# Mercury Dynamics in Finger Lakes Fish and Invertebrates

Summary Report | Report Number 20-37 | December 2020



# **NYSERDA's Promise to New Yorkers:**

NYSERDA provides resources, expertise, and objective information so New Yorkers can make confident, informed energy decisions.

### **Our Vision**:

New York is a global climate leader building a healthier future with thriving communities; homes and businesses powered by clean energy; and economic opportunities accessible to all New Yorkers.

### **Our Mission**:

Advance clean energy innovation and investments to combat climate change, improving the health, resiliency, and prosperity of New Yorkers and delivering benefits equitably to all.

# Mercury Dynamics in Finger Lakes Fish and Invertebrates

#### Summary Report

Prepared for:

#### New York State Energy Research and Development Authority

Albany, NY

Diane Bertok Project Manager

Prepared by:

#### Hobart and William Smith Colleges

Geneva, NY

L.B. Cleckner N.R. Razavi S.F. Cushman J.D. Halfman

NYSERDA Report 20-37

## Notice

This report was prepared by Hobart and William Smith Colleges in the course of performing work contracted for and sponsored by the New York State Energy Research and Development Authority (hereafter "NYSERDA"). The opinions expressed in this report do not necessarily reflect those of NYSERDA or the State of New York, and reference to any specific product, service, process, or method does not constitute an implied or expressed recommendation or endorsement of it. Further, NYSERDA, the State of New York, and the contractor make no warranties or representations, expressed or implied, as to the fitness for particular purpose or merchantability of any product, apparatus, or service, or the usefulness, completeness, or accuracy of any processes, methods, or other information contained, described, disclosed, or referred to in this report. NYSERDA, the State of New York, and the use of any product, apparatus, process, method, or other information will not infringe privately owned rights and will assume no liability for any loss, injury, or damage resulting from, or occurring in connection with, the use of information contained, described, disclosed, or referred to in this report.

NYSERDA makes every effort to provide accurate information about copyright owners and related matters in the reports we publish. Contractors are responsible for determining and satisfying copyright or other use restrictions regarding the content of reports that they write, in compliance with NYSERDA's policies and federal law. If you are the copyright owner and believe a NYSERDA report has not properly attributed your work to you or has used it without permission, please email <u>print@nyserda.ny.gov</u>

Information contained in this document, such as web page addresses, are current at the time of publication.

# **Preferred Citation**

New York State Energy and Research Development Authority (NYSERDA). 2020. "Mercury Dynamics in Finger Lakes Fish and Invertebrates." NYSERDA Report Number 20-37. Prepared by Hobart and William Smith Colleges, Geneva, NY. nyserda.ny.gov/publications

## Abstract

The Finger Lakes are a series of eleven elongated glacially formed freshwater lakes in the Lake Ontario basin located in western and central New York State. Angling for both cold and warm water fish species is a popular recreational activity in the region and is a large component of the annual \$2 billion of economic activity associated with tourism. To understand more about mercury (Hg) concentrations in Finger Lakes fish, the Finger Lakes Mercury Study was launched in 2015. As part of this study, fish and invertebrate communities in five Finger Lakes and three streams for each lake were analyzed for mercury concentrations. These lakes were selected based on their varying limnology and morphometry including differences in nutrient status, volume, surface area, and retention time.

Results showed that several fish species exceed the United States Environmental Protection Agency (EPA) methylmercury (MeHg) criterion of 300 nanograms per gram (ng/g), including greater than 30% of sampled Lake Trout and Largemouth Bass as well as 80% of sampled Walleye. No water chemistry or lake morphology variables predicted fish Hg concentrations in the Finger Lakes despite sampling a range of trophic statuses from oligotrophic to eutrophic, suggesting that fish food web structure and fish growth rates may be driving differences in Hg concentrations.

By comparing and contrasting stream to in-lake levels of Hg in biota across proximal lakes in the Finger Lakes, a comprehensive assessment of Hg concentrations in sport fish and lower trophic organisms was completed. This information will be integral for understanding future changes in mercury associated with other disturbances such as land use, nutrient supply, climate change, and air pollution.

### **Keywords**

Finger Lakes, bioaccumulation, sportfish, watershed, streams, macroinvertebrates

# Acknowledgments

This research was funded by the New York State Energy Research and Development Authority under the direction of Gregory Lampman and Diane Bertok. Additional support was provided by the Finger Lakes Institute at Hobart and William Smith Colleges. The authors thank numerous collaborators from across the Finger Lakes region including John Foust and Bruce Gilman from Finger Lakes Community College, Webster Pearsall and Peter Austerman from the New York State Department of Environmental Conservation, Jacques Rinchard from The College at Brockport, and Jon Gaulke. The authors also thank Hobart and William Smith Colleges' staff members Rob Beutner and Patrick Gunn; students Alex Gatch, Nikki Andrzejczyk, and Kayleigh Buffington; as well as Patricia Thompson from Finger Lakes Community College for field and laboratory support. For more information on the results of the work summarized in this report, please see the full articles in *Ecotoxicology and Environmental Safety* and *Ecotoxicology*. The full citations for these articles are as follows:

Razavi, N.R., S.F. Cushman, J.D. Halfman, T. Massey, R. Beutner, L.B. Cleckner. 2019a. Mercury bioaccumulation in stream food webs of the Finger Lakes in central New York State, USA. Ecotoxicology and Environmental Safety. 172: 265-272.

Razavi N.R., J.D. Halfman, S.F. Cushman, T. Massey, R. Beutner, J. Foust, B. Gilman, L.B. Cleckner. 2019b. Mercury concentrations in fish and invertebrates of the Finger Lakes in central New York, USA. Ecotoxicology. https://doi.org/10.1007/s10646-019-02132-z

# **Table of Contents**

Notice	ii
Preferred Citation	ii
Abstract	ii
Keywords	ii
Acknowledgments	v
List of Figures	/i
List of Tables	/i
1 Study Overview	1
1.1 Study Context	1
2 Finger Lakes Mercury Study—Lakes	3
2.1 Field Methods	4
2.1.1 Plankton, Invertebrate, Water Chemistry Collection, and Processing	4
2.1.2 Fish Collection and Processing for Mercury	5
2.2 Laboratory Methods	5
2.2.1 Total Mercury Analysis	5
2.2.2 Methylmercury Analysis	6
2.2.3 Water Chemistry Analysis	6
2.2.4 Data Analysis	9
2.3 Results and Discussion	9
2.3.1 Zooplankton and Invertebrate Mercury Concentrations	
2.3.2 Fish Mercury Concentrations	
2.4 Conclusions	
3 Finger Lakes Mercury Study—Streams1	9
3.1 Study Methods	
3.2 Results and Discussion	
4 Conclusions	7
5 References	8

# List of Figures

Figure 1. Dominant Land Cover and Location of the Finger Lakes Sampled in this Study	3
Figure 2. Monthly MeHg Concentrations (ng/g dw) in Finger Lakes Zooplankton by	
Lake from May to September 2015	10
Figure 3. Methylmercury Concentrations (ng/g dw) in Finger Lakes Quagga Mussels	
by Lake from May to September 2015	11
Figure 4. Methylmercury Concentrations (ng/g dw) in Finger Lakes Amphipods by	
Lake from May to September 2015	12
Figure 5. Size-Adjusted Yellow Perch THg Concentrations (ng/g ww) by Lake	14
Figure 6. Size-Adjusted Brown Bullhead THg Concentrations (ng/g ww) by Lake	15
Figure 7. Size-Adjusted Largemouth Bass THg Concentrations (ng/g ww) by Lake	15
Figure 8. Size-Adjusted Lake Trout THg Concentrations (ng/g ww) by Lake	16
Figure 9. Size-Adjusted Walleye THg Concentrations (ng/g ww) by Lake	16
Figure 10. Stream Sampling Locations in the Finger Lakes Watershed	19
Figure 11. Stream Fish THg Concentrations (ng/g dw) versus Total Length for	
Blacknose Dace and Creek Chub	23
Figure 12. Stream Macroinvertebrate MeHg Concentrations (ng/g dw) by Functional	
Feeding Group	25

# List of Tables

Table 1. Physical Characteristics and Sample Sites of Study	4
Table 2. Water Chemistry Summary of Lakes Studied in the Finger Lakes Mercury Study	
Table 3. Summary Statistics of Total Mercury Concentrations in Fish Species Collected	
in the Finger Lakes	13
Table 4. Mean Methylmercury Concentrations (ng/g dw) in Macroinvertebrates	
Collected from Finger Lakes Streams	21

### 1 Study Overview

Mercury (Hg) concentrations in multiple trophic levels of aquatic organisms across five Finger Lakes and their watersheds were investigated through this study. This was accomplished by (1) collecting monthly samples of zooplankton and benthic invertebrates in Honeove, Canandaigua, Seneca, Cayuga, and Owasco Lakes from May through September 2015 and (2) analyzing the samples for methylmercury (MeHg). In addition, two different trophic levels of fish were collected from each of the five lakes once during the same period and analyzed for total Hg, since it is assumed that most of the mercury in fish, especially in higher trophic levels, is MeHg (Bloom 1992). While a more recent analysis has shown that this assumption is not true for all fish species, sizes, and trophic levels (Lescord et al. 2018), the size of the fish and trophic levels sampled in this study indicated that the results would likely demonstrate that the majority of total Hg would be comprised of MeHg. In addition, three tributaries from each lake were sampled for periphyton, macroinvertebrates, and small fish, and then analyzed for MeHg. Tributaries were chosen based on prior knowledge of water quality, contrasting land use in the watershed, and discharge. Combined, the lake and stream Hg portions of this study provide contemporary information about the concentrations of MeHg in sport fish as well as lentic and lotic food webs of the Finger Lakes. This information, in turn, provides insight about the relative risks of consuming different types of Finger Lakes fish due to Hg concentrations and differences among specific lakes and watersheds.

