**Methylmercury Sources and Distribution in the Torch Lake Watershed**

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## Abstract

This project aimed to assess the relative importance of mining-related activities, catchment wetlands, and the lake itself as sources of methyl mercury to Torch Lake. To make this determination, concentrations and loadings in tributaries to Torch Lake were compared with previous studies of streams in the region. A mass balance for inflows and outflows of total and methyl mercury for Torch Lake was constructed based on project measurements of MeHg concentrations to clarify the major sources. A bioaccumulation model was created to assess whether measured concentrations of methyl mercury in Torch Lake are adequate to cause the Hg concentrations reported for fish from this lake.

Results demonstrate that the majority the lake's inventory of methyl mercury is brought by tributaries. Mining related activities account, at most, for about 25% of the methyl mercury flowing into the lake from tributaries. Catchment wetlands are inferred to be the major source of the other 75% of tributary methyl mercury inputs to the lake. In-lake methylation contributes at least 20% of the inventory of methyl mercury in the lake in summer.

Bioaccumulation modeling demonstrated that measured concentrations of methyl mercury in Torch Lake are adequate to cause the fish mercury concentrations found in the lake. The model further predicted that a reduction in methyl mercury concentrations in the lake would would cause a corresponding reduction in fish mercury concentrations within a few years.



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## Introduction

Mercury in Michigan's Upper Peninsula - Although mercury is a naturally occurring substance, emissions from human activities exceed natural emissions (Allan et al. 2013; Amos et al. 2015; Chen et al. 2014; Corbitt et al. 2011; Driscoll et al. 2013; Enrico et al. 2017; Mason et al. 1994; Selin 2009; Streets et al. 2011). Large anthropogenic emissions of mercury combined with the volatility of elemental mercury result in the global spread of this pollutant. Even remote regions such as Michigan's Upper Peninsula receive mercury deposition from human activities occurring thousands of miles away (Zhang et al. 2021). Fish from lakes throughout the Upper Peninsula have mercury concentrations above levels deemed as safe for frequent human consumption (Evers et al. 2011; Perlinger et al. 2018).

Michigan's Upper Peninsula has local sources of mercury in addition to inputs from distant sources. Historically, copper smelters, taconite-processing plants, and coal-fired power plants have been the largest sources of atmospheric mercury emissions (Kerfoot et al. 1999a; Kerfoot et al. 2006; Kerfoot et al. 2016a; Kerfoot et al. 2020; Kerfoot et al. 2016b; Kerfoot et al. 2018) in the Upper Peninsula. Most point-sources of atmospheric emissions of mercury in the Upper Peninsula have been greatly reduced in magnitude or been closed (Kwon et al. 2015; MDEQ 2008). However, metal ores are frequently enriched in mercury, and dissemination of mine residues (poor rock, tailings or stamp sands) may result in release of mercury to surface waters (Kerfoot et al. 2001). Mine tailings exposed to surface or ground waters can remain a potential source of mercury contamination for many years to centuries.

Mercury in Torch Lake - There are several known mining-related sources of mercury to Torch Lake that include streams and mine tailings deposits. There are two known mine drainages that flow ultimately into Torch Lake; drainage from Osceola Mine Shaft #4 and drainage from the Kingston Mine. Hammell Creek receives substantial water flows from artesian drainage from the Osceola #4 mineshaft. This mineshaft may be interconnected with numerous shafts further north on the Keweenaw Peninsula; because the connected shafts have surface openings at higher elevations than that of Osceola #4, there is enough pressure to force the water through the shaft cap (unconsolidated poor rock) at flow rates that range from ~0.014 to 0.11 $m^3/s$ (cubic meters per second, cms, Barry et al. 2021). Discharge peaks in mid-summer. Mercury concentrations in the discharge range from 38 to 130 ng/L (Barry et al. 2021; Degraeve and McCauley 2003; MDEQ 2002), well above values typical of Upper Peninsula rivers and streams (THg – 0.01-20 ng/L, MeHg – 0.01-1.4 ng/L refs) (Janssen et al. 2024; Knauer et al. 2011). The Kingston mine, located near Copper City, also has very high mercury concentrations (~300 ng/L) in its discharge; that discharge flows into Fulton Creek which, in turn, flows in Slaughterhouse Creek to Scales Creek to the Traprock River to Torch Lake.

Mine tailings on the Keweenaw Peninsula have been shown to leach mercury and to cause elevated mercury concentrations in streams that flow through or receive drainage from mine tailings (Kerfoot et al. 1999b; Kerfoot et al. 2004; Kerfoot et al. 2016b; Kerfoot et al. 2018). The mine tailings that are most likely to contribute mercury to Torch Lake are the ~200,000 metric tons that reside within Torch Lake and occupy 50% of its former volume. The slow dewatering if these tailings due to compaction forces a slow flow of water through the tailings into the lake, but there are no measurements of mercury concentrations in this upflowing water. Tailings reaching above the lake level (i.e., the capped areas of Superfund Operational Unit I) receive rainfall and snowmelt that percolates through the cap into the lake. Mercury

concentrations in this seepage have been reported as high (MDEQ 2016). The magnitude of all mercury inputs to the lake will be tabulated and compared later in the report.

Project goals - Prior to this project, there were no measured concentrations of methylmercury in tributaries to Torch Lake nor within the lake itself. For that reason, the goal of this project was to measure concentrations of methylmercury (MeHg) in Torch Lake and its tributaries, and to estimate the relative contribution of mining- and non-mining sources of MeHg to the inventory within the lake. Bioaccumulation modeling was performed to determine the potential for reductions in fish mercury content as a result of remediation activities

**Methods**

The general plan for the project was to collect water samples seasonally from Torch Lake and its tributaries (Fig. 1), and to use those samples to create a mass balance for MeHg. In summer 2021, the Michigan Dept. of Energy, the Great Lakes, and Environment (EGLE) sampled Torch Lake using clean sampling techniques on four occasions and measured total and methyl mercury (Fig. 2). Those results also are utilized for the mass balance calculations in this study.

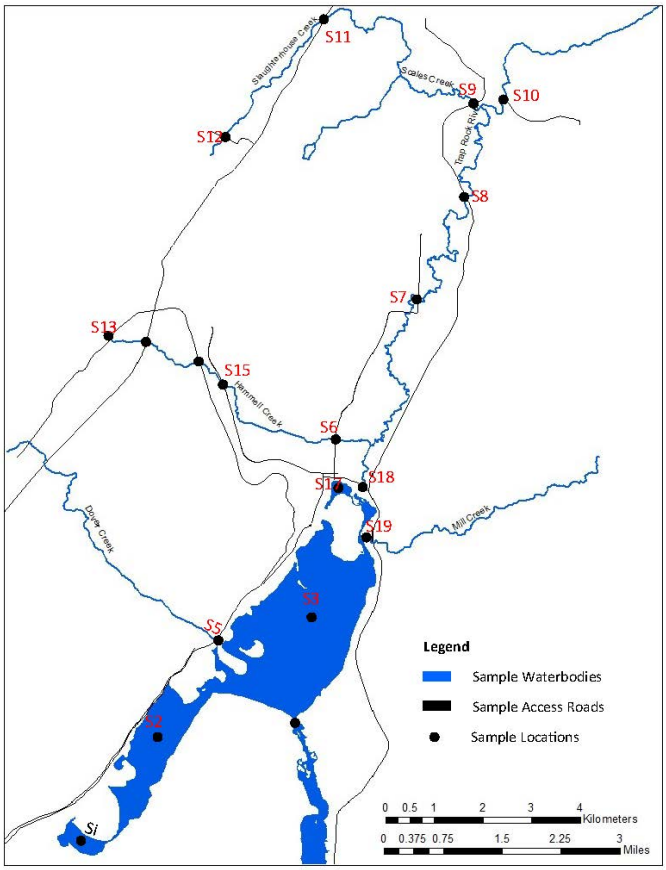


**Figure 1.** Project sampling sites designated S1 through S19. Sampling was conducted at only three stations (S6, S13, S15) on Hammell Creek. The S4 sampling site near the outflow was moved further into Torch Lake.

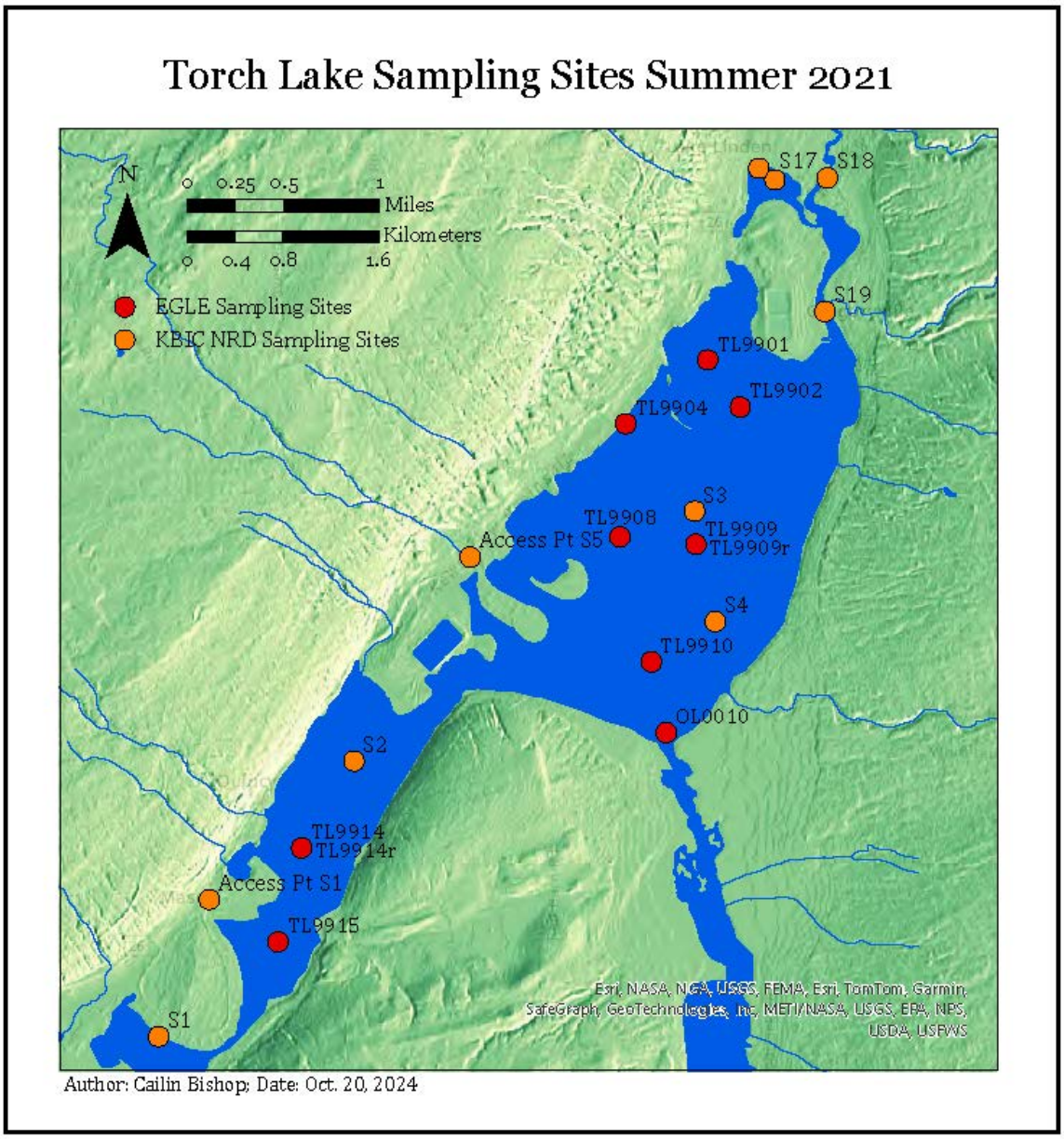


**Figure 2**. Locations of sampling sites on Torch Lake where samples for MeHg analysis were obtained for this study (orange circles) and for a separate study (red circles) conducted by Michigan Dept. Environment, Great Lakes and Energy (EGLE).

