Elevated Methylmercury in Water and Aquatic Food Webs in Lagoons in the Apostle Islands National Lakeshore (Lake Superior)

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Abstract. We assessed mercury contamination of water, sediment, and selected aquatic biota from two lagoons in the Apostle Islands National Lakeshore (southern Lake Superior). These nearshore lagoon systems appear to be mercury-sensitive environments with unusually high rates of production of methylmercury, a highly toxic compound that readily bioaccumulates in aquatic food webs. Concentrations of methylmercury in oxic, near-surface water from these systems were unusually high (averaging 1.3 ng L^{-1} in Outer Lagoon and 2.5 ng L^{-1} in Stockton), with observed values greatly exceeding reported concentrations for Lake Superior and inland lakes of the region. Methylmercury concentrations in bulk samples of zooplankton from these systems were also high (averaging 481 ng g^{-1} dry weight in Outer Lagoon and 270 ng g^{-1} in Stockton) and substantially exceeded values reported in the literature or measured in samples taken from regional inland lakes. In contrast, concentrations of *total* mercury in surface water (averaging 4.5 ng L^{-1} in Outer and 10 ng L^{-1} in Stockton) and sediment from these systems were not unusual, and were within or near the range of observed values for regional lakes. The fraction of total mercury present as methylmercury in sediment was much less than that in water, leading us to hypothesize that the high concentrations of aqueous methylmercury in the lagoons resulted from high rates of mercury methylation in the water column. Concentrations of total mercury in whole northern redbelly dace *Phoxinus eos*, a prey fish sampled from the Stockton lagoon, averaged 0.105 µg g^{-1} (parts per million) wet weight and ranged from 0.070 to 0.193 µg g^{-1}. Total mercury in axial muscle tissue of northern pike *Esox lucius* from Outer lagoon averaged 0.78 µg g^{-1} wet weight and ranged from 0.25 to 1.15 µg g^{-1}, exceeding the U.S. Environmental Protection Agency methylmercury criterion of 0.3 µg g^{-1} wet weight in 15 of 17 fish analyzed. We conclude that these lagoon systems are mercury-sensitive environments that actively produce methylmercury, a toxic compound that may be bioaccumulating to harmful concentrations in organisms in upper trophic levels of food webs in these lagoon systems.

Introduction

Lagoons on the Apostle Islands National Lakeshore in southern Lake Superior exhibit several characteristics that have been associated with high rates of methylmercury production and its bioaccumulation to high concentrations in aquatic biota. Such characteristics include low aqueous pH, warm temperature in summer, adjoining wetlands, and moderate to high concentrations of dissolved organic carbon, and dense submersed vegetation (Table 1). These lagoons contain resident aquatic biota and are used as foraging sites by migratory and breeding birds and aquatic mammals, providing a pathway for dietary exposure of sensitive early life stages to methylmercury.

Toxicological concerns about mercury (Hg) pollution of aquatic ecosystems focus appropriately on methylmercury, a highly toxic compound that readily accumulates in exposed aquatic organisms and biomagnifies in food webs (Wiener et al. 2003). Although most of the mercury in atmospheric deposition exists as inorganic forms, nearly all of the mercury accumulated by fish and higher trophic levels is methylmercury (Grieb et al. 1990, Bloom 1992, Hammerschmidt et al. 1999). Methylmercury readily crosses external and internal biological membranes (Pickhardt et al. 2006), is eliminated slowly

relative to its rate of uptake (Trudel and Rasmussen 1997), and accumulates to concentrations in aquatic organisms that vastly exceed those in surface water. In fish, for example, concentrations of methylmercury commonly exceed those in the water in which they reside by a factor of 10^6 to 10^7 or more (Wiener et al. 2003). Direct uptake from water is important for organisms, such as algae, in the lowest trophic levels (Pickhardt et al. 2002, Gorski et al. 2006), whereas aquatic organisms, such as fish, in higher trophic levels obtain methylmercury almost entirely from the diet (e.g., Rodgers 1994, Hall et al. 1997, Harris and Bodaly 1998). Aquatic food webs are the primary pathway for exposure of humans and wildlife to methylmercury (NRC 2000, Mergler et al. 2007, Scheuhammer et al. 2007). In contrast to methylmercury, inorganic mercury in natural waters is not readily transferred through successive trophic levels and does not biomagnify (Watras et al. 1998, Pickhardt et al. 2002).