#### 1.1 Study Context

Little is known about Hg dynamics in the Finger Lakes, although there have been relatively recent publications and presentations about Hg levels in sediment cores (Callinan 2001; Bookman et al. 2008), which are useful for determining long-term trends in Hg from pre-industrial times (late 1700s) to today. However, sediment cores are less useful for understanding the impact of changes in recent atmospheric loadings of Hg, the most likely source of Hg to surface waters and to biota (Hammerschmidt and Fitzgerald 2006).

Mercury contamination of fish is a global concern due to deleterious health effects in humans and wildlife associated with ingesting fish with elevated Hg levels. The most toxic form of Hg is MeHg, and this chemical form most readily bioaccumulates through food webs (Evers et al. 2011). A key to understanding elevated fish Hg levels is to examine MeHg dynamics at the base of the food web; in lakes

1

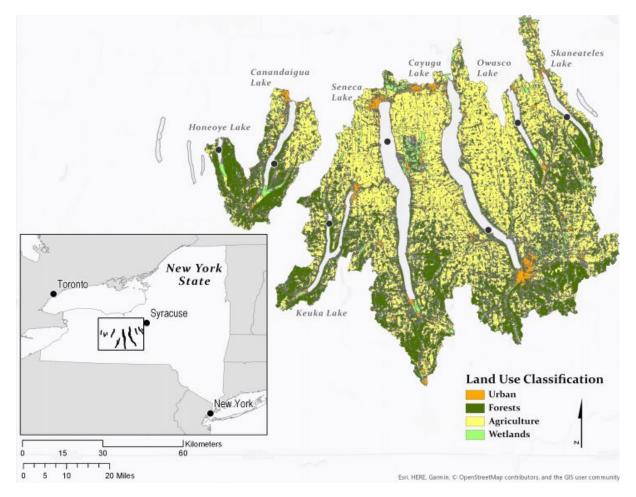
this includes algae and zooplankton and for streams this includes periphyton and macroinvertebrates. Previous to this study, concentrations of MeHg in Finger Lakes biota comprising the base of the aquatic food web were virtually unknown. The Finger Lakes Mercury Study addressed this data gap and presents data on the extent of Hg bioaccumulation in aquatic biota in select Finger Lakes and sub-watersheds.

Research conducted through the study has helped provide a better understanding of Hg levels in fish in several large lakes in a region that had not been widely studied to date. The focus on fish that humans consume makes the data gathered even more relevant for understanding potential risks associated with eating fish caught in the Finger Lakes. Perhaps most importantly, this Finger Lakes research will contribute to an increased understanding of Hg levels in invertebrates and other lower trophic level organisms. Since these organisms tend to spend their lives in a small geographic area and have relatively short lives, they can be used as bioindicators that may signal ecosystem responses to changes, such as varying atmospheric deposition rates of Hg, alterations of food webs due to the introduction of invasive species, and changes in methylation and demethylation rates in response to land use changes that water sampling and higher trophic organisms cannot measure without intense sampling and costs. Finally, this research provides more information about total Hg and MeHg in aquatic food webs for both lake and tributary systems. As a result, an increased understanding of recent Hg levels in the Finger Lakes region and across multiple trophic levels was achieved.

# 2 Finger Lakes Mercury Study—Lakes

The Finger Lakes are a series of eleven elongated glacially formed freshwater lakes in the Lake Ontario Basin located in western and central New York State. With the exception of one lake (Honeoye Lake, 9 meters [m] maximum depth), the median maximum depth of the remaining 10 lakes is 55 m (ranging from 18 to 198 m). Five Finger Lakes were selected for this study, namely, from west to east, Honeoye, Canandaigua, Seneca, Cayuga, and Owasco (Figure 1). These lakes were selected based on their varying limnology and morphometry including differences in nutrient status, volume, surface area, and retention time (Table 1). The land use in the region is dominated by agriculture and forest lands (Figure 1).





#### Table 1. Physical Characteristics and Sample Sites of Study

Finger Lake	Lake Code	Sample Site Latitude / Longitude <sup>a</sup>	Mean; Max (Sampled) Depth (m) <sup>b</sup>	Surface Area (km2) <sup>b</sup>	Watershed Area (km2) <sup>b</sup>	Lake Trophic Status <sup>c</sup>
Honeoye	HN	42° 44.32 N / 77° 30.72 W	4.9; 9.2 (7)	7.1	95	Eutrophic
Canandaigua	CN	42° 49.27 N / 77° 16.58 W	38.8; 83.5 (78)	42.3	477	Oligotrophic
Seneca	SN	42° 46.28 N / 76° 57.00 W	88.6; 198.4 (116)	175.4	1181	Mesotrophic
Cayuga	CY	42° 37.92 N / 76° 40.33 W	54.5; 132.6 (110)	172.1	1145	Mesotrophic
Owasco	OW	42° 49.15 N / 76° 30.45 W	29.3; 54 (51)	26.7	470	Mesotrophic

Finger Lakes are listed from west to east.

<sup>a</sup> Location for sample collection other than fish

<sup>b</sup> Callinan 2001

° Halfman 2017

#### 2.1 Field Methods

The five Finger Lakes chosen as part of this study were sampled every month for water, plankton, benthic invertebrates, and fish from May through September 2015. Since 2006, these lakes have been the focus of monthly water chemistry sampling from May to September (Halfman 2017).

#### 2.1.1 Plankton, Invertebrate, Water Chemistry Collection, and Processing

Bulk zooplankton were sampled monthly by vertical tow (metal-free net, 153 micrometer [ $\mu$ m] mesh size) through a water column from 2 to 3 meters above the sediment. Low-level Hg sampling and processing protocols (Back et al. 2003) were followed to prevent sample contamination. Upon return to the laboratory, zooplankton were filtered immediately onto ashed glass fiber filters (0.7  $\mu$ m pore size) using Teflon equipment. Three separate samples were filtered for weight determination (Gorski et al. 2003).

Benthic invertebrates were also sampled monthly at the same location as were the zooplankton sampling, which took place using a Ponar dredge. Three dredges were taken at each location to try to ensure sufficient benthos were collected. Most of the biomass was comprised of amphipods and quagga mussels, but not all benthic organisms were present in all studied lakes. Back at the laboratory, amphipods were rinsed with lake water, placed in Teflon jars, and frozen at <sup>-</sup>20°C until analysis. Quagga mussels were measured for length and weight, and soft tissue was extracted from shells prior to storing in Teflon jars. Methylmercury measurements were conducted on composite benthic samples from each lake each month.

For water quality, grab water samples from each lake were collected monthly and the secchi disk depth was recorded. Epilimnetic water was collected at a depth of about 0.5 m using a plastic bucket while hypolimnetic water was collected about 1 m above the sediment using a Go-Flo bottle. Subsamples of these waters were analyzed on the boat for temperature, pH, and conductivity via handheld probes and for dissolved oxygen and alkalinity via titration (Halfman 2017). Subsamples of both depths were further processed in the laboratory as follows: unfiltered water was saved for total phosphorus, while samples for dissolved nutrients including soluble reactive phosphorus, silicate, and nitrate were filtered through 0.45 µm nitrocellulose filters. Samples for chlorophyll-a and total suspended solids were filtered onto 0.7 µm glass fiber filters and frozen until analysis.

#### 2.1.2 Fish Collection and Processing for Mercury

Fish samples were collected monthly between May and September 2015. A range of lengths for three predatory species (Largemouth Bass, Lake Trout, and Walleye), and three prey species (Brown Bullhead, Golden Shiner, and Yellow Perch) were collected. Fish were sampled by boat electrofishing, angling, and gill netting by the New York State Department of Environmental Conservation and through dedicated efforts of anglers in New York State. All fish were measured for total length and weight and were placed on ice in the field. In the lab, a dorsal muscle plug was sampled and weighed for wet weight, freeze dried, and then weighed again to determine percent moisture.

#### 2.2 Laboratory Methods

#### 2.2.1 Total Mercury Analysis

Total Hg (THg) analyses were conducted on all fish, assuming 95-100% of Hg is present as MeHg (Bloom 1992). Most fish were analyzed in triplicate (range = 2.6-16.8% and average = 5.3% coefficient of variation [CV], n = 282). Total Hg analyses were conducted using atomic absorption spectrophotometry (Milestone DMA-80). A minimum of a four-point standard curve was run every day of analysis, and blanks were analyzed every five samples. Standards and certified reference materials were analyzed every ten samples. For quality assurance/quality control (QA/QC), the recovery of TORT-3 (lobster hepatopancreas, National Research Council of Canada) was 98.5% ( $288 \pm 2.2$ 

standard error [SE] ng/g dry weight (dw, n = 51) and DORM-3 (fish protein, National Research Council of Canada) was 102% ( $390 \pm 2.1$  SE ng/g dw, n = 100). Fish Hg concentrations were converted to wet weight (ww) for comparisons to risk thresholds using % moisture calculated for each individual fish after freeze-drying plug samples.

#### 2.2.2 Methylmercury Analysis

Methylmercury analyses were performed on zooplankton and benthic invertebrates using cold vapor atomic fluorescence spectrophotometry (Brooks Rand Model III). EPA Method 1630 (U.S. EPA 2001) was followed for sample digestion and QA/QC. When possible, 20 milligrams (mg) of freeze-dried tissue was digested using an alkaline digestion, which included 3 hours in 25% potassium hydroxide/methanol (KOH/MeOH) that was then diluted with pure methanol to a ratio of 0.39 of 25% KOH/MeOH to MeOH. Volumes were adjusted based on the amount of tissue available. When 5–10 mg of tissue was available, digestions were more concentrated. All statistical analyses were conducted on THg concentrations in wet weight for fish and MeHg concentrations in dry weight for zooplankton and benthic invertebrates. Quality assurance/quality control included running a five point curve of MeHg (0.5–250 picograms [pg] methylmercury hydroxide [MeHgOH]) for every new run, analyzing a second source MeHg standard (methylmercuric chloride, MeHgCl) and blanks every ten samples (criteria for acceptance < 0.2 pg), and running two certified reference materials per digestion batch. Recoveries for certified reference materials were 107% (73–125%, n = 4) for NIST-2976 (mussel tissue, National Institute of Standards and Technology) and 92% (71–125%, n = 6).