Sampling – Stream and lake samples were collected by personnel from Keweenaw Bay Indian Community's (KBIC) Department of Natural Resource (DNR). Personnel were trained in EPA's trace metal clean sampling techniques. Samples were collected in summer (7/12-13) and fall (10/18-26) of 2021 and in spring (5/17) 2022. Winter sampling could not be accomplished because of dangerous conditions by the streams due to high snowfall. Samples were collected using the clean hands-dirty hands technique whereby a pre-cleaned glass bottle obtained from the analytical lab was stored and transported in two plastic bags. One person (dirty hands) opened

the outer bag, and the second person (wearing gloves) opened the inner bag and immersed the bottle in the water upstream of her/himself, capped the sample and closed the inner bag before the first person closed the outer bag. Because KBIC personnel had no equipment to enable clean sampling from the hypolimnion of Torch Lake, only surface water samples were obtained. Sampling locations are shown in Figure 1.

Analysis – Analyses were contracted through Whitewater Associates (Amasa, MI), and they supplied, with directions, the pre-cleaned containers for sampling. Whitewater Associates shipped the samples to Eurofins Canton (Barberton, OH) for measurement of methylmercury. Analysis was performed according to EPA Method 1630 which involves distillation of the sample, ethylation with sodium tetraethyl borate, purging with nitrogen onto a graphite trap, thermal desorption followed by pyrolytic decomposition to $Hg^0$ and measurement by cold-vapor atomic fluorescence spectrometry. Quality assurance measures included field and lab blanks, a lab control sample, replicate analyses, and a surrogate standard (n-propyl mercury chloride).

Mass balance calculations for methylmercury – A simple mass balance was constructed to illustrate the relative magnitudes of MeHg inputs from different catchments and to compare those inputs with the inventory in the lake. Flow rates for each stream that was sampled were estimated by taking the flow at the Traprock River USGS gaging station and multiplying by the ratio of the stream watershed area to that of the gaged watershed. Total flows for each season (Spring – March-May, Summer – June-August, Fall – September-November, Winter – December-February) were calculated in this fashion. The measured concentrations were assumed to be representative of the season and multiplied by the seasonal flow to yield seasonal fluxes (mg MeHg per season). Because no concentrations were measured in winter, a winter concentration was estimated as the average of fall and spring values for each stream. To calculate the MeHg inventory in the lake epilimnion and hypolimnion, the measured concentrations were multiplied by the volumes of each lake stratum as determined from a hypsographic curve. The depth of the thermocline was set at 15 m.

Modeling of fish mercury concentrations

This project funded the masters thesis project of Michelle Bollini who developed models of bioaccumulation of mercury and PCBs (polychlorinated biphenyl compounds) in Torch Lake fish. All of the details of the model development, testing, and use for prediction of future scenarios are detailed in Bollini's published thesis (Bollini 2023) which is available through Digital Commons. Excerpts from the thesis are copied into the Appendix A for this report.

**Results**

Methylmercury measurements in streams – Quality assurance standards were met with but minor exceptions. All lab blanks (n = 6) were below the detection limit (0.018 ng/L). All filter and trip blanks (n = 11) also were below the detection limit with but two exceptions. All surrogate standard recoveries (n = 77) were within the guidelines (36-133%). Accuracy was 96 $\pm$ 17% as indicated by recovery of MeHg standard spikes into samples (n = 20); all recoveries but one were within the targeted range (67-138%). Precision was $\pm$ 0.009 ng/L as determined by 7 pairs of replicated spiked samples.

**Table 1.** Measured MeHg Concentrations in Torch Lake Tributaries.

| Stream | Location | Site | Season | MeHg (ng/L) |
|---|---|---|---|---|
| Quincy Ck | Not sampled (ns) | | | |
| McCallum Ck | Not sampled (ns) | | | |
| Dover Ck | Mouth | S5 | Summer 2021 | 0.030 |
| | | | Fall 2021 | 0.100 |
| | | | Spring 2022 | 0.094 |
| Sawmill Ck | | S19 | Summer 2021 | 0.030 |
| | | | Fall 2021 | 0.066 |
| | | | Spring 2022 | ns |
| Hammell Ck | Gregory St. | S6 | Summer 2021 | 0.038 |
| | | | Fall 2021 | 0.048 |
| | | | Spring 2022 | 0.034 |
| | Douglas-Houghton Falls | S15 | Summer 2021 | 0.060 |
| | | | Fall 2021 | 0.087 |
| | | | Spring 2022 | 0.049 |
| | Old County Rd | S13 | Summer 2021 | 1.2 |
| | | | Fall 2021 | 0.11 |
| | | | Spring 2022 | 0.071 |
| Traprock River | Mouth | S18 | Summer 2021 | 0.049 |
| | | | Fall 2021 | 0.053 |
| | | | Spring 2022 | ns |
| | USGS station | S7 | Summer 2021 | 0.053 |
| | | | Fall 2021 | 0.063 |
| | | | Spring 2022 | 0.070 |
| | Angman Rd. | S8 | Summer 2021 | 0.059 |
| | | | Fall 2021 | ns |
| | | | Spring 2022 | 0.087 |
| | Upper TR | S10 | Summer 2021 | 0.890 |
| | | | Fall 2021 | 0.100 |
| | | | Spring 2022 | 0.052 |
| Scales Creek | Mouth | S9 | Summer 2021 | 0.120 |
| | | | Fall 2021 | 0.120 |
| | | | Spring 2022 | 0.090 |
| Slaughterhouse Ck | | S11 | Summer 2021 | <DL |
| | | | Fall 2021 | ns |
| | | | Spring 2022 | <DL |
| | | S12 | Summer 2021 | 0.025 |
| | | | Fall 2021 | 0.025 |
| | | | Spring 2022 | 0.069 |

Metal concentrations in Torch Lake – Samples were collected from Torch Lake for methyl mercury as part of this project only in summer and fall 2021. Methylmercury was below the detection limit (0.018 ng/L) in all but two of the samples; the two samples in which MeHg was found were from the southernmost and northernmost basins of the lake. These two areas of the

lake have abundant macrophytes, relatively stagnant water and abundant organic matter in the sediments all of these conditions may promote low oxygen in the bottom waters and mercury methylation. The sampling of surface waters for this project revealed lower concentrations than those measured by the EPA in summer 2021; reasons for this discrepancy are not clear.

**Table 2.** Summary of methyl mercury concentrations measured in Torch Lake for this project.

| Station ID | Location | Closest EGLE site | Date | MeHg (ng/L) |
|---|---|---|---|---|
| S1 | Southern-most basin | None comparable | 7/13/2021 | 0.019 |
| | | | 10/26/2021 | <0.018 |
| S2 | South basin | TL9914, 9915 | 7/13/2021 | <0.018 |
| | | | 10/26/2021 | <0.018 |
| S3 | Main basin | TL9009, 9010 | 7/13/2021 | <0.018 |
| | | | 10/26/2021 | <0.018 |
| S4 | Outflow to Portage L. | OL0010 | 7/13/2021 | <0.018 |
| | | | 10/26/2021 | <0.018 |
| S17 | Northern basin | None comparable | 7/13/2021 | <0.018 |
| | | | 10/26/2021 | 0.028 |

The state (EGLE) also sampled Torch Lake on four occasions in summer 2021 and samples were submitted to Whitewater Assoc. for trace metal (Cu, Pb, THg, MeHg) analyses. The nine sampling sites (Figure 2) were in the north and south basins and near the lake outflow. Sampling was performed on June 30, July 8, 15 and 22. A sample was collected from the epilimnion and hypolimnion at each station.

**Table 3**. QA parameters for EGLE trace metal sampling in Torch Lake

| Metal | Copper (Cu) | Lead (Pb) | Total Hg (THg) | MethylHg (MeHg) |
|---|---|---|---|---|
| Units | µg/L | µg/L | ng/L | ng/L |
| Detection limit | 0.22 | 0.41 | 43 | 0.018 |
| Average Field blank* | 0.25 | 0.20 | 22 | 0.015 |
| Precision (S.D.) | 3.5 | NA | NA | 0.004 |

For both lead and total mercury, few valid measurements were obtained for Torch Lake. For lead, detectable concentrations in the epilimnion were measured only on one of four sampling dates at one of nine sampling stations. Detectable lead concentrations in the hypolimnion were measured at three of nine sampling stations but only on one of four sampling dates. All detectable lead concentrations were well below all of Michigan's Rule 57 Aquatic Life values and also below the action level for drinking water. The stations where lead was detected were near the Lake Linden Recreational Area and the Hubbell Smelter Area. The high detection limit (43 ng/L) for total mercury precludes meaningful measurements. Total mercury was above the detection limit at only two stations (of nine) on one sampling date. The measured concentrations were, however, quite high (67, 58 ng/L) compared to most upper peninsula lakes in Michigan (Perlinger et al. 2018) albeit still below Michigan's Rule 57 Aquatic Life values.

Copper concentrations were fairly uniform throughout the lake and ranged from 14 to 25 µg/L. These concentrations are all above Michigan's Rule 57 Final Chronic Value (6.0 µg/L) and many are above the Final Acute Value for Torch Lake as well (17.4 µg/L). While some spatial variability exists, it is generally small. The single high hypolimnetic value (24 µg/L) was measured in the Hubbell Smelter Area.

Methylmercury was consistently measurable in top and bottom waters of the lake. Sampling was too sparse to determine if any spatial patterns exist, but concentrations were markedly higher in the hypolimnion (0.026-0.124, mean 0.078 $\pm$ 0.049 ng/L) than in the epilimnion (0.017-0.036, mean 0.024 $\pm$ 0.008 ng/L) Concentrations were generally low, ranging from nondetectable (< 0.018 ng/L) to 0.124 ng/L. Values were similar to the range measured at the mouth of the Traprock River into Torch Lake (0.049-0.053 ng/L), but higher than river values in the epilimnion and lower in the epilimnion. Because total mercury was below the detection limit at the stations where methylmercury was measured, the percent of mercury occurring as methylmercury could not be calculated.

**Table 4.** Summary of EGLE trace metal measurements in Torch Lake, summer 2021

| Site | Epilimnion | | | | Hypolimnion | | | |
|---|---|---|---|---|---|---|---|---|
| | Cu (µg/L) | Pb (µg/L) | THg (ng/L) | MeHg (ng/L) | Cu (µg/L) | Pb (µg/L) | THg (ng/L) | MeHg (ng/L) |
| TL9001 | 16.5 | < DL | < DL | nm | 16.1 | 1.9 | < DL | nm |
| TL9002 | 16.0 | 0.7 | < DL | nm | 16.2 | 3.3 | 67.0 | nm |
| TL9004 | 16.8 | < DL | < DL | nm | 18.1 | 0.5 | 58.5 | nm |
| TL9008 | 16.1 | < DL | < DL | nm | 16.1 | < DL | < DL | nm |
| TL9009 | 16.0 | < DL | < DL | 0.022 | 16.0 | < DL | < DL | 0.115 |
| TL9010 | 15.9 | < DL | < DL | nm | 15.6 | < DL | < DL | nm |
| TL9014 | 17.1 | < DL | < DL | 0.020 | 15.6 | < DL | < DL | 0.026 |
| TL9015 | 17.1 | < DL | < DL | 0.036 | 20.3 | < DL | < DL | 0.045 |
| OL0010 | nm | nm | nm | 0.017 | Nm | nm | nm | 0.124 |

nm – not measured; < DL – less than the detection limit

River flows – The US Geological Survey maintains a water gaging station on the Traprock River (Traprock River near Lake Linden, MI – 04043050); the drainage area above the gage (72 $km^2$) is only 69% of the total river drainage area. ArcGIS Pro was used in conjunction with a BLANK-resolution digital elevation map to determine the drainage areas for the streams listed in Table 5 below. Daily average river flows for the Traprock River the period 6/1/2021-5/31/2022 were retrieved from the USGS web site (html). For the other streams in the table, daily flows for the same time period were calculated as the Traprock River daily flow times the ratio of the stream drainage area to the Traprock River drainage area.

