mercury data are also limited for the Nemadji. Data have been occasionally collected coincident with the USGS gage at Superior, WI. These include 18 samples (THg only) collected in 1997-

1998 as part of the harbor toxics study (MPCA, 1999), 6 samples collected in 2015 (dissolved and particulate, THg and MeHg; RTI 2016), and 9 samples collected in 2021 (dissolved and particulate, THg and MeHg; Janssen and Tate, 2022). These limited data show that high THg concentrations can be present in the Nemadji, with a maximum observed value of 27 ng/L.

The flow from the Nemadji enters the SLRE directly across from the Superior entrance and much of the load from the Nemadji likely goes directly into Lake Superior. Nonetheless, these loads need to be characterized for the WASP model.

Examination of the 33 available samples from the Nemadji reveals a strong positive correlation between THg concentration and flow (Figure 5-5). While this relationship appears strong it is unlikely that THg concentrations will increase without limit at extreme flows. Further, the linear regression is highly leveraged by the highest concentration value. Therefore, an alternative power function fit is used (Figure 5-6), which has the advantage of damping concentrations at extreme flows while also passing through the intercept.

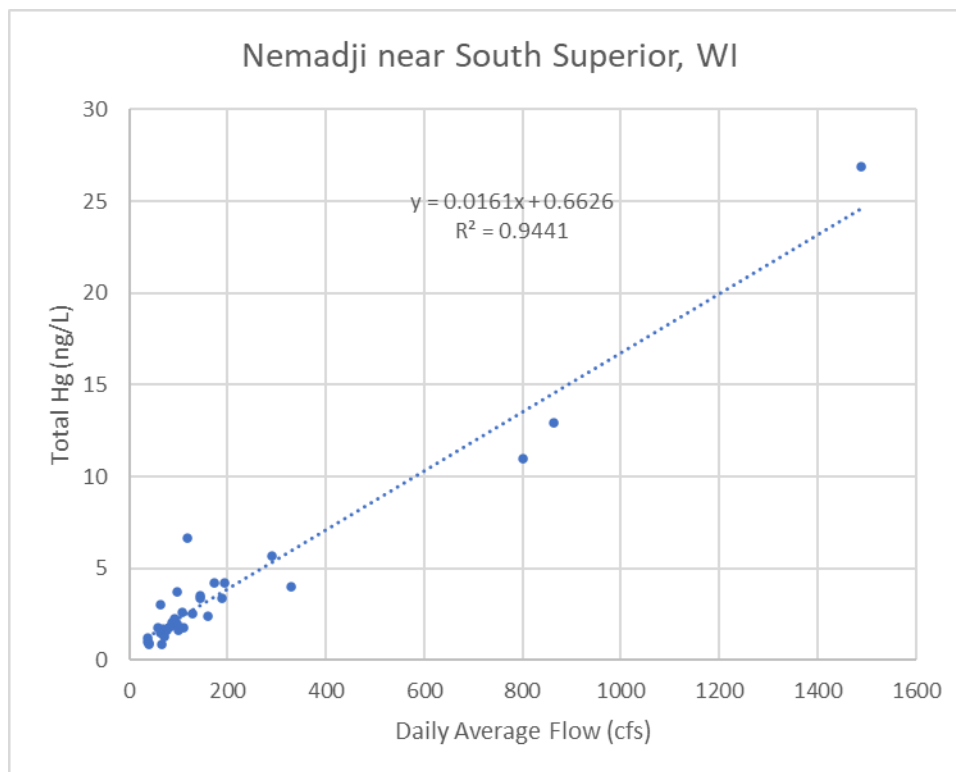


Figure 5-5. Relationship of THg and flow, Nemadji River at South Superior, WI (USGS Gage 05011002), with linear regression

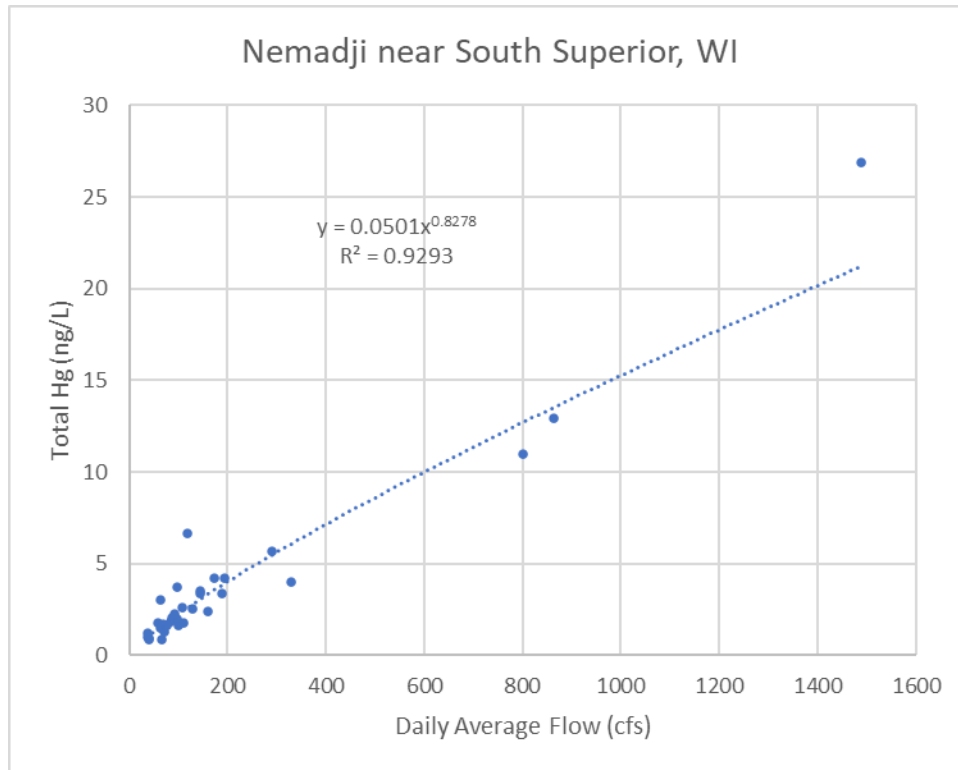


Figure 5-6. Relationship of THg and flow, Nemadji River at South Superior, WI (USGS Gage 05011002), with power regression

The WASP model also requires estimates of boundary concentrations of sand, fine inorganic sediment, and particulate organic matter for the Nemadji. These series are based on relationships at South Superior, WI established in earlier modeling of the Nemadji (Tetra Tech, 2016b). Total suspended solids (TSS) are also positively correlated with flow and also fit with a power regression (Figure 5-7). The observed data do not distinguish the components of TSS, so these are assigned, based on the results of HSPF modeling in Tetra Tech (2016b), as 2.32% sand, 12.47% particulate organic matter, and the remainder as fines (silt and clay). These relationships are then used to create daily timeseries based on flow at the USGS gage.

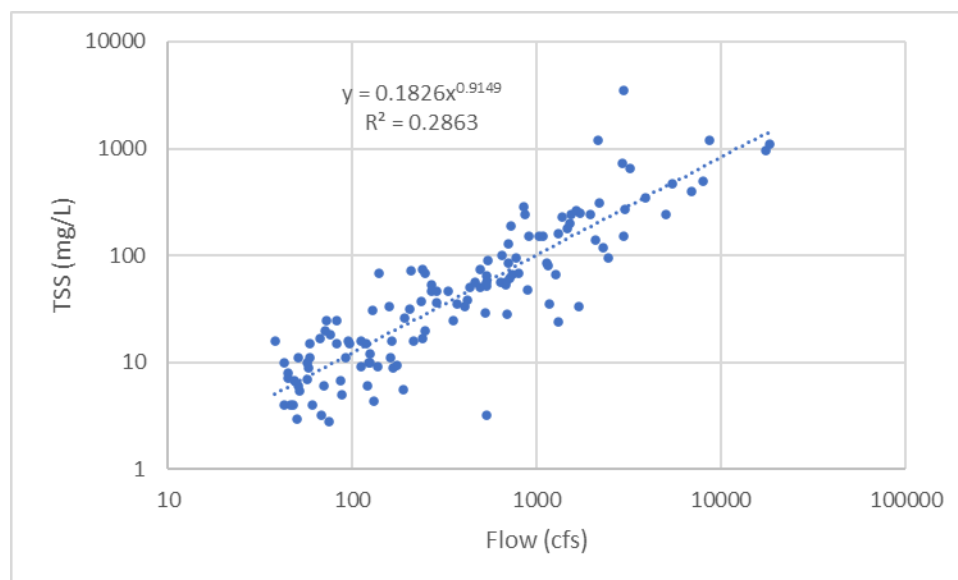


Figure 5-7. Relationship of TSS and flow, Nemadji River at South Superior, WI (USGS Gage 05011002), with power regression

5.2.4 Direct Atmospheric Deposition

Wet and dry atmospheric deposition of mercury to water surfaces in the WASP model was estimated as is described for the HSPF model in Section 4.1.3.

5.2.5 Lake Superior Boundary Condition

Mercury concentrations within the open water of Lake Superior are low and relatively consistent over time (Jeremiason et al., 2009; Ogorek et al., 2021). Mercury concentrations at the WASP model boundary with Lake Superior are set consistent with Jeremiason et al. at constant values of 210 pg/L (0.210 ng/L) THg, consisting of 189 pg/L Hg(II), 7 pg/L MeHg, and 14 pg/L Hg(0).

5.2.6 Sediment Initial Conditions

WASP requires specification of initial conditions in surface sediment for both the sediment itself and mercury species. Both are represented in WASP as volumetric measurements (i.e., mg/L), which requires correcting for porosity. The primary data source was the massive amounts of data available in the NOAA DIVER database for the St. Louis River Area of Concern (<https://www.diver.orr.noaa.gov/st-louis-river-aoc>). We queried the DIVER database on 2/28/2023, at which time it contained sediment mercury data through 10/19/2018.

For mercury concentrations we augmented the DIVER data compilation with several additional sources not included in the database to ensure better spatial coverage throughout the estuary. These are:

- 2014-2015 sampling conducted by Johnson et al. (2016; data tables provided electronically in email from Dr. Nathan Johnson, University of Minnesota – Duluth to Jennifer Brentrup, MPCA, January 6, 2023).
- 2015 sampling conducted by Research Triangle Institute (RTI, 2016).

- 2021 USGS data for Lake Superior tributaries reported in Janssen and Tate (2022). Detailed data tables provided electronically by email from Jennifer Brentrup, MPCA to Jonathan Butcher, Tetra Tech on 12/08/2022).

Only sediment data collected since 1/1/2005 were used to characterize mercury in sediment of the SLRE due to concerns about changes over time. It is likely that there have been some significant changes since 2005 as well (e.g., remediation efforts), but data collection has been sporadic and there is not a comprehensive coverage for a single point in time. Some of the largest changes to mercury sediment concentrations likely occurred in 2010, 2016, and 2018 when sediments contaminated with heavy metals in the Minnesota Slip, Slip 2, Slip 3, Slip C, and St Louis River/ Interlake/Duluth Tar were capped and armored. Thus, the sediment mercury concentrations used in the WASP model might be higher than the concentrations post-remediation; this can be considered part of an implicit MOS for the TMDL calculations.

To characterize sediment physical properties, we relied on the DIVER database from which we extracted data on porosity, total organic carbon, percent total fines (silt and clay), and percent sand and larger particulates. The size classes are reported separately from the total organic carbon content. Most of the organic carbon was assumed to be in the total fines class with organic carbon constituting 57% of the organic sediment mass. The percent fines (and in some cases part of the sand fraction) were corrected to account for organic matter and inorganic fine sediment as separate classes. The percentages reported are for dry weights and must be converted to a weight per total volume basis for WASP. This was done by adjusting for porosity and assuming dry bulk densities of 2.7 g/cm³ for sand, 2.0 g/cm³ for fine inorganic sediment, and 1.35 g/cm³ for organic material, consistent with the WASP model.

The DIVER sediment samples are composites over depth. To obtain surface sediment concentrations we analyzed those samples with a starting sample depth of 0. The depth over which samples were composited is, however, highly variable ranging from 3 to 203 cm with an average of 21 cm. It is thus likely that the surface sample averages over a WASP segment may not be representative of the mercury in the sediment that is in direct contact with the water column.

Elemental mercury (Hg(0)) concentrations have generally not been reported for sediment samples and are assumed to be zero for initial conditions. Most samples report total mercury (THg) and methyl mercury (MeHg) concentrations as mass per mass of sediment (ng/g). As with sediment size classes, these concentrations must be converted to a mass per volume basis (ng/L) after adjusting for porosity. THg encompasses MeHg, and so must be corrected to prevent double counting, then converted to a volumetric basis by adjusting for porosity. In addition, WASP specifications for initial conditions should account for both the sorbed and dissolved fractions of THg and MeHg – although the dissolved fraction is generally an insignificant component of total mass per volume. This is accomplished by adjusting the mass per volume to include both the reported solids concentration (per gram of sediment) and the implied dissolved porewater mass. Under assumptions of equilibrium partitioning, the dissolved fraction in pore water is equal to the sorbed mass times 1/K_d, corrected for porosity, where K_d is the assumed partition coefficient for each solids class as defined in the WASP parameterization (L/kg).

5.2.7 Estuarine Macrodispersion

The WASP model Net Flow approach does not directly simulate tidal and seiche mixing. These are approximated through a tidal dispersion coefficient. Initial analysis of tidal dispersion was done for approximately steady-state conditions using the fraction of freshwater approach outlined in Thomann and Mueller (1987), developed for estimating tidal dispersion from dye tests under steady state conditions. This was applied to approximate dispersion coefficients in the Duluth estuary by selecting time periods where conditions in the Harbor are approximately steady-state relative to normal summer conditions and avoid higher flow periods with freshwater inflows greater than 100 m³/s.

Notation and assumptions:

Segment numbers generally increase in the downstream direction; Segment 1 represents an upstream freshwater boundary condition (e.g., Fond du Lac Dam)

C_i	Concentration in segment i
$C_{i,j}$	Concentration at the boundary between segments i and j .
C_B	Subscript B indicates the boundary concentration in the downstream receiving water (e.g., Lake Superior)
Q	Flow (m^3/s)
$(QC)_{i,j}$	Mass transfer (product of flow and concentration between segments i and j)
E'	Bulk dispersion coefficient (L^3/T)
E	Tidal dispersion coefficient = $E' \times$ average length of adjacent segments (or distance between their centroids) / cross-sectional area (L^2/T)

The fraction of freshwater method is usually applied to a one-dimensional estuarine analysis without branching but can be extended to joined or split flows. Dispersion coefficients typically differ for each model segment interface, resulting in an under-determined set of equations. However, with the assumption of approximate steady-state conditions and a concentration of interest initially present only at the downstream end of the model the system of equations becomes solvable by reducing the number of coefficients to be estimated to the number of segments. This occurs because the steady-state approximation implies that, at the interface between the most downstream estuarine segment and the boundary (e.g., Lake Superior), the mass entering the last segment from the boundary via dispersion must be balanced by the mass flux leaving the last segment to the boundary via advection. If this balance did not occur, then a nonsteady buildup or loss of mass would occur. This assumption makes it possible to solve for the dispersion coefficient for the most downstream boundary segment(s). Once this is made, one can then proceed upstream to solve succeeding segments.