Table 1. Characteristics of the studied lagoons on Outer and Stockton Islands. Morphometric data (area, depth) were provided by the National Park Service. Values for dissolved organic carbon (DOC) and pH are from *in situ* measurements (pH) and analyses of water samples (DOC) taken during the present study in late July 2005.

Variable	Outer	Stockton
Surface area (ha)	51	19
Maximum depth (m)	~2	~2
Mean DOC (mg/L)	18.6 ±0.5	46.5 ±0.4
Mean pH (s.u.)	6.45	6.12

Atmospheric deposition is the primary source of the mercury accumulating in watersheds and lakes in the Great Lakes region, and analyses of lacustrine sediment cores from this and other regions have conclusively shown that most of this atmospherically deposited mercury is derived from anthropogenic sources (Swain et al. 1992, Engstrom and Swain 1997, Lockhart et al. 1998, Lorey and Driscoll 1999, Lamborg et al. 2002). In addition, a growing body of evidence indicates that atmospheric deposition is the primary source of mercury accumulating as methylmercury in aquatic food webs and freshwater fish (Fitzgerald et al. 1998, Wiener et al. 2006, Munthe et al. 2007, Harris et al. 2007).

In this study, we quantified concentrations of total mercury and methylmercury in physical and biotic components in two lagoons of the Apostle Islands National Lakeshore. Our study objectives were (1) to assess contamination of the lagoons, by quantifying concentrations of total mercury in water and sediment, and (2) to assess methylmercury accumulation in selected components of the aquatic food webs of the lagoons. These data provide a foundation for assessing the potential ecotoxicological

significance methylmercury exposure in biota that forage in lagoon systems in the Apostle Islands National Lakeshore.

Methods

Sampling was performed in late July 2005 to coincide with the seasonal period of warm temperatures and active microbial production of methylmercury. We sampled water, seston (mostly algae), bulk zooplankton, surficial sediment, and fish from each lagoon.

Water

Near-surface samples (~ 0.1 m) of water were sampled from a small inflatable boat at five sites in each lagoon. Clean techniques were used during the collection and analysis of water samples to reduce handling contamination. Water samples were promptly acidified and held on ice in the dark until analysis for total mercury and methylmercury. Dissolved oxygen and pH were determined on-site with portable meters. Water samples were also analyzed for dissolved organic carbon (DOC). Total mercury in water was determined by oxidizing the sample with BrCl, followed by analysis by cold vapor atomic fluorescence spectrophotometry (Olson et al. 1997). Methylmercury in water was determined by steam distillation, ethylation, separation by gas chromatography and analysis by cold vapor atomic fluorescence spectrophotometry (Tekran model 2500 detector; Horvat et al. 1993, Olson et al. 1997).

Seston

Seston were sampled at a depth of ~ 0.5 m by passing water through an in-line filter capsule containing an ashed quartz fiber filter with a nominal pore size range of 0.7 to 2.0 μm when whetted. Samples were held in the dark on ice in the field and then frozen until processing in the laboratory. Methylmercury in seston were determined by steam distillation, ethylation, separation by gas chromatography, and analysis by cold vapor atomic fluorescence spectrophotometry (Horvat et al. 1993, Olson et al. 1997). Samples of bulk suspended particles for simple mass analysis were similarly sampled onto quartz fiber filters, frozen, oven-dried, and weighed with a microbalance.

Zooplankton

Samples of bulk zooplankton were obtained with a 0.5-m diameter, acid-cleaned 143-μm Nitex hoop net towed at a depth of about 0.5-1.0 m at two locations in each studied lagoon. Samples of bulk zooplankton were held on ice in a portable cooler while in the field and then frozen until processing in the laboratory. Methylmercury in zooplankton was determined by filtering the collection through ashed quartz fiber filters, followed by steam distillation, ethylation, separation by gas chromatography, and analysis by cold vapor atomic fluorescence spectrophotometry (Horvat et al. 1993, Olson et al. 1997).