To facilitate calculation of the mass of methyl mercury exiting the mouths of each of the streams, total flows ($m^3$) were calculated for each of four seasons: summer (6/1/2021-8/31/2021), fall (9/1/2021-11/30/2021), winter (12/1/2021-2/28/2022) and spring (3/1/2022-5/31/2022). Seasonal flows (summarized in Table 5 below) were calculated as the product of average daily flow rate ($m^3/s$) and the number of seconds within the season. Seasonal water flows were multiplied by the seasonal methylmercury concentrations measured at the mouth of each stream (Table 2) to determine the seasonal fluxes (mg) of methylmercury for each stream (Table 6). Because ice was not thick enough to obtain winter methylmercury samples, the winter

concentrations were calculated as the average of fall and spring concentrations. At most stream sampling locations there was little seasonal variation in MeHg concentrations; for this reason, the use of a single concentration for the whole season and the averaging of fall and spring concentrations to obtain a winter concentration are not though to introduce large errors in the calculated fluxes.

**Table 5.** Stream drainage areas and seasonal flows.

| Stream | Drainage area ($km^2$) | Summer flow (million $m^3$) | Fall flow (million $m^3$) | Winter flow (million $m^3$) | Spring flow (million $m^3$) | Annual (million $m^3$) |
|---|---|---|---|---|---|---|
| Upper Traprock R. | 25 | 1.09 | 1.74 | 2.13 | 12.9 | 17.9 |
| Slaughterhouse Ck. | 6.5 | 0.28 | 0.45 | 0.55 | 3.36 | 4.64 |
| Scales Ck | 12.5 | 0.54 | 0.87 | 1.07 | 6.47 | 8.95 |
| Hammell Ck | 4.8 | 0.21 | 0.33 | 0.41 | 2.48 | 3.43 |
| Whole Traprock R. | 120 | 5.22 | 8.34 | 10.2 | 62.1 | 85.9 |
| Sawmill Ck. | 10.2 | 4.44 | 0.71 | 0.87 | 4.6 | 10.6 |
| McCallum Ck | 15.4 | 0.67 | 1.07 | 1.31 | 5.47 | 8.52 |
| Dover Ck | 10.2 | 0.44 | 0.71 | 0.87 | 5.28 | 7.30 |
| Quincy Ck | 5.1 | 0.22 | 0.35 | 0.44 | 2.64 | 3.65 |

**Table 6.** Seasonal fluxes of methylmercury (mg/season) leaving each river.

| Stream | Summer 2021 MeHg Flux (mg) | Fall 2021 MeHg Flux (mg) | Winter 2021-22 MeHg Flux (mg) | Spring 2022 MeHg Flux (mg) | Annual MeHg Flux (mg) |
|---|---|---|---|---|---|
| Upper Traprock R. | 967 | 174 | 163 | 686 | 1990 |
| Slaughterhouse Ck. | 3 | 4 | 5 | 30 | 42 |
| Scales Ck | 65 | 104 | 117 | 582 | 869 |
| Hammell Ck | 8 | 16 | 16 | 84 | 125 |
| Whole Traprock R. | 256 | 442 | 522 | 3168 | 4387 |
| Sawmill Ck. | 13 | 47 | 42 | 221 | 323 |
| McCallum Ck | Not measured | Not measured | Not measured | Not measured | Not measured |
| Dover Ck | 13 | 71 | 65 | 496 | 645 |
| Quincy Ck | Not measured | Not measured | Not measured | Not measured | Not measured |

The river fluxes used above were combined with ancillary data to estimate a mass balance or budget for total and methyl mercury in Torch Lake (Table 7). Methylmercury inflows from rivers are based on values for 2023 given in Table 6. For McCallum and Quincy Creeks,

the average concentration in all other streams (0.058 ng/L) was used together with the computed water runoff for those catchments. Values for total mercury concentrations in the rivers are taken from the 2003 GLEC study (Degraeve and McCauley 2003). Outputs from the lake are calculated as the average epilimnetic (upper water column) and hypolimnetic (lower water column) concentrations measured in this study and the EGLE 2021 measurements (Tables 2, 4), the volumes of both portions ($1.08x10^8$ and $3.94x10^7$ $m^3$) of the lake calculated from a hypsographic curve, and water residence time of the lake (~ 1 yr) (Urban et al. 2016). The outflow for total mercury is highly uncertain; THg was not measured in this study, and all but two hypolimnetic measurements in the EGLE study were less than the detection limit. To calculate an average, values of one half the detection limit were used for all non-detectable concentrations. The two values above the detection limit are very high (67, 58 ng/L) and probably cause an overestimate for the hypolimnetic concentration. The "unknown source/sink" in the bottom row of Table 7 is the sum of all inputs (positive) and outputs (negative). At face value, these unknown sources would indicate there must exist a large additional source of THg to the lake; this could be groundwater flowing in through stamp sand deposits or dissolution of Hg in the sediments and diffusion into the lake. For MeHg, the results suggest that there must be an additional sink for MeHg from the lake; this could be either volatilization or demethylation. Both processes were concluded to be important in a previous modeling study of mercury in Torch Lake (Hendricks 2018).

**Table 7**. Budgets for total and methyl mercury in Torch Lake

| Category | Specific source/sink | THg input/output (g/yr) | MeHg input/output (mg/yr) |
|---|---|---|---|
| Atmospheric Deposition | | 93.4 (17%) | |
| River inflows | Traprock R. | 404 (73%) | 4,387 (60%) |
| | McCallum Ck | 9 (1.7%) | 493 (7%) |
| | Sawmill Ck | 12 (2.1%) | 323 (4%) |
| | Dover Ck | 8 (1.5%) | 645 (9%) |
| | Quincy Ck | 4 (0.7%) | 211 (3%) |
| | Remainder of catchment | 23 (4.1%) | 1,200 (16%) |
| | Total rivers | 459 (83%) | 7,259 (100%) |
| Lake Outflow | | -631,000 | -5,700 |
| Unknown source/sink | | 630,119 | -1,659 |

## I. Discussion

### Sources and sinks of Hg within river drainage basins

#### *i. Hammell Creek*

Although we have known since 2002 that Hammell Creek contains high concentrations of total mercury (130 ng/L) where it receives discharge from the Osceola #4 mineshaft (MDEQ 2002), this is the first time that methylmercury has been measured in this stream. This idyllic stream provides the water flowing down Houghton Douglas Falls, the tallest waterfall in the state of

Michigan. The mine discharge water constitutes, on average, 56% of the water flowing over Houghton Douglas Falls (Barry et al. 2021).

While the Osceola mines were operating, the brackish mine water was pumped into a canal that emptied into Hammell Creek. Yanko (1969) reported in his master's thesis that the fauna in the stream had species typical of salt water environments. Spain used the chloride plume from this stream to trace water flows from Torch Lake to Portage Lake and the subsequent mixing of Portage Lake water with Lake Superior water (Spain and Andrews 1970; Spain et al. 1976). Following closure of the Osceola mines, all of the shafts were capped (Fig. 3). However, the poor rock that was dumped into Osceola shaft #4 was not adequate to prevent an outflow of water that continues to this day. The mine discharge flows approximately 100 m through a channel that empties into Hammell Creek just a short distance on the east side of Tecumseh Road. It is thought that mine shafts are interconnected from Osceola some distance to the north. It is possible that meteoric water percolating into mines at higher elevations discharges at the Osceola #4 shaft (elevation 1188 ft asl). The water flowing out of the mine shaft has a temperature of 10°C year round and a dissolved oxygen concentration of zero. The conductivity ranges from 1200-1500 µS/cm according to records from MTU class surveys. Recent measurements of trace metal concentrations were not unusually high (Cu 23 µg/L, As 1.7 µg/L) with the exception of mercury (38 ng/L; Barry et al. 2021).

**Figure 3.** Satellite image (Google Earth Pro) showing locations of Osceola mine shafts. Mine discharge occurs from shaft #4. Figure created by Barry et al. 2021.

In 2002 Michigan's Dept. of Environmental Quality listed Hammell Creek as an impaired water on the state's 303(d) listing and created a Total Maximum Daily Load report for the site on account of the high mercury concentrations (MDEQ 2002). They did not recommend any remedial actions because they observed that mercury concentrations decreased much more rapidly than did conductivity downstream from the mine discharge. It was surmised that the mercury in the mine water was in the elemental form ($Hg^0$) and that it quickly volatilized from the stream.

The current BIA funded project is the first to measure MeHg concentrations in Hammell Creek. Concentrations were measured at three locations as shown in Figure 1. These MeHg concentrations are graphed together with historical measurements of total Hg (THg) in Figure 4. The MeHg concentrations show the same pattern as does THg; concentrations are high in the vicinity of the mine discharge but are nearly 10-fold lower in the in lower reaches of the river. A curious phenomenon shown by this graph is that concentrations of THg decline from 95 ng/L to

12.6 ng/L in a short (100-m) stretch of the stream between Old County Road and Highway 41. This short section of stream is shown in the aerial image in Figure 5. The MeHg concentrations provided by this project support the decision of the MDEQ not to remediate the stream. The MeHg concentrations near the mine outflow include the highest value (1.2 ng/L) measured in this study. However, concentrations closer to the mouth of the stream (0.034-0.048) are typical of most stream locations measured in this study and are lower than those at the mouth of Dover Creek (0.030-0.100 ng/L) which has no known mining influence. At all three sites along the stream, MeHg represents less than 1% of THg which suggests that, despite the large area of wetlands through which the stream passes, there is relatively low conversion of inorganic to methyl mercury. Based on the literature, it is common to find MeHg equal to 1 to 20% of THg in other rivers and streams. As will be presented below, there is no evidence that the high discharge of Hg into Hammell Creek results in large fluxes of either THg or MeHg to Torch Lake.

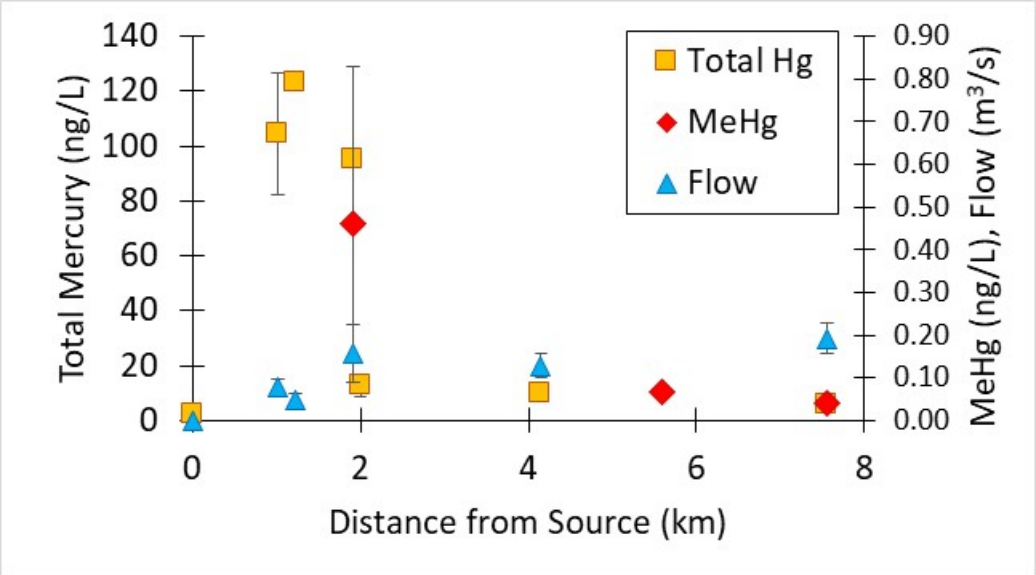


**Figure 4.** Compilation of recent and historical concentrations of THg and MeHg in Hammell Creek shown together with water flow rates along the stream. Sites extend from the relatively stagnant waters ponded near stamp sand piles along Osceola Road (0 km from the source) to the stream culvert under Gregory Road in Lake Linden (7.6 km from the source). Shown are the averages of THg concentrations at each station compiled from measurements by the state of Michigan (MDEQ 2002), by Great Lakes Environmental Consulting (Degraeve and McCauley 2003), and by a Senior Design class at Michigan Tech (Barry et al. 2021). Water flow measurements were compiled from the same sources. The MeHg concentrations are the averages of the seasonal values reported in Table 2. Error bars represent standard errors; when not visible they are smaller than the symbol.

