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Spatial and temporal variation in mercury bioaccumulation by zooplankton in Lake Champlain (North America)

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ABSTRACT

Trophic transfer of Hg across lakes within a region has been related to multiple environmental factors, but the nature of these relationships across distinct basins within individual large lakes is unknown. We investigated Hg bioaccumulation in zooplankton in basins of differing trophic status in Lake Champlain (Vermont, USA) to determine the strongest predictors of Hg bioaccumulation. Zooplankton were sampled in Malletts Bay (oligotrophic) and Missisquoi Bay (eutrophic) in 2005–2008. Zooplankton in the eutrophic basin had lower concentrations of total Hg and MeHg than those in the oligotrophic basin in all years but 2007, when no bloom occurred in Missisquoi. In addition, Hg concentrations in seston and small zooplankton, sampled during 2009 at 12 sites spanning the lake, decreased with increasing phytoplankton and zooplankton biomass. Thus, Hg bioaccumulation in zooplankton across basins in Lake Champlain is related to trophic status, as observed previously in multiple lake studies.

1. Introduction

Large lakes such as Lake Champlain (1127 km^2) and the Great Lakes are physically complex and contain basins with distinct trophic characteristics that can span the range of conditions found across multiple lakes in a broad region. In numerous multi-lake studies conducted throughout the US, mercury (Hg) bioaccumulation and trophic transfer in lakes was related to physical, chemical, and ecological factors, including positive relationships to lake and watershed area, and negative relationships to human land use, nutrient concentrations, pH, alkalinity, and abundances of phytoplankton and zooplankton (Watras et al., 1998; Kamman et al., 2004; Chen et al., 2005; Driscoll et al., 2007; Yu et al., 2011). In general, when compared to lakes of other trophic status, eutrophic lakes have lower Hg concentrations in top trophic level fish compared to lakes with lower productivity, in part due to higher zooplankton biomass and lower Hg concentrations in zooplankton (Chen and Folt, 2005; Chen et al., 2005).

Although these spatial patterns in Hg bioaccumulation and trophic transfer have been documented for different lakes within a region, studies have not been conducted within larger lakes, where trophic conditions can vary within their basins. Large lakes such as the Laurentian Great Lakes in the Upper Midwest and Lake Champlain in Vermont and New York (USA) have extensive and varying watersheds surrounding basins that are often hydrologically distinct. These separate basins can vary in trophic status ranging from highly eutrophic to oligotrophic, the same range of conditions captured in past studies of multiple lakes. Although the differences in trophic status among basins have been documented in these large lake ecosystems (McCarty et al., 2004), the influence of such differences on Hg bioaccumulation and transfer in the food web has not been examined.

We hypothesize that the mechanisms influencing between-lake differences in Hg bioaccumulation would also cause differences among basins within large lakes.

Eutrophic lakes have chemical and ecological attributes that may result in reduced Hg bioaccumulation and food web transfer relative to oligotrophic lakes. Increases in lake water pH and alkalinity may reduce the MeHg available for bioaccumulation in the food web (Driscoll et al., 2007). In addition, fish in eutrophic lakes

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may exhibit growth dilution of mercury when food is abundant, reducing concentrations in tissues relative to those in fish inhabiting oligotrophic lakes (Essington and Houser, 2003; Ward et al., 2009, in review). Nutrient conditions in eutrophic lakes stimulate algal blooms that spread the pool of dissolved inorganic and MeHg over a greater biomass of algal cells (Pickhardt et al., 2002; Luengen and Flegal, 2009), thereby reducing Hg and MeHg concentrations in algae and their zooplankton grazers (Chen and Folt, 2005; Chen et al., 2005). The increase in algal biomass may also alter other factors (e.g., biogeochemical) that could change MeHg production or the degree of Hg uptake via absorption or ingestion of non-living particulate organic matter.

Studies of temporal variability of Hg bioaccumulation in lakes have most often focused on intra-annual changes demonstrating that variability in Hg bioaccumulation through the growing season differs greatly between lakes (Herrin et al., 1998; Monson and Brezonik, 1998; McCarty et al., 2004; Ward et al., in review). However, little is known about inter-annual variation within a single lake or a single basin within a lake. Algal blooms can vary from year to year in lakes, with major nuisance algal blooms in some years and none in others. These temporal changes within lake systems could greatly influence the bioaccumulation of Hg by lower trophic levels and transfer of Hg to higher trophic levels.