#### 2.2.3 Water Chemistry Analysis

Water collected was analyzed by spectrophotometry following standard methods for total phosphorus (TP), soluble reactive phosphorus (SRP), dissolved silicate, nitrate, and chlorophyll-a, and measurements were made of total suspended solids (Wetzel and Likens 2000). Laboratory precision was assessed by replicate analyses (mean standard deviations: total suspended sediments  $\pm 0.2$  milligrams per liter [mg/L], phosphate  $\pm 0.1$  micrograms per liter [µg/L, both TP and SRP], silica  $\pm 5$  µg/L, and nitrate  $\pm 0.1$  mg/L; Halfman 2017). Dissolved organic carbon (DOC; mg/L, detection limit = 0.5 mg/L; 5% reproducibility on multiple injects/scans) and absorbance were measured on a Total Organic Carbon (TOC) analyzer (Shimadzu TOC-L, Kyoto, Japan) and spectrometer (Horiba Aqualog, New Jersey, USA), respectively. All lake water chemistry results are presented in Table 2.

#### Table 2. Water Chemistry Summary of Lakes Studied in the Finger Lakes Mercury Study

Water quality parameters include dissolved organic carbon (DOC, mg/L); Secchi depth (Secchi, m); temperature (Temp, °C); conductivity (Cond,  $\mu$ S/cm); pH; dissolved oxygen determined from titration (DO\_ti, mg/L); alkalinity (Alk, mg/L); total suspended solids (TSS, mg/L); total phosphorus (TP,  $\mu$ g/L); soluble reactive phosphorus (SRP,  $\mu$ g/L); nitrate (Nit, mg/L); silica ( $\mu$ g/L); and chlorophyll-a (Chla,  $\mu$ g/L); and \_s and\_b indicate measurements taken in the epilimnion and hypolimnion, respectively.

Date	ake Code	DOC	Secchi	Temp_s	Temp_b	Cond_s	Cond_b	pH_s	d_Hq	D0_ti_s	DO_ti_b	Alk_s	Alk_b	TSS_s	TSS_b	TP_s	TP_b	SRP_s	SRP_b	Nit_s	Nit_b	Silica_s	Silica_b	Chla_s	Chla_b
5-21-15	SC	2.01	4	9.3	5.3	713	738	8.2	8.1	10	10.6	108	116	1.6	0.3	17.6	13.6	0.2	1.3	0.0	0.1	312	347	1.4	0.4
5-22-15	CN	8.07	4	12.1	8.5	423	431	8.4	8.3	9.4	9.4	135	132	1.3	0.6	12.8	6.7	0.6	0.5	0.1	0.3	641	729	2.7	0.4
5-22-15	HN	8.64	3.5	17.8	17.7	277	276	8.2	8.2	6.8	6	100	100	1.2	1.2	19.0	21.9	0.6	0.6	0.0	0.0	548	566	3.8	3.2
5-26-15	CY	1.99	2.7	13.2	6.9	453	464	8.6	8.2	9.8	11	132	134	1.9	1.4	23.1	17.6	0.4	2.0	0.4	0.6	474	669	2.2	0.4
5-26-15	OW	2.16	4.2	13.4	8.3	346	361	8.4	8.23	10.6	9.4	162	164	1.3	4.0	21.5	10.3	0.2	0.8	1.1	2.1	1029	1210	2.7	0.5
6-18-15	SC	2.58	2.3	17.8	7.4	676	732	8.9	8.6	10.8	11.4	108	138	3.0	0.0	8.1	8.6	0.0	4.9	0.0	0.0	93	367	5.4	0.3
6-19-15	CN	2.50	1.9	20	6.1	408	444	8.6	8.4	8.1	9.9	124	136	3.6	1.5	7.2	4.6	0.2	0.8	0.1	0.2	765	911	1.1	0.4
6-19-15	HN	3.59	0.99	21.9	21.7	268	269	8.4	8.4	7.6	7.2	88	88	7.3	7.4	16.5	13.3	1.0	0.2	0.0	0.0	539	576	4.7	2.2
6-23-15	OW	2.04	3.4	20.4	8.5	348	365	8.3	8.1	8.8	11	136	150	1.6	2.4	12.8	9.6	0.1	0.2	0.2	0.9	863	1181	5.4	0.3
6-24-15	CY	2.09	2.3	18.6	6.7	445	472	8.7	8.1	10.2	11	120	120	2.7	1.6	21.5	15.9	0.2	4.0	0.9	0.6	498	659	3.8	0.5
7-21-15	OW	2.07	4	23.1	8.7	335	368	8.3	8	6.4	7.8	160	168	1.5	4.3	16.1	7.3	2.0	2.0	1.6	0.3	576	1261	0.2	1.0
7-22-15	CY	2.20	2.9	21.7	6.7	444	484	8.5	8.2	9.2	11.5	147	124	3.1	2.1	14.6	10.3	0.2	8.2	0.7	1.1	91	632	7.8	0.5
7-23-15	SC	2.38	2.1	20.6	8.2	670	738	8.7	8.3	9	11.2	114	112	2.4	0.6	20.1	19.6	0.8	2.9	0.2	1.0	77	380	6.0	0.2
7-24-15	CN	2.47	5.2	22.7	7.7	422	467	8.2	8.1	8.2	10.2	158	160	1.0	1.5	7.1	7.6	1.3	1.7	0.1	0.1	999	885	1.8	0.5
7-24-15	HN	3.54	1.5	24.7	24.3	277	279	8.9	8.8	9	7.8	85	95	5.3	4.5	27.1	37.8	1.7	1.7	0.0	0.0	889	914	20.5	16.4
8-18-15	ow	2.45	3.3	26.7	8	351	414	7.5	7.2	8.3	7.4	160	162	2.7	2.2	10.9	7.8	0.4	1.4	0.2	0.1	265	1443	4.8	0.7
8-19-15	CY	2.25	2	23.1	7.3	475	555	7.8	7.6	9	10.4	150	122	1.8	1.0	8.7	11.5	0.7	5.7	0.4	1.4	251	791	7.9	0.6
8-20-15	SC	1.32	2.3	23.8	7.4	736	840	8.5	7.4	8.4	11.8	133	108	3.5	0.6	16.3	10.1	0.4	6.0	0.0	0.9	144	429	8.1	0.3

#### Table 2 continued

Date	Lake Code	DOC	Secchi	Temp_s	Temp_b	Cond_s	Cond_b	pH_s	q⁻Hq	DO_ti_s	DO_ti_b	AIK_s	Alk_b	TSS_s	d_SST	TP_s	d_TP_b	SRP_s	SRP_b	Nit_s	Nit_b	Silica_s	Silica_b	Chla_s	Chla_b
8-21-15	CN	2.82	6.7	23.3	6.8	459	516	8	7.4	8.1	10	146	160	1.2	1.2	6.4	3.6	0.0	0.4	0.1	0.1	646	1118	3.0	0.7
8-21-15	HN	4.05	0.8	25	24.6	304	310	9	8.5	8.5	7.3	87	98	9.6	4.9	42.7	38.9	3.2	3.2	0.0	0.0	864	969	42.9	22.6
9-28-15	CY	2.13	4.2	20.5	7.3	450	507	8.6	8	9.4	9.8	76	64	2.5	4.7	16.2	25.9	0.0	13.6	0.2	0.1	178	1370	4.6	0.5
9-29-15	OW	2.39	3.5	20.1	7.9	337	394	8.2	8.1	6.6	8	156	168	1.2	1.1	14.4	11.4	0.3	0.0	0.7	0.1	779	2412	5.1	0.5
9-30-15	HN	4.37	0.95	18.3	18	273	276	9.4	9.4	8.8	7.4	88	88	8.1	10.9	46.8	52.0	0.5	0.3	0.0	0.0	63	81	24.4	24.6
10-1-15	SC	2.50	5	17.4	6.8	594	641	8.7	8.4	8.4	11.4	134	130	2.3	0.4	10.3	8.3	0.0	4.7	0.2	0.4	145	670	4.2	0.2
10-2-15	CN	2.79	3.6	16.1	5.9	361	392	9.1	8.3	9.8	9.8	150	172	1.5	1.3	9.6	7.8	0.2	0.0	0.0	0.2	987	1656	3.9	0.5

#### 2.2.4 Data Analysis

For the lake portion of this study, THg concentrations were size-adjusted when there was a significant lake-species THg-total length regression. An analysis of variance (ANOVA) was used to compare size-adjusted THg concentrations within species among lakes, followed by a Tukey-Kramer test to assess which groups were significantly different. Results are presented as boxplots and statistically significant differences among groups are indicated by differing letters above the THg and MeHg concentrations. ANOVAs were also performed to test for differences among lakes in zooplankton and benthos MeHg concentrations. Significance level was set at 0.05 for all tests.