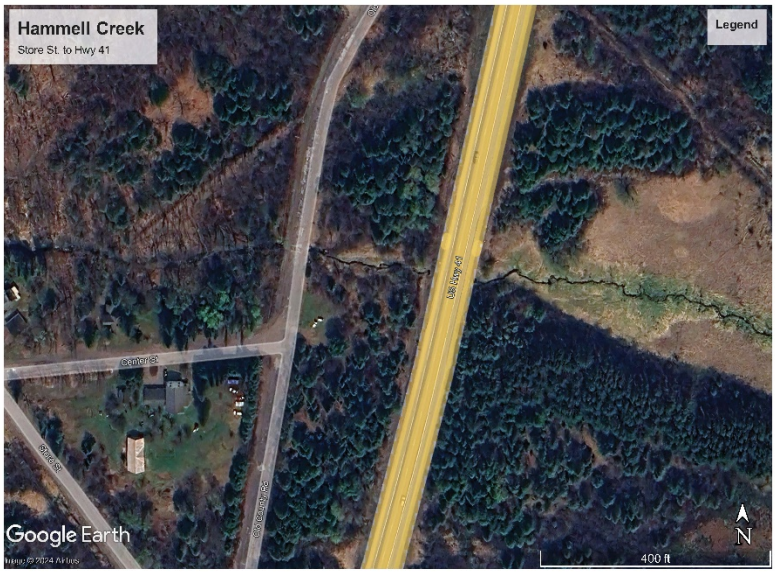


**Figure 5.** Satellite image of Hammell Creek section between Old County Rd and Hwy 41. In this short 100-m section of stream the THg concentration was reported in 2001 to decline from 95 to 13 ng/L. This steep decline should be confirmed and investigated as to its cause.

*ii. Traprock River*

There was a marked decrease in MeHg concentrations from the Upper Traprock River (above confluence with Scales Creek) to the mouth at Torch Lake. The average concentration at the Upper Traprock River location was 0.35 ng/L; concentrations peaked at 0.89 ng/L in summer at this station. There is little anthropogenic disturbance of this part of the watershed; wetlands represent >20% of the drainage area in the upper catchment. The high summertime MeHg concentration is thought to reflect high rates of methylation in the wetlands during summer. Methylation of atmospherically deposited Hg in wetlands has been widely reported (Marcel, Knauss, Watras refs).

Scales Creek which empties into the Traprock River less than a km downstream from the Upper Traprock sampling station is known to be heavily impacted by mining. The river channel was moved to prevent it from flowing through stamp sand deposits that caused elevated copper concentrations. The outflow from the Kingston mine which was reported to have a THg concentration of 310 ng/L (Degraeve and McCauley 2003) runs through a short stream that empties into Scales Creek. Slaughterhouse Creek, another tributary to Scales Creek is also known to be heavily impacted by mining activities. Slaughterhouse Creek begins as the outflow from Calumet Lake, an impoundment created to provide a source of water for mining operations. Concentrations of MeHg in Slaughterhouse Creek north of Calumet Lake started at 0.040 ng/L but decreased to less than 0.018 ng/L a few kilometers downstream. Concentrations of MeHg in Scales Creek were found in this study to be relatively high (0.090-0.120 ng/L), but still lower than in the upper Traprock River.

Only 1.5 km downstream of the Upper Traprock River sampling point, at the Angman Rd sampling station, the average concentration was nearly four times less (0.073 ng/L) than that in the upper Traprock River (Fig. 6). A further 4.2 km downstream the average concentration remained at 0.073, but decrease to 0.051 ng/L 4.8 km further downstream at the mouth of the river. Thus the load of MeHg reaching Torch Lake in the Traprock River clearly has a large component that is unrelated to mining.

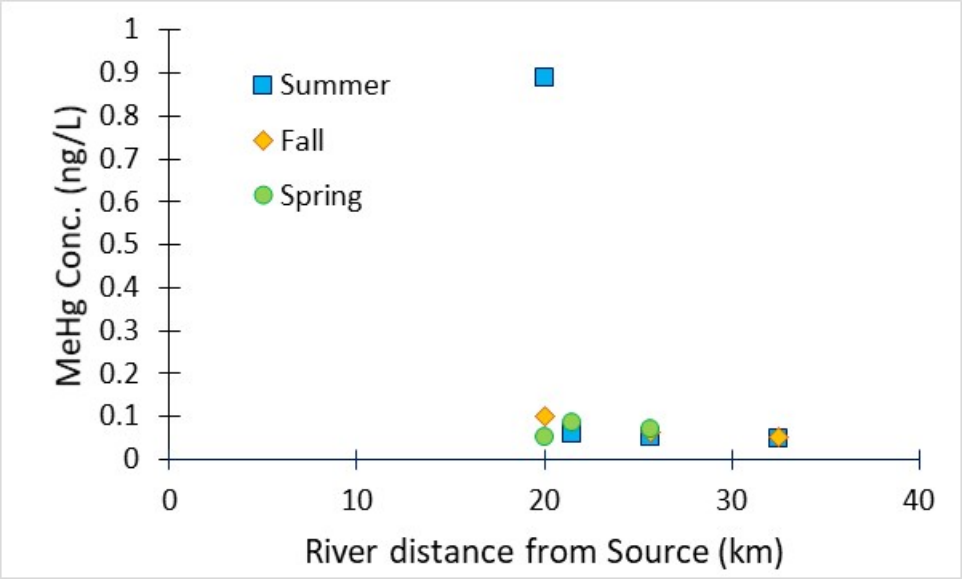


**Figure 6.** Methylmercury Concentrations along the Traprock River. At each of four sampling stations are shown the concentrations measured in summer, fall and spring. There is a slight decline in concentration from the upper Traprock River station to the river mouth. The high summer concentration at the upper Traprock River Station might result from high rates of methylation in the large area of wetlands in the upper catchment.

Inputs of Mercury to Torch Lake – Mining vs. non-mining sources

Potential sources of Hg to Torch Lake include local mining activities, mobilization from the catchment, and long-range atmospheric transport from distant sources. It is well established that historical mining in Michigan's Upper Peninsula caused an enrichment of Hg above "background" concentrations in many environmental media. The iron, copper, silver and gold ores found in the U.P. are all highly enriched in Hg (1-1000 µg/g or 20 to 20,000 times concentrations in uncontaminated soil) (Kerfoot et al. 2002). Consequently, mine residues are also enriched in mercury relative to soil or rock not associated with mining. Mine residues include poor rock (9-281 ng Hg/g), stamp sands (i.e., coarsely ground, extracted mine tailings; 3-265 ng/g), mine tailings (i.e., finely ground, extracted ore; 17-95 ng/g), soils (60-200 ng/g), and lake sediments (50-600 ng/g) (Kerfoot et al. 2002). Mapping of surface soils of the contiguous U.S. by the USGS showed elevated mercury concentrations (> 150 ng/g) in surface soil and soil A horizons in Marquette, Baraga and Ontonagon counties; all of these were historically areas of mining activity (Smith et al. 2013). A report to the MDNR (Knauer et al. 2011) reported elevated total Hg concentrations in sediments of mining-impacted lakes in the Marquette iron mining region. Clearly, the potential for mercury inputs into Torch Lake from legacy mining activities exists.

Further, it is known that Hg continues to be released into stream waters from mines in the Torch Lake catchment. Drainage from the Kingston mine (Copper City) was found to have a Hg concentration of 310 ng/L (i.e., $3.1 \times 10^{-7}$ g/L) and discharged 0.36 g/d (Degraeve and McCauley 2003). Slaughterhouse Creek which receives drainage from multiple mines had a Hg concentration of 39 ng/L ($3.9 \times 10^{-8}$ g/L) in summer 2002 and a Hg flux of 0.57 g/d (Degraeve and McCauley 2003). Osceola mine #4 was estimated to discharge 0.8 g/d of Hg in fall 2001 when flow from the mine was relatively low; the Hg concentration in the outflow was 130 ng/L or

$1.3x10^{-7}$ g/L (MDEQ, 2002). For comparison, the average rate of atmospheric deposition of Hg to Torch Lake is 0.27 g/d. Clearly, the potential exists for mine drainage to contribute significantly to the mercury inputs to Torch Lake.

Using the data gathered in this study and other recent measurements (e.g., atmospheric deposition from the Mercury Deposition Network, https://nadp.slh.wisc.edu/networks/mercury-deposition-network/) we have estimated a mass balance or budget for total and methylmercury in Torch Lake (Table 7). While there are many uncertainties in the results, several factors become immediately apparent from these estimates. The two known and measured inputs to the lake for both total and methyl mercury are atmospheric deposition and river inflows. For THg, atmospheric deposition represents 17% of the total, and for MeHg it is thought to be negligible. Of the river inputs, the Traprock river provides 88% for THg and 60% for MeHg. Of the load of MeHg carried by the Traprock River, the two tributary streams impacted by mining (Scales Ck, Hammell Ck) contribute 23% although these streams contribute only 14% of the water flow. Hence remediation of these mining-impacted streams could reduce MeHg inputs to Torch Lake only by about one fourth. About 45% of the Traprock River's total load of MeHg is contributed by the wetland-rich headwaters area that is largely unimpacted by mining. Another 32% is not accounted for by any of the measured tributary inputs and must be produced either in catchments of other tributaries or in the riparian wetlands along the river below the confluence with Scales Creek.

It is clear that some MeHg is formed in the deep waters (hypolimnion) of Torch Lake. The average MeHg concentration in the Traprock River is 0.051 ng/L, while the average in the summer epilimnion is 0.024 and that in the hypolimnion is 0.078. This suggests that 35% of the MeHg in the summer hypolimnion was formed within the lake; this is equal to 20% of the total MeHg in the lake in summer or about 15% of the total, annual tributary input of MeHg to the lake. It is not surprising that some river inputs of MeHg are lost in the epilimnion; microbial and photo-demethylation are known to occur in lakes (Benoit et al. 2003; Korthals and Winfrey 1987; Poste et al. 2015). Demethylation also is likely to occur in the hypolimnion which would render the estimate of in-lake methylation above a net rate that likely underestimates the total or gross rate.

This same dynamic situation of methylation and demethylation may occur in the rivers as well. Methylation in organic-rich sediments or associated with filamentous algal mats has been reported in rivers (Tsui et al. 2014; Tsui et al. 2009; Wasserman et al. 2003). Simultaneous methylation by iron- and sulfate-reducing bacteria and demethylation by methanogens has been reported in river sediments. While our calculation of river loads and allocation of sources above implies that the MeHg is conservative once in the river, in reality, methylmercury can be very dynamic with half-lives as low as two days in some rivers (Bento and Hintelmann 2024). This may account for the disappearance of MeHg in summer between the sampling point for the upper Traprock River (MeHg flux 967 mg/summer) and the mouth of the river (MeHg flux 256 mg/summer). Hence, the attribution of 23% MeHg in the Traprock River to mining sources is an upper bound because some of the MeHg contributed to the Traprock River from Scales and Hammell Creeks may be demethylated before reaching the mouth of the river.