Fish

Northern redbelly dace (*Phoxinus eos*) in the Stockton Island Lagoon were sampled on July 28, 2005 with a small-mesh bag seine hauled in littoral habitat. Northern pike (*Esox lucius*) in the Outer Island Lagoon were sampled on July 25 and 27 by angling and seining. No prey fish were obtained in Outer Island by several hauls of a small-mesh bag seine in littoral habitat. All fish were held on ice in a portable cooler in the field and stored in a portable freezer on the date of sampling. In the laboratory, each fish was lightly thawed, identified to species, measured (total length to nearest 1 mm), weighed (northern pike to 0.1 g; northern redbelly dace to 0.01 g), dissected (axial muscle of northern pike), placed into a labeled Ziploc® bag, and stored in a conventional freezer (-30°C) until lyophilization at -50°C to a constant dry weight. Lyophilized samples of fish (whole body of northern redbelly dace; axial muscle of northern pike) were ground and homogenized in a stainless steel blender. A 50- to 150-mg sample of the homogenate from each fish was acid digested with procedures modified from EPA Method 1631 (US Environmental Protection Agency 2001). Briefly, a mixture of 7:3 (vol:vol) HNO_3 and H_2SO_4 were added to each sample and the digestate heated to 95 °C for 3 hours followed by digestion with BrCl for 8 hours at 40^oC. Each digestate was analyzed for total mercury by flow injection cold-vapor atomic fluorescence spectrophotometry with a Leeman Laboratory Hydra AF Gold Plus Mercury Analyzer.

Most of the mercury in whole prey fish (Wiener et al. 2007) and in the axial muscle tissue of predatory fish (Bloom 1992) is present as methylmercury. The analyses of these samples for total mercury, therefore, yielded a valid estimate of methylmercury concentration.

Sediment

Surficial sediment (uppermost 4 cm) was taken at 10 sites in each lagoon with a hand-operated Ekman dredge. Sediments were held on ice in a portable cooler in the field and transferred later the same day to a domestic freezer. Analysis of sediment for total mercury followed the analytical procedures of Olson et al. (1997), Bloom and Crecelius (1983), and Bloom and Fitzgerald (1988). Briefly, samples were lyophilized, homogenized, and microwave-digested in a 5:2 (v/v) mixture of concentrated H_2SO_4:HNO_3 acids in Teflon containers. Digested samples were analyzed by the purge-trap cold vapor atomic fluorescence spectrophotometry technique with a Tekran 2500 detector. Methylmercury in sediment was determined by steam distillation, ethylation, separation by gas chromatography, and analysis by cold vapor atomic fluorescence spectrophotometry (Horvat et al. 1993, Olson et al. 1997).

Quality Assurance

The accuracy and precision of mercury determinations were verified by concomitant analyses of (1) standard reference materials, (2) spiked (before digestion) subsamples, (3) replicate subsamples, and (4) procedural blanks and standards. About 40% of the total analytical workload associated with this project was devoted to quality assurance.

Methylmercury analyses conducted on solids (filters, sediments) had a method detection limit of 0.010 ng g^{-1} dry weight. Analytical duplicates averaged 19.8 % difference (n = 6), and spiked samples were recovered at 98%. For reference material Mussel-2976 (NIST Certified Reference Material), 6 of 9 analyses were within the certified range (27.8 ± 1.1 ng g^{-1} dry weight), and our average concentration was 104% of the accepted value. Analyses of total mercury in solids yielded a detection limit of 1.0 ng g^{-1} dry weight, analytical duplicates averaged 25.5% difference (n = 18), and the mean spike recovery was 98% (n = 3). Analysis of 4 of 7 samples of the reference material MESS-3 (estuarine sediment, National Research Council Canada) yielded results within the accepted concentration range of 91 ± 9 ng g^{-1} dry weight, and our average concentration from the MESS-3 analyses was 97% of the accepted value. The detection limit for methylmercury in aqueous samples was 0.054 ng L^{-1}. These samples had an average spike recovery of 112% (n = 4), and the average coefficient of variation from triplicate analyses (n = 3) averaged 6.7%. No reference material was available to apply to our aqueous methylmercury samples.