Lake Champlain is a spatially complex large lake that experiences elevated Hg levels in fish, leading to fish consumption advisories for top trophic level species such as walleye, *Sander vitreus* (Vermont Department of Health, 2007). This is despite the low water column concentrations of total mercury (THg) and MeHg as compared to smaller lakes in the region (Shanley et al., 1999; Kamman et al., 2004; Gao et al., 2006). Trophic status and Hg inputs vary greatly across different basins in Lake Champlain (Gao et al., 2006; Miller et al., in review). The most oligotrophic basin in the lake is Malletts Bay in the mid-reach of the lake and the most eutrophic is Missisquoi Bay at the northernmost end bordering Canada. Missisquoi Bay has received substantial nutrient inputs from the surrounding agricultural watershed that have stimulated annual algal blooms. Most of the remaining basins in the lake are mesotrophic, surrounded by watersheds with mixed land uses dominated by forest and agriculture (LCBP, 2010).

In this study, we address the overarching questions of whether basins within a large lake ecosystem like Lake Champlain differ significantly in the degree to which Hg enters the base of the food web. We investigated factors controlling Hg bioaccumulation in zooplankton across contrasting basins in Lake Champlain to identify the strongest chemical and ecological predictors of Hg bioaccumulation in zooplankton, which are important in the trophic transfer of MeHg to fish. To do this, we used two different approaches. In the first, we compared two basins within the lake, one eutrophic and the other oligotrophic, over 4 consecutive years to determine if bioaccumulation of THg and MeHg in large zooplankton differed between basins and whether differences changed through time. In the second, we conducted a broader spatial analysis of 12 sites within Lake Champlain during one season and identified chemical and ecological factors that predict elevated Hg concentrations in particulate and zooplankton size fractions.

2. Methods

2.1. Two-basin comparison

2.1.1. Sampling

In 2005, 2006, 2007 and 2008, we compared Hg bioaccumulation in zooplankton from Malletts Bay and Missisquoi Bay in mid-summer. Two size fractions of zooplankton, small (45–202 μm) and large (>202 μm), were sampled each year. The smaller size fraction incorporates taxa that are primarily herbivores and the larger size fraction incorporates large omnivores. Past studies indicate that the size fractions represent 2 different trophic levels with higher MeHg concentrations in the larger fraction (Chen et al., 2000; Ward et al., in review). Zooplankton were collected with multiple tows in the deepest portion of each site in the lake from 0.5 m above the bottom to the surface with a cone net (202-μm nylon mesh) for large zooplankton, and a Wisconsin net (45-μm nylon mesh) for small zooplankton until enough sample was obtained for each size fraction (>50 mg DW). The contents of the 45-μm net were filtered through a 202-μm filter (with >202 μm material discarded) to generate a sample representing the 45–202-μm size range. Zooplankton samples were taken from one location in each basin on one date in late August of each year (except in 2007, when samples were taken in June and July). Multiple plankton tows (3–5) were usually taken for each replicate sample. Triplicate samples for Hg speciation analysis were collected for both zooplankton size fractions. Samples were placed on ice in the dark and transported to the laboratory, where they were transferred to pre-weighed trace-metal clean glass vials, weighed, freeze dried, and reweighed to determine sample dry weight.

To minimize contamination, zooplankton sampling was conducted with great care with previously established protocols (Chen et al., 2000). Zooplankton samples were collected with trace-metal clean technique and non-metallic sampling gear, deployed from an aluminum boat with outboard motor. Prior to field sampling, Teflon™ sample vials and sampling apparatus were acid cleaned in sequential concentrated nitric acid, dilute HCl, and trace-metal grade, dilute nitric acid baths. Plankton nets were rinsed in Citranox and deionized water.

Data for phytoplankton abundance (measured as chlorophyll *a*, phytoplankton biovolume, and phytoplankton density), zooplankton density, and water quality parameters (total phosphorus (TP), total nitrogen (TN), dissolved organic carbon (DOC)) for 2005–2008 were obtained from the water quality monitoring conducted by the Vermont Department of Environmental Conservation (VTDEC) Lake Champlain Monitoring Program (LCMP, 2010). We used data obtained during LCMP sample dates that were closest to those dates when our sampling was conducted.

2.1.2. Hg and MeHg analyses

All freeze-dried zooplankton samples were analyzed at the Trace Element Analysis (TEA) Facility at Dartmouth College. Hg speciation of small and large zooplankton was conducted with isotope dilution and alkaline digestion followed by purge and trap GC-ICPMS. The zooplankton samples were first spiked with appropriate amounts of enriched Hg^{199} and $MeHg^{201}$ and then extracted by standard alkaline extraction procedures. Our previous work (which describes these techniques in detail) has shown that this double-spiking method can produce accurate and precise measurements of both inorganic Hg and MeHg from biological tissues (Taylor et al., 2008; Jackson et al., 2009). Quality control was achieved by analyses of two standard reference materials, TORT-2 (NRC-CNRC Canada $n = 1$) and Mussel 2976 (NIST, Gaithersburg, MD, $n = 11$). Recoveries of MeHg and total Hg were 120% and 118% for TORT 2, respectively, and 102% and 101%, respectively, for NIST 2976. Coefficients of variation for MeHg and total