Potential for reductions in fish mercury by lake and watershed remediation

Mercury was the first contaminant above recommended health guidelines to be found in Torch Lake fish, and fish consumption advisories because of mercury have been in place since 1993 (Urban et al. 2016). In the 31 years since that advisory was instituted, there has been no

discernible decrease in fish mercury concentrations (Fig. 7). The state agencies have long maintained that the mercury in Torch Lake is unrelated to local mining activities because mercury contamination is widespread across all of mercury. Indeed, a state-wide fish consumption advisory was imposed in 1993 on account of mercury and remains in place to the present. Neither lake (THg and MeHg) nor fish mercury concentrations in Torch Lake are outside the range of concentrations reported in other Michigan lakes (cf. Hendricks 2018; Perlinger et al. 2018; Priyadarshini 2018). This study is the first to prove that in-lake mercury methylation occurs within Torch Lake, although that, in itself, does not prove that the methylated mercury was derived from mining sources.

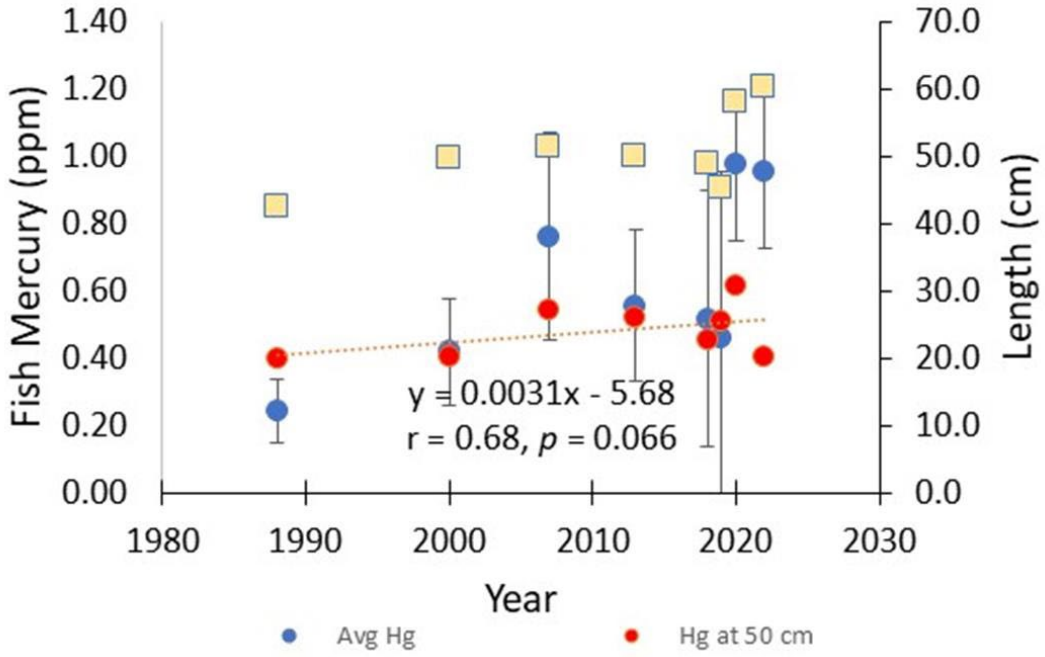


**Figure 7.** Historical trajectory of fish mercury content in Torch Lake. Shown are mercury concentrations in male walleye. Because average size of walleye caught for Hg content analysis has changed over time, there have been sizable shifts in measured fish walleye concentration. When concentrations are calculated for fish of the same size in each year, there is a slight increasing trend of fish Hg concentrations over time. Data from 1988-2013 are from MDEQ; data for years 2018-2022 are from GLIFWC

As quantified above, mining-related sources of THg and MeHg exist in both Scales and Hammell Creeks. We have pointed to the rapid removal of both THg and MeHg from Hammell Creek through natural attenuation processes. It is likely that remediation in the Scales Creek watershed or directly in the stream could accelerate mercury removal from that stream as well. Because mercury is methylated by iron- and sulfate-reducing bacteria as well as methanogens, raising the oxidation potential of the hypolimnion has been suggested as a possible remediation strategy (Ji et al. 2020; Mailman et al. 2006). To evaluate the possible reduction in fish Hg content, we modeled fish Hg bioaccumulation in scenarios with the current levels of MeHg in lake water and one in which MeHg concentrations were lowered by 50%. A 50% reduction in MeHg resulted in a two-fold reduction in both bullhead and walleye Hg content to be achieved within a two-year time span (Bollini 2023). As discussed above, our current prediction of the contribution of in-lake methylation to lake MeHg concentrations is 15-35%. The model results

suggest that if MeHg concentrations could be reduced by 15-35%, we would achieve a corresponding reduction in walleye Hg content within a few years.

## II. Conclusions

From this study, several clear conclusions can be drawn. First, despite the mine drainage into Hammell Creek, this creek is not a significant source of methylmercury to Torch Lake. The majority of the methylmercury entering Torch Lake via the Traprock River and other tributaries appears to be derived from methylation of atmospherically deposited mercury; wetlands are a likely locus for methylation. Scales Creek has relatively high concentrations of MeHg, possibly as a result of mercury in the stream from mining-related sources; clean-up of this watershed could potentially reduce both inputs of total and methyl mercury to Torch Lake via the Traprock River. Fish mercury content has been increased slightly since 1988; this suggests that lake MeHg concentrations also have not changed greatly over that time period. Bioaccumulation modeling indicates that a reduction in methylmercury concentrations in Torch Lake would result in lower fish Hg concentrations within a few years.

This study also points to some clear data gaps. There is a need for measurements of total mercury in Torch Lake and its tributaries to clarify if the lake is a source of Hg to downstream waters including Lake Superior. Seasonal measurements of MeHg in Torch Lake surface and bottom waters would help to quantify the amount of in-lake methylation. Isotopic measurements of MeHg and fish Hg in Torch Lake are the only way to determine if mine tailings are an important source of methylated and bioaccumulated mercury.

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# Appendix A. Excerpts from MS Thesis of M. Bollini (2023).

### 1.1.1 MeHg adapted bioaccumulation model

The bioaccumulation of mercury was modeled in a similar format to that of PCBs. However, the uptake and elimination mechanisms differ between PCBs and Hg (Li et al., 2015). For example, PCBs undergo passive partitioning between the different phases (e.g., water, lipid, and non-lipid organic matter; NLOM)) in organisms. In contrast, Hg exhibits a strong association with sulfur-rich proteins and is poorly associated with tissue lipids (Li et al., 2015). The dominant species of Hg in aquatic organisms is MeHg; thus, the inorganic form was ignored (Trudel & Rasmussen, 2006; Li et al., 2015). The bioaccumulation model for MeHg in fish was adapted from that of Trudel & Rasmussen (2001). The model is relatively simple and can predict the mercury concentration in freshwater fish species based on exposure through contaminated prey.

The kinetic mass balance model for MeHg bioaccumulated burden used for fish is shown in the equation below:

$$\frac{dM_{fish}}{dt} = (E_D \times C_D \times I \times W_B) - k_{tot} \times M_{fish} \quad (20)$$

The uptake of dissolved MeHg from the water accounts for less than 0.1% of the mercury accumulated in fish, therefore bioconcentration is assumed to be negligible (Trudel & Rasmussen, 2001). The uptake mechanism in the diet is modeled as a function of the assimilation efficiency ($E_D$, unitless), concentration of Hg in diet ($C_d$, mg/g), food ingestion rate ($I$, g food/g organism/d), and weight of the organism ($W_B$, g). The Trudel & Rasmussen (2001) study compared the predictions of this model and its bioenergetic equations with a feeding rate based on measured uptake of radiolabeled cesium ($^{137}$ Cs). There are no measurements of feeding rates or activity costs for Torch Lake walleye; therefore, the general bioenergetic relationship that was used in the PCB model above was implemented. The feeding rate for trophic level 3 was based on the bioenergetics model for brown bullhead (Hartman, 2017). The model calculations are shown in the forage fish and predator fish section of Table 9.

The elimination of MeHg is much faster as compared to PCBs; however, the physiological mechanism of Hg elimination is largely unknown for fish (Li et al., 2015). Hypothesized mechanisms include demethylation biotransformation reactions, protein turnover during routine metabolism, or hormonally controlled elimination (Madenjian et al., 2014b). Because Hg elimination is less understood and the bioenergetics have not been analyzed for Torch Lake walleye, an overall elimination rate constant ($k_{tot}$) is implemented based on an updated empirical equation of Trudel & Rasmussen (1997). A study by Yoa & Drouillard (2019) compared three different empirical elimination models based on Trudel & Rasmussen (1997) and data published after 1997. The Trudel & Rasmussen (1997) original model is represented by Model 1 and has been commonly used in bioenergetic-toxicokinetic models. Model 2 included a thermal category (TC) to incorporate the relationship between fish metabolic rate and temperature. The TC 1, 2, or 3 represented cold, cool, and warm water fish, respectively. Model 2 performed best even against Model 3, which included species specific routine metabolic rate (RMR) as estimated from the Wisconsin Fish Bioenergetic Model (Deslauriers et al., 2017). Therefore, Model 2 was used to estimate the elimination rate constant for forage and predatory fish in the bioaccumulation model. The empirical model is a function of body weight, temperature, and thermal category (TC).

$$\ln\ k_{tot} = -0.52\ \pm 0.05\ \times ln\, W_B + 1.89 \pm 0.73\ \times ln(T) + 4.29 \pm 1.15\ \times TC - 1.44\ \pm 0.44 \times (ln\, T \times\ TC) - 9.19\ \pm 1.78 \quad (21)$$

Walleye were assumed to be cool water fish, corresponding to a TC of 2. Brown bullhead were assumed to be warm water fish species corresponding to TC of 3. The calculated $k_{tot}$ for a temperature of 10 °C for bullhead and walleye were 0.0058 $d^{-1}$ and 0.0013 $d^{-1}$, respectively. Walleye have an optimum temperature preference of 22ºC (~75°F). Thus, $k_{tot}$ may be underestimated at a temp of 10°C (Kitchell et al., 1997).

The MeHg model treats the fish as a single compartment with uptake only from the diet, and elimination via all pathways (including growth) are combined into one in the second term. The model assumes a homogenous distribution of MeHg, and thus the concentrations in the muscle tissue and whole body are equal. Additionally, the model assumes that the daily losses from the body tissue to the gonads are negligible in comparison to other pathways because of the association with the protein matrix rather than with lipids (Harris et al. 2003; Trudel and Rasmussen, 2006). For simplicity, the release of Hg-contaminated eggs and sperm during spawning is assumed to be negligible. Because most mercury in fish is in the MeHg form, the model assumes that the assimilation of inorganic Hg in the intestine of fish from the consumed prey is negligible. The assimilation efficiency ($E_D$) for Hg in piscivorous fish typically ranges between 0.6 and 0.95; with a middle value of approximately 0.8 often used (Trudel & Rasmussen, 2001). MeHg is covalently bonded to sulfur in proteins that have an assimilation efficiency of around 80%. Therefore, it is assumed that $E_D$ is equal to 0.8.

The bioaccumulation model for fish is driven by the concentration of Hg in the prey in the fish diet, but there are no empirical observations in Torch Lake except for top-predator fish species (e.g., walleye, northern pike, and small mouth bass). Therefore, the concentration of MeHg in the diet ($C_d$) was predicted based on modeling from measurements of the dissolved phase concentration in the water column. There are fewer bioaccumulation models for lower trophic level organisms for MeHg in comparison to PCBs. However, this project implemented a model based on Schartup et al. (2018) for Northwest Atlantic Ocean phytoplankton and zooplankton. Phytoplankton take up MeHg via diffusion from lake water across the cell membrane. The Schartup (2018) steady-state phytoplankton model combined studies from Lee & Fisher (2016) and Luengen et al (2012) to model the aqueous uptake (*U,* amol $\mu m^{-3}$ nM) as a function of cell size and DOC concentration. Note it is assumed that the phytoplankton achieve equilibrium with the water over 4 hours (Lee & Fisher, 2016).

$$C_{phyto}\left(\frac{ng}{g}\right) = \frac{U * C_{WD,T} * V}{W_B} x200.59\ x10^{-12} \quad (22)$$

Therefore, the steady state predicted MeHg concentration is shown in Equation 22 as a function of aqueous uptake rate constant, MeHg concentration in the water ($C_{WD,\,T}$, pM), and the volume of the cell ($V$, $\mu m^3$). The radius of the phytoplankton cell in Torch Lake (r, µm) was assumed to be 25 µm, contributing to a surface area ($SA$, $\mu^2$) to volume ratio of 0.12.