Results and Discussion

Water

Concentrations of methylmercury in oxic surface water averaged 1.3 ng L^{-1} in Outer Lagoon and 2.5 ng L^{-1} in Stockton Lagoon, greatly exceeding concentrations in Lake Superior and inland lakes of the region, including Voyageurs National Park (Table 2). Corresponding mean concentrations of total mercury were 4.5 ng L^{-1} in the Outer lagoon and 10.0 ng L^{-1} in Stockton lagoon. The fraction of total mercury present as methylmercury in water was unusually high (Table 2), averaging 31% in Outer lagoon and 25% in Stockton lagoon. In comparison, methylmercury generally accounts for about 0.1% to 5% and seldom exceeds 10% of total mercury in oxic surface water (Wiener et al. 2003).

Nearly all of the waterborne inorganic mercury and methylmercury in inland surface waters is associated with organic matter (Lamborg et al., 2003). The relation of aqueous total mercury concentrations to waterborne organic carbon in the lagoons was similar to that observed for inland lakes in Voyageurs National Park (Figure 1). In contrast, aqueous methylmercury in the lagoons was much more enriched relative to DOC than in lakes at Voyageurs National Park (Figure 1).

Dissolved oxygen concentrations in both lagoons were significantly under-saturated relative to the atmosphere. Stockton Lagoon ranged from 3.8 mg L^{-1} at the surface to 0.2 mg L^{-1} at mid-depth (1 m) and near the sediment-water interface (2 m). Similarly, Outer Lagoon exhibited low dissolved oxygen (3.5 mg L^{-1}) at mid-depth (1 m) and 0.5 mg L^{-1} at the sediment-water interface (2 m). Such low-oxygen conditions are characteristic of mercury-methylating environments, where rates of microbial respiration of organic matter and oxygen consumption are elevated.

Table 2. Means (and ranges) of total mercury, methylmercury, and percent methylmercury in oxic, near-surface water from lagoons in the Apostle Islands National Lakeshore (APIS), Lake Superior, and inland lakes of Voyageurs National Park (VOYA).

Location	Methylmercury (ng L^{-1})	Total mercury (ng L^{-1})	Percent methylmercury (median & range)	Source
APIS lagoons				
Outer	1.3 (0.97-2.1)	4.5 (4.1-4.8)	27 (20-52)	This study
Stockton	2.5 (1.2-3.1)	10.0 (6.6-12.6)	25 (19-36)	This study
Lake Superior* (16 sites)	0.006 (0.003-0.013)	0.47 (0.28-0.67)	1.0 (0.5-3.8)	Rolfhus et al. 2003
VOYA (17 lakes)**	0.16 (<0.04-0.30)	2.1 (0.45-3.3)	7.5 (5.6-13)	Wiener et al. 2006

*Samples taken August 2000; **Samples taken May 2001 & May 2002

Sediment

Mean concentrations of total mercury in surficial sediment (upper 4 cm) were 163 ng g^{-1} dry weight in Outer Lagoon and 157 ng g^{-1} in Stockton (Table 3). Methylmercury in surficial sediment averaged 1.3 ng g^{-1} dry weight in Outer Lagoon and 0.7 ng g^{-1} in Stockton (Table 3). The fraction of total mercury present as methylmercury in sediment (Table 3) was much less than that in water (Table 2), averaging 0.77% in Outer Lagoon and 0.81% in Stockton. The concentrations of total mercury in surficial sediment from the two lagoons were within the ranges of values reported for surficial sediments from 20 northeastern Minnesota lakes (Engstrom et al. 2007) and six northern Wisconsin lakes (Rada et al. 1993); thus, the concentrations of total mercury in lagoon sediments were not elevated relative to lakes in the region. These observations lead us to hypothesize that the high concentrations of aqueous methylmercury in the lagoons resulted from high rates of mercury methylation in the overlying water column of the lagoons.