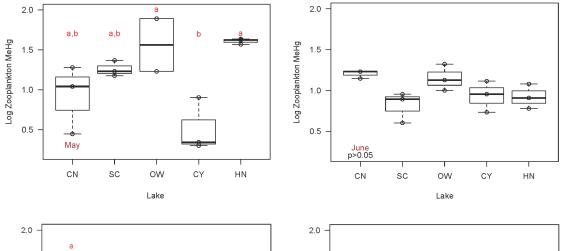
#### 2.3 Results and Discussion

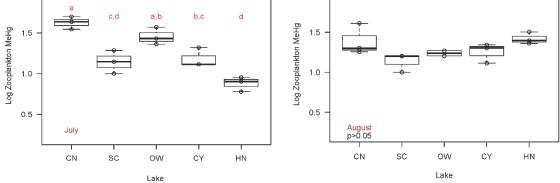
#### 2.3.1 Zooplankton and Invertebrate Mercury Concentrations

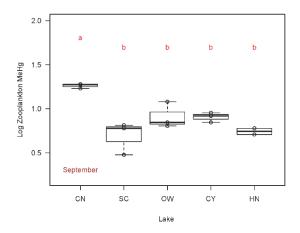
Consistently low MeHg concentrations were found in bulk zooplankton collected from May through September 2015 across the Finger Lakes (Figure 2). While individual months showed statistically significant differences, zooplankton from a single lake did not consistently exhibit higher MeHg concentrations in comparison to other lakes in the study. Compared to other studies, the range of MeHg concentration for bulk zooplankton collected with the 153  $\mu$ m net (2–78 ng/g dw) from the Finger Lakes was lower than reported for similarly sized bulk zooplankton from Lake Champlain (202  $\mu$ m net, 3–99 ng/g dw; Chen et al. 2012), but higher than similarly sized bulk zooplankton from the St. Lawrence River (150  $\mu$ m net, –12 ng/g dw; Ridal et al. 2010). The relatively lower MeHg concentrations in the Finger Lakes may be due to high zooplankton densities, but this was not assessed in the present study.

# Figure 2. Monthly MeHg Concentrations (ng/g dw) in Finger Lakes Zooplankton by Lake from May to September 2015

Lakes are presented left to right in order of increasing trophic status as indicated by chlorophyll-a concentrations (lake codes are presented in Table 1). Different letters denote statistically significant differences in zooplankton MeHg concentrations between lakes. Even though significant differences exist, there is no consistent pattern of MeHg in zooplankton among lakes over the season. No statistically significant differences in zooplankton MeHg concentrations among lakes were observed in June and August.



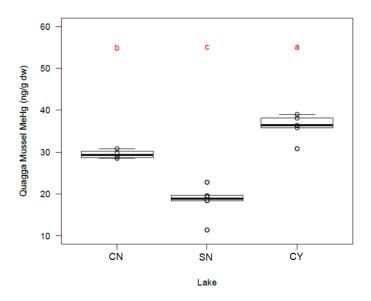




For benthic invertebrates (Figures 3 and 4), MeHg concentrations  $(48 \pm 3 \text{ ng/g dw})$  were significantly higher compared to zooplankton  $(20 \pm 4 \text{ ng/g dw})$ . Of the lakes with sufficient benthic invertebrate biomass for analysis, amphipods from Cayuga and Owasco Lakes were significantly higher in MeHg concentrations compared to Canandaigua and Seneca Lakes. For quagga mussels, Cayuga Lake invertebrates had the highest MeHg concentrations when compared to Canandaigua and Seneca Lakes. In general, MeHg concentrations measured in quagga mussels were higher in the Finger Lakes  $(29 \pm 8 \text{ ng/g dw})$  than offshore  $(12 \pm 3 \text{ ng/g dw})$  or nearshore  $(17 \pm 4 \text{ ng/g dw})$  quagga mussels reported for Lake Michigan (Lepak et al. 2015). This suggests that Finger Lakes food webs that are more closely tied to benthic energy pathways will lead to higher MeHg transfer.

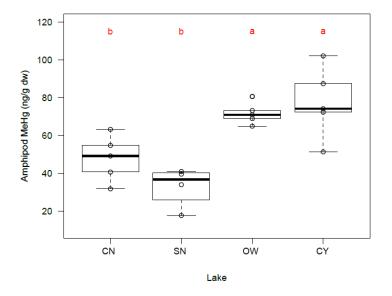
# Figure 3. Methylmercury Concentrations (ng/g dw) in Finger Lakes Quagga Mussels by Lake from May to September 2015

Lakes are presented left to right in order of increasing trophic status as indicated by chlorophyll-a concentrations (lake codes are presented in Table 1). Different letters denote statistically significant differences in quagga mussel MeHg concentrations between lakes from May to September 2015.



# Figure 4. Methylmercury Concentrations (ng/g dw) in Finger Lakes Amphipods by Lake from May to September 2015

Lakes are presented left to right in order of increasing trophic status as indicated by chlorophyll-a concentrations (lake codes are presented in Table 1). Different letters denote statistically significant differences in amphipod MeHg concentrations between lakes from May to September 2015.



#### 2.3.2 Fish Mercury Concentrations

Total Hg concentrations in fish showed high variation for most species sampled across the Finger Lakes (Table 3). However, factors previously shown to be important explanatory variables of fish Hg concentrations, such as length, age, and species (Eagles-Smith et al. 2018) were all significant predictors for Finger Lakes fish Hg concentrations. Concentrations varied six-fold for Lake Trout and up to 20-fold for Brown Bullhead. Variations in THg concentrations for Largemouth Bass were in part due to the variation in fish sizes collected (i.e., smaller individuals).

 Table 3. Summary Statistics of Total Mercury Concentrations in Fish Species Collected in

 the Finger Lakes

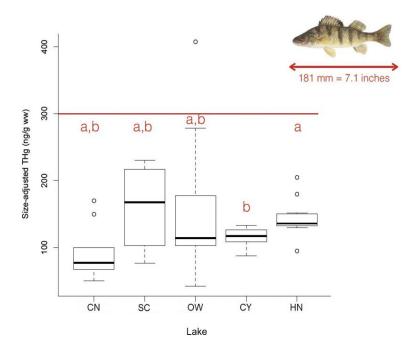
Species (Species Code)	Lake	Sample size	Total length (mm) Min–Max	Arithmetic Mean	THg (ng/g ww) Min–Max	Arithmetic Mean
Lake Trout	Honeoye	-				
(LT)	Canandaigua	8	374–476	416 ± 30	187–305	247 ± 47
	Seneca	17	281–740	559 ± 144	208–703	342 ± 128
	Cayuga	10	350–652	574 ± 96	110–300	217 ± 61
	Owasco	9	558–686	638 ± 39	371–686	517 ± 97
Largemouth Bass	Honeoye	12	110–420	278 ± 98	161–535	302 ± 135
(LB)	Canandaigua	11	241–431	362 ± 54	173–810	464 ± 205
	Seneca	10	180–429	320 ± 82	56–601	297 ± 183
	Cayuga	14	50–430	208 ± 146	21–881	201 ± 270
	Owasco	9	78–115	96 ± 12	26–95	51 ± 20
Walleye	Honeoye	10	475–606	537 ± 47	498–824	630 ± 112
(WA)	Owasco	10	464–617	569 ± 46	1212–1905	1529 ± 250
Yellow Perch	Honeoye	11	70–287	175 ± 75	84–256	141 ± 46
(YP)	Canandaigua	10	104–262	180 ± 62	33–194	90 ± 49
	Seneca	5	151–307	248 ± 63	51–330	159 ± 127
	Cayuga	11	95–236	134 ± 40	31–178	72 ± 39
	Owasco	12	88–252	207 ± 54	26–335	168 ± 91
Brown Bullhead	Honeoye	10	330–426	391 ± 38	31–74	52 ± 15
(BH)	Canandaigua	10	245–361	278 ± 32	42–260	85 ± 65
	Seneca	14	191–365	308 ± 41	70–352	221 ± 98
	Cayuga	12	175–270	227 ± 33	17–80	38 ± 19
	Owasco	10	291–353	322 ± 20	112–220	164 ± 36
Golden Shiner	Honeoye	10	72–227	154 ± 50	45–98	75 ± 16
(GS)	Canandaigua	9	63–204	139 ± 51	36–125	72 ± 31
	Seneca	4	66–194	150 ± 58	17–68	48 ± 23
	Cayuga	10	130–207	182 ± 26	22–83	41 ± 19
	Owasco	10	75–123	95 ± 14	11–32	25 ± 6

Across the lakes sampled, all species except for Golden Shiner had individuals that exceeded the EPA criterion of 300 ng/g ww, which represented approximately 24% (85/360 individuals) of all fish sampled (Table 3). The proportion of fish that exceeded the 300 ng/g ww consumption guideline by species were as follows: 9% for Brown Bullhead (6/66 individuals), 5% for Yellow Perch (3/64 individuals), 36% for Largemouth Bass (20/56 individuals), 36% for Lake Trout (36/100 individuals), and 83% for Walleye (20/24 individuals). All of the Owasco Lake Walleye sampled exceeded the United States Food and Drug Administration (FDA) action level of 1,000 ng/g ww (10/10 individuals); no other species was found to exceed the FDA standard.

Significant differences in THg concentrations were found for all fish species among lakes except Largemouth Bass. For Yellow Perch, significant differences in THg concentrations were found between Cayuga and Honeoye Lakes (Figure 5). For Brown Bullhead, Owasco, Seneca, and Canandaigua Lakes have significantly higher concentrations of THg compared to Cayuga Lake and Honeoye Lake (Figure 6). Seneca Lake has significantly higher concentrations of THg in Brown Bullhead compared to Canandaigua Lake. The lack of differences in THg concentrations in Largemouth Bass among lakes is apparent (Figure 7) and sampled fish THg concentrations often exceeded 300 ng/g. For Lake Trout, Canandaigua Lake and Cayuga Lake have significantly lower concentrations of THg compared to Seneca Lake and Owasco Lake (Figure 8). For Finger Lakes with Walleye, Owasco Lake has significantly higher concentrations of THg in Walleye compared to Honeoye Lake (Figure 9).

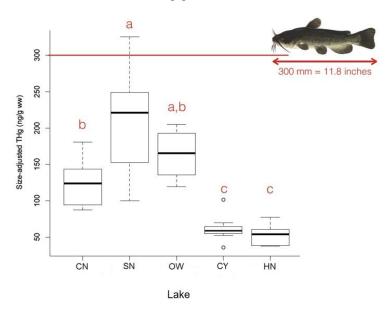
#### Figure 5. Size-Adjusted Yellow Perch THg Concentrations (ng/g ww) by Lake

Lakes are presented left to right in order of increasing trophic status as indicated by chlorophylla concentrations (lake codes are presented in Table 1). Different letters denote statistically significant differences in size-adjusted Yellow Perch THg concentrations between lakes. The EPA criterion of 300 ng/g ww is shown.