For the St. Louis estuary it is necessary to deal with instances where flows spilt or join, complicating the analysis. We describe several different configurations that apply to the St. Louis WASP model:

- 1. Downstream Boundary Segment.** These are the segments that drain to Lake Superior via the Duluth and Superior harbor entries. Consider a segment i connection to a boundary segment B. The steady-state assumption requires that the advective flow out of the segment is consistent with the advective exchange that yields the observed (average) concentration in segment i :

$$Q_{i,B} C_{i,B} = E'_{i,b} (C_B - C_i)$$

This in turn implies

$$E'_{i,b} = Q_{i,B} C_{i,B} / (C_B - C_i)$$

- 2. Upstream One-Dimensional Segment.** Where there is only one adjacent upstream segment, E' for the interface with the upstream segment is readily solved once the downstream segment E' is obtained. Under approximate steady-state assumptions, the mass balance at a given cell i is given by:

$$(QC)_{i-1,i} - (QC)_{i,i+1} + E'_{i,i+1} (C_{i+1} - C_i) - E'_{i-1,i} (C_i - C_{i-1}) = 0$$

This can be solved to yield

$$E'_{i-1,i} = [(QC)_{i-1,i} - (QC)_{i,i+1} + E'_{i,i+1} (C_{i+1} - C_i)] / (C_i - C_{i-1})$$

where $E'_{i,i+1}$ has already been determined.

- 3. Split Flow – Segment with Two Downstream Segments:** Suppose flow from segment i flows to both segment $i+1$ and segment j , and that the relative fractions of flow are known. Upstream flow comes from segment $i-1$. The mass balance for segment i at steady state is then:

$$(QC)_{i-1,i} - (QC)_{i,i+1} - (QC)_{i,j} - E'_{i-1,i} (C_i - C_{i-1}) + E'_{i+1,i} (C_{i+1} - C_i) + E'_{j,i} (C_j - C_i) = 0$$

Solving this first requires determining $E'_{i+1,i}$ and $E'_{j,i}$, which can be accomplished using the method for the case of the upstream one-dimensional segment. Then:

$$E'_{i-1,i} = [(QC)_{i-1,i} - (QC)_{i,i+1} - (QC)_{i,j} + E'_{i+1,i} (C_{i+1} - C_i) + E'_{j,i} (C_j - C_i)] / (C_i - C_{i-1})$$

- 4. Segment with Two Upstream Segments:** Suppose flow into segment i derives from two upstream segments, $i-1$ and k . There is one downstream segment $i+1$. The mass balance for segment i is given by:

$$(QC)_{i-1,i} + (QC)_{k,i} - (QC)_{i,i+1} + E'_{i+1,i} (C_{i+1} - C_i) - E'_{i-1,i} (C_i - C_{i-1}) - E'_{k,i} (C_i - C_k) = 0$$

Here there are two equations for two unknowns:

$$E'_{i-1,i} = [(QC)_{i-1,i} + (QC)_{k,i} - (QC)_{i,i+1} + E'_{i+1,i} (C_{i+1} - C_i) - E'_{k,i} (C_i - C_k)] / (C_i - C_{i-1})$$

$$E'_{k,i} = [(QC)_{i-1,i} + (QC)_{k,i} - (QC)_{i,i+1} + E'_{i+1,i} (C_{i+1} - C_i) - E'_{i-1,i} (C_i - C_{i-1})] / (C_i - C_k)$$

This set of equations does not have a unique solution unless an additional constraint is added. One way to do this is to assume that the two upstream bulk dispersion coefficients are equal, in which case

$$E'_{i-1,i} = E'_{k,i} = [(QC)_{i-1,i} + (QC)_{k,i} - (QC)_{i,i+1} + E'_{i+1,i} (C_{i+1} - C_i)] / (2 C_i - C_{i-1} - C_k)$$

The resulting effective tidal dispersion coefficients (E) will differ depending on the area of the intersection and the distance between centroids of the two cells. Note that the equations presented above are undefined when the concentrations in two adjacent cells are equal.

The initial analysis showed that estimated dispersion coefficients varied considerably from year to year, whereas WASP requires constant values of E for each segment pair. In addition, it is clear that conditions in the estuary are dynamic, not steady state, while the lack of a unique solution for case (4) is also problematic. We therefore revised the approach to simultaneously optimize values of E' that minimize the squared error in predicted average concentration in each WASP segment.

The mass balance for each segment can be written in terms of coefficients applied to the concentrations in the subject and adjacent (two or more) segments in the following form, for segment i :

$$a_{i,i-1}C_{i-1} + a_{i,i}C_i + a_{i,i+1}C_{i+1} = W_i,$$

where $a_{i-1,i} = -Q_{i-1,i} - E'_{i-1,i}$, $a_i = Q_{i,i+1} + E'_{i-1,i} + E'_{i,i+1}$, $a_{i+1,i} = -E'_{i,i+1}$, and W_i represents any sources or sinks. For an upstream boundary segment, $a_{i,i-1}$ is not used and $W_i = Q_{B,i}C_B$. For a downstream boundary segment, $W_i = E'_{i,B}C_B$, and for all non-boundary segments, $W_i = 0$. The complete system of equations can then be written in matrix form as $\mathbf{A} \times \mathbf{C} = \mathbf{W}$. If there are a total of n segments, $\mathbf{A}$ is an n -by- n matrix with entries corresponding to segment number:

$$\begin{bmatrix} a_{11} & a_{12} & 0 & 0 & 0 & 0 \\ a_{21} & a_{22} & a_{23} & 0 & 0 & 0 \dots \\ 0 & a_{31} & a_{33} & a_{34} & 0 & 0 \\ \dots & & & & & \end{bmatrix}$$

and so on. $\mathbf{C}$ and $\mathbf{W}$ are vectors of length n . Multiplying both sides of the system of equations by the inverse of $\mathbf{A}$ yields a prediction of the complete set of concentrations: $\mathbf{A}^{-1} \times \mathbf{A} \times \mathbf{C} = \mathbf{A}^{-1} \times \mathbf{W}$, or $\mathbf{C} = \mathbf{A}^{-1} \times \mathbf{W}$. The inverse of $\mathbf{A}$ can be estimated for each simulation year using the Excel MINVERSE function.

From here, we use the Excel Solver function to find a set of E' estimates that minimize the squared error in concentration predictions simultaneously across all five years simulated by USGS with EFDC. As

expected, the highest macrodispersion values are estimated for the Duluth Harbor area. WASP cells upstream of W₁₂ require minimal macrodispersion to match observed concentrations; these cells are in the dominantly advective reaches upstream of the harbor and below Fond du Lac Dam.

The optimization across all years simulated by USGS yields a relatively good fit (Figure 5-8). It will be noted, however, that the regression line is dragged down by results for 2015. For the 2015 simulations USGS lacked a hydrodynamic model for the Bay (relying instead on interpolating water surface elevations from buoy data) and also lacked direct gaging data for many of the Duluth-area direct tributaries to the Harbor. Therefore, the 2015 results are likely less reliable. Eliminating 2015 from the optimization yields a much more precise fit (Figure 5-9).

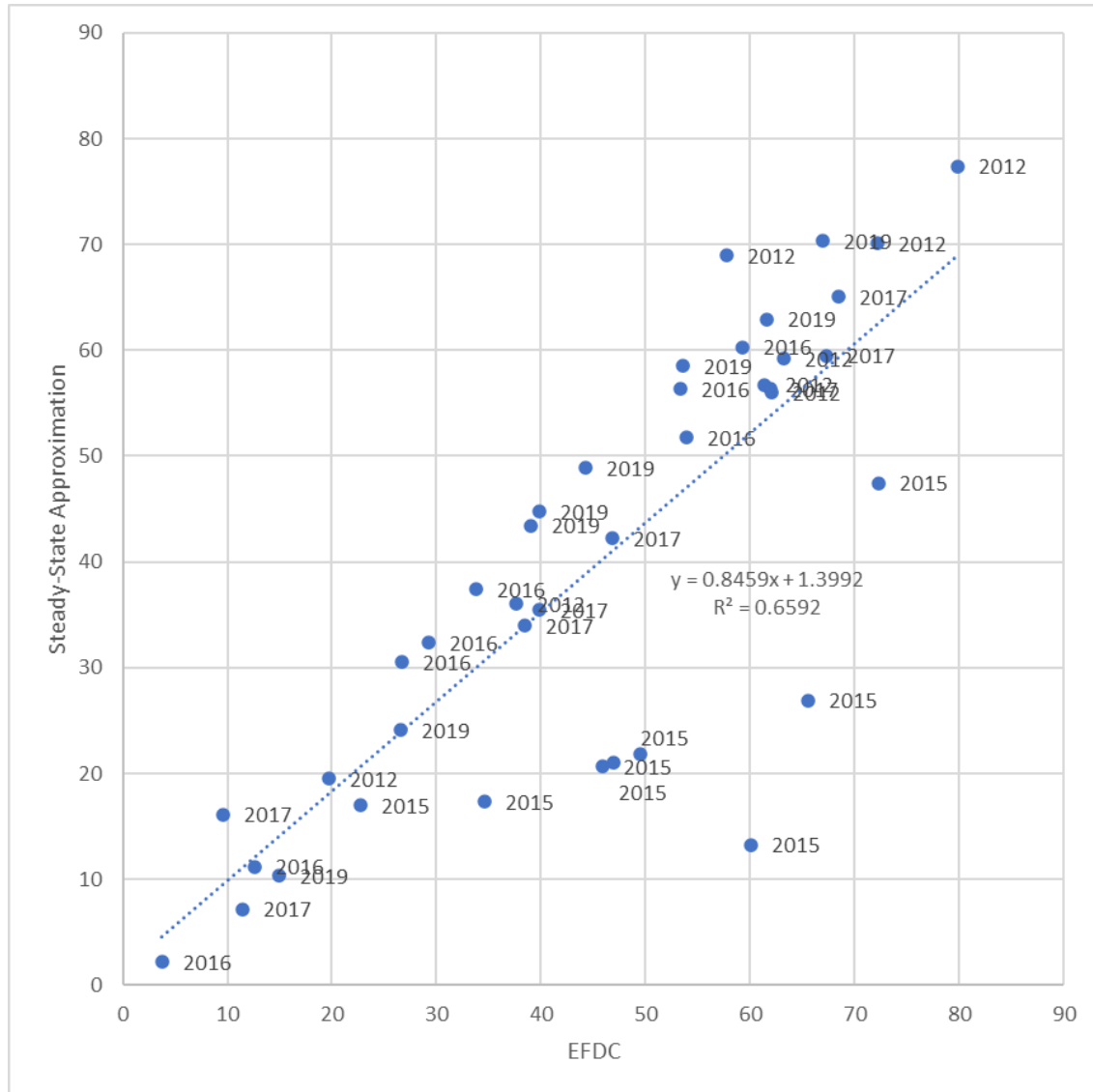


Figure 5-8. Optimized fit of macrodispersion coefficients to average WASP segment concentration for 2012, 2015, 2016, 2017 and 2019

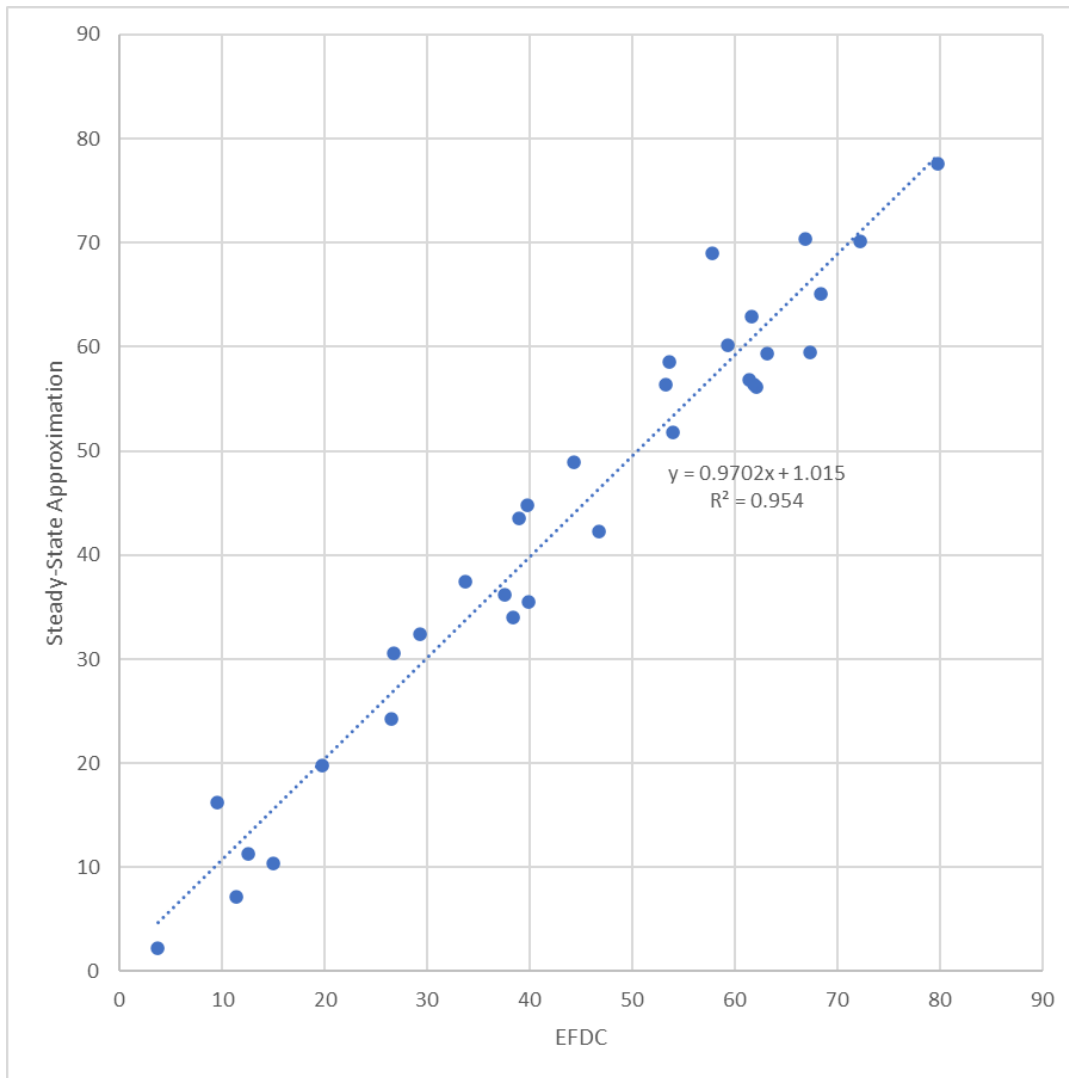


Figure 5-9. Optimized fit of macrodispersion coefficients to Average WASP segment concentration for 2012, 2016, 2017 and 2019

The resulting macrodispersion coefficients estimated without the 2015 simulation results are provided in Table 5-2.