Seston and Zooplankton

The methylmercury content of seston in the lagoons was somewhat elevated relative to typical inland lakes (Table 4). These concentrations are lower than that of bulk zooplankton, reflecting the contribution of low-methylmercury material such as detritus and algae in seston. Concentrations of methylmercury in bulk samples of zooplankton were high, exceeding values reported in the literature (Watras et al. 1998) or measured in samples from regional inland lakes (Table 4). The unusually high concentrations of methylmercury in water and zooplankton (i.e., lower trophic levels) indicate a significant potential for biomagnification of methylmercury in food webs of these lagoons.

Table 3. Means (and ranges) of total mercury, methylmercury, and percent methylmercury in surficial sediment from lagoons in the Apostle Islands National Lakeshore.

APIS lagoon	Methylmercury (ng g^{-1} dry wt)	Total mercury (ng g^{-1} dry wt)	Percent methylmercury
Outer	1.3 (0.14-3.6) *n = 10*	163 (20-333) *n = 6*	0.77 (0.21-1.44) *n = 6*
Stockton	0.71 (0.05-1.3) *n = 10*	157 (25-239) *n = 7*	0.81 (0.26-2.42) *n = 7*

Table 4. Mean methylmercury (MeHg) in northern pike, age-1 yellow perch, bulk zooplankton, seston, and water in two lakes from Voyageurs National Park, MN (see footnote) and in two lagoons in the Apostle Islands National Lakeshore.

Variable	Voyageurs National Park*		Apostle Islands National Lakeshore	
	Mukooda Lake	Ryan Lake	Outer Lagoon	Stockton Lagoon
THg in northern pike (ng g^{-1} dry wt)	1130 (55-cm)	9725 (55-cm)	4436 (41-cm)	--
THg in age-1 yellow perch (ng g^{-1} dry wt)	181	943	No prey fish	--
MeHg in zooplankton (ng g^{-1} dry wt)	30	224	678	269
MeHg in seston (ng g^{-1} dry wt)	14	32	78	25
MeHg in near-surface water (ng L^{-1})	0.12	0.23	1.3	2.5
BioAccumulation Factor (zoop/water)	10$^{5.4}$	10$^{6.0}$	10$^{5.7}$	10$^{5.0}$
BioAccumulation Factor (pike/water)	10$^{7.0}$	10$^{7.6}$	10$^{6.5}$	--

*Mukooda and Ryan lakes respectfully contain the lowest and highest concentrations of methylmercury in water and fish in 17 studied lakes in Voyageurs National Park, and Ryan Lake contains northern pike (*Esox lucius*) with the highest mercury concentrations found in surveys of ~1000 Minnesota lakes.

Fish

Concentrations of mercury in fish from the lagoons were also elevated. Mercury in axial muscle of northern pike (total length range, 19-43 cm) averaged 0.78 μg g^{-1} (parts per million) wet weight, ranged from 0.25 to 1.15 μg g^{-1}, and increased with fish length (Figure 2), a widely observed pattern for methylmercury in fish (Wiener et al. 2007).

Concentrations in fillets of 15 of the 17 northern pike exceeded the US Environmental Protection Agency Tissue Residue Criterion of 0.3 µg g^{-1} wet weight for methylmercury, which was established to protect the health of humans who eat noncommercial fish (Borum et al. 2001). Mercury levels in 25 whole northern redbelly dace (total length range, 5.5-8.1 cm) from the Stockton Island lagoon averaged 0.105 µg g^{-1} wet weight, ranged from 0.070 to 0.193 µg g^{-1}, and increased with fish length (Figure 3).

Ecotoxicological Implications

Processes that affect the mass of methylmercury in aquatic ecosystems or its concentration at the base of the aquatic food web strongly affect its concentration in all trophic levels (Paterson et al. 1998, Benoit et al. 2003, Wiener et al. 2003). The unusually high concentrations of methylmercury in lower trophic levels of these lagoon systems indicate a significant potential for biomagnification of methylmercury to concentrations that could adversely affect wildlife that forage in these lagoons. The food webs in the lagoons appear to contain fewer trophic levels than those in most inland lakes of the region. For example, biological surveys of these lagoons by the National Park Service and the results of our fish-sampling efforts indicate that Outer Lagoon contains a population of northern pike but no forage fish, whereas Stockton lagoon contains several species of forage fish but no piscivorous fish (Julie Van Stappen, National Park Service, Apostle Islands National Lakeshore, personal communication).