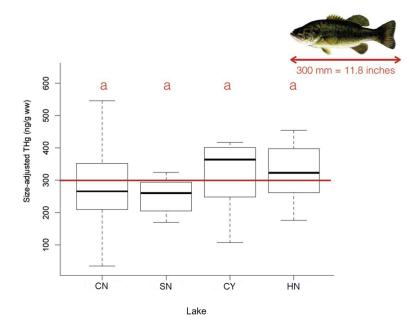
#### Figure 6. Size-Adjusted Brown Bullhead THg Concentrations (ng/g ww) by Lake

Lakes are presented left to right in order of increasing trophic status as indicated by chlorophylla concentrations (lake codes are presented in Table 1). Different letters denote statistically significant differences in size-adjusted Brown Bullhead THg concentrations between lakes. The EPA criterion of 300 ng/g ww is shown.



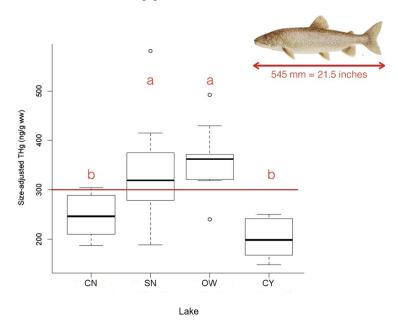
#### Figure 7. Size-Adjusted Largemouth Bass THg Concentrations (ng/g ww) by Lake

Lakes are presented left to right in order of increasing trophic status as indicated by chlorophylla concentrations (lake codes are presented in Table 1). Different letters denote statistically significant differences in size-adjusted Largemouth Bass THg concentrations between lakes. The EPA criterion of 300 ng/g ww is shown.



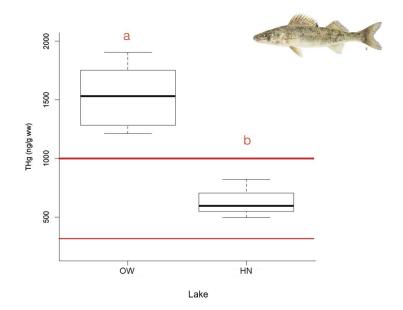
#### Figure 8. Size-Adjusted Lake Trout THg Concentrations (ng/g ww) by Lake

Lakes are presented left to right in order of increasing trophic status as indicated by chlorophylla concentrations (lake codes are presented in Table 1). Different letters denote statistically significant differences in size-adjusted Lake Trout THg concentrations between lakes. The EPA criterion of 300 ng/g ww is shown.



#### Figure 9. Size-Adjusted Walleye THg Concentrations (ng/g ww) by Lake

Lakes are presented left to right in order of increasing trophic status as indicated by chlorophylla concentrations (lake codes are presented in Table 1). Different letters denote statistically significant differences in size-adjusted Walleye THg concentrations between lakes. The EPA criterion of 300 ng/g ww and FDA action level of 1,000 ng/g ww are shown.



Based on otolith analysis, Walleye were significantly older in Owasco Lake (average age ~16 years) compared to Honeoye Lake (average age ~12 years). Lake Trout were also significantly older in Owasco Lake (average age ~13 years) compared to Cayuga and Canandaigua Lake (average age ~8 and 5 years, respectively), but not significantly different from Seneca Lake (average age ~11 years).

No water chemistry (Table 2) or lake morphology variables predicted fish Hg concentrations despite the Finger Lakes representing a range of trophic statuses from oligotrophic to eutrophic. Similarly, no water chemistry variables predicted zooplankton MeHg concentrations. This is surprising due to differences in primary productivity among the sampled lakes. This may result from the narrow ranges for several of the commonly reported explanatory water chemistry variables. For example, the pH range in the Finger Lakes measured during this study (7.4 to 9.4) was in the neutral to alkaline range, whereas relationships previously observed between fish Hg concentrations and pH have included acidic lakes in regional studies, such as those found in the Adirondacks (Driscoll et al. 1994; Yu et al. 2011), or in broader geographical surveys such as previous surveys in New York State (Simonin et al. 2008) and across northeastern North America (Kamman et al. 2005).

Chlorophyll-a, a proxy for lake trophic status, which is another commonly found predictor of fish Hg concentrations in lakes (Chen and Folt 2005; Razavi et al. 2015), was not a significant predictor. This may be due to sample sizes not being sufficiently large for the study. A previous survey of New York State lakes found chlorophyll-a to be a significant predictor of Largemouth Bass Hg concentrations (Simonin et al. 2008). Dissolved organic carbon and specific ultraviolet absorbance (SUVA) were also not predictors, but the range in DOC and SUVA across the Finger Lakes was very narrow (1.29 to 4.37 mg/L and 1.18 to 3.09 mg/L, respectively) compared to other studies where DOC could be used as a predictor (e.g., DOC range 2–20 mg/L in Adirondack Lakes in Driscoll et al. 1995; 2–23 mg/L in tundra lakes in French et al. 2014).

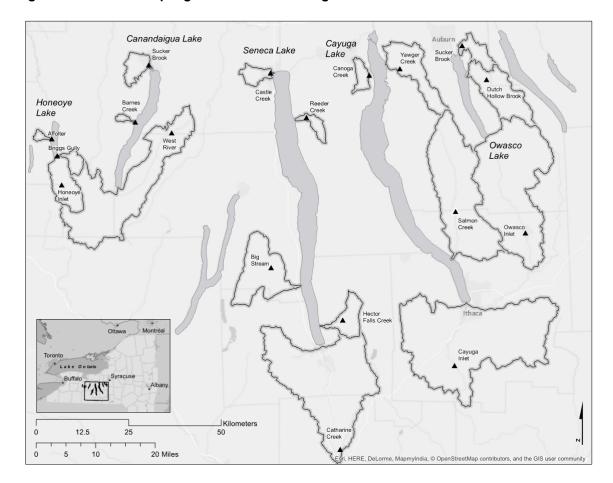
#### 2.4 Conclusions

For the lakes portion of this study, variables previously shown to be important explanatory variables of fish Hg concentrations, such as length, age, and species (Eagles-Smith et al. 2018), were all significant predictors for Finger Lakes fish Hg concentrations. Significant differences in Hg concentrations among lakes were species specific. For instance, age explained why Hg concentrations were higher in Walleye from Owasco Lake compared to Honeoye Lake. However, differences in age did not explain differences in Hg concentrations between Lake Trout from Cayuga Lake and Seneca Lake. One hypothesis is that differences in prey availability between Cayuga and Seneca Lakes may explain differences in Hg concentrations. Specifically, the Round Goby (Neogobius melanostomus) has invaded Cayuga Lake and become a dominant prey of the Lake Trout (NYSDEC, pers. comm.); Round Goby have not yet invaded Seneca Lake. The presence of Round Goby in the diets of sportfish can result in greater (Crane and Einhouse 2016) or decreased growth efficiency (Lantry et al. 2019). Based on what was observed during this study, one can hypothesize that the growth efficiency of Cayuga Lake Trout is greater than that of uninvaded Finger Lakes, thus resulting in lower Hg concentrations due to growth dilution (Karimi et al. 2007; Lepak et al. 2012). No difference in Hg concentrations was observed for Largemouth Bass, suggesting that this species exploits different prey resources that can compensate for differences in growth due to the presence of Round Goby in Cayuga Lake. Forage species such as Yellow Perch and Golden Shiner showed highly variable THg concentrations and no clear high-to-low pattern exists among the lakes, suggesting that Hg bioavailability is lake specific.

Lastly, lower trophic level MeHg concentrations were also not found to be significant predictors of Hg concentrations in Finger Lakes fish. Zooplankton MeHg concentrations did not vary significantly among Finger Lakes sampled monthly. A recent meta-analysis found seston, as opposed to zooplankton MeHg concentrations, were a significant predictor of fish Hg concentrations (Wu et al. 2019). Trends in benthic invertebrate Hg concentrations were opposite those of fish Hg concentrations. For example, Lake Trout Hg concentrations were significantly higher in Seneca Lake compared to Cayuga Lake, whereas the opposite trend was observed in the mussels and amphipods. Thus, this study suggests that the fish food web structure and fish growth rates are driving differences in Hg concentrations, as opposed to lower trophic level Hg uptake. Ultimately, future work to understand sportfish Hg uptake among the Finger Lakes should include assessments of diet and fish growth rates to assess how growth efficiency affects Hg bioaccumulation among lakes.

## 3 Finger Lakes Mercury Study—Streams

To date, no stream biota Hg studies have been conducted in the Finger Lakes region. Given the importance of Finger Lakes streams to fish biodiversity (Carlson et al. 2016) and recreational fishing, this study fills a gap in knowledge. The objectives of the streams' component of the Finger Lakes Mercury Study were to (1) quantify Hg concentrations at several trophic levels of Finger Lakes stream food webs, (2) assess water chemistry, land cover, and lower food web MeHg as predictors of biota Hg concentrations, and (3) determine whether Finger Lakes stream fish Hg concentrations are of concern to wildlife. Three tributaries including the inlets from each of the five lakes sampled for the lake component of the Finger Lakes Mercury Study (Figure 10) were selected based on land cover characteristics with a range of types prioritized for sampling. Further information about the land cover information for the study can be found in Razavi et al. 2019a.