Table 5-2. Macrodispersion coefficients for WASP optimized from USGS EFDC modeling

WASP Segment Interface	$E'(m^3/s)$	$E(m^2/s)$	m^2/d
Bay-14	59.023	0.560	0.019
Bay-18	148.574	0.640	0.021
19-18	155.559	0.269	0.009
18-17	139.336	1.465	0.049
17-16	446.201	251.882	8.461
16-15	1849.003	502.579	16.882
15-13	39.354	32.350	1.087
15-14	2.495	0.547	0.018
13-12	5.016	1.262	0.042
12-10	0.500	0.602	0.020
11-10	0.500	0.239	0.008
10-7	0.500	0.308	0.010

For comparison, Table 3.3 in Thomann and Mueller (1987) provides a summary of estuarine longitudinal dispersion coefficients estimated from dye studies, primarily from coastal tidal estuaries, which range from 0.5 to 62 m^2/d , but are likely to be somewhat larger than those for the SLRE due to the greater marine tidal range compared to the Lake Superior seiche.

The RTI (2013b) report also discusses conducting a series of short-term dye tracing simulations to estimate macrodispersion coefficients from inter-segment flux rates using their EFDC model and states that the calculated values of E were mostly in the range of 5 – 10 m^2/s . However, examination of the RTI WASP model input file supplied to MPCA shows that E was set to 3 m^2/s for all surface water exchange pairs contrary to the documentation. Results using the USGS EFDC model, which has much finer spatial resolution and more rigorous calibration than the RTI model, are expected to be more reliable. Therefore, the updated WASP model presented in this section uses the macrodispersion coefficients shown in Table 5-2.

5.3 WASP MODEL SENSITIVITY ANALYSIS

The model calibration process tested the sensitivity of THg and MeHg simulation results to changes in the parameters and inputs, within plausible bounds suggested in the literature (Ambrose et al., 2005; Knightes, 2010; Knightes et al., 2014; Wool et al., 2020). Water column data are available for multiple locations, but sample sizes are small, with a maximum of 14 samples per station during the 2011-2022 calibration period, mostly from 2014-2015.

There are not sufficient observed data to conduct a robust numerical analysis of variance propagation in the estuary WASP model; therefore we present a more qualitative sensitivity analysis.

Mercury predictions from the model were most sensitive to boundary condition loads at Fond du Lac Dam. The estuary is predominantly depositional and water column concentrations throughout the system are strongly affected by those specifications. Loads from the Nemadji River are locally important but primarily affect concentrations near the Superior Entrance and in Allouez Bay. Loads from local

tributaries and the WLSSD wastewater discharge are minor components of the mass balance (see Section 5.5).

Predictions are also strongly sensitive to sediment deposition and resuspension rates. These rates (along with dispersive exchange and porewater flux) control the exchange of mercury species between the sediment and the water column. Model predictions are extremely sensitive to these rates, which can also induce model instability in certain combinations.

Model predictions are also moderately sensitive to the following:

- Atmospheric deposition: Because of the large surface area of the estuary, concentrations of Hg(II) are sensitive to the atmospheric deposition rate. This rate is believed to be fairly well constrained, but direct measurements over the estuary are not available.
- Partition coefficients: Model inputs include partition coefficients that specify sorption of each form of mercury to sand, fine sediment, organic particulate matter, and DOC. These affect rates of settling and concentrations of dissolved mercury in porewater. Increasing the first three sets of partition coefficients increases net settling rates while complexing to DOC, which does not settle, reduces such rates. These changes, however, produce smaller effects than changes in the overall deposition and resuspension rates.
- Demethylation rates: MeHg concentration predictions are sensitive to demethylation rates. These have only a small impact on Hg(II) concentrations because MeHg is a small fraction of THg.
- Methylation rates: MeHg concentrations are also sensitive to methylation rates. Because most of the estuary is well mixed by wind and seiche it is logical to assume that methylation occurs primarily or solely in the sediment layer. Changing the methylation rate in the sediment indirectly affects water column concentrations of MeHg but depends on the rates of resuspension, porewater exchange, and diffusive exchange.

Model sensitivity was low to most other active parameters in the version of the mercury module described in the WASP documentation.

5.4 WASP MODEL CALIBRATION AND VALIDATION

The simulated WASP THg and MeHg concentrations in surface water were calibrated to existing observations. The location of THg and MeHg observations are presented in Figure 5-10. Water column mercury observations were compiled from multiple sources (see Section 2.3) and underwent quality checks to identify potential outliers before being used for model calibration. The measurements were collected between May 2014 and August 2018, resulting in a total of 100 observations for THg and 94 observations for MeHg. The majority of these observations were collected in St. Louis Estuary channel and there are only limited observations available at or outside the harbor entrances from Lake Superior.

The WASP calibration process aimed to achieve agreement between simulations and observations by adjusting model parameters for Hg (II), Hg (0), and MeHg simulations. For Hg (II) model calibration, parameters such as methylation and reduction rates were adjusted, along with the partition coefficient to dissolved organic carbon and simulated solids (sand, silt, and organic matter). The same calibration parameters were applied to the MeHg simulation, except for methylation which was replaced by demethylation. Calibration parameters for MeHg and Hg(0) also included photo-reduction and photo-oxidation rates, respectively, for ten different wavelengths. Additionally, settling and resuspension rates for solids were calibrated to represent the deposition to and load of mercury from the sediment. The calibrated parameter values for WASP are presented in Table 5-3.

The model application suggests that mercury methylation within the estuary is a relatively minor contributor to estuarine MeHg concentrations compared to the delivery of MeHg from the SLRW upstream of Fond du Lac Dam. Low rates of methylation are plausible for the energetic, well-mixed parts of the

water column where oxygenated conditions are maintained but seems less likely for the fringing wetlands along the upper reaches of the estuary. Janssen et al. (2021) suggested that a portion of the MeHg in the Lower Estuary originates from methylation processes occurring in the side marshes of model segments near the St. Louis River entrance, referred to as the Upper Estuary (WASP model segments 1-5). Similarly, White et al. (2022) observed “shallow, vegetated areas of the Upper Estuary contain MeHg concentrations in sediment, surface water, and biota that are elevated compared to deep areas without vegetation and the Lower Estuary” and suggested that these shallow areas “are an important contributor of MeHg to surface water and biota.” The final model calibration was improved by assigning a methylation rate in surface sediment within the shallow side areas of segments 1-5 that is five times higher than in other surface sediments of the SLRE, consistent with the findings of Janssen et al. and White et al. However, it is also possible that MeHg concentrations may be higher in some nearshore areas of the Upper Estuary because these are locations that trap and accumulate MeHg associated with fine sediment delivered from upstream sources rather than because of high rates of local MeHg production.

The surface sediment methylation rate arrived at through the model calibration effort ($1.0\text{E-}8$ per day in the Upper Estuary and $2\text{E-}09$ in the Lower Estuary) is much lower than the rate of 0.04 per day recommended in a recent review by Helmrich et al. (2022), while the calibrated sediment demethylation rate ($3.75\text{E-}5$ per day) is less than Helmrich et al.’s recommendation of 0.05 per day. The sediment methylation and demethylation rates affect observed concentrations in conjunction and are difficult to calibrate individually; however, the Helmrich et al. methylation rate recommendations are for wetland soils and may not be applicable to the more dynamic conditions of the SLRE. In the SLRE model the demethylation rate in the water column is assigned a relatively high value (0.75 per day) which could be compensating for an over-estimation of MeHg crossing Fond du Lac Dam.

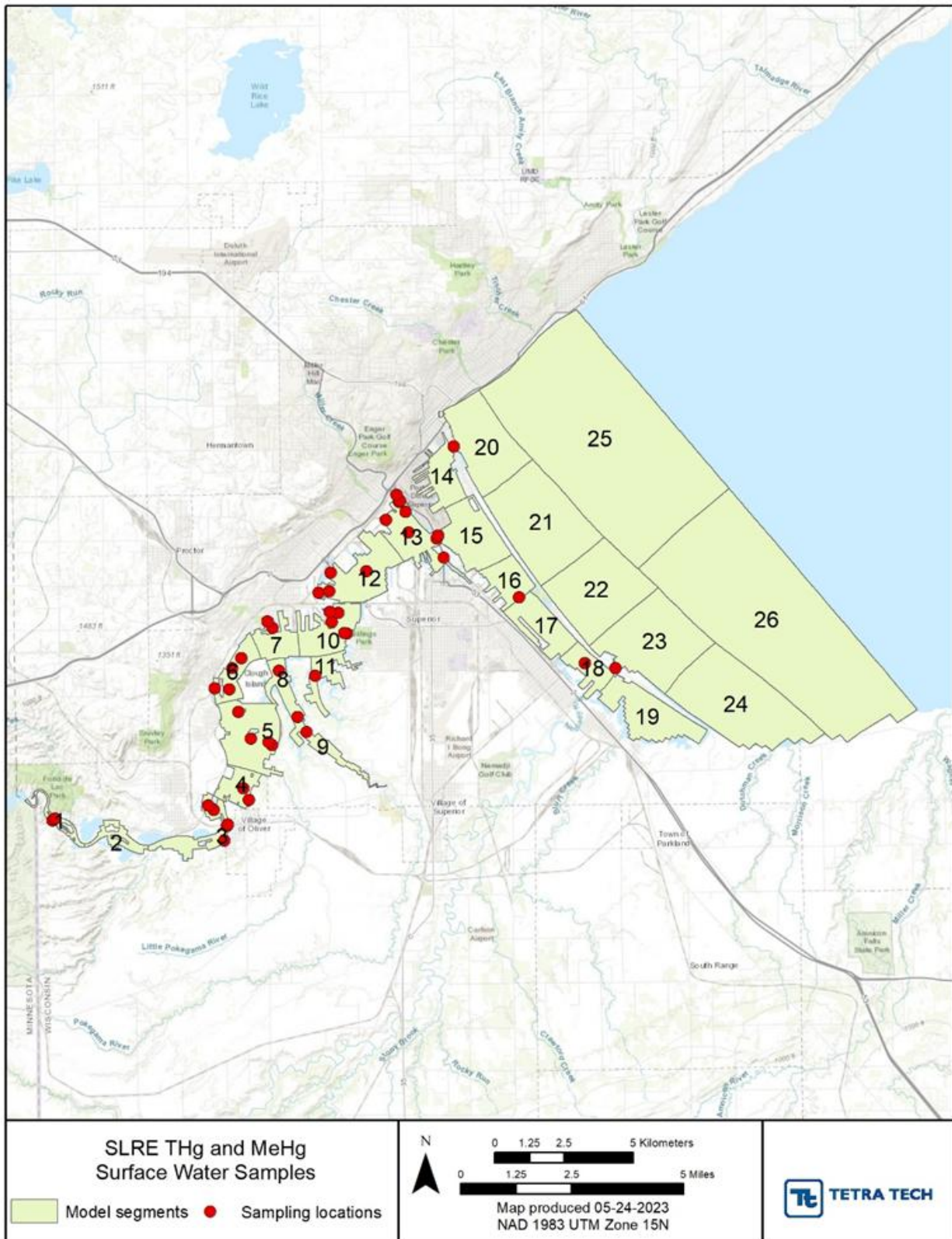


Figure 5-10. Sampling locations for THg and tMeHg in surface water

Table 5-3. Calibrated parameter values in WASP for simulating THg and tMeHg.

Constant Group	Parameter or Constant	Units	Value
Mercury Partitioning	Molecular weight	g/mole	200
	Partition coefficient of reactive Hg(II) to DOC	L/kg	249,408
	Partition coefficient of methylmercury to DOC	L/kg	750,000
	Partition coefficient of reactive Hg(II) to Sand	L/kg	1250
	Partition coefficient of reactive Hg(II) to Fines	L/kg	200,000
	Partition coefficient of reactive Hg(II) to Organic Matter	L/kg	500,000
	Partition coefficient of reactive methylmercury to Sand	L/kg	75
	Partition coefficient of reactive methylmercury to Fines	L/kg	147.000
	Partition coefficient of reactive methylmercury to Organic Matter	L/kg	375,000
Hg(II) Methylation	Methylation rate constant in water column	1/day	0
	Methylation rate constant in sediment	1/day	2.0E-9, 1.0E-8
MeHg Demethylation	MeHg demethylation rate in water column	1/day	0.75
	MeHg demethylation in surface sediment	1/day	3.75E-5
	MeHg demethylation rate in subsurface sediment	1/day	0
Hg(II) Reduction	Hg(II) reduction rate in water column	1/day	0.001
	Hg(II) reduction rate in surface sediment	1/day	0
	Hg(II) reduction rate in subsurface sediment	1/day	0.001
MeHg Reduction	MeHg reduction rate in water column	1/day	0.005
	MeHg reduction rate in surface sediment	1/day	0.008
	MeHg reduction rate in subsurface sediment	1/day	0.01
Hg0 Photo-oxidation	Photolysis rate constant- wavelength 1-10	(1/day)/(W/m ²)	0.001
	Volatilization rate (Henry's Law Constant)	atm/(mole/m ³)	0.0071
MeHg Photo-Reduction	Reduction efficiency	[fraction]	0.93
	Photolysis rate constant- wavelength 1-10	(1/day)/(W/m ²)	0.01
Solids Resuspension and Deposition	Sand settling	m/d	5.0
	Fines and organic matter settling	m/d	0.2
	Sand resuspension	m/d	0
	Silt and organic matter resuspension	m/d	7.5E-08 – 1.9E-05

The performance of the calibrated model was assessed using metrics Root Mean Square Error (RMSE), Mean Absolute Error (MAE), and percent or mean error (Pbias). Table 5-4 and Figure 5-11 present the model's performance in simulating Hg and MeHg concentrations for the calibration segments that have a minimum of 4 observations between 2011 and 2022. Figure 5-11 shows strong correlation between simulated and observed values with the coefficient of determination (R^2) indicating that the model explains about 78% of the variability in THg and 58% of the variability in observed MeHg. Figure 5-12 and Figure 5-13 display the simulated and observed THg and MeHg concentration timeseries.

For most stations model Pbias is below ± 25 percent with an average across stations below ± 5 percent; nonetheless, the relative discrepancies are large at some stations. Overall, considering the limited number of samples, the model demonstrates reasonable performance in replicating observations. In several cases where the Pbias is large it appears that this may be in part due to small discrepancies in the simulated timing of loading events. The first 9 months of 2011 are a model spin up period to allow the water column concentrations to equilibrate with the surface sediment. In a few segments (e.g., 10 and 13 – 16) this results in a relatively large adjustment, possibly indicating inaccuracies in the initial sediment specification. For segment 1 there are observations in both the center channel (1b) and the right-side area (1d). The differences between these sub-segments are perhaps due to the complex workings of Fond du Lac Dam, which has the turbine outlets on one side of the river and the spillway on the other side with an island separating them.