Recent experiments have shown that exposure to environmentally realistic concentrations of methylmercury can impair the health and reproduction of fish (Latif et al. 2001, Hammerschmidt et al. 2002, Drevnick and Sandheinrich 2003). In recent field studies, fish from a number of national park units have exhibited adverse sublethal effects of methylmercury exposure (Moran et al. 2007, Drevnick et al. 2008, Schwindt et al. 2008). The concentrations of mercury in several northern pike from Outer lagoon exceeded those in northern pike from Isle Royale that exhibited adverse sublethal effects of methylmercury exposure (Drevnick et al. 2008); however, the fish sampled in the present study were not histologically examined for tissue damage.

In birds and mammals, methylmercury in reproducing females readily passes to the developing egg or embryo, life stages that are much more sensitive than the adult to methylmercury exposure (Wiener et al. 2003, Scheuhammer et al. 2007). Reproductive impairment has been associated with environmentally realistic methylmercury exposures in field studies of several aquatic and marsh birds (Heath and Frederick 2005, Schwarzbach et al. 2006, Scheuhammer et al. 2007). Burgess and Meyer (2008) showed that productivity of nesting common loons (*Gavia immer*) decreases as methylmercury exposure increases. In their study, maximum observed loon productivity declined 50% when mercury levels in prey fish were 0.21 µg g^{-1} (wet weight), and reproduction of loons failed completely when mercury concentrations in prey fish were 0.41 µg g^{-1}. The mercury levels in fish in the studied lagoons of the Apostle Islands National Lakeshore are sufficiently high to adversely affect the reproduction of common loons and possibly other piscivorous avian species that forage in these systems.