While the Finger Lakes tributaries support large trout, both native (Lake Trout; Salvelinus namaycush) and non-native (Rainbow and Brown Trout; Oncorhynchus mykiss and Salmo trutta), the smaller tributaries are home to other fish species, primarily minnows (Cyprinidae), suckers (Catostomidae), and darters (Percidae). Two minnow species, the Blacknose Dace (BND; Rhinichthys atratulus) and Creek Chub (CKB; Semotilus atromaculatus), were targeted for collection during this study. These fishes are ideal for comparing mercury availability across sub-watersheds because of their broad distribution across New York State and their previous use in stream Hg bioaccumulation studies (Riva-Murray et al. 2011; Burns and Riva-Murray 2018).

This study also focused on macroinvertebrates, which are important food sources for fish and higher trophic levels. Different macroinvertebrates were classified into functional feeding groups (FFG), which are based on how macroinvertebrates obtain food rather than taxonomy. This classification lends itself for comparing MeHg concentrations across various habitats and streams of the Finger Lakes region since MeHg is obtained primarily through food consumption.

#### 3.1 Study Methods

Streams were sampled between June and July 2015 (Table 4). Four streams were resampled between September and October 2015 because insufficient biota was collected the first time. Resampled streams include Affolter Creek (Hn2-F), Brigg's Gully (Hn3-F), Catharine's Creek (Sc4-F) and Dutch Hollow (Ow3-F). Barnes Gully (Cn3) was sampled twice but insufficient biota biomass was collected both times.

#### Table 4. Mean Methylmercury Concentrations (ng/g dw) in Macroinvertebrates Collected from Finger Lakes Streams

Sample sizes indicated in parentheses if greater than n=1. Note for Cambaridae this indicates individual crayfish, whereas others are combined samples.

Stream name	Stream	Periphyton	Colle	ectors	Scrapers	Shre	dders	Predators			
	Code		Gatherers	Filterers	Heptageniidae	Gammaridae	Tipulidae	Cambaridae	Perlidae		
			Elmidae	Hydro- psychidae							
Honeoye Lake											
Honeoye Inlet	Hn1	17.5	-	62.1	56.1	-	86.1 (2)	62.1	167.1		
Affolter Creek	Hn2	-	-	49.1	-	-	2.9	82.8	30.1		
Briggs Gully	Hn3	3.0	-		40.0	-	-	-	84.3		
	Hn2-F	2.7	-	11.3	-	-	0.9 (2)		-		
	Hn3-F	1.6	-	-	-	-	-	-			
Canandaigua Lake											
Sucker Brook	Cn1	5.3	18.3	-	40.7	52.3	17.0 (2)	45.2 ± 11.5 (5)	-		
Barnes Creek	Cn2	-	-	-	22.4	-	41.4 (2)		-		
West River (Inlet)	Cn3	2.2	24.6	82.3	-	-		60 ± 7.6 (3)	-		
Seneca Lake											
Castle Creek	Sc1	16.8	-	53.7	-	64.6	14.1 ± 1.2 (5)	50.7 ± 7.4 (6)	-		
Reeder Creek	Sc2	5.7	20.7	121.0	-		27.5	51.8 ± 35.4 (3)	161.6		
Big Stream	Sc3	2.8	12.5	34.6	37.2	-	31.0	65.3 ± 27.7 (4)	74.8 ± 48.3 (3)		
Catherine's Creek	Sc4	-	18.1	-	37.7	-	43.0 (2)	-	-		
Hector Falls	Sc5	3.6	14.4	77.7	39.7	-	-	48.3 ± 12.1 (3)	126.9 (2)		
	Sc5-F	4.2	85.3	-	-	160.2	-	112.5 ± 67.9 (3)	232.7 (2)		
Cayuga Lake											
Yawger Creek	Cy1	1.5	-	-	-	-	-	148.4 ± 114.6 (3)	-		
Canoga Creek	Cy2	40.5	52.3	-	130.2	193.3	74.4 (2)	-	-		
Cayuga Inlet	Cy3	2.3	-	55.3	36.0		55.8 ± 26.3 (4)	69.9 (2)	48.3 ± 32.1 (3)		
Owasco Lake											
Sucker Brook Creek	Ow1	3.6	21.8	82.8	42.7	110.3	30.9 ± 6.2 (5)	87.4 ± 16.5 (3)	114.6		
Dutch Hollow Creek	Ow2	2.3	18.4	-	42.7	18.0	-	75.8 ± 28.5 (5)	103.1		
Owasco Inlet	Ow3	19.1	17.5	60.8	61.9	8.9	42.9 (2)	134.0 ± 89.7 (5)	73.8		
	Ow2-F	4.0	-	55.0	66.8	140.1	31.1	56.1 ± 19.3 (4)	-		

For sampling, stream reaches of  $\sim$ 50 m were sampled for water chemistry, periphyton,

macroinvertebrates, and fish. Periphyton was scraped off rocks into Ziplock bags. Macroinvertebrates were collected using hand-held aquatic D-nets ( $12 \times 10$  centimeter (cm) opening,  $1200 \mu m$  netting; Wildco, Yulee, Florida, USA) and efforts were made to sample in a variety of habitats including riffles and submerged roots of the stream reaches. Macroinvertebrates were identified to family level (Voshell 2014) and included representatives from six FFGs, namely Scrapers, Shredders, Collector-Gatherers, Collector-Filterers, Omnivores, and Predators. More specific information regarding specific taxonomic representatives can be found in Table 4. At each stream, in situ pH, conductivity, dissolved oxygen and temperature were assessed using a YSI 556 Multiprobe system. Grab samples were also collected for unfiltered and dissolved nutrients, total suspended solids, and DOC to be analyzed in the laboratory.

Stream fish were sampled by electrofishing (Smith-Root LR 20B backpack electrofisher, Vancouver, Washington, USA). Targeted species included Blacknose Dace (species code BND) and Creek Chub (species code CKB). Fish were euthanized immediately upon capture in buffered MS-222 (500 mg/L, Western Chemical) to standards established by the institutional animal care and use committee at Hobart and William Smith Colleges. Fish were measured for total length to the nearest mm and weighed to the nearest 0.1 g in the field, stored in labeled plastic bags with site water, and kept cool until they were further processed in the lab. Whole fish were stored separately in bags after being rinsed in ultra-pure water. For fish larger than 100 millimeters (mm), a skinless fillet was removed and stored separately for analysis because analysis of whole fish was not possible due to the associated excessively long freeze-drying times. All samples were stored at <sup>-20°</sup>C. Prior to Hg analyses, all stream biota samples were freeze dried for a minimum of 24 hours. Similar to the lake portion of this study, fish THg as well as periphyton and invertebrate MeHg concentrations were analyzed using methods as described previously in sections 2.2.1 and 2.2.2. Similarly, water chemistry analysis followed methods described in section 2.2.3.

Similar to the lake study, THg concentrations were size adjusted when there was a significant regression relationship between stream species THg and total length. Nonparametric tests (Wilcoxon signed ranked test) were conducted to assess stream fish differences in (1) total length and (2) size-adjusted THg concentrations between the two fish species. Nonparametric analyses (Kruskal-Wallis test) were conducted for multiple comparisons to assess macroinvertebrate differences in MeHg concentrations among the (1) functional feeding groups and (2) functional feeding groups and periphyton. In all multiple comparisons, a non-parametric Steel-Dwass test was conducted to assess which groups were significantly different. Significance level was set at 0.05 for all tests.

#### 3.2 Results and Discussion

A statistically significant difference between Blacknose Dace (BND) and Creek Chub (CKB) total length was found, with CKB having significantly longer total lengths (Figure 11). For this reason, THg concentrations were size adjusted to account for the difference in length between species. Significantly higher mean THg concentrations were found for BND compared to CKB (arithmetic means for all unadjusted fish were 229 ng/g dw versus 195 ng/g dw, respectively).

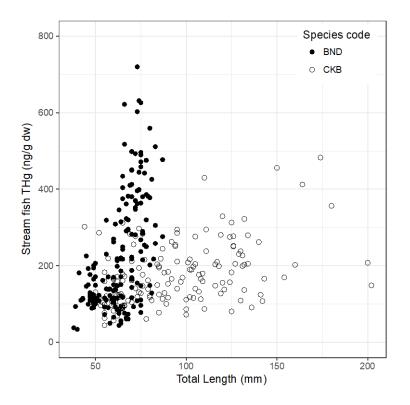


Figure 11. Stream Fish THg Concentrations (ng/g dw) versus Total Length for Blacknose Dace and Creek Chub

Across the watersheds and among streams, Hg concentrations in fish were not associated with water chemistry measurements (Razavi et al. 2019a). This is likely due to the relatively narrow range of values observed for parameters such as pH and DOC (1.6–8.9 mg/L) across the Finger Lakes watersheds compared to other ecosystems such as the Adirondacks (DOC range of 2.5–27.6 mg/L; Burns and Riva-Murray 2018). Further, it is important to remember that the water samples were collected as one-time grab samples while fish and other biota integrate water quality conditions over time. Future work should consider longer term water quality sampling to more fully describe the relationship between water quality parameters and Hg in fish and their biota in the Finger Lakes.

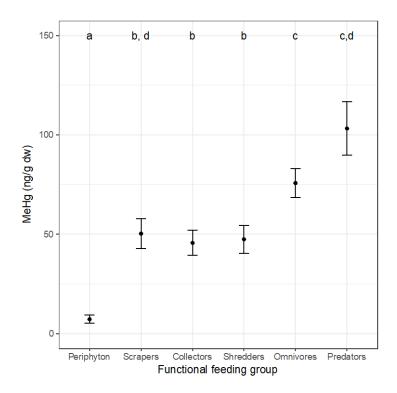
Based on the number of invertebrates collected at all sites (Table 4), macroinvertebrates were consolidated into different FFGs across all sites for statistical analysis to determine if MeHg concentrations varied among FFGs across the Finger Lakes region rather than by lake or watershed. Median macroinvertebrate MeHg concentrations ranged from 18 ng/g dw (range = 13–85) in collector-gatherers to 88 ng/g dw (range = 24–246) in predators (Table 4).