Table 5-4. Performance of WASP model in simulating THg and MeHg, paired data, 2011-2022

	Model Segment	Observed (ng/L)		Simulated (ng/L)	RMSE	MAE	Pbias
		Count	Average	Average	(ng/L)	(ng/L)	Percent
THg	1b	7	4.22	4.65	2.11	1.52	10.19
	1d	8	4.75	4.48	1.00	0.93	-5.61
	3b	14	3.99	4.12	1.58	1.27	3.26
	6b	8	3.52	3.84	1.74	1.10	9.07
	10d	9	4.66	4.90	1.47	1.18	5.06
	12b	5	3.63	3.58	1.16	0.92	-1.41
	13b	6	3.90	3.65	1.07	0.95	-6.57
	14b	5	1.15	1.93	1.36	1.02	67.06
	15b	5	4.07	3.21	1.18	1.11	-21.11
	16b	6	3.15	2.83	1.39	0.97	-10.12
	23b	6	2.77	2.22	1.30	1.01	-19.82
MeHg	1d-S	7	0.27	0.28	0.20	0.13	3.23
	1c-S	6	0.38	0.21	0.31	0.20	-45.68
	3c-S	13	0.26	0.23	0.16	0.12	-14.35
	6c-S	8	0.20	0.23	0.14	0.09	16.3
	10d-S	8	0.23	0.25	0.14	0.10	9.44
	12c-S	5	0.17	0.19	0.08	0.08	11.43
	13c-S	5	0.13	0.16	0.07	0.06	27.46
	14-S	5	0.05	0.06	0.06	0.05	18.67
	15c-S	5	0.17	0.09	0.10	0.08	-48.11
	16c-S	6	0.08	0.13	0.13	0.09	55.36
	23-S	6	0.08	0.06	0.05	0.04	-33.47

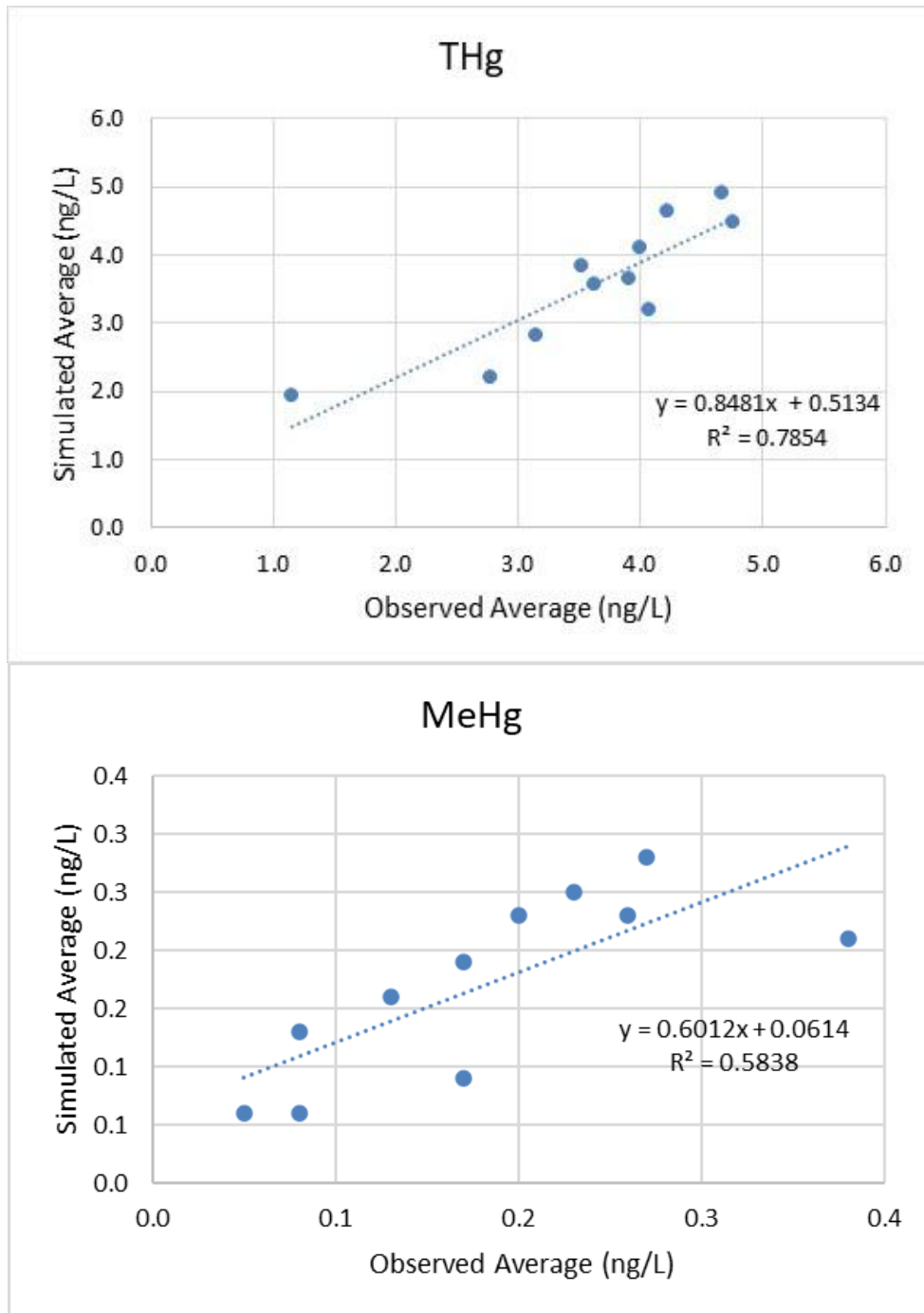
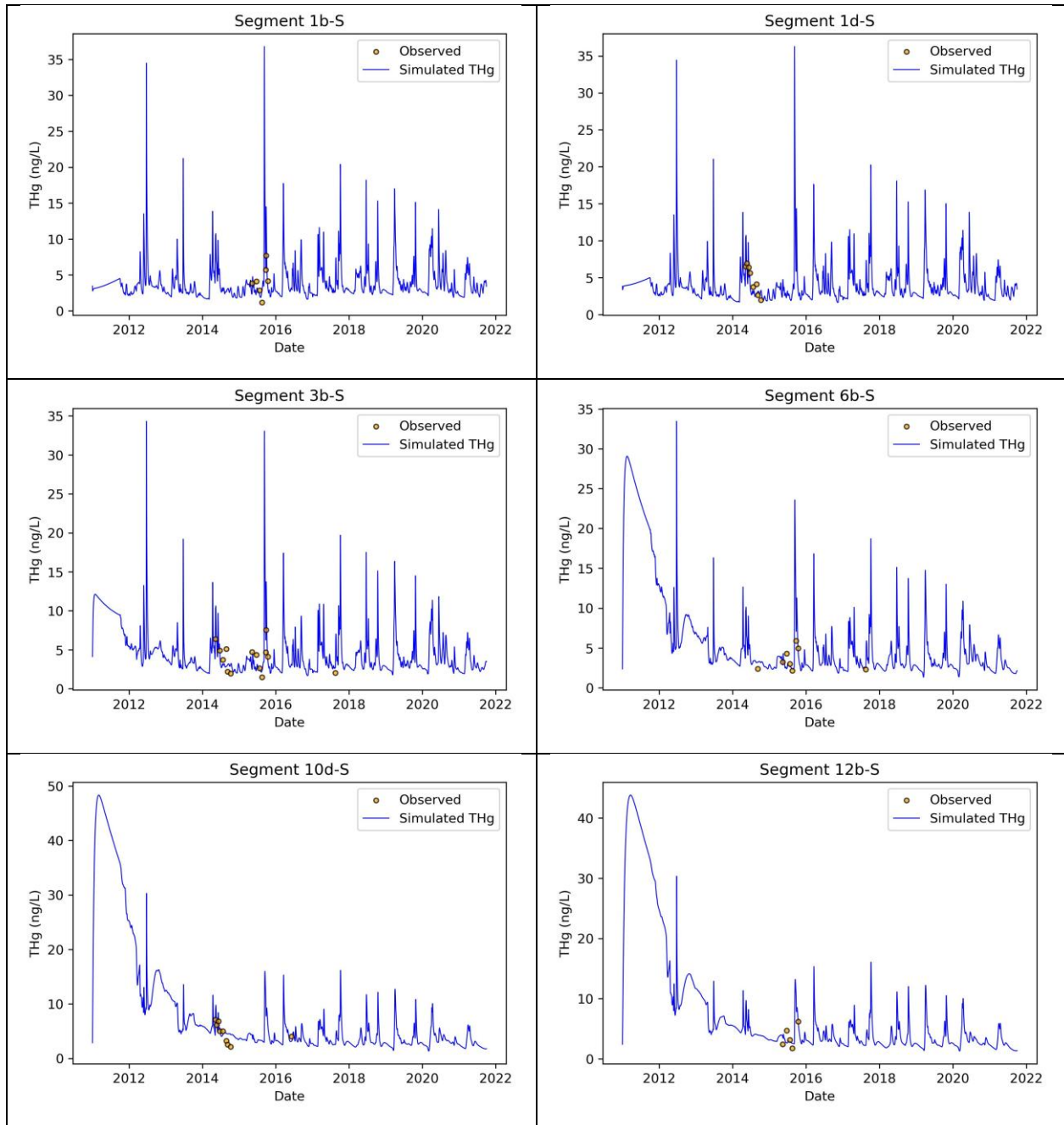


Figure 5-11. Simulated vs. observed station averages for THg (top) and MeHg (bottom)



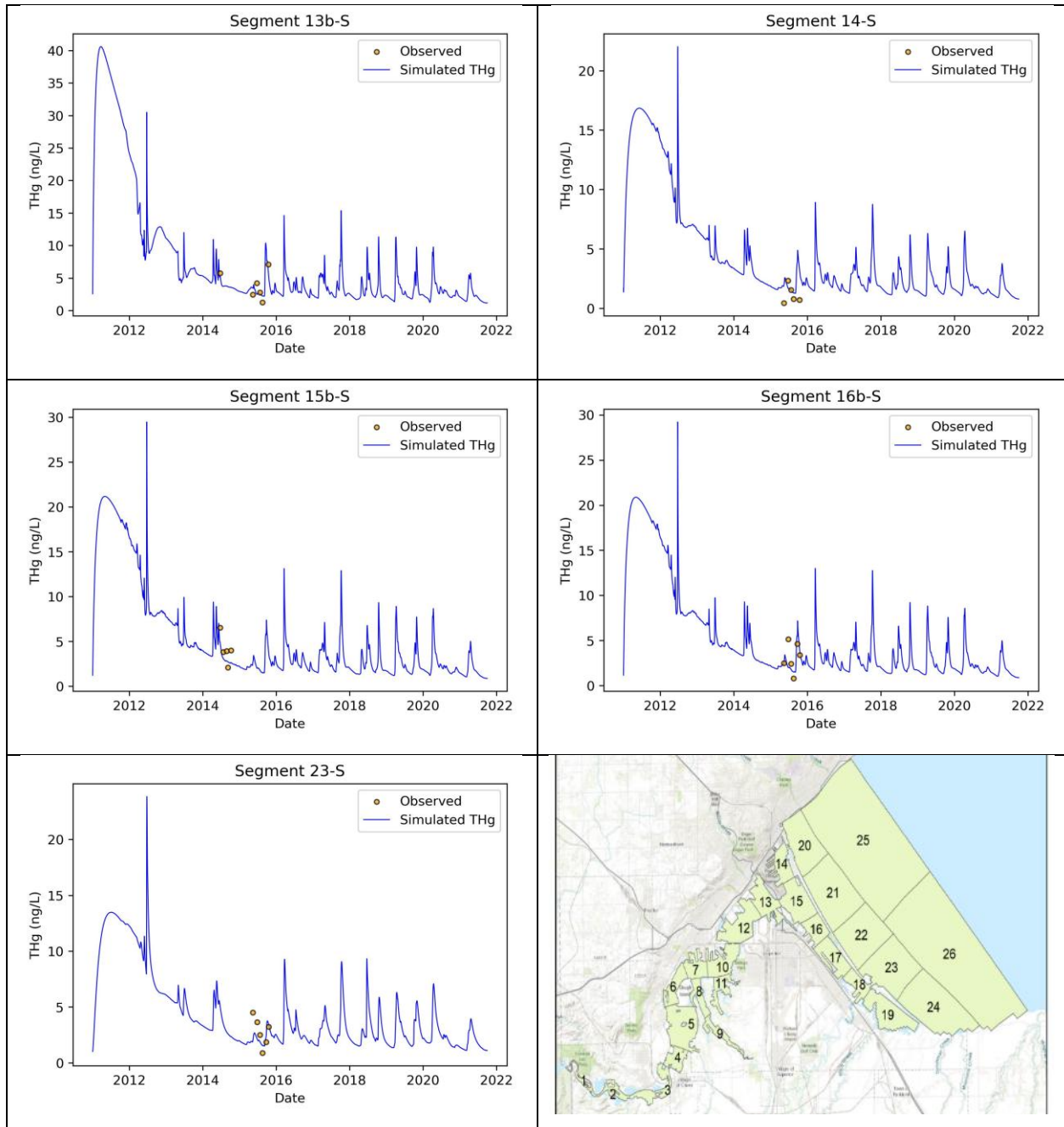
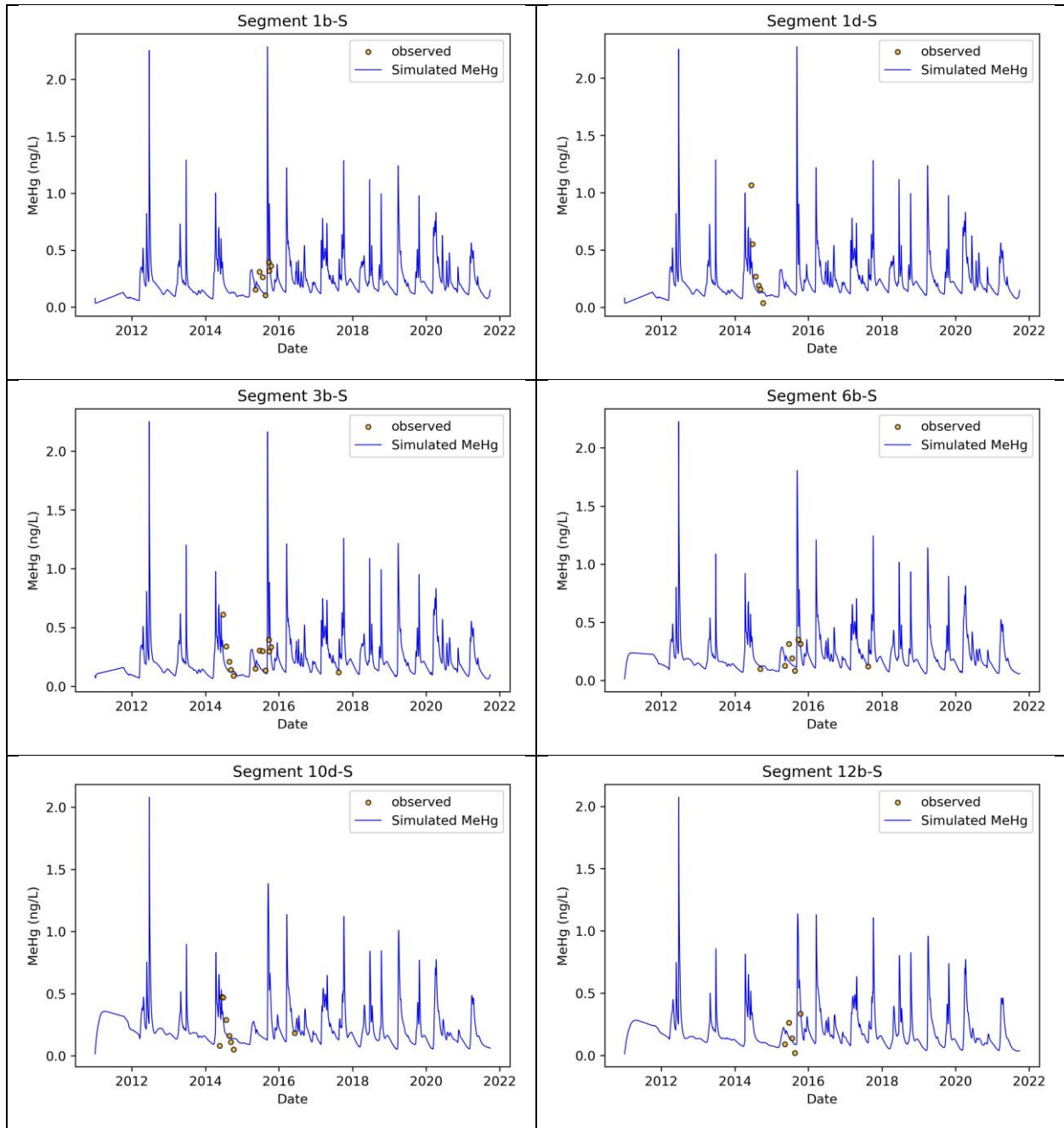


