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Mercury biomagnification and contemporary food web dynamics in lakes Superior and Huron

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ABSTRACT

Trophic structure is an integral part of understanding the flow of contaminants within an aquatic system. Persistent, bioacccumulative, and toxic substances and food web perturbations by invasive species are critical ecological issues with far-reaching consequences for the health of the Laurentian Great Lakes. The historically-different aquatic ecosystems of Lakes Superior and Huron were evaluated for mercury (Hg) biomagnification using stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope ratios. The results showed that δ values vary significantly with sampling depth, particularly for the lower food web components, reflecting depth- and diet-specific patterns of δ values. The stable isotope assessment of the Lake Superior food webs was consistent with previous results, underscoring the temporal stability of this ecosystem. However, based on stable isotope data, the Lake Huron lake trout appear to be incorporating the exotic round goby in their diet, possibly compensating for the collapse of alewife populations, historically their principal food. Our results suggest that the well-documented perturbations in the Lake Huron ecosystem have likely contributed to increasing Hg concentrations in the lake trout. Similar Hg biomagnification rates were observed suggesting strong similarities in the contemporary contaminant flow in Lakes Superior and Huron.

Introduction

Pollutants and invasive species represent two of the most important issues for the Laurentian Great Lakes, and have focused the efforts of state, tribal and federal agencies to protect these international resources. Of the five Great Lakes, Lake Superior, outside of harbors, remains the only lake free of the dreissenid mussels (*Dreissena* spp.), and has had a relatively intact food web structure characterized by sustained naturally reproducing populations of both native lake trout (*Salvelinus namaycush*) and the deepwater coregonines (Schmidt et al., 2009; Vanderploeg et al., 2002).

In contrast, multiple exotic species, particularly the round goby (*Neogobius melanostomus*), the spiny water flea (*Bythotrephes longimanus*), and the quagga/zebra mussels (*Dreissena* spp.) that were introduced in the Great Lakes beginning in the late 1980s, have been implicated in the dramatic and rapid alterations in the food web structure of the affected ecosystems, especially in Lake Huron (Barbiero et al., 2009; Bunnell et al., 2012; Schaeffer et al., 2005; Vanderploeg et al., 2002). The sequestration of particulate nutrients driven by the efficient filtering of seston from the water column by *Dreissena* spp. is suspected to have precipitated declines in the Lake Huron spring phytoplankton bloom (Barbiero et al., 2011, 2012). Excessive planktivory by *Bythotrephes longimanus*, a well-known predator of herbivorous Cladocera, is thought to have likely contributed to the observed alterations in the overall zooplankton community population dynamics in the 2000s (Bunnell et al., 2011, 2012). At the same time, the Lake Huron native benthic macroinvertebrates (McNickle et al., 2006; Nalepa et al., 2009) and the deepwater demersal fish (Riley et al., 2008) showed substantial declines in abundances likely induced, in part, by nutrient limitations associated with the filtering activities of the *Dreissena* spp.

The cumulative impacts of these perturbations, which occur on multiple trophic levels, likely influence the bioaccumulation and trophic level transfer of toxic and bioaccumulative contaminants such as mercury (Hg). For example, substantial declines in abundances of key macroinvertebrate species (e.g., *Diporeia* and *Mysis*) in Lake Huron are responsible for declines in forage fish growth and condition (McNickle et al., 2006). Declining fish growth rates would produce increases in Hg and other contaminant concentrations (Munthe et al., 2007).

Additionally, because the round goby can forage on the dreissenid mussels, their establishment in the Great Lakes potentially introduces

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an alternative pathway of energy and contaminant transfer, particularly if the round goby are utilized by top predators (e.g., the lake trout, Johnson et al., 2005). Johnson et al. speculated that the foraging costs for predators that rely on the round goby are lower, resulting in increased mean length-at-age. Alternatively, a switch to a less calorically dense prey such as the round goby (Johnson et al., 2005 but see Ruetz et al., 2009) could potentially negatively impact the lake trout growth rates. If so, such changes in the growth response of goby-reliant predators could affect Hg bioaccumulation.

The primary goal of this study is to assess the average rate of Hg biomagnification in a stable Great Lake ecosystem (Lake Superior) relative to Lake Huron, which has recently undergone significant food web changes. This study utilizes the stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope ratios of food web components from both lakes to describe food web structures and to assess the rate of Hg biomagnification (e.g., Kidd et al., 2012; Lavoie et al., 2010; Poste et al., 2012; Rolfhus et al., 2011).

Methods

Sample collection

Food web components (seston, zooplankton, macroinvertebrates, forage, and piscivorous fishes) were collected from the two Lake Superior and Lake Huron sites routinely monitored as part of the Great Lakes Fish Monitoring and Surveillance Program (GLFMSP, EPA, 2012; Zananski et al., 2011). In Lake Superior, samples were collected from two shallow sites, the Apostle Islands (AI) and the Keweenaw Point (KP, Table 1, Fig. 1) aboard the U.S. EPA *R/V Lake Guardian* in June and July of 2011. Two lake trout morphotypes, the adult lean lake trout (*Salvelinus namaycush*) and juvenile siscowet lake trout (*Salvelinus namaycush siscowet*) were sampled at both of the Lake Superior sites (Table 1). In Lake Huron, samples were collected from the nearshore Port Austin (PA) and the offshore Rockport (RP) sites aboard the U.S. EPA *R/V Lake Guardian* in July of 2012. The different food web components sampled from both lakes are listed in Tables 2 and 3. No forage fish were found at the offshore Lake Huron site (RP), but deepwater sculpin, rainbow smelt, and the round goby were collected at an alternate offshore site (44° 48′ 0″ N, 83° 0′ 49″ W), approximately 50 km south of the RP site (Fig. 1). Additionally, quagga mussels were virtually absent at the nearshore Lake Huron site (PA) and additional samples were collected at an alternate nearshore site (44° 05′ 42″ N, 82° 43′ 3″ W), 10 km north of the PA site (Fig. 1). The water depth at the alternate nearshore and offshore sites were 39 m and 118 m, respectively.