Within the fish species sampled in this study, invertivorous BND, which are known to consume diatoms, midges and aquatic insects (Ryan 2008), were found to be significantly higher in THg concentrations compared to CKB, which feed on invertebrates as well as small fish (Garman and Moring 1993). This trend of higher Hg concentrations in BND compared to CKB has also been observed in the Adirondack Mountains (Burns and Riva-Murray 2018). Both BND and CKB demonstrated a connection to the base of the food web as scrapers were highly correlated with periphyton in the Finger Lakes study (Razavi et al. 2019a). Stream fish indirect dependence on periphyton (i.e., autochthonous), rather than terrestrial (i.e., allochthonous) food sources may expose them to higher MeHg concentrations, as periphyton communities are known sites of Hg methylation (Cleckner et al. 1999; Hamelin et al. 2015).

Significant differences in MeHg concentrations among FFGs were found (Figure 12). Specifically, predators had significantly higher mean MeHg concentrations compared to collector-gatherers and shredders. Omnivores also had significantly higher mean MeHg concentrations compared to collector-gatherers, shredders, and scrapers. No significant differences were found among the other FFGs. Relative to periphyton, all FFGs were significantly higher in MeHg concentrations. Concentrations of MeHg in stream biota of the Finger Lakes increased from primary producers to consumers as has been demonstrated for streams elsewhere in New York State and the northeast (Chasar et al. 2009; Riva-Murray et al. 2011, 2013; Tsui et al. 2014). In general, increases in MeHg across trophic levels in stream food webs are expected (Ward et al. 2010). However, no difference between consumers of algae versus consumers of detritus (scrapers vs. shredders) were observed. Riva-Murray et al. (2011) found that scrapers in an Adirondack Mountain stream had twice the Hg concentrations compared to shredders. Others have also observed this higher uptake of Hg in consumers of periphyton compared to detritus (Tsui et al. 2009; Jardine et al. 2012). Additional studies using stable isotopes to determine the trophic position and feeding strategy of macroinvertebrate FFGs would provide greater clarification regarding the sources of Hg they represent (Riva-Murray et al., 2013; Tsui et al., 2014).

# Figure 12. Stream Macroinvertebrate MeHg Concentrations (ng/g dw) by Functional Feeding Group

Different letters denote statistically significant differences in stream macroinvertebrate MeHg concentrations between functional feeding groups.



Overall, omnivorous crayfish (Cambaridae) MeHg concentrations were higher (12–290 ng/g dw) on average than observed by Schmitt et al. (2011) in Ozark streams (30–70 ng/g dw) with a similar limestone geology to the Finger Lakes, while mean predatory Perlidae were lower in the Finger Lakes (104 ng/g dw) compared to eastern Canada (370 ng/g dw; Jardine et al., 2012). Except for the collector-gatherers, all other FFGs exceeded the European directive on Environmental Quality Standards for Hg of 100 ng/g dw (EC 2013). No FFG exceeded hazard concentrations of 400 ng/g dw recently proposed by Rodriguez et al. (2018).

For fish and the current risk threshold of 200 ng/g ww (Beckvar et al. 2005), no risk was found across sampled Finger Lakes streams for BND and CKB. One individual BND exceeded the limit for risk for low-sensitivity avian species of 180 ng/g ww, while the risk for highly sensitive avian species of 90 ng/g ww was exceeded in ~22% of the BND and ~5% of CKB, suggesting ecological risk for consumers especially of BND. Furthermore, lower thresholds to assess biological health include a benchmark of 30 ng/g ww for the Belted Kingfisher (Lazorchak et al. 2003), a threshold of

40 ng/g ww for dietary thresholds above which can result in lower reproduction in piscivorous fish (Depew et al. 2012), and a 70 ng/g ww level for mink (Lazorchak et al. 2003; Rolfhus et al. 2015). In stream fish collected from Grand Portage National Monument, 79% and 23% of stream fish exceeded the 30 ng/g and 70 ng/g ww thresholds (Rolfhus et al. 2015), compared to 71% and 23% of stream fish in the Finger Lakes. This indicates there is considerable risk to the most highly sensitive consumers of stream fishes in the Finger Lakes region. This also suggests that atmospheric point sources (i.e., coal fired power plants) in the Finger Lakes and regionally can have an equivalent impact to stream food webs affected by the historic fur trade, in addition to atmospheric sources, such as in the Grand Portage National Monument (Rolfhus et al. 2015). A variety of predators including the Belted Kingfisher, Barred Owl, Great Blue Heron, Mink, Northern Water Snake, as well as frogs (Ryan 2008) may be affected by Hg concentrations found in Finger Lakes stream fish and macroinvertebrates.

### 4 Conclusions

The completion of the Finger Lakes Mercury Study adds to the baseline understanding of Hg levels in fish and invertebrates in several large lakes and their tributaries in a region of New York State that has not been widely studied. Results showed that several Finger Lakes fish species exceeded the EPA MeHg human health criterion of 300 ng/g, including greater than 30% of sampled Lake Trout and Largemouth Bass as well as greater than 80% of sampled Walleye. No water chemistry or lake morphology variables predicted fish Hg concentrations in the Finger Lakes studied, despite sampling a range of trophic statuses from oligotrophic to eutrophic. Mercury concentrations in lower trophic level biota such as zooplankton, quagga mussels, and dreissenid mussels were also not associated with fish Hg concentrations across lakes. Thus, this study suggests that the fish food web structure and fish growth rates are driving differences in Hg concentrations, as opposed to lower trophic level Hg uptake. Ultimately, future work to understand sportfish Hg uptake among the Finger Lakes should include assessments of diet and fish growth rates to assess how growth efficiency affects Hg bioaccumulation among lakes.

The Finger Lakes region contains many important stream habitats for wildlife, yet little was previously known about the risk Hg poses to the watersheds. This study showed elevated THg concentrations in an abundant stream fish, Blacknose Dace (BND). High Hg concentrations in BND were best predicted by fish length ( $\geq 65$  mm) and total suspended solids (TSS), but other land cover and water chemistry parameters typically found to explain Hg concentrations in stream fish such as pH and DOC did not predict Hg concentrations. Significant differences in MeHg concentrations among invertebrate FFGs were found with higher trophic levels exhibiting higher MeHg concentrations. In general, the risk to stream fish is likely to be low, but Hg concentrations found in this study could cause impairment in sensitive consumers of stream fish and invertebrates.

Finally, this research provides more information about Hg in aquatic food webs for both lake and tributary systems. By comparing and contrasting stream to in-lake levels of Hg in biota across proximal lakes in the Finger Lakes and across NYS, there is now a comprehensive assessment of Hg concentrations in sportfish and lower trophic organisms that will be integral for understanding future changes in mercury concentrations in biota associated with other disturbances such as land use, nutrient supply, climate change and air pollution.

### 5 References

- Back, R.C., P.R. Gorski, L.B. Cleckner, J.P. Hurley. 2003. Mercury content and speciation in the plankton and benthos of Lake Superior. The Science of the Total Environment, 304: 349-54.
- Beckvar, N., T.M. Dillon, L.B. Read. 2005. Approaches for linking whole-body fish tissue residues of mercury or DDT to biological effects thresholds. Environmental Toxicology and Chemistry. 24:2094-2105.
- Bookman, R. C.T. Driscoll, D.R. Engstrom, S.W. Effler. 2008. Local to regional emission sources affecting mercury fluxes to New York lakes. Atmospheric Environment. 42: 6088-97.
- Bloom, N.S. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. Canadian Journal of Fisheries and Aquatic Sciences. 49:1010-1017.
- Burns, D.A., K. Riva-Murray. 2018. Variation in fish mercury concentrations in streams of the Adirondack region, New York: A simplified screening approach using chemical metrics. Ecological Indicators. 84:648–661.
- Callinan, C.W. 2001. Water Quality Study of the Finger Lakes, New York State Department of Environmental Conservation Division of Water.
- Carlson, D.M., Daniels, R.A., Wright, J.J. 2016. Atlas of Inland Fishes of New York. New York State Museum Record 7.
- Chasar, L.C., B.C. Scudder, A.R. Stewart, A.H. Bell, G.R. Aiken. 2009. Mercury cycling in stream ecosystems. 3. Trophic dynamics and methylmercury bioaccumulation. Environmental Science and Technology. 43: 2733–2739.
- Chen C.Y., C.L. Folt. 2005. High plankton densities reduce mercury biomagnification. Environ Science and Technology. 39:115–121.
- Chen, C., N. Kamman, J. Williams, D. Bugge, V. Taylor, B. Jackson, E. Miller. 2012. Spatial and temporal variation in mercury bioaccumulation by zooplankton in Lake Champlain (North America). Environmental Pollution. 161:343–349.
- Cleckner, L.B., C.G. Gilmour, J.P. Hurley, D.P. Krabbenhoft. 1999. Mercury methylation in periphyton of the Florida Everglades. Limnology and Oceanography. 44: 1815-1825.
- Crane D.P., D.W. Einhouse. 2016. Changes in growth and diet of smallmouth bass following invasion of Lake Erie by the round goby. Journal of Great Lakes Research. 42:405–412.
- Depew, D.C., N. Basu, N.M. Burgess, L.M. Campbell, E.W. Devlin, P.E. Drevnick, C.R. Hammerschmidt, C.A. Murphy, M.B. Sandheinrich, J.G. Wiener. 2012. Toxicity of dietary methylmercury to fish: derivation of ecologically meaningful threshold concentrations. Environmental Toxicology and Chemistry. 31:1536–1547.