Figure 5-12. Calibration timeseries plots for total Hg, St. Louis River Estuary



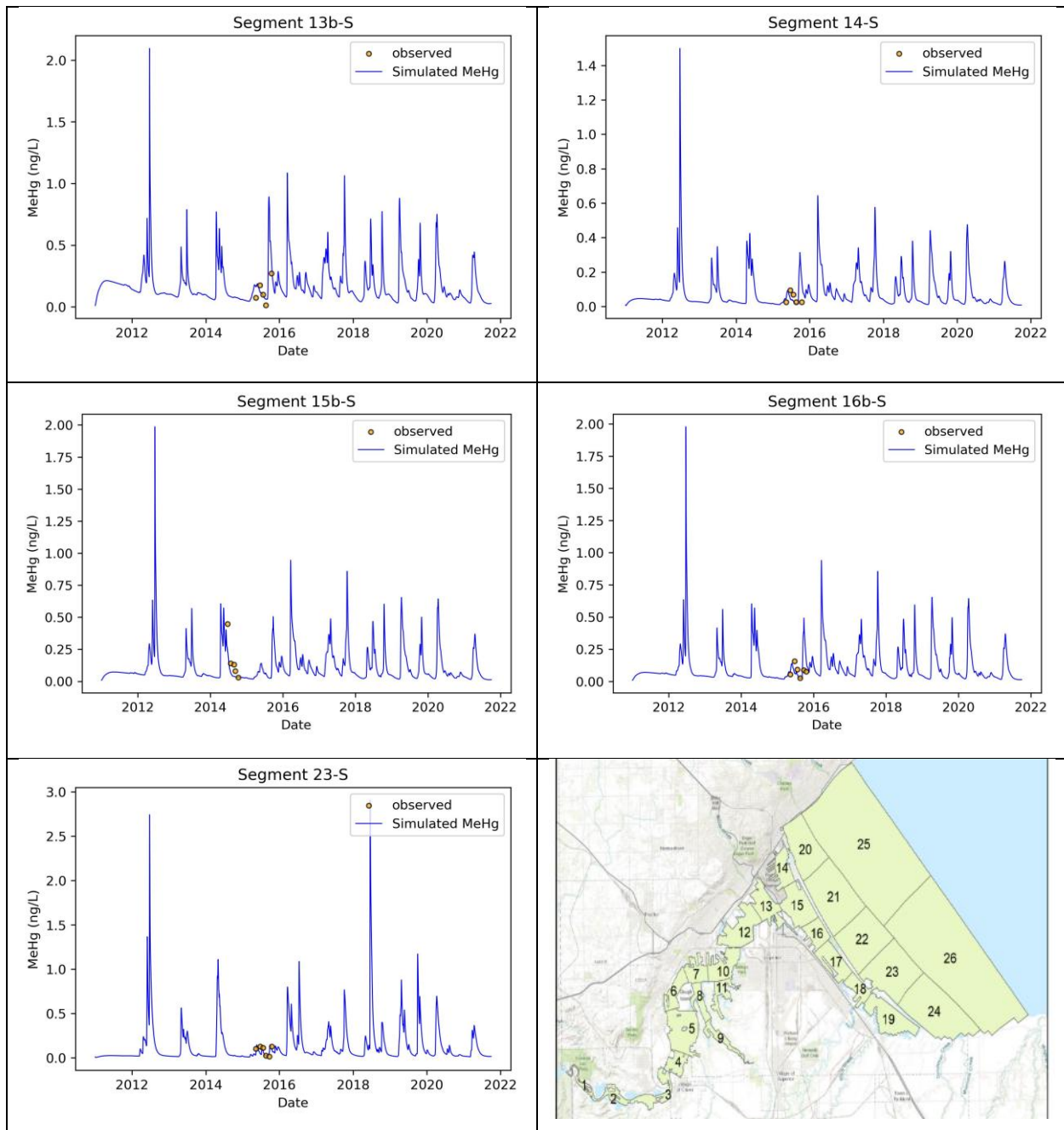


Figure 5-13. Calibration timeseries plots for MeHg, St. Louis River Estuary

The model predicts that THg concentrations over the full simulation period are persistently greater than the state chronic criterion of 1.3 ng/L. However, the simulated results for THg appear to be biased high by large initial concentrations that persist through 2013 and limited observation data show a few measured concentrations less than 1.3 ng/L at five out of 11 stations. The percentage of simulated THg concentrations greater than 1.3 ng/L at the calibration stations for calendar years 2014 – 2021 is shown in Table 5-5. These frequencies are close to 100 percent throughout the St. Louis River mainstem and are largely dependent on the simulation of THg entering the estuary at Fond du Lac Dam.

Table 5-5. WASP simulated frequency of THg concentrations in the St. Louis River Estuary greater than the state chronic criterion of 1.3 ng/L, 2014 – 2021

WASP Model Segment	Percent of Days with THg > 1.3 ng/L
1b	100%
1d	100%
3b	100%
6b	100%
10d	100%
12b	99.9%
13b	98.3%
14	84.5%
15b	94.0%
16b	94.0%
23	96.4%

There are not sufficient observation timeseries data to estimate temporal trends in surface sediment concentrations and the WASP model setup is not conducive to a detailed evaluation of predicted trends. Over time there is ongoing settling from the water column to the sediment. The SLRE model has two sediment layers - surface sediment layer with an initial depth of 0.01 m and an underlying subsurface sediment layer with an initial depth of 0.5 m, as recommended in the WASP guidance. The dynamic bed volume option is selected, with recalculation occurring every 5 days (benthic time step). The thin surface sediment layers, which represent an oxidized interfacial zone, are reset to their initial volume and depth each benthic time step. In a net depositional system, excess mass is passed downward to the subsurface benthic segment at the end of every benthic time step. The subsurface benthic segments are passive. They transport mass upward or downward depending on whether the overlying segment is erosional or depositional. Excess volume and mass are passed downward to the next benthic layer or out of the system while maintaining the bulk density and porosity of the layer (Ambrose et al., 2017).

For the SLRE model there are not additional layers underneath the first subsurface benthic layer. In a net depositional system this results in a net loss of mass that represents deep burial. The loss of this sediment mass also results in a loss of sediment-associated mercury.

In the SLRE model runs during the initial model spin-up period there is diffusive transfer of mercury from the surface sediment to the water column. This likely suggests that the data-based specification of initial sediment mercury concentrations was likely too high for the surface sediment layer and out of equilibrium with the water column concentrations. As noted in Section 5.2.6, these surface sediment concentration measurements are composites over variable depths and may not be representative of mercury within the surface sediment layer that is in direct contact with the water column.

Within the subsurface sediment layers the simulated segment depth and solid concentrations increase over time. This in turn causes the initial THg concentration in the subsurface sediment layers to decrease over time as some of the THg mass is forced out of the bottom of the layer and the remainder is diluted with somewhat cleaner sediment.

5.5 MERCURY MASS BALANCE FOR THE ST. LOUIS RIVER ESTUARY

This section summarizes the mass balances for mercury in the SLRE, defined as the area from the two harbor entrances to Fond du Lac Dam and to the mouth of the Nemadji River. The structure of the mercury module in WASP does not readily facilitate mass balance calculations because the available output is primarily for concentrations and transformation rates and does not provide cumulative mass flux summaries directly. Mass fluxes must be calculated by the user and, for some components such as outflow to Lake Superior, these are inevitably approximations. Nonetheless, a reasonably accurate estimate of the mass balance simulated by the model can be calculated. This is done for Water Years 2012 – 2021 (i.e., omitting the spin-up period of 1/1/2011 – 9/30/2011) in Table 5-6.

Table 5-6. Simulated mercury mass balance for the St. Louis River Estuary, water years 2012-2021

	Component	Hg(II) (g/yr)	MeHg (g/yr)	Hg(0) (g/yr)	THg (g/yr)
Inputs					
	St. Louis River	12,790	934	0	13,724
	Nemadji River	9,993	697	0	10,690
	Tributaries to Estuary	15	2	0	16
	Point Source	116	2	0	119
	Atmospheric Deposition	692	0	0	692
	Total Input	23,606	1,635	~0*	25,240
Outputs					
	To Lake Superior	11,733	848	1653	14,233
	Hg(0) volatilization			371	371
	Total Output	11,733	848	2,023	14,604
Net Exchanges with Sediment		-11,867	-11,872	-787	1,653
	Retention in Estuary	50.3%	50.29%	48.16%	

* We assume minimal Hg(0) load from the tributaries because (1) little monitoring for Hg(0) is available, and (2) it is likely that most Hg(0) will be lost to the atmosphere in the hydropower and dam spillway releases from the St. Louis River and in high flows from the Nemadji River. All mass loads are rounded to the nearest g/yr.

The mercury balance is dominated by the inorganic ionic form (Hg(II)). Table 5-6 indicates that the estuary is a net sink for mercury. It is estimated that about 43 percent of the total mercury entering the estuary ends up in estuary sediment including 50 percent of the influent Hg(II). Apparent retention of MeHg is less primarily because there is net production of MeHg in the estuary (Janssen et al., 2021). Some MeHg may also be converted to gaseous Hg(0) and lost to the atmosphere.

The external source attribution is shown for ionic (Hg(II)) and methyl (MeHg) mercury in Figure 5-14. Loads of both species of mercury are estimated to be dominated by loads from the St. Louis River with a substantial contribution from the Nemadji River – although the Nemadji loads have only a small impact on

the up-estuary portions of the SLRE. Contributions from direct tributaries (which include the Duluth, MN and Superior, WI MS4 areas), the WLSSD point source, and direct atmospheric deposition to the water surface are estimated to be small in comparison to the upstream loads.

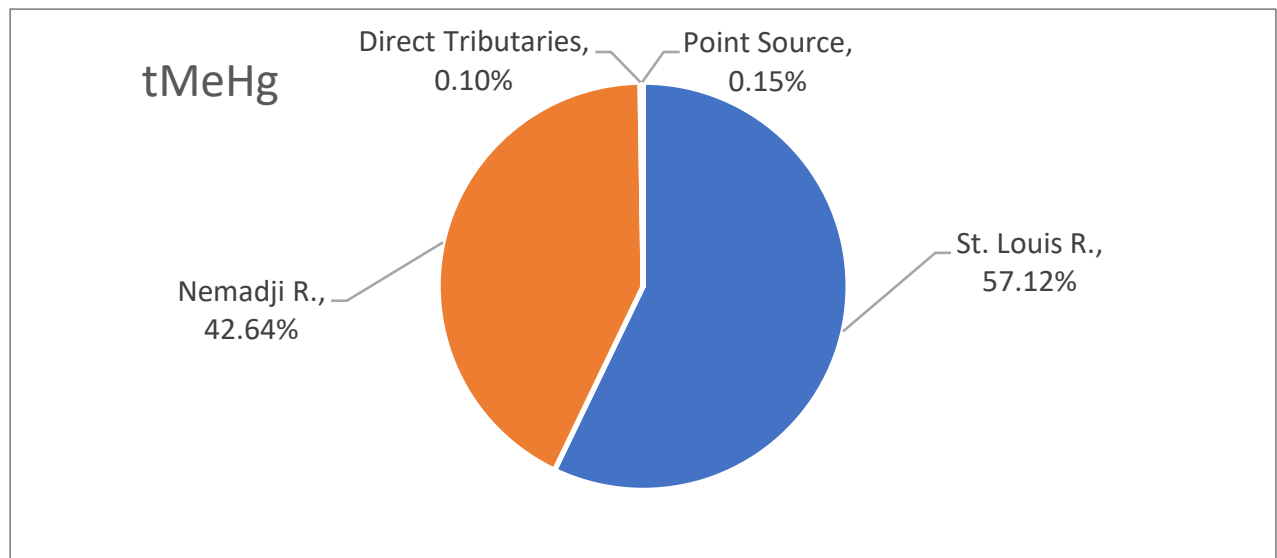
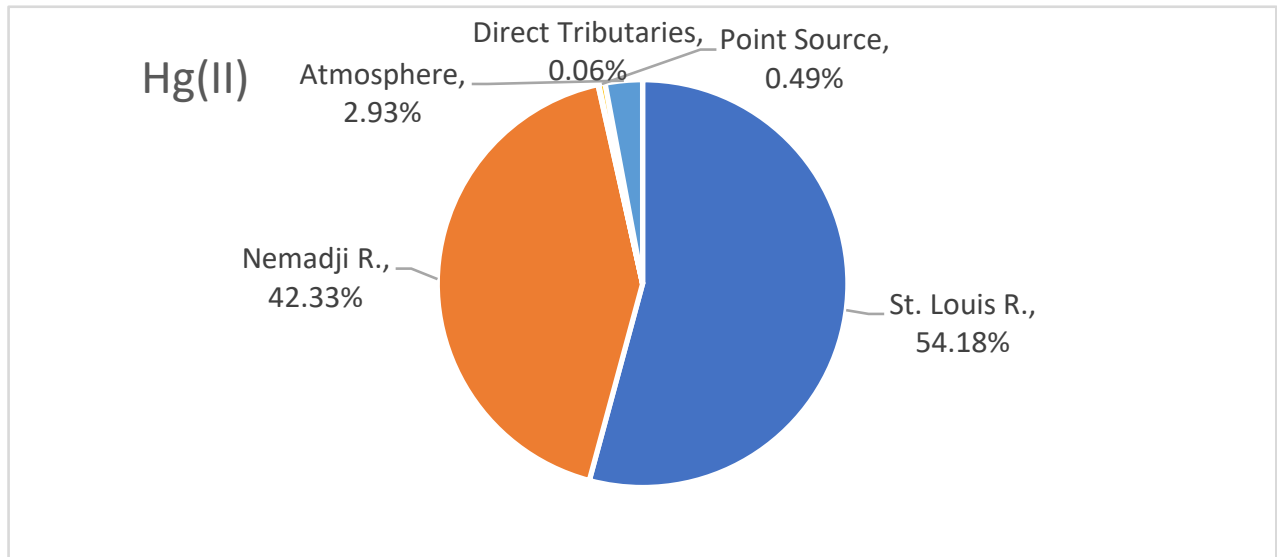


Figure 5-14. Source attribution for external mercury loads to St. Louis River Estuary, water years 2012-2021

6.0 MERCURY BIOACCUMULATION IN FISH TISSUE

BAFs were calculated to translate the fish tissue standard (0.2 mg/kg) to water MeHg concentration targets for TMDL development. For the TMDL calculations, one BAF was calculated for the estuary impairments; upstream of the estuary one BAF was calculated for the lake/reservoir impairments (lentic) and one BAF was calculated for the river/stream (lotic) impairments. Separate BAFs were calculated for the estuary to account for habitat differences and contaminated sediment in the estuary. In addition to food chain differences, separate BAFs for the lake/reservoir impairments and river/stream impairments were also calculated to account for the potential for higher MeHg concentrations in the reservoirs from water level changes that may enhance MeHg release from the sediments (See Section 4.1.4; Sorensen 2019, Eckley et al., 2015).