***Table 1.*** *Phytoplankton equations used in the Torch Lake MeHg bioaccumulation model (Schartup et al., 2018).*

| Equation Description | Units | Equation |
|---|---|---|
| Empirical relationship between net MeHg uptake rate and cell $S_A$:V | amol $\mu m^{-3}$ $nM^{-1}$ | $U = t\frac{0.118S_A}{V}\exp(-0.008 \times DOC)$ $where\ t = 4h$ |
| Volume of cell | $\mu m^3$ | $V = \frac{4}{3}\pi r^3$ |
| Surface area to volume ratio (spherical) | $\mu m^{-1}$ | $S_A{:}V = 3/r$ |

The Schartup et al. (2018) model implemented a non-steady state bioaccumulation model for herbivorous (small) and omnivorous (large) zooplankton. Bioconcentration is significant for zooplankton, and thus the equation has a similar structure as for PCBs. The zooplankton mass balance equation is shown below (Equation 23). The variables for this equation are listed in Table 7.

$$\frac{dM_{zoo}}{dt} = (W_B\{(k_1 * C_{wDO}) + (k_D * C_D)\}) - (k_{tot} * M_{zoo}) \quad (23)$$

The uptake included both respiratory intake through the gills ($k_1$) and ingestion of contaminated phytoplankton ($k_D$). The aqueous uptake rate is a function of the gill chemical uptake efficiency ($E_D$, unitless), as estimated in the Arnot & Gobas (2004) model, in addition to the clearance rate ($F$, L/d) and weight of the organism ($W_B$, g). The dietary uptake rate constant is a function of the effective depth-averaged suspended particle matter (SPM) concentration ($E_{SPM}$, g/L) which was assumed to be 75% of the SPM. In addition, the $k_D$ was modeled as a function of the clearance rate, dietary assimilation efficiency ($E_D$, unitless) and body weight. The $E_D$ for zooplankton ranges between 50% and 70% and therefore is simulated probabilistically using a uniform distribution; this is equivalent to setting $E_D$ to 60% (Schartup et al., 2018). The phytoplankton represents 100% of the diet for zooplankton. The fecal elimination ($k_{tot}$, $d^{-1}$) is dependent on the body burden and water temperature. Pseudo-elimination via growth dilution was included in the Schartup et al. (2018) model, but the results indicated a balance between uptake and growth. The zooplankton were growing faster but consuming more contaminated food. However, studies of freshwater systems have indicated the importance of growth dilution, which is discussed in section 4 (Pickhardt et al., 2002; Barber et al., 2015).

***Table 2***. *Biological input parameters used in Torch Lake MeHg bioaccumulation model.*

| Variable Name | Units | Symbol | Trophic Level Values | | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | |
| Weight of biomass | g | $W_B$ | $5.7 \times 10^{-4}$ | $5.7 \times 10^{-5}$ | 500 | 1,450 | 1,2 |
| Dietary chemical transfer efficiency | - | $E_D$ | 0 | 0.60 | 0.80 | 0.80 | 3,4 |

*Source References Used in this Table: MI EGLE fish data[1], Arnot & Gobas (2004)[2], Schartup et al. (2018)[3], Trudel & Rasmussen (2001)[4].*

***Table 3***. *Chemical input parameters used in Torch Lake MeHg bioaccumulation model.*

| Variable Name | Units | Symbol | Value | Ref. |
|---|---|---|---|---|
| Octanol-water partition coefficient | - | $K_{ow}$ | $10^{1.7}$ | 1 |
| Truly dissolved water concentration | ng/L | $CwdO$ | 0.151 | 2 |
| Molecular weight of Hg | g/mol | $MW_{Hg}$ | 201 | |
| Molar Truly dissolved water concentration | pM | $CwdO_M$ | 0.751 | |

*Source References Used in this Table: Schartup et al. (2018)[1], EGLE (unpub.)[2]*

***Table 4***. *Bioenergetic equations Torch Lake MeHg bioaccumulation model.*

| Equation Description | Units | Equation | Eqn. No. | Ref |
|---|---|---|---|---|
| **Zooplankton** | | | | |
| Aqueous clearance rate constant | L/g × $d^{-1}$ | $k_1 = E_W \times F/W_B$ | 24 | 2 |
| Gill chemical uptake efficiency | - | $E_W = \left(1.85 + (155/K_{OW})\right)^{-1}$ | 25 | 1 |
| Clearance rate | L/d | $F = 1.777 \times e^{0.234 \times T} \times (0.002 \times W_B \times 10^5)^{0.681} \times exp(0.0199 \times T)$ | 26 | 2 |
| Dietary uptake clearance rate constant | g SPM/g organism × $d^{-1}$ | $k_D = F \times E_{SPM} \times E_D/W_B$ | 27 | 2 |

| Equation Description | Units | Equation | Eqn. No. | Ref |
|---|---|---|---|---|
| Particle Scavenging efficiency | g SPM /L | $E_{SPM} = 0.75 \times SPM$ | 28 | 2 |
| Elimination rate constant | $d^{-1}$ | $k_{tot} = 0.00335 \times W_B^{-0.195} \times \exp(0.0066 \times T)$ | 29 | 2 |
| **Forage & Predatory Fishes** | | | | |
| Dietary uptake clearance rate constant | g food/g organism × $d^{-1}$ | $k_D = E_D \times G_D / W_B$ | 30 | 1 |
| Feeding rate | kg food/d | $G_D = 0.022 \times W_B^{0.85} \times \exp(0.06 \times T)$ | 31 | 1 |

The MeHg model was encoded in a format in MATLAB software similar to the PCB bioaccumulation model. The mass balance equations for zooplankton and fish were solved with separate functions because of the negligible magnitude of bioconcentration as compared to biomagnification. The ODE (ode15s) solver was implemented to solve the dynamic mass balance equations over a 10-year period with a daily time step. The initial mass for each trophic level was assumed to be close to zero ($1 \times 10^{-17}$ ng of MeHg). The MATLAB code is available in the Appendix (Appendix).

### 1.1.1 Model validation, and sensitivity and uncertainty analyses

#### *1.1.1.1 Model Validation*

The MeHg bioaccumulation model was validated with the average observed walleye concentrations obtained from MI EGLE and GLIFWC. The box-and-whisker plot of walleye measured mercury concentrations is shown in the Figure 13 below:

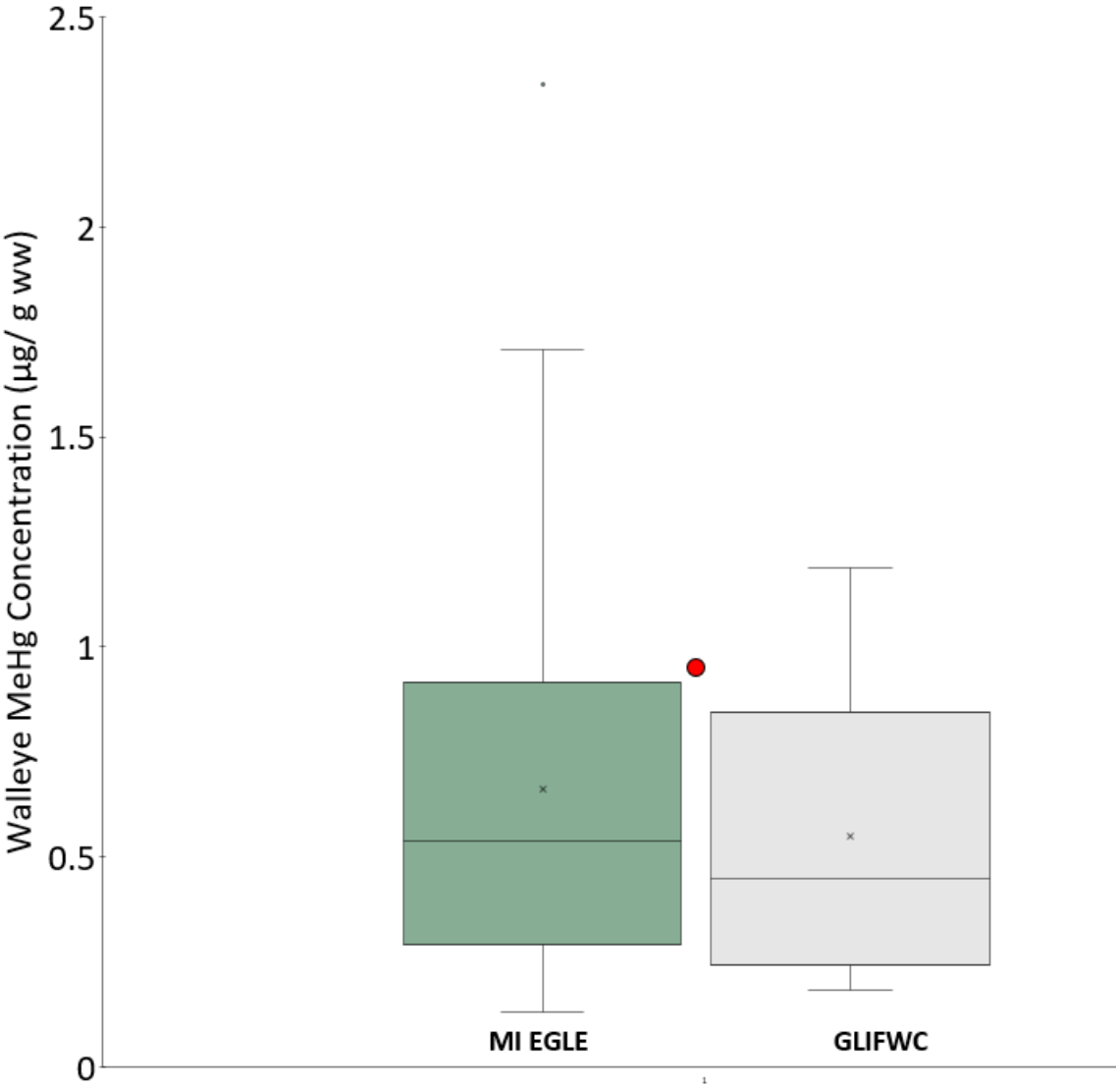


***Figure 1.*** *Box- and -whisker plots of measured MeHg concentrations in walleye concentration in Torch Lake obtained from Michigan EGLE (2000, 2007, 2013, and 2018) and Great Lakes Indian Fish and Wildlife Commission (GLIFWC) for years 2018-2021 for model validation. The model predicted value is indicated by the red circle.*

There are no data are available for the other trophic levels in Torch Lake, however, a Bioaccumulation Factor (BAF) has been previously used in mercury mass balance models (Hendricks, 2018). The BAF is defined by the ratio of the contaminant concentration in fish tissue to the dissolved contaminant concentration in the lake water, Equation (24):

$$BAF = \frac{C_{fish}\ (\mu g/kg)}{C_{water}\ (\mu g/L)} \tag{24}$$

The BAF is a simple steady-state calculation to estimate the concentration in aquatic species ($C_{fish}$) based on the water concentration ($C_{water}$). The mercury BAF of trophic levels 3 and 4 were estimated from the 5$^{th}$, 25$^{th}$, 50$^{th}$, 75$^{th}$, and 95$^{th}$ percentiles presented in Knightes (2008). The predicted BAF from the

MATLAB bioaccumulation non-steady state model was compared with the empirical BAF values shown in Table 10.