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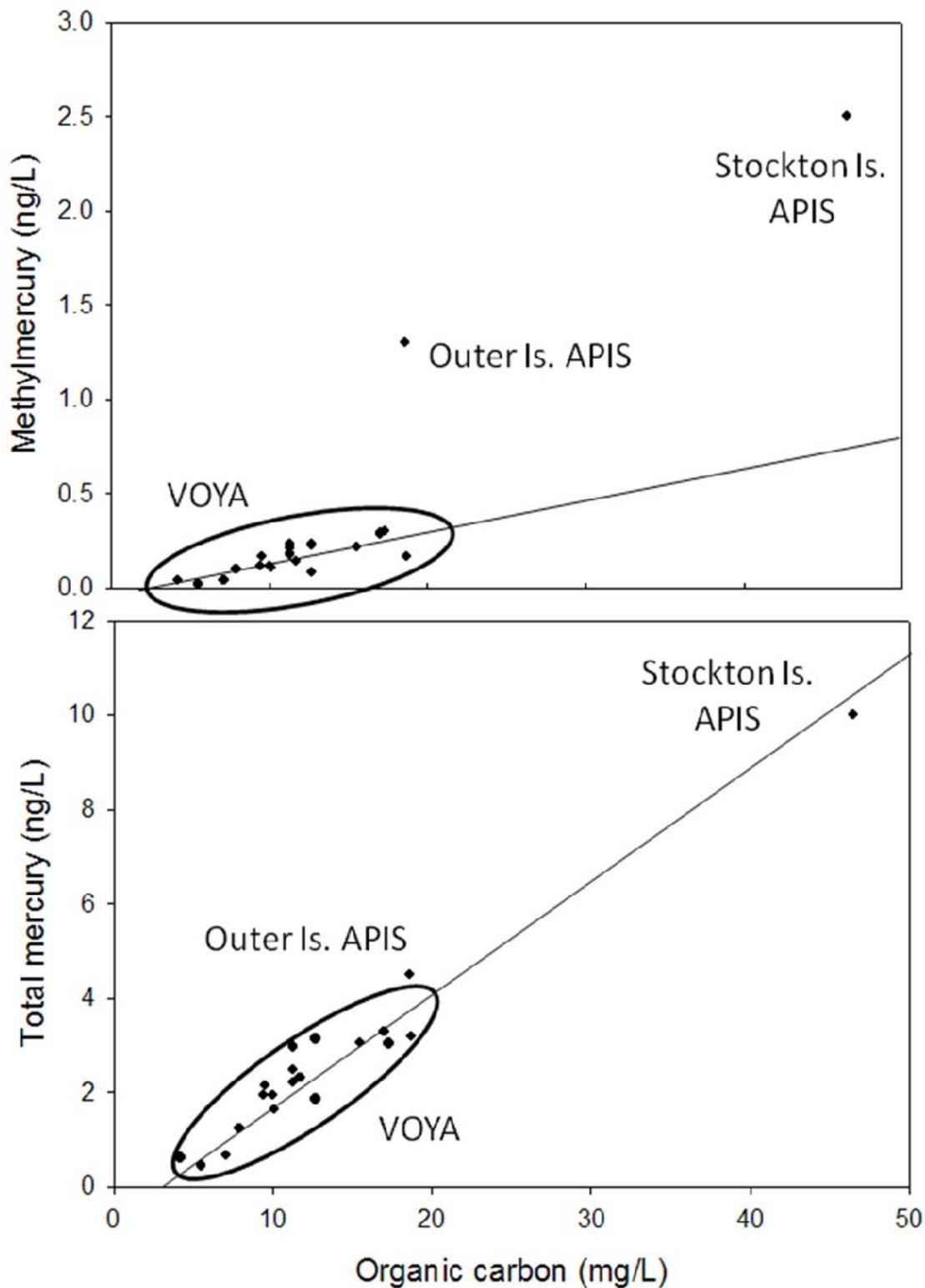
Figure 1. Concentrations of methylmercury and total mercury in relation to organic carbon in near-surface waters from two lagoons in the Apostle Islands National Lakeshore and from inland lakes of the Voyageurs National Park, MN (VOYA). Data for the Voyageurs National Park are from Wiener et al. (2006).
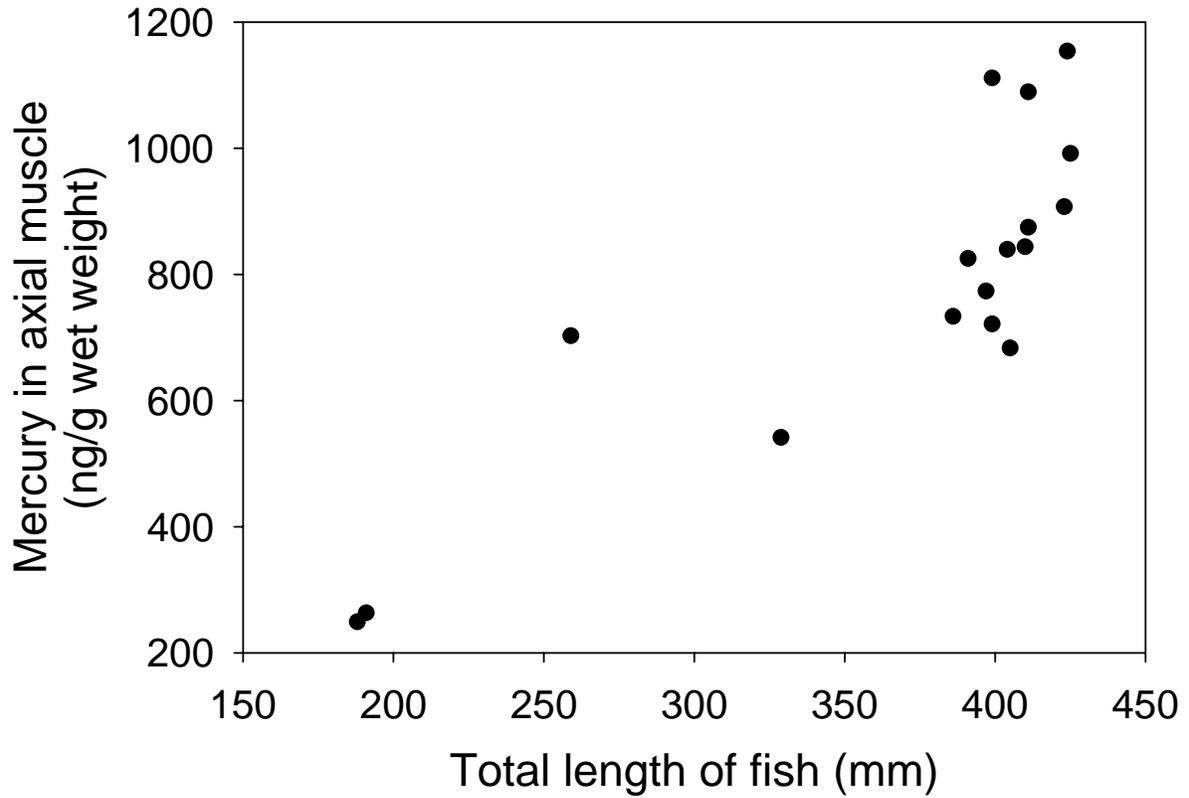