- Driscoll, C.T., C. Yan, C.L. Schofield, R. Munson, J. Holsapple. 1994. The mercury cycle and fish in the Adirondack Lakes. Environmental Science and Technology. 28:136–143.
- Driscoll C.T., V. Blette, C. Yan, C.L. Schofield, R. Munson, J. Holsapple J. 1995. The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes. Water Air and Soil Pollution. 80:499–450.
- Evers, D.C., J.G. Wiener, C.T. Driscoll, D.A. Gay, N. Basu, B.A. Monson, K.F. Lambert, H.A. Morrison, J.T. Morgan, K.A. Williams, A.G. Soehl. 2011. Great Lakes Mercury Connections: The Extent and Effects of Mercury Pollution in the Great Lakes Region. Biodiversity Research Institute. Gorham, Maine. Report BRI 2011-18. 44 pp.
- French T.D., A.J. Houben, J-P.W. Desforges et al. 2014. Dissolved organic carbon thresholds affect mercury bioaccumulation in Arctic Lakes. Environmental Science and Technology. 48:3162–3168.
- Garman, G.C. and J.R. Moring. 1993. Diet and annual production of two boreal river fishes following clearcut logging. Environmental Biology of Fishes. 36:301-311.
- Gorski, P.R., L.B. Cleckner, J.P. Hurley, M.E. Sierszen, D.E. Armstrong. 2003. Factors affecting enhanced mercury bioaccumulation in inland lakes of Isle Royale National Park, USA. The Science of the Total Environment, 304: 327-48.
- Halfman J.D. 2017. Decade scale water quality variability in the eastern Finger Lakes, New York. Clear Waters.47:20-35.
- Hamelin, S., D. Planas, M. Amyot. 2015. Mercury methylation and demethylation by periphyton biofilms and their host in a fluvial wetland of the St. Lawrence River (QC, Canada). Science of the Total Environment. 512–513: 464–513.
- Hammerschmidt, C., W.F. Fitzgerald. 2006. Methylmercury in mosquitoes related to atmospheric mercury deposition and contamination. Environmental Science and Technology, 39: 3034-39.
- Jardine, T.D., K.A. Kidd, J.B. Rasmussen. 2012. Aquatic and terrestrial organic matter in the diet of stream consumers: implications for mercury bioaccumulation. Ecological Applications. 22, 843–855.
- Kamman, N.C., N.M. Burgess, C.T. Driscoll, H.A. Simonin, W. Goodale, J. Linehan, R. Estabrook, M. Hutcheson, A. Major, A.M. Scheuhammer, D.A. Scruton. 2005. Mercury in Freshwater Fish of Northeast North America – A Geographic Perspective Based on Fish Tissue Monitoring Databases. Ecotoxicology. 14:163-180.
- Karimi R., C.Y. Chen, P.C. Pickhardt, N.S. Fisher, C.L. Folt. 2007. Stoichiometric controls of mercury dilution by growth. Proceedings of the National Academy of Sciences of the United States of America. 104: 7477-7482.
- Lantry, B.F., S.L. Furgal, M.J. Connerton, D. Gorski. 2019. Lake Trout rehabilitation in Lake Ontario, 2018. YSDEC Lake Ontario Annual Report 2018.

- Lazorchak, J.M., F.H. McCormick, T.R. Henry, A.T. Herlihy. 2003. Contamination of fish in streams of the Mid-Atlantic Region: an approach to regional indicator selection and wildlife assessment. Environmental Toxicology and Chemistry. 22:545–553.
- Lepak J.M., K-D Kinzli, E.R. Fetherman, W.M. Pate, A.G. Hansen, E.I. Gardunio, C.N. Cathcart, W.L. Stacy, Z.E. Underwood, M.M. Brandt, C.A. Myrick, B.M. Johnson. 2012. Manipulation of growth to reduce mercury concentrations in sport fish on a whole system scale. Canadian Journal of Fisheries and Aquatic Sciences. 69:122–135.
- Lepak R.F., D.P. Krabbenhoft, J.M. Ogorek, M.T. Tate, H.A. Bootsma, J.P. Hurley. 2015. Influence of Cladophora–quagga mussel assemblages on nearshore methylmercury production in Lake Michigan. Environmental Science and Technology. 49:7606–7613.
- Lescord, G.L., T.A. Johnston, B.A. Branfieun, J.M. Gunn. 2018. Percentage of Methylmercury in the Muscle Tissue of Freshwater Fish Varies with Body Size and Age and Among Species. Environmental Toxicology and Chemistry. 37: 2682-2691.
- Razavi N.R., M. Qu, D. Chen, Y. Zhong, W. Ren, Y. Wang, L.M. Campbell. 2015. Effect of eutrophication on mercury (Hg) dynamics in subtropical reservoirs from a high Hg deposition ecoregion: Hg dynamics in subtropical reservoirs. Limnology and Oceanography. 60:386–401.
- Razavi, N.R., S.F. Cushman, J.D. Halfman, T. Massey, R. Beutner, L.B. Cleckner. 2019a. Mercury bioaccumulation in stream food webs of the Finger Lakes in central New York State, USA. Ecotoxicology and Environmental Safety. 172: 265-272.
- Razavi N.R., J.D. Halfman, S.F. Cushman, T. Massey, R. Beutner, J. Foust, B. Gilman, L.B. Cleckner. 2019b. Mercury concentrations in fish and invertebrates of the Finger Lakes in central New York, USA. Ecotoxicology. https://doi.org/10.1007/s10646-019-02132-z
- Ridal J.J., L.E. Yanch, A.R. Fowlie, N.R. Razavi, T.M. Delongchamp, E.S. Choy. 2010. Potential causes of enhanced transfer of mercury to St. Lawrence River Biota: implications for sediment management strategies at Cornwall, Ontario, Canada. Hydrobiologia. 647:81–98.
- Riva-Murray, K., L.C. Chasar, P.M. Bradley, D.A. Burns, M.E. Brigham, M.J. Smith, T.A. Abrahamsen. 2011. Spatial patterns of mercury in macroinvertebrates and fishes from streams of two contrasting forested landscapes in the eastern United States. Ecotoxicology 20:1530–1542.
- Riva-Murray, K., P.M. Bradley, L.C. Chasar, D.T. Button, M.E. Brigham, B.C. Scudder Eikenberry, C.A. Journey, M.A. Lutz. 2013. Influence of dietary carbon on mercury bioaccumulation in streams of the Adirondack Mountains of New York and the Coastal Plain of South Carolina, USA. Ecotoxicology 22:60–71.
- Rodriguez, P., L. Méndez-Fernández, I. Pardo, N. Costas, M. Matinez-Madrid. 2018. Baseline tissue levels of trace metals and metalloids to approach ecological threshold concentrations in aquatic macroinvertebrates. Ecological Indicators. 91:395–409.

- Rolfhus, K.R., J.G. Wiener, R.J. Haro, M.B. Sandheinrich, S.W. Bailey, B.R. Seitz. 2015. Mercury in streams at Grand Portage National Monument (Minnesota, USA): assessment of ecosystem sensitivity and ecological risk. Science of the Total Environment. 514:192–201.
- Ryan, J. 2008. Adirondack Wildlife: a Field Guide. University of New Hampshire Press. 296 pp.
- Schmitt, C.J., C.A. Stricker, W.G. Brumbaugh. 2011. Mercury bioaccumulation and biomagnification in Ozark stream ecosystems. Ecotoxicology and Environmental Safety. 74:2215-2224.
- Simonin, H.A., J.J. Loukmas, L.C. Skinner, K.M. Roy. 2008. Strategic monitoring of mercury in New York State fish. New York State Energy Research and Development Authority, Albany, NY. Report 08-11.
- Tsui, M.T.K., J.C. Finlay, E.A. Nater. 2009. Mercury bioaccumulation in a stream network. Environmental Science and Technology. 43:7016-22.
- Tsui, M.T.K., J.D. Blum, J.C. Finlay, S.J. Balogh, Y.H. Nollet, W.J. Palen, M.E. Power. 2014. Variation in terrestrial and aquatic sources of methylmercury in stream predators as revealed by stable mercury isotopes. Environmental Science and Technology. 48:10128–10135.
- US EPA. 2001. Water quality criterion for the protection of human health: methylmercury. Office of Science and Technology Office of Water, Washington, DC [EPA- 823-R-01-001].
- Voshell, J.R., 2014. A guide to common freshwater invertebrates of North America. McDonald & Woodward Publishing Company. 456 pp.
- Ward, D.M., Nislow, K.H., Folt, C.L., 2010. Bioaccumulation syndrome: identifying factors that make some stream food webs prone to elevated mercury bioaccumulation. Ann. NY Acad. Sci. 1195, 62–83.
- Wetzel, R.G. and G. Likens. 2000. Limnological Analyses. Springer, 3rd edition. 429 pp.
- Wu P., M.J. Kainz, A.G. Bravo, S. Akerblom, L. Sonesten, K. Bishop. 2019. The importance of bioconcentration into the pelagic food web base for methylmercury biomagnification: a meta-analysis. Science of the Total Environment. 646:357–367.
- Yu X., C.T. Driscoll, M. Montesdeoca, D. Evers, M. Duron, K. Williams, N. Schoch, N.C. Kamman. 2011. Spatial patterns of mercury in biota of Adirondack, New York lakes. Ecotoxicology. 20:1543–1554.

NYSERDA, a public benefit corporation, offers objective information and analysis, innovative programs, technical expertise, and support to help New Yorkers increase energy efficiency, save money, use renewable energy, and reduce reliance on fossil fuels. NYSERDA professionals work to protect the environment and create clean-energy jobs. NYSERDA has been developing partnerships to advance innovative energy solutions in New York State since 1975.

To learn more about NYSERDA's programs and funding opportunities, visit nyserda.ny.gov or follow us on Twitter, Facebook, YouTube, or Instagram.

#### New York State Energy Research and Development Authority

17 Columbia Circle Albany, NY 12203-6399 toll free: 866-NYSERDA local: 518-862-1090 fax: 518-862-1091

info@nyserda.ny.gov nyserda.ny.gov



State of New York Andrew M. Cuomo, Governor

New York State Energy Research and Development Authority Richard L. Kauffman, Chair | Doreen M. Harris, Acting President and CEO