***Table 5.*** *Mercury Bioaccumulation Factors (BAF) in fish (Knightes, 2008; Hendricks, 2018)*

| Percentile | Trophic level 3 $\times 10^6$ | Trophic level 4 $\times 10^6$ |
|---|---|---|
| $5^{th}$ | 0.46 | 3.3 |
| $25^{th}$ | 0.95 | 5.0 |
| $50^{th}$ | 1.6 | 6.8 |
| $75^{th}$ | 2.6 | 9.2 |
| $90^{th}$ | 5.4 | 14 |

The validation of the bioaccumulation models (PCB and MeHg) with observed measurements characterizes the overall model error, including model parameterization errors and natural variability with measured values (Arnot & Gobas, 2004). The model performance was assessed by calculating the percent error, shown in the equation below:

$$percent\ error = \frac{|C_{pred,i} - C_{obs,i}|}{C_{obs,i}} \times 100 \quad (24)$$

where, the percent error is a function of the steady-state predicted ($C_{pred,i}$)and measured concentrations ($C_{obs,i}$) for each of the seven congeners divided by the number of observations ($n$).

#### *1.1.1.1 Sensitivity Analysis*

The sensitivity analyses of the PCB and MeHg bioaccumulation models were performed by the parameter perturbation method. The objective of this method is to determine the sensitivity of the model to an individual parameter. The selected individual model parameters were varied by $\pm$ a fixed amount while holding all other terms constant (Chapra et al. 2008). The parameters that were selected for the sensitivity analysis of PCB model included the uptake and elimination rate constants (± 10%), partition coefficients (± factor of 2), water temperature (± 5°C), and fish wet weight (± factor of 2). These parameters were chosen because they are thought to be values that strongly impact the predicted concentrations.

#### *1.1.1.2 Uncertainty Analysis*

The uncertainty analyses of the PCB and MeHg bioaccumulation models were performed with Monte Carlo simulations. This method uses random values to generate a series of outcomes to create a distribution of the predicted concentrations (Chapra et al., 2014).

The random values selected for each selected parameter were assumed to follow a normal distribution and estimated using the Matlab function *normrnd*, which is dependent on the mean, standard deviation, and size of the array (Mathworks, 2023b). The standard deviation was estimated, with literature review values of dietary uptake of PCBs in fish estimated from assimilation efficiency, which can be easily measured. The trophic transfer efficiency ($E_D$) is the efficency with which the contaminant in the food ingested by predator is transported through the gut wall (Madenjian et al., 2014a). The transfer efficiency is an important parameter for modeling bioaccumulation, and laboratory and field studies suggest that $E_D$ can be influenced by the feeding rate and digestibilty of the dietary matrix.

The four most sensitive parameters selected for the PCB Monte Carlo simulation included: $T$, $k_D$, $C_{wd}$, and $K_{ow}$. The literature review values of assimilation efficiency of modeled PCB congeners based on species type used for the uncertainty analysis shown below:

***Table 6**. Literature review values of dietary assimilation efficiency for PCB congeners in fish based on species type.*

| Estimated dietary assimilation efficiency ($E_D$) | | | | | | | Species | Ref |
|---|---|---|---|---|---|---|---|---|
| PCB 33 | PCB 52 | PCB 99 | PCB 101 | PCB 149 | PCB 153 | PCB 180 | | |
| 0.25 | 0.35 | 0.34 | 0.39 | 0.40 | 0.64 | 0.56 | Marbled sole | 1 |
| 0.10 | 0.19 | 0.12 | 0.29 | 0.47 | 0.65 | 0.46 | Koi | 2 |
| 0.25 | 0.24 | 0.10 | 0.30 | 0.36 | 0.37 | 0.30 | Koi | 2 |
| | | 0.38 | 0.28 | 0.39 | 0.44 | 0.44 | Goldfish | 3 |
| 0.47 | 0.49 | 0.51 | 0.54 | 0.50 | 0.50 | 0.56 | Goldfish | 4 |
| | 1.001 | 0.551 | | | | | Whitefish | 5 |
| 0.775 | 0.775 | 0.775 | 0.775 | 0.775 | 0.775 | 0.775 | Walleye | 6 |
| 0.848 | 0.911 | 0.675 | 0.705 | 0.628 | 0.653 | 0.681 | Lake trout | 7 |

*Source references used in this table: Kobayasni et al. (2011)[1], Lui et al. (2010)[2], Li et al. (2015)[3], Bruggeman et al. (1981)[4], Madenjian et al. (2008)[5], Barber et al. (2008)[6], Madenjian et al. (2014a)[7].*

The three most sensitive parameters selected for the MeHg Monte Carlo simulation were: $T$, $E_D$, *and* $k_{TOT}$. The dietary assimilation efficiency and total elimination rate constant based on literature values are shown in Tables (12-13) below:

***Table 7.** Literature review values of dietary assimilation efficiency for MeHg in fish based on species type.*

| Estimated dietary assimilation efficiency ($E_D$) for MeHg | Species | Ref |
|---|---|---|
| 0.64 | Lake whitefish | 1 |
| 0.77 | Lake trout | 2 |
| 0.98 | Goldfish | 3 |

| | | |
|---|---|---|
| 0.89 | Redear sunfish | 4 |
| 0.94 | Tilapia | 5 |
| 0.85 | Tilapia | 5 |
| 0.68 | Rabbitfish | 6 |
| 0.94 | Largemouth bass | 7 |

*Source references used in this table: Madenjian and O'Connor (2008)[1], Madenjian et al. (2012)[2], Li et al. (2015)[3], Pickhardt et al. (2006)[4], Wang et al (2010)[5], Peng et al. (2016)[6], Bowling et al. (2011)[7].*

The total elimination rate constant can be easily measured in laboratory and field studies. Studies such as, The Mercury Experiment to Assess Atmospheric Loading in Canada and the United States (METAALICUS), have utilize mercury stable isotopes to analyze fate and transport in the environment and whole-ecosystem response to changes in loadings (Harris et al., 2007 ; Blanchfield et al., 2021). The total elimination rate constant can be estimated by transferring fish from a spiked environment to a different lake (VanWellegham et al., 2007 ; VanWalleghem et al., 2013).

***Table 8.*** *Literature review values of total elimination rate constant for MeHg in fish based on species type.*

| **Estimated total elimination rate constant ($k_{TOT}$, 1/d) for MeHg** | **Species** | **Ref** |
|---|---|---|
| $1.42 \times 10^{-3}$ | Yellow perch | 1 |
| $6.32 \times 10^{-4}$ | Northern pike | 2 |
| $3.80 \times 10^{-4}$ | Lake Trout | 3 |
| $9.50 \times 10^{-4}$ | Whitefish | 3 |
| $7.30 \times 10^{-4}$ | Whitefish | 4 |
| $2.44 \times 10^{-4}$ | Lake Trout | 5 |

*Source references used in this table: VanWalleghem et al, (2007)[1], VanWalleghem et al., (2013)[2], Blanchfield et al. (2022)[3], Madenjian and O'Connor (2008)[4], Madenjian et al. (2012)[5]*

The bioaccumulation models were adapted to output only the trophic level 4 concentrations with the parameter variations to estimate the uncertainty in the walleye concentration. The model included 10,000 iterations (N = 10,000) to estimate the corresponding output concentrations. The 95% confidence interval of the PCB congener and MeHg concentrations were estimated in MATLAB with the built-in function *paramci*. To compute the mean and standard deviation of the walleye concentrations, the results were fit to a normal distribution with the MATLAB function *fitdist*.

### 1.1.2 Model Experiments

The different scenarios of Torch Lake with the kinetic bioaccumulation models of PCBs and MeHg to understand the dynamics of PCB bioaccumulated burdens depending on changes in PCB sources, remediation efforts, and food web characteristics. The objective was to answer the questions posed in this study:

(1) What are the expected PCB and MeHg concentrations in Torch Lake fish if remediation now under consideration is performed?

(2) How long must fish reside in Torch Lake in order to acquire the observed PCB and MeHg concentrations?

This section outlines the methods used in the modeling experiments to answer the above questions. There was only one scenario involved for the mercury modeling due to the natural background concentration not associated with the mining activities.

#### *1.1.2.1 MeHg modeling questions*

Estimating the remediation effectiveness with mercury is different than for PCBs due to the background concentrations from methylation in the lake and surrounding watershed (i.e., wetlands). The spatial and temporal distribution in tributaries of the Torch Lake suggested 50% of MeHg is produced from wetlands discharging water into Trap Rock River. The other ~50% was concluded to be produced from in-lake methylation (Greene and Urban, 2022). Therefore, to answer the first question in regard to mercury, the measured MeHg concentration was reduced by 50% to eliminate the source of in-lake methylation (EGLE, unpub.). Under these conditions, the model can estimate the effects of potential remediation actions that focus on the elimination of in lake sources to decrease the concentrations of MeHg available for bioaccumulation.

The same method was performed for MeHg as for PCBs for answering the second question. The initial concentrations in trophic levels 1-3 were set to their predicted steady-state concentrations. However, the trophic level 4 MeHg initial concentration was set to zero. Therefore, the bioaccumulation of MeHg could be modeled under steady-state conditions in the other trophic levels.

# Results

## 1.2 MeHg Modeling Results

This section gives an overview of the MeHg bioaccumulation model results in Torch Lake. Figure 21 displays the whole-ecosystem recovery of Torch Lake aquatic ecosystem over the 10-yr period. The sensitivity and uncertainty analysis results show the limitations to the non-steady state model and assist with future model improvements. The experimental modeling of reducing the dissolved MeHg concentrations in the lake water examines the response of the walleye MeHg concentration to source eliminations.

### 1.2.1 Non-steady state MeHg bioaccumulation model results

The predictions of the MeHg bioaccumulation model for Torch Lake are displayed in Figure 21 for the walleye concentrations (μg/g ww or ppm) over a 10-year period. The model was run for 10 years because this is the estimated age of walleye of the weight modeled (e.g., 1.45 kg). Trophic levels 1 and 2 reach steady state within one year, but it requires about two years for trophic level 3 and 10 years for trophic level 4. Trophic level 4 has a steady state concentration about 10 times higher than trophic level 3 which is about 10-fold higher than trophic level 1. Concentrations in trophic level 2 plateau at a value within a factor of two of the steady state concentration in trophic level 3.

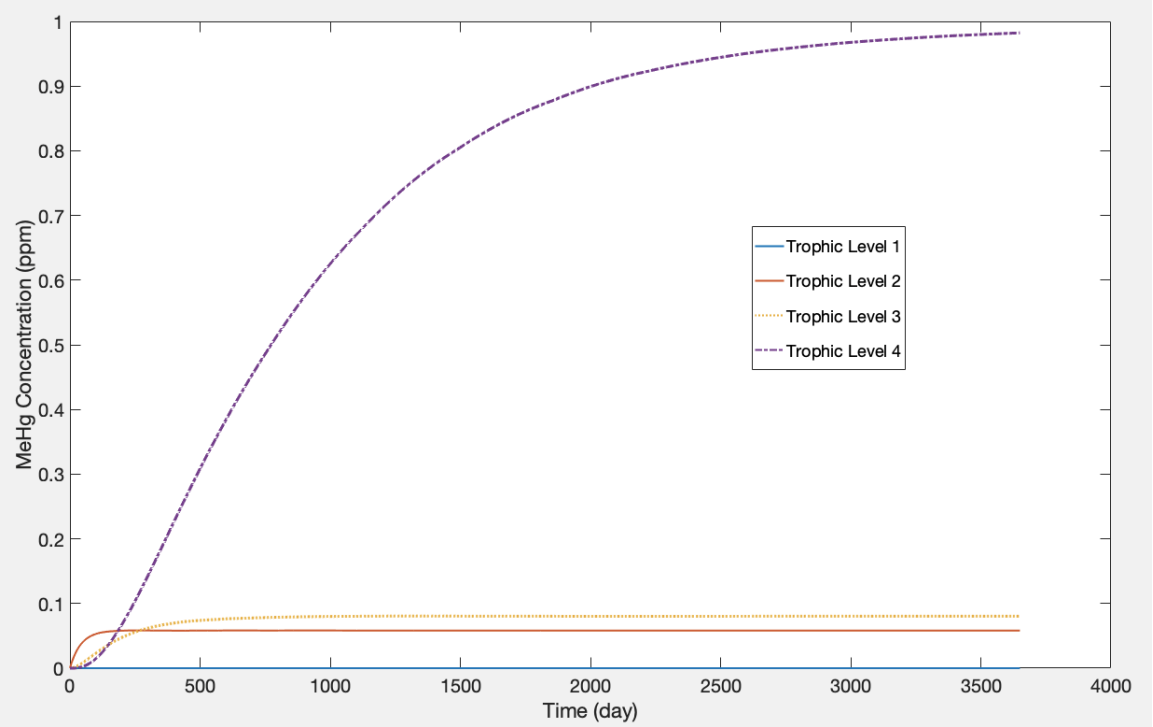


**Figure 2**. The non-steady state MATLAB predicted MeHg concentration in walleye over 10-year period.

## 1.2.1 Model validation, and sensitivity and uncertainty analyses results

### *1.2.1.1 Walleye Model Validation Results*

The MATLAB predicted concentration of mercury in walleye were about two-fold higher than the observed concentrations from GLIFWC and MI EGLE (see Table 17). The percent error between the model-predicted concentrations and the measured walleye concentration was estimated to be 78% using Equation 24. There are limitations of the model that may have resulted in values higher than those measured. For example, the model assumes a constant organism body weight; thus, it ignores the potential impacts of growth dilution. The implications will be discussed later together with recommendations for model improvement.