Bulk zooplankton (ZOO*b*) and seston were collected by pumping lake water from approximately five (5) m below the surface through 150 μm and 10 μm nested nets to separate the zooplankton and seston, respectively. Bulk zooplankton (ZOO*a*) were also collected in Lake Huron using vertical tows of a 150 μm zooplankton net. The sampling depths were 20 m and 60 m for the nearshore (PA) and offshore (RP) sites, respectively. Macroinvertebrates (*Mysis diluviana*, *Diporeia*, Chironomidae, Oligochaeta, and *Dreissena* spp.) were sampled using benthic trawls. At least two 10 min tows were performed per site, whereupon samples were pooled and individual animals grouped by taxon, rinsed with deionized water and immediately frozen in 125 mL glass jars with Teflon screw lids. All composited samples were thawed at room temperature and homogenized prior to analyses. The collection method for forage and top predator fish was similar to the method described for lake trout in Zananski et al. (2011). Briefly, samples were collected by the use of gill nets, trap nets, or trawls. Whole fish were immediately frozen, kept at ≤ −20°C, then transported to the homogenization laboratory (Aquatec Biological Sciences, Inc., Burlington, VT) where samples were then slowly thawed and ground until a smooth, creamy paste was obtained. All forage fish from each site in each lake were homogenized and composited by taxa, resulting in one (1) to four (4) composited samples per species (Tables 1 and 2). Homogenized adult lean lake trout were not composited. Composited samples and individual lake trout (whole body tissues) were analyzed for both total mercury (THg) and stable isotopes of carbon and nitrogen.

Sample analyses for total mercury, methylmercury, and stable isotopes

Total Hg (THg) analyses were performed on wet tissues based on the U.S. EPA Method 7473 using a DMA-80 Direct Mercury Analyzer (Milestone Srl, Bergamo, Italy; see Zananski et al., 2011). Primary calibrations were performed using the DOLT-3 certified reference material (CRM, National Resource Council, Toronto, Canada, $n = 7$), in which quadratic regression curves with an r^2 value of >0.99 were selected for use in quantifying THg in samples. Approximately 0.1 to 0.2 g of each homogenate was used for THg analysis. Before each daily analysis, calibration checks were performed using the DOLT-3 CRM ($n = 4$) and the Lake Superior Fish Tissue 1946 Standard Reference Material (NIST; National Institute of Standards and Technology, Gaithersberg, MD, $n = 4$). The average % recovery from the DOLT-3 ($n = 70$) and the Lake Superior Fish Tissue SRM ($n = 70$) were 104 ± 4.1% and 103 ± 3.8%, respectively. All samples ($n = 47$ and $n = 58$ for Lake Superior and Huron, respectively) were analyzed in duplicate to assess reproducibility, and the average % relative difference was 4.6 ± 3.3%. The accuracy of the analysis was tested using the Lake Superior Fish Tissue SRM, which was run after every sample batch (10 samples run in duplicate). Samples were reanalyzed if the % recovery for the 1946 NIST SRM fell outside of the 90% to 110% range. Method blanks ($n = 77$) assessed by analyzing three empty nickel sampling boats between the last sample in an analytical batch and the 1946 NIST SRM were all less than 5% of the lowest measured mass (0.6 ng THg). Therefore, measured THg concentrations were not corrected for blanks. Measured THg concentrations are reported in units of ng/g whole body, wet weight.

Analyses of methylmercury (MeHg) concentrations for the lower food web samples (bulk zooplankton and macroinvertebrates, $n = 22$) were performed at Brooks Rand Laboratories (Seattle, WA, USA) using a Brooks Rand MERX-M Model III CVAFS system and following the U.S. EPA Method 1630. Tissue samples were prepared by alkaline digestion in 25% KOH in methanol and oven digestion at 65 °C for 3 to 4 hours. Samples were analyzed by ethylation, Tenax trap collection, gas chromatography separation, isothermal decomposition, and cold

Table 1
Characteristics of the Lake Superior and Lake Huron sites.

	Lake Superior		Lake Huron	
	Apostle Islands	Keweenaw Point	Port Austin	Rockport
Latitude	46.9164 N	47.4025 N	44.0803 N	45.2536 N
Longitude	90.4164 W	87.6036 W	82.7281 W	83.0139 W
Depth (m)	16 ± 1	15 ± 1	43 ± 8	131 ± 20
pH	8.4 ± 0.06	~	8.62 ± 0.61	7.74 ± 1.74
Conductivity (μS/cm)	100.3 ± 0.2	~	175.3 ± 22.2	166.3 ± 30
Dissolved oxygen (mg/L)	10.7 ± 0.2	~	10.4 ± 1.6	10.6 ± 2.9
Lake surface temperature (°C)	14.5 ± 0.1	10.9 ± 0.4	22.3 ± 0.3	21.6 ± 0.3