6.1 DATA PROCESSING

MPCA provided datasets containing water column mercury and fish tissue concentrations. Data processing and analysis was performed using R routines (R Core Team 2022). The variables of interest were water column concentration (tMeHg and dMeHg; ng/L), fish tissue concentration (total Hg, wet-weight mg/kg, which is typically predominantly MeHg), and fish length (cm, an approximate surrogate for age). Top predator fish (trophic level [TL] 4 species) are expected to have the highest Hg body burdens and also include species likely to be consumed by humans. Three species in TL 4 are well-represented in the monitoring data: northern pike (*Esox lucius*; NOP), walleye (*Sander vitreus*, synonym *Stizostedion vitreum*; WAE), and channel catfish (*Ictalurus punctatus*; CCF). TL 3 fish, such as perch were also sampled, but have lower Hg body burdens and lower BAFs such that setting targets based on TL 4 species will also be protective of human consumption of TL 3 species.

Filletts (both with and without skin) or dorsal muscle plugs were used to assess fish tissue concentration in the tissue usually eaten by humans. We restricted the analysis to more recent data to limit the possible impacts of temporal trends and used water column data collected between 2005 and 2021 and fish tissue data collected between 2000 and 2019. Fish tissue data were included back to 2000 to provide broader spatial coverage; no fish Hg data are available for 2020 – 2021. Fish data were collected from streams, rivers, lakes, and reservoirs throughout the SLRW, and in the SLRE adjoining Duluth, MN and Superior, WI (Figure 6-1). The fish and water column data were grouped by waterbody type as river/stream, lake/reservoir, and estuary (downstream of the Fond du Lac dam).

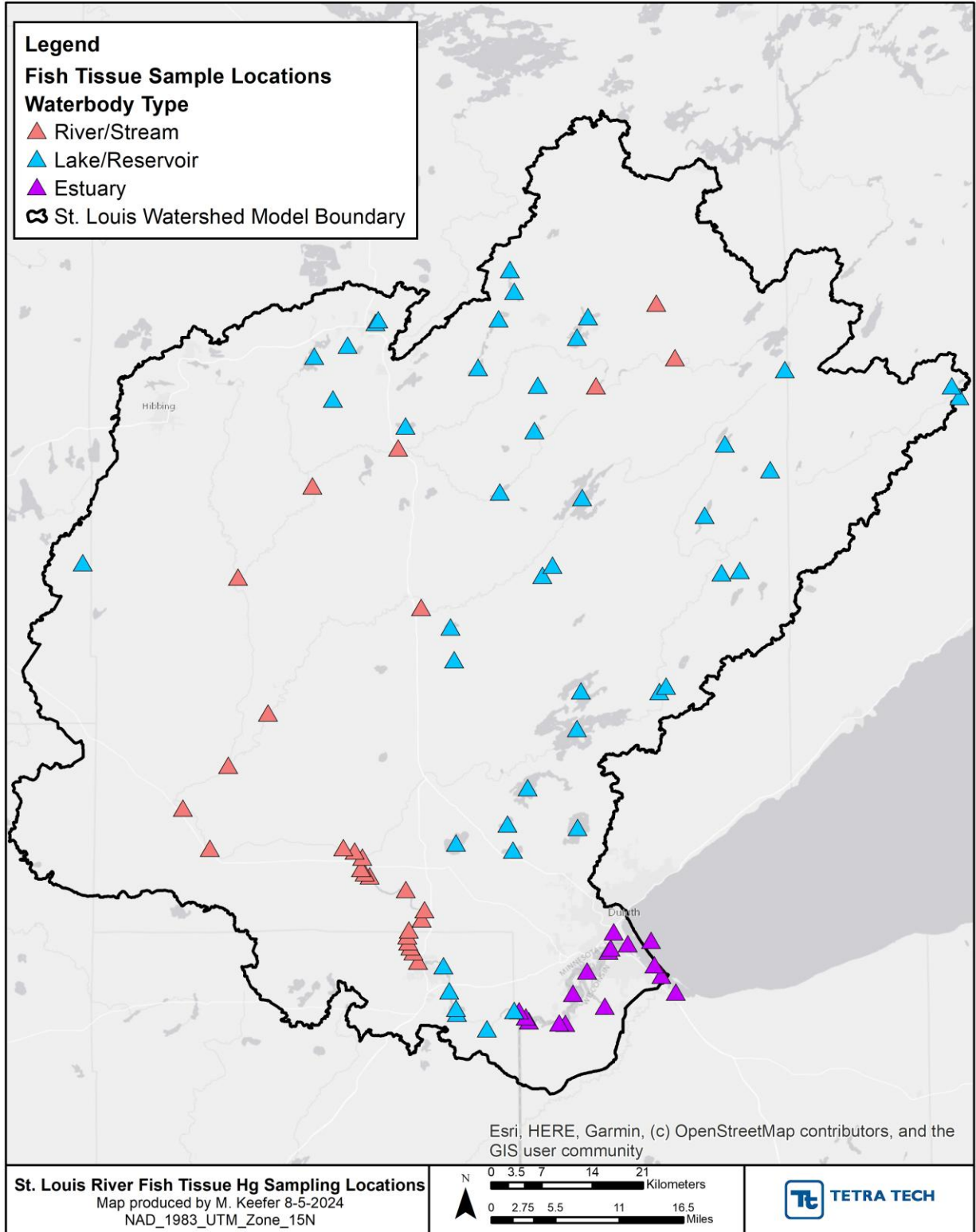


Figure 6-1. Map of fish tissue sampling locations 2000-2019, colored by waterbody type

Data were checked for quality assurance. Physically impossible values (e.g., negative concentrations) were screened – none were found. Zero values for concentration were also screened – none were found. Nondetect (censored) data were replaced with one-half the reported censoring level. In total, five out of 572 (0.87%) of the water samples and zero of the fish samples were identified as censored. It is well established that calculating statistics with replacement of censored data with one-half the detection limit can yield suboptimal or biased estimates, and a variety of sophisticated methods are available to address this problem (e.g., Helsel, 2005; Bolks et al., 2014); however, because the count of censored data was small use of one-half the detection limit does not introduce significant bias in this study.

The final processed dataset contained 2,119 fish tissue samples collected between 2000 and 2019 (Table 6-1). Each fish concentration sample had a paired length value. The majority (73.8%) of fish samples were from lakes/reservoirs, while the majority (83.0%) of water samples were from rivers and streams. Channel catfish (6.8%) were sampled less frequently than northern pike (47.3%) or walleye (45.9%). There were no catfish samples from smaller tributary streams.

Table 6-1. BAF analysis sample counts by waterbody type and species

Water Type	Fish Species			Total by Water Type	Percent of Fish	Water Samples*	Percent of Water Samples
	CCF	NOP	WAE				
River/Stream	47	28	46	121	5.7%	463	72.0%
Lake/Reservoir	14	818	731	1,563	73.8%	50	8%
Estuary	84	156	195	435	20.5%	130	20%
Total	145	1,002	972	2,119	-	642	-

Note: This table summarizes fish tissue samples for 2000 – 2019 and water column samples for 2005 – 2021.

* Water sample count for river/stream and lake/reservoir categories is for dMeHg; count for the estuary is for tMeHg samples.

Data were visually explored using boxplots and cumulative distribution function (CDF) plots. Fish tissue distributions were similar across species (Figure 6-2). However, fish tissue distributions varied somewhat across waterbody types, with similar medians but larger concentration ranges observed in the estuary and lakes/reservoirs (Figure 6-3). In these plots, the “box” shows the interquartile range (IQR), enclosing the median value; the “whiskers” extend 1.5 x IQR.

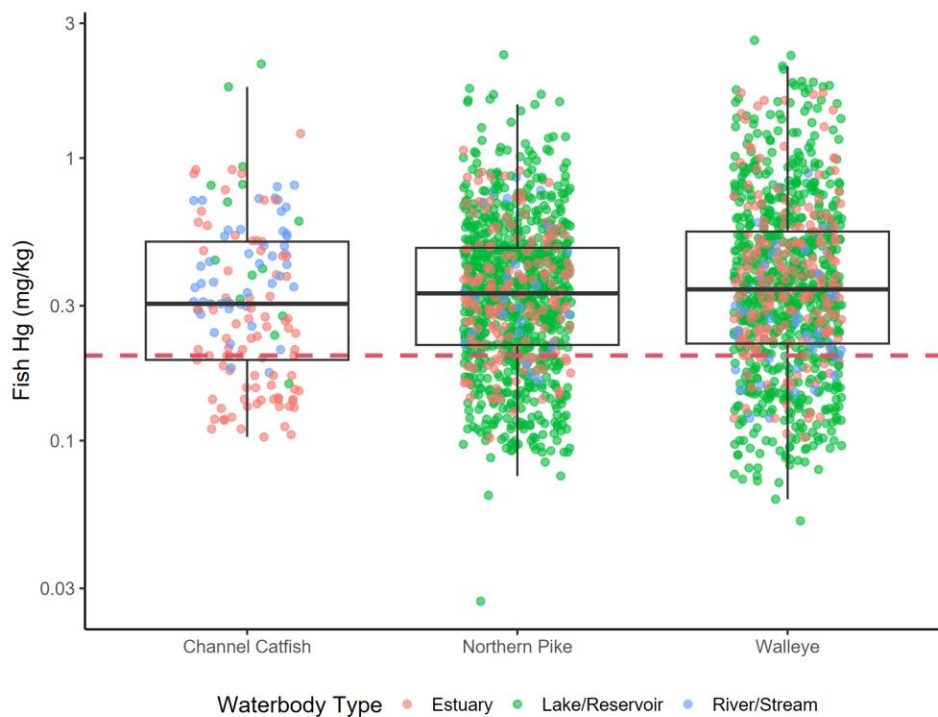


Figure 6-2. Boxplots of fish tissue Hg by species. Horizontal red dashed line denotes the Minnesota fish tissue criterion.

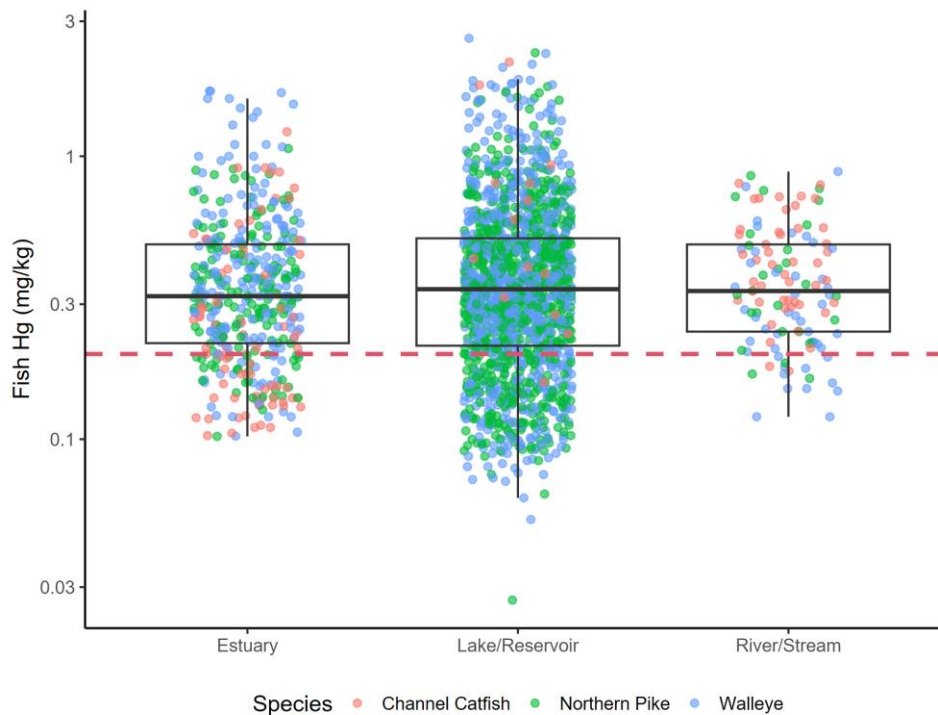


Figure 6-3. Boxplots of fish tissue Hg by waterbody type. Horizontal red dashed line denotes the Minnesota fish tissue criterion (0.2 mg/kg).

Fish length serves as an approximate surrogate for fish age. Hg in fish tissue is expected to increase continuously with age. Fish tissue Hg concentrations are evaluated at a standard length representative of individuals likely to be consumed by humans. MPCA (2007) defines the standard length as “a set total fish length that is used to compare mercury concentrations among lakes and over time.” The standard lengths used in the MPCA (2007) statewide TMDL are 55 cm for northern pike and 40 cm walleye, which are applied here, and MPCA indicated that we should use a 48 cm standard length for channel catfish (email from Bruce Monson, MPCA, to Michelle Schmidt, Tetra Tech, 8/29/2022). Mercury concentrations for a standard-length fish are determined from a regression of measured mercury fish tissue concentration versus fish length. Sampled fish lengths varied across species, with the median sampled lengths slightly below the standard lengths (Figure 6-4 and Figure 6-5).