**Table 9.** Torch Lake walleye mercury modeled and observed concentrations from MI EGLE (1988, 2000, 2007, 2013, 2018) and GLIWC (2018, 2019).

| **Torch Lake Walleye Mercury Concentration (µg/g ww)** | | |
|---|---|---|
| MATLAB predicted (10-yr period) | GLIFWC average measured (2018-2019) | MI EGLE average measured (1988-2018) |
| 0.98 | 0.55 | 0.61 |

The predicted BAF from the non-steady state bioaccumulation model are reported in Table 18 below:

**Table 10.** Predicted MeHg Bioaccumulation Factor (BAF) for trophic levels 3 and 4.

| Trophic level 3 | Trophic level 4 | Literature values trophic level 4 log BAF[1] |
|---|---|---|
| $0.53 \times 10^6$ | $6.5 \times 10^6$ | $10^{6.5}$-$10^{7.69}$ |

*Source references used in this table: Raymond and Rossmann (2009)[1]*

The BAF for trophic level 3 was higher than the 90$^{th}$ percentile and trophic level 4 was higher than measured BAF values indicated in Table 10 in methods.

The zooplankton measurements from northern Wisconsin lakes presented in Back and Watras (1995) were used to compare the model-predicted concentrations. The zooplankton were collected from twelve different lakes and separated by taxa. The ranges of MeHg based on taxa are presented in Table 19. The results from this study showed a decrease in zooplankton bioconcentration of Hg as an increase in lake DOC.

**Table 11**. Zooplankton MeHg concentrations reported by Back and Watras (1995).

| Zooplankton taxa | Measured MeHg range (ng/g dry wt) |
|---|---|
| Herbivorous | 1 - 479 |
| Omnivorous | 24 - 30 |

The model-predicted herbivorous zooplankton concentrations were within the range with a value of 58 ng/g ww. The study by Back and Watras (1995) revealed that zooplankton from lakes <10 mg/L DOC had higher bioconcentration of both Hg and MeHg. The dissolved organic carbon concentration in the Torch Lake water was assumed to be 7.9 mg/L based on the 10-year average (Mandelia, 2016).

#### *1.2.1.2 Sensitivity Analysis Results*

The parameter perturbation method for the MeHg bioaccumulation model was performed in a similar manner to the PCB bioaccumulation model. The uptake and elimination rate constants were varied by ± 10% shown in Figures 24 and 25. It should be noted that the rate constants were included in the analysis because the steady-state assumption for the MeHg concentration in phytoplankton. The MeHg model was most sensitive to the total elimination rate constant ($k_{TOT}$) in trophic levels 2 and 3, the bioconcentration uptake rate in trophic level 2 ($k_1$) and the ingestion rate in trophic levels 3 and 4 ($I$).

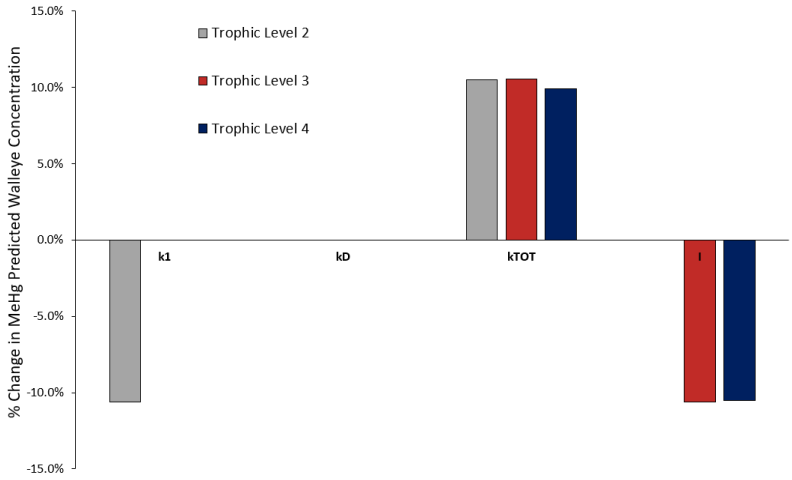


**Figure 3**. Change in walleye MeHg concentration caused by decreasing the model rate constants for trophic levels 2 (gray), 3 (red), and 4 (blue) by 10%.

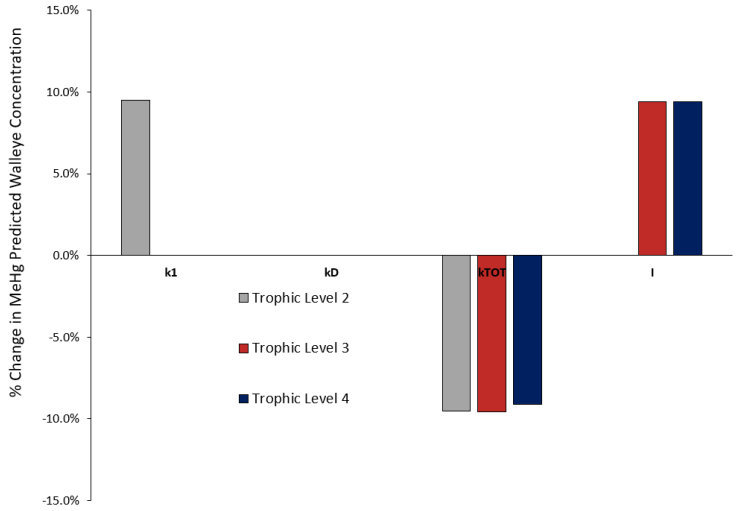


**Figure 4**. Change in walleye MeHg concentration caused by increasing the model rate constants for trophic levels 2 (gray),3 (red), and 4 (blue) by 10%.

#### *1.2.1.1 Uncertainty Analysis Results*

The Monte Carlo simulation was run for 10,000 iterations of the MeHg bioaccumulation model. Values for the dietary assimilation efficiency ($E_D$), total elimination ($k_{TOT}$) rate constants and temperature ($T$) followed a normal distribution and were randomly and independently selected. The simulation results are shown in Figure 26. The calculated mean MeHg concentration, standard deviation, and 95% confidence interval from the Monte Carlo Simulation are displayed in Table 20.

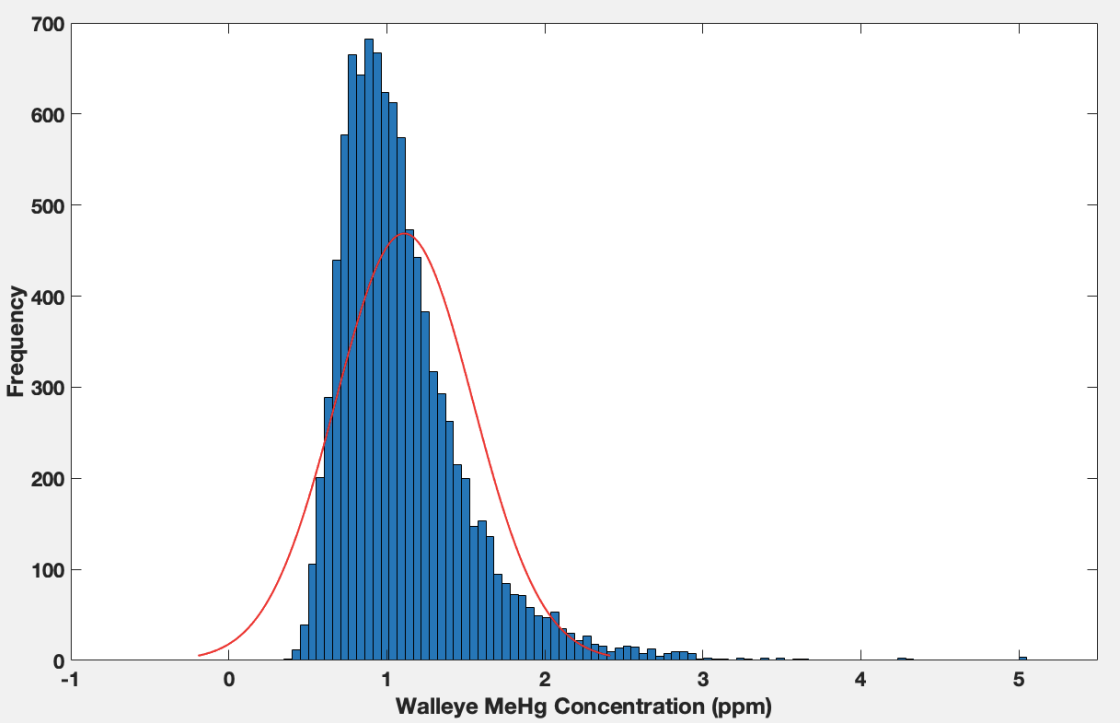


**Figure 5.** Walleye MeHg Monte Carlo simulation output concentration histogram. Normal distribution curve (redline).

**Table 12**. Torch Lake Walleye MeHg Monte Carlo simulation mean concentration, standard deviation, upper and lower 95% confidence interval selected at the end of 10-year period modeled.

| Mean Concentration (µg/g ww) | Standard deviation (µg/g ww) | Lower 95% confidence interval | Upper 95% confidence interval |
|---|---|---|---|
| 1.11 | 0.43 | 1.10 | 1.12 |

The results from the Monte Carlo simulation show that the model predictions did not follow a normal distribution. As a percent of the mean, the 95% confidence interval was 1.8%. The uncertainties are, therefore, small relative to the predicted concentrations (0.98 µg/g ww). Nevertheless, the range of values predicted by "reasonable values" of the parameters in the Monte Carlo simulation is large (~ 3 µg/g ww) relative to measured concentrations (< 1 µg/g ww). If bias exists in the model predictions, it would be easy to tune the model to predict lower values.

### 1.2.1 Modeling Experiment Results

The lake water dissolved MeHg concentration was set to half of the value measured in 2021 to represent the reduction in MeHg if there was no ongoing source in the lake due to in-lake methylation. The model-predicted 10-year steady state concentration in walleye was 0.49 µg/g ww; therefore, a 50% reduction in MeHg in the lake caused a reduction in the bioaccumulated burden by 50%. The simulation results highlight the dependence of the predicted walleye concentrations on dissolved MeHg concentrations. In addition, the results show the maximum potential impact of remediation actions on in-lake methylation.

The results of the second model experiment to determine the time to reach the average measured bioaccumulated burden in Torch Lake walleye to be 619 days, or ~2 years.