Figure 2. Concentrations of total mercury in axial muscle tissue of northern pike from the Outer Island lagoon (Apostle Islands National Lakeshore) in relation to total length of fish.
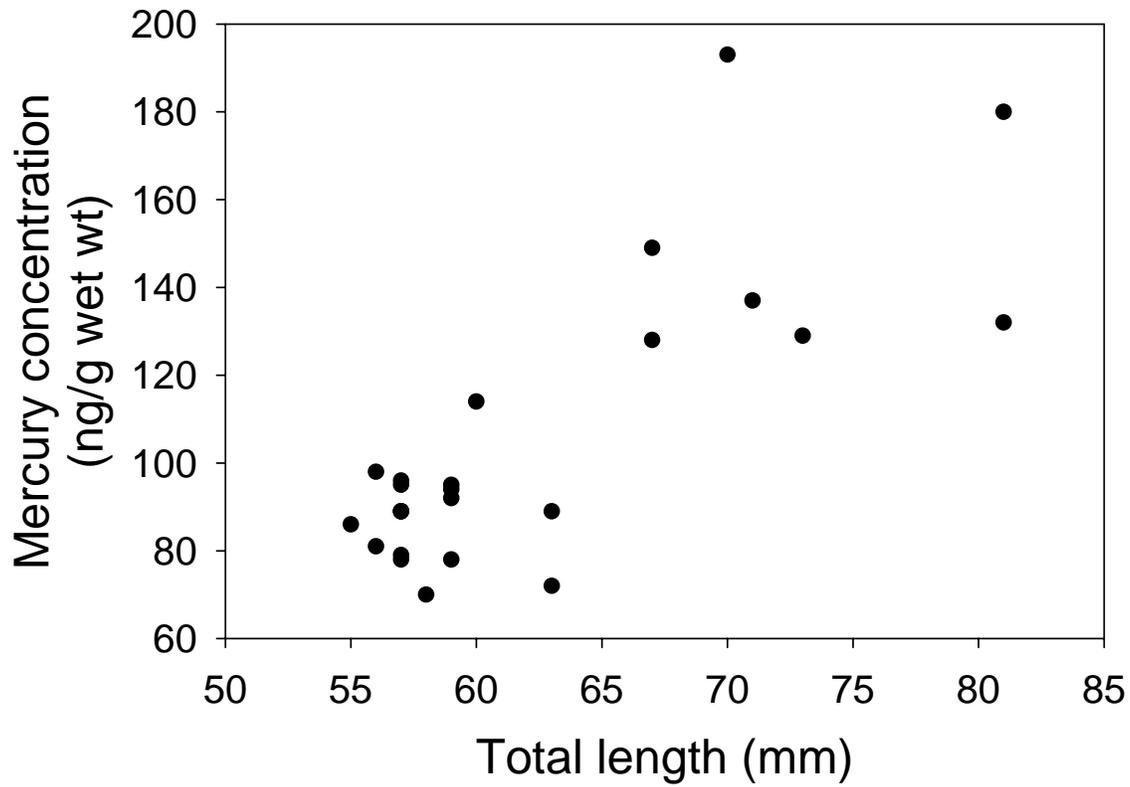
Figure 3. Concentrations of total mercury in whole northern redbelly dace from the Stockton Island lagoon (Apostle Islands National Lakeshore) in relation to total length of fish.