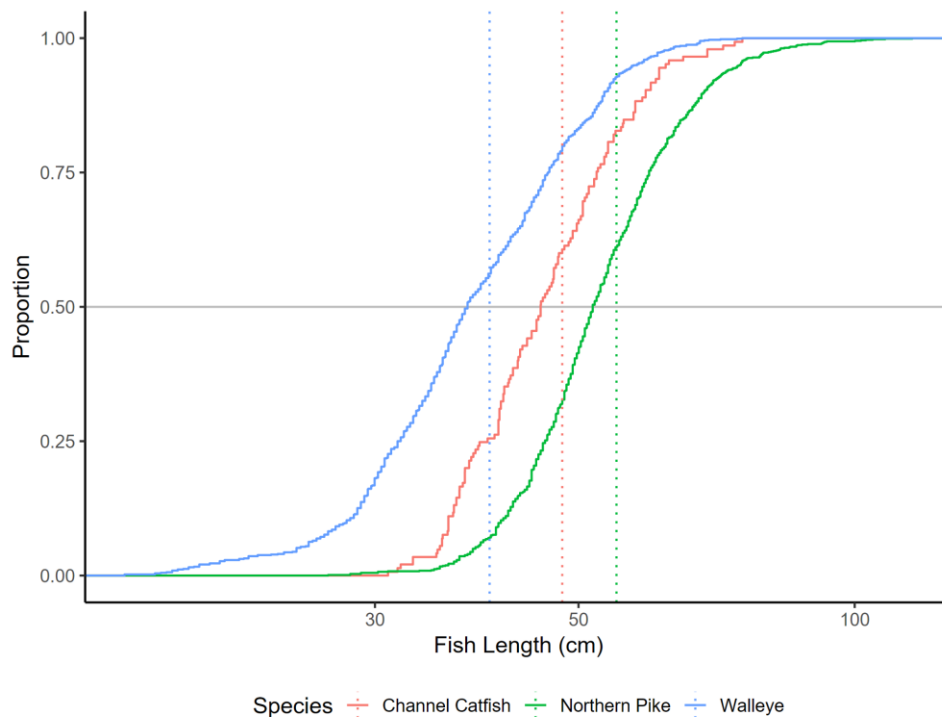


Figure 6-4. Cumulative distribution function (CDF) of fish length by species. Vertical colored dashed lines denote the standard length for each species. Solid grey line represents the median.

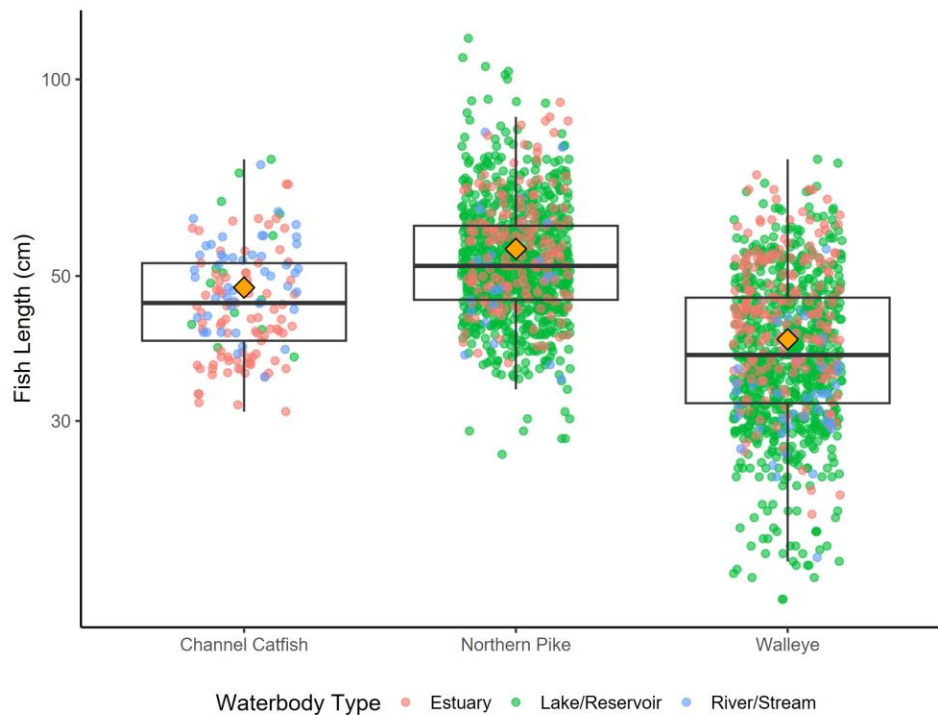


Figure 6-5. Box plots of fish length by species. Orange diamond denotes standard length.

Reported water concentrations (tMeHg) vary somewhat across waterbody types, with lotic concentrations from rivers and streams generally slightly higher than lentic samples from lakes, reservoirs, and the estuary (Figure 6-6), which corresponds well with the DOC distribution among these water types and supports the inference that Hg and MeHg partitioning to DOC is the primary transport mechanism in the SLRW.

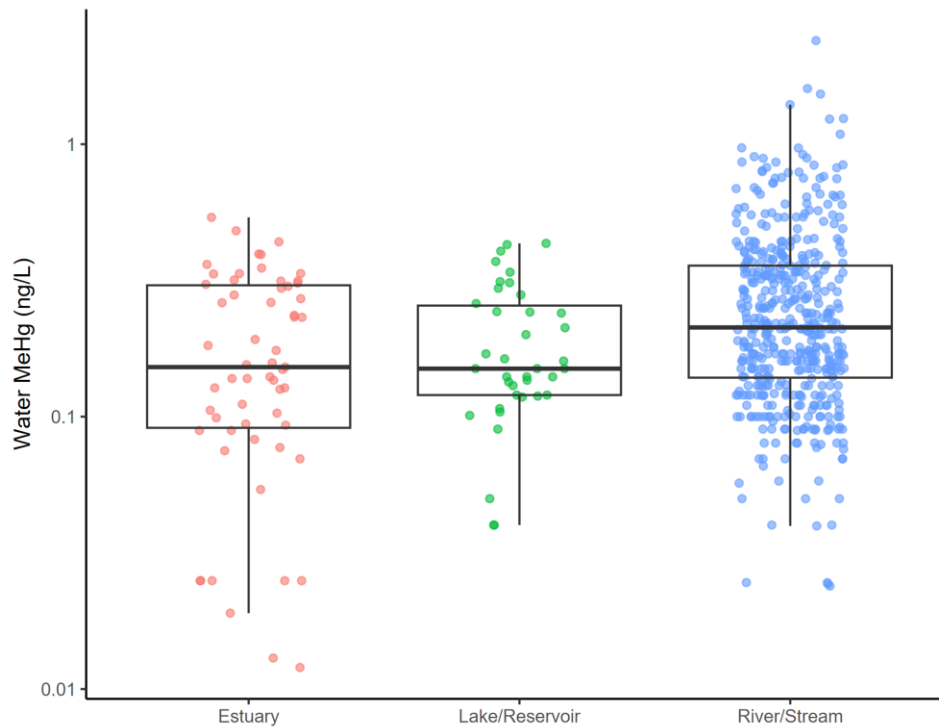


Figure 6-6. Boxplots of MeHg concentrations in water by waterbody type

Scatterplots of fish tissue vs length show a steeper slope for fish tissue concentration versus length for catfish compared to the other species (Figure 6-7), which may reflect fewer samples from a more restricted set of habitats. Calculation of the BAF stratified to waterbody type reduces the large amount of scatter observed in the northern pike and walleye relationships to fish length.

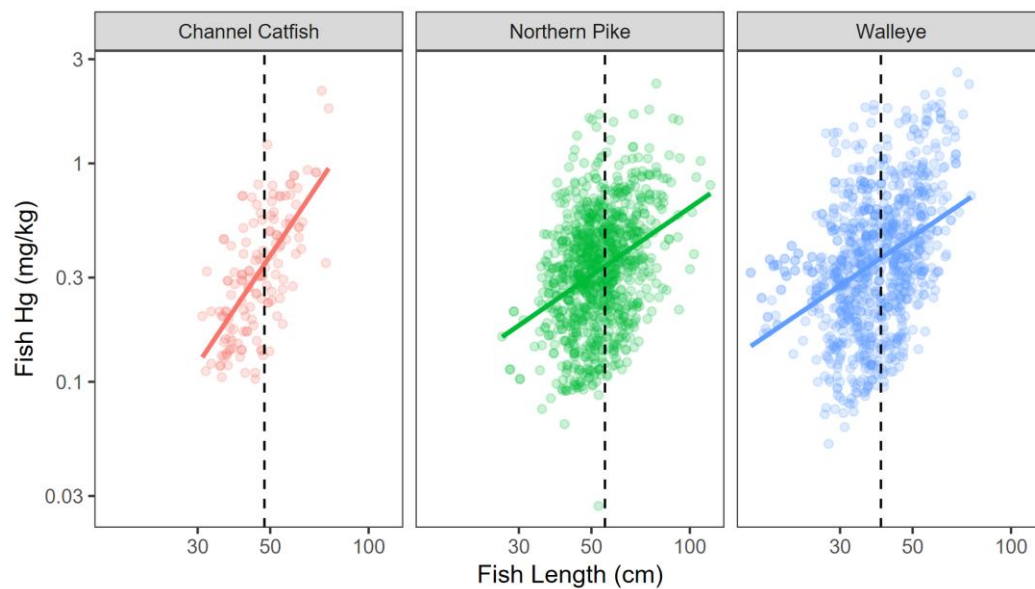


Figure 6-7. Scatterplots of fish tissue vs length. Solid line denotes linear fit. Vertical dashed line denotes the standard length. Summary statistics by species and waterbody type are presented in Table 6-2.

Table 6-2. Summary statistics, grouped by waterbody type and species

Waterbody Type	Species/Media	Variable	N	Min	10 th %le	25 th %le	Median or GM*	Mean	Std Deviation	75 th %le	90 th %le	Max
River/Stream	CCF	Fish Tissue (Hg mg/kg)	47	0.174	0.249	0.305	0.414	0.437	0.172	0.545	0.710	0.802
River/Stream	CCF	Length (cm)	47	35.0	41.0	45.2	49.4	50.0	7.5	53.8	57.7	74.0
River/Stream	NOP	Fish Tissue (Hg mg/kg)	28	0.164	0.200	0.240	0.330	0.398	0.202	0.496	0.731	0.854
River/Stream	NOP	Length (cm)	28	34.8	38.9	45.8	52.3	53.5	11.8	60.4	65.6	83.0
River/Stream	WAE	Fish Tissue (Hg mg/kg)	46	0.120	0.155	0.205	0.266	0.317	0.168	0.386	0.529	0.883
River/Stream	WAE	Length (cm)	46	18.5	26.9	30.0	33.5	34.1	6.6	37.8	43.1	55.0
River/Stream	Water	Water (tMeHg ng/L)	482	0.03	0.10	0.13	0.22	0.28	0.24	0.34	0.55	2.40
River/Stream	Water	Water (dMeHg ng/L)	463	0.0025	0.061	0.11	0.2	0.30	0.3	0.37	0.61	2.48
Lake/Reservoir	CCF	Fish Tissue (Hg mg/kg)	14	0.159	0.248	0.334	0.517	0.714	0.586	0.806	1.530	2.152
Lake/Reservoir	CCF	Length (cm)	14	37.6	39.6	42.6	51.1	52.3	12.3	61.1	69.8	75.4
Lake/Reservoir	NOP	Fish Tissue (Hg mg/kg)	818	0.027	0.136	0.214	0.334	0.390	0.263	0.484	0.691	2.321
Lake/Reservoir	NOP	Length (cm)	818	26.7	40.9	45.7	52.3	53.4	11.5	59.2	68.1	115.6
Lake/Reservoir	WAE	Fish Tissue (Hg mg/kg)	731	0.052	0.130	0.210	0.343	0.455	0.367	0.578	0.904	2.611
Lake/Reservoir	WAE	Length (cm)	731	16.0	27.2	31.0	37.2	38.6	10.3	45.6	52.8	75.4
Lake/Reservoir	Water	Water (tMeHg ng/L)	14	0.101	0.153	0.244	0.313	0.358	0.195	0.43	0.467	0.89
Lake/Reservoir	Water	Water (dMeHg ng/L)	50	0.005	0.025	0.06	0.137	0.351	0.6	0.34	0.879	2.880
Estuary	CCF	Fish Tissue (Hg mg/kg)	84	0.103	0.124	0.140	0.210	0.305	0.231	0.382	0.632	1.220
Estuary	CCF	Length (cm)	84	31.0	35.5	37.1	43.3	44.1	8.6	49.1	57.5	69.1
Estuary	NOP	Fish Tissue (Hg mg/kg)	156	0.102	0.177	0.229	0.325	0.371	0.191	0.471	0.650	1.065
Estuary	NOP	Length (cm)	156	36.8	44.2	48.0	55.2	56.2	11.2	62.1	69.8	92.2
Estuary	WAE	Fish Tissue (Hg mg/kg)	195	0.103	0.183	0.247	0.366	0.459	0.328	0.528	0.846	1.700

Waterbody Type	Species/Media	Variable	N	Min	10 th %ile	25 th %ile	Median or GM*	Mean	Std Deviation	75 th %ile	90 th %ile	Max
Estuary	WAE	Length (cm)	195	21.6	31.7	36.7	43.1	44.3	9.9	52.1	57.7	71.4
Estuary	Water	Water (tMeHg ng/L)	130	0.012	0.05	0.089	0.151	0.216	0.183	0.314	0.475	1.07
Estuary	Water	Water (dMeHg ng/L)	126	0.020	0.040	0.070	0.127	0.188	0.174	0.258	0.457	1.04

* Column shows median (50th percentile) for fish tissue concentrations; geometric mean (GM) for other measures.

6.2 RELATING EXPOSURE CONCENTRATION TO FISH TISSUE MERCURY TARGETS

Target concentrations for tMeHg and dMeHg in water can be derived using a fish tissue criterion and a BAF (USEPA, 2010). The formula for the BAF is:

$$BAF = \frac{FishTissueConcentration}{WaterConcentration} \times 10^6$$

where fish tissue is in units of mg/kg, and water is in ng/L, and BAF is in L/kg. BAFs were calculated for each waterbody type–species combination, using length standardized median values for fish tissue and geometric means for water concentrations.

The fish tissue concentration for a given species and waterbody type is standardized to the predefined length by fitting a linear regression. The equation used for each sample i is:

$$\ln(FishTissue_i) = \alpha + \beta * \ln(FishLength_i) + e_i$$

where α is an intercept term, β is the slope coefficient relative to the natural logarithm of fish length, i is the sample index, and e_i denotes a residual error term accounting for deviation of the sample from the regression line. Variables were (natural) log transformed to account for skew, approximate linearity, and ensure positive results.

The length standardization regression parameters are estimated across all data for each fish species and waterbody type combination to account for different food chain and habitat conditions. Fitted parameters are shown in Table 6-3.

Table 6-3. Regression Parameters for length standardization of mercury tissue concentrations in fish

Waterbody Type	Species	Intercept	Slope	Standard Error of Intercept	Standard Error of Slope
Estuary	CCF	-8.679	1.931	1.155	0.306
Lake/Reservoir	CCF	-10.378	2.485	2.443	0.620
River/Stream	CCF	-7.274	1.633	1.228	0.315
Estuary	NOP	-6.079	1.238	0.726	0.181
Lake/Reservoir	NOP	-4.969	0.970	0.397	0.100
River/Stream	NOP	-8.895	1.985	0.824	0.208
Estuary	WAE	-6.760	1.538	0.571	0.152
Lake/Reservoir	WAE	-4.346	0.910	0.339	0.094
River/Stream	WAE	-7.173	0.1.681	0.960	0.273

After fitting the parameters, the regression equation for each waterbody type species combination is used to calculate the mercury concentration for the standard-length fish. The standardized fish tissue concentration in mg/kg units is the exponentiated (data were natural log transformed) results of the predicted value at the standard length (40 cm, 48 cm, and 55 cm for walleye, catfish, and northern pike, respectively). Note that the linear regression fits to the mean of the natural logarithms. Therefore, fitting log-transformed data and back-transforming is akin to fitting to the geometric mean of the untransformed observations. If the underlying true distribution is accurately represented by the lognormal distribution the geometric mean and median of the

untransformed data would be the same. We prefer to use the median of the fish data because it is a more robust estimator that is less affected by anomalous or extreme outliers in smaller samples.

Figure 6-8 includes two examples of the linear regression results and the standardized fish tissue concentration for channel catfish in the estuary (0.3 mg/kg) and northern pike in the lake/reservoir (0.34 mg/kg).

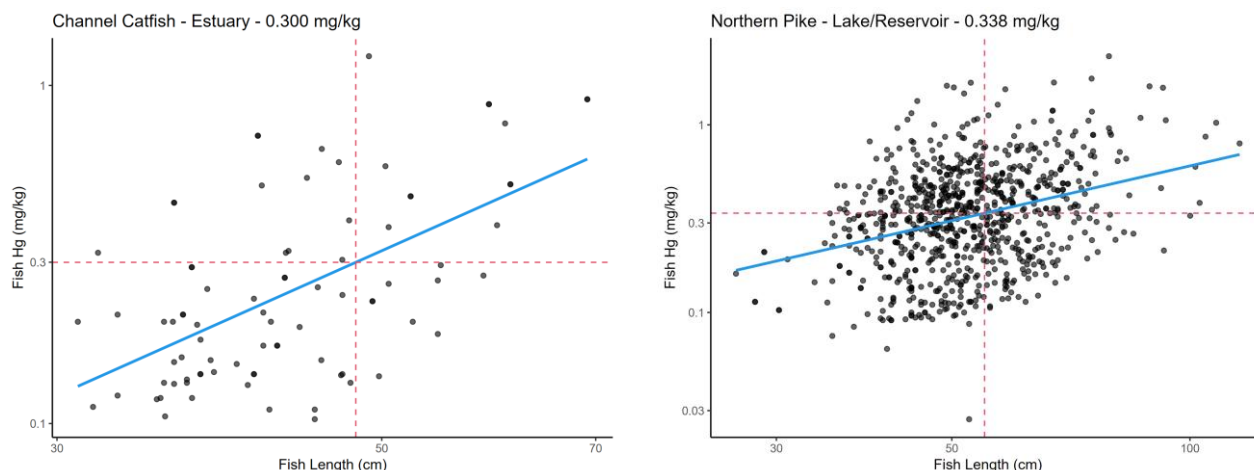


Figure 6-8. Scatterplots of channel catfish-estuaries (LEFT) and northern pike-lakes (RIGHT) relationship of tissue concentration to fish length.

Solid line denotes linear fit. Vertical dashed red line denotes standard length. Horizontal dashed red line denotes the estimated mercury concentration (back transformed) at the standard length (also reported above).

For each individual fish specimen, the mercury concentration is standardized to account for differences from the standard-length fish concentration. To standardize the observed fish tissue concentrations, the plotted point of each fish tissue sample was essentially "slid" parallel to the regression line toward the species standard length (vertical red dashed line in Figure 6-8). For fish specimens below the line of best fit (blue line in Figure 6-8), if that specimen were to grow to standard length, we expect the fish tissue concentration to be less than the standard length mercury concentration (horizontal red dashed line in Figure 6-8). For fish specimens above the line of best fit, if that specimen were to grow to standard length, we would expect the fish tissue concentration to be greater than the standard length mercury concentration. This calculation is performed by adding the residual concentration from the difference of the individual specimen to the regression line to the standard length mercury concentration for that species-waterbody type combination. The residual term is calculated as the difference between the natural logarithm of the observed concentration and the predicted average concentration at the observed length with $e_i = 0$. This standardization process was performed for each individual fish specimen, based on the relevant linear regression model.

Once all the individual fish specimen data have been length standardized, the median (50th percentile) of the standardized fish tissue concentration is calculated and used to determine the BAF. The median was chosen because it is less subject to outliers than the geometric mean. It is also the same summary statistic that EPA recommends for the national BAF (USEPA, 2001). For the area upstream of Fond du Lac Dam, BAFs were calculated for each TL4 species (northern pike, walleye, and channel catfish) for the waterbody type groups rivers/streams and lakes/reservoirs. One BAF for the lake/reservoir group and one BAF for the rivers/streams group were calculated by taking the geometric mean of the BAFs for the three TL 4 fish species. These BAFs were used to calculate two dMeHg concentration targets that in turn are used to calculate loading capacities for lakes/reservoirs or river/stream sections with fish impairments upstream of the estuary. A separate BAF was

calculated for the estuary due to differences in the food web and relationship of MeHg to THg in this area using the same approach by taking the geometric mean of the BAFs for the three fish species. This BAF was used to calculate one tMeHg concentration target for fish impairments in the estuary.

A tMeHg or dMeHg water concentration target associated with a desired fish tissue target is calculated using the formula:

$$WaterTarget = \frac{FishTissueTarget}{BAF} * 10^6$$

where 10^6 is for unit conversion from a fish tissue criterion in mg/kg and BAF in L/kg to a water target in units of ng/L.

The standardized length fish tissue concentration (or its summary measure) is compared to Minnesota's fish tissue criterion, which is 0.2 mg/kg wet weight. The Fond du Lac Band uses the EPA fish tissue criterion of 0.3 mg/kg; however, the impaired segments for which this criterion applies are all along the boundaries of the reservation, so the more stringent Minnesota criterion will apply.

The water column MeHg concentration target to achieve the fish tissue criterion and calculate the TMDL can be computed from either a BAF or from a reduction factor (RF) calculated from the standardized fish tissue concentration. The RF is the percent reduction needed to achieve the 0.2 mg/kg Hg tissue criterion for the median of the standard-length fish mercury concentration. For the median fish tissue concentration, the RF is:

$$RF = \frac{50\%le\ Fish\ Concentration - 0.2}{50\%le\ Fish\ Concentration}, \quad Water\ Target = (1 - RF) * Water_{GM}$$

The results obtained using either the RF or BAF method are mathematically identical. Results for walleye in the estuary relative to tMeHg (see Table A-1) are shown for example:

$$Water\ Target = (1 - RF) * Water_{GM} = \left[1 - \frac{(Fish_{50} - Fish\ target)}{Fish_{50}} \right] * Water_{GM} =$$

$$\left[1 - \frac{(0.321 - 0.2)}{0.321} \right] * 0.138 \frac{ng\ dMeHg}{L} = 0.086\ ng\ tMeHg/L$$

$$Water\ Target = Fish\ target / BAF_{50} = \frac{0.2 \frac{mg}{kg}}{\left(\frac{Fish_{50}\ mg/kg}{Water_{GM}\ ng/L} \right)} =$$

$$\frac{0.2 \frac{mg}{kg}}{\left(\frac{0.321\ mg/kg}{0.138\ ng/L} \right)} = 0.086\ ng\ tMeHg/L$$

Reduction targets for individual species and waterbody combinations based on median fish tissue concentrations range from 39% to 65%. The largest estimated reductions to achieve tissue targets are for channel catfish in lakes/reservoirs. However, this fish – waterbody combination has a relatively small sample size for fish tissue concentrations (n = 14). The resulting water column targets are similar for tMeHg and dMeHg, consistent with observations that dMeHg is typically close to tMeHg concentration. (Because many samples did not include analyses for both tMeHg and dMeHg the geometric sample mean concentration for dMeHg is higher than that for tMeHg in the river samples.)

To simplify the approach for addressing fish tissue-based impairments, MPCA decided to calculate a single reduction target to achieve the MeHg fish tissue criterion across all TL4 fish for each waterbody type. This involved the following steps:

1. Calculate the median (50th percentile) tissue concentration for each of the three TL 4 species by waterbody type.

2. Estimate the Reduction Factor by comparing the median fish tissue concentration to the Minnesota criterion of 0.2 mg/kg
3. Calculate the dMeHg BAF for each species-waterbody type combination based on the ratio of the THg concentration median in fish to the geometric mean water exposure concentration (dMeHg in lakes/reservoirs and rivers/streams, tMeHg in the estuary) .
4. Calculate an aggregated BAF for the waterbody type as the geometric mean across the three TL 4 species.
5. Calculate the overall water column target (dMeHg or tMeHg) by dividing the fish tissue criterion by the BAF.

The resulting calculations and MeHg targets are shown in Table 6-4.

Table 6-4. Aggregated BAFs and MeHg target concentration results

Waterbody Type	Species	Water MeHg Count *	Geometric Mean Water MeHg (ng/L) *	Fish Count	Median Standardized Fish THg (mg/kg)	Reduction Fraction	BAF (L/kg) *	Aggregated BAF (L/kg) *	MeHg Target (ng/L) *
Estuary	Channel Catfish	130	0.151	84	0.265	25%	1.75E+06	2.01E+06	0.099
	Northern Pike			156	0.331	40%	2.19E+06		
	Walleye			195	0.321	38%	2.13E+06		
Lake/ Reservoir	Channel Catfish	50	0.137	14	0.524	62%	3.82E+06	3.06E+06	0.065
	Northern Pike			818	0.362	45%	2.64E+06		
	Walleye			731	0.388	48%	2.83E+06		
River/ Stream	Channel Catfish	463	0.2	47	0.381	48%	1.91E+06	1.83E+06	0.109
	Northern Pike			28	0.367	46%	1.84E+06		
	Walleye			46	0.35	43%	1.75E+06		

* Calculations for water MeHg, BAFs, and MeHg target are based on tMeHg for the Estuary and on dMeHg for lake/reservoir and river/stream waterbody types. The reduction factor is calculated relative to the Minnesota criterion of 0.2 mg/kg MeHg.

Overall, BAFs are lower and water column targets are higher for river/stream waterbodies than for other waterbody types. More fish samples were available for the estuary and lakes/reservoirs, while more water samples were taken in lotic waterbodies. The most stringent MeHg targets are for lake/reservoir waterbodies.

As part of the development of the MeHg criterion, USEPA (2001, Appendix A) undertook a thorough re-evaluation of data on MeHg BAFs with a specific focus on BAFs for dMeHg. Tables A-1 through A-9 in USEPA (2001) summarize BAF estimates, including separation by lentic versus lotic systems. The lentic and lotic results were in the end combined because there was not a statistically significant difference between the two, although the lentic results tended to be higher. Table A-9 in USEPA (2001) gives the final recommendations for national BAFs, summarized as the median of the distribution but also providing the 95th percentile value. USEPA's discussion of uncertainty in the BAF calculation notes that the lotic BAFs are primarily based on data from canals in the Everglades and a point-source-contaminated stream in Tennessee, while the lentic BAF data are biased toward northern oligotrophic lakes, primarily in the Great Lakes region, which is more appropriate for the SLRW. For trophic level 4 fish (which includes northern pike, walleye, and channel catfish), EPA (2001) recommended national BAF relative to dMeHg is 2.67×10^6 L/kg – consistent with dMeHg aggregated BAFs for TL4 fish species shown in Table 6-4 as well as those based on the median tissue concentration for different species and waterbody combinations, which range from 1.83×10^6 L/kg to 3.40×10^6 L/kg. The similarity between BAFs calculated here and EPA's national recommendations increases confidence in the results.

The water column targets shown in Table 6-4 are substantially higher than the open water concentrations of tMeHg in Lake Superior, reported as being 14 ± 8 pg/L (0.014 ± 0.008 ng/L) Jeremiason et al. (2009). Elevated mercury tissue levels in fish in Lake Superior has long been somewhat of a puzzle as the open waters have extremely low concentrations of both THg and MeHg yet have elevated Hg concentrations in fish and high BAFs. Ogorek et al. (2021) “hypothesize two critical differences between the Laurentian Great Lakes and previous work on inland lakes and the oceans that might play a critical role in our observed BAF differences: (1) an overwhelming dominance of autochthonous carbon (and/or photochemically bleached allochthonous carbon) as the MeHg ligand relative to other well-studied systems and (2) a lack of chloride anions to complex MeHg in the water column. Together, these conditions likely result in MeHg-ligand complexes that are both highly unstable (evidenced by high photo-demethylation rates) and readily incorporated at the base of the food web (high BAFs), leading to a high degree of efficiency for MeHg bioaccumulation in the Laurentian Great Lakes, which ultimately leads to increased fish Hg.” This hypothesis provides another possible cause for higher tMeHg BAFs in the SLR estuary where the ligand characteristics are likely more similar to Lake Superior.

The dMeHg and tMeHg targets are not directly translatable to THg targets for comparison purposes because the THg:dMeHg and THg: tMeHg ratios vary. The ratio of THg to MeHg also appears to be on average higher in the estuary samples. For the non-estuary samples there are 278 paired THg and dMeHg measurements. The combined river/stream and lake/reservoir THg:dMeHg ratios have a range from 4.9 to 158 with an average of 16.9, median of 15.0. Applying the median ratio to the non-estuary dMeHg fish tissue-based target in Table 6-4 suggests that an equivalent THg target (as a long-term average exposure concentration) would be in the range of 1.0 to 1.6 ng/L, which is similar to the Minnesota THg water column criterion of 1.3 ng/L but higher than the Fond du Lac Band water column criterion of 0.77 ng/L THg. The median THg:tMeHg ratio for the 59 estuary/bay paired samples is 22.7. Applying this ratio, the estuary tMeHg target would also correspond to a THg concentration of about 2.2 ng/L.

6.3 FINAL MERCURY CONCENTRATION TARGETS

For the SLRW upstream of Fond du Lac Dam, the HSPF model predicts dMeHg. Therefore, the river/stream target of 0.109 ng/L dMeHg and the lake/reservoir target of 0.065 ng/L dMeHg (Table 6-4) are applicable to mercury impairments due to fish tissue concentrations upstream of Fond du Lac Dam. For the St. Louis River Estuary, the WASP model provides estimates of tMeHg. Therefore, the estuary target of 0.099 ng/L tMeHg from Table 6-4 is applicable.

Various waterbody segments in the watershed are listed as impaired relative to Minnesota's chronic criterion for THg of 1.3 ng/L or the Fond du Lac Band's chronic criterion of 0.77 ng/L. TMDL allocations for these waterbody segments are estimated through direct comparison of THg concentrations predicted by the HSPF model to the applicable chronic target. In this calculation the modeled THg concentration is the average of the daily modeled

concentrations in the reach over the assessment period of water years 2012 - 2021. This is equivalent to the average of the annual averages for these water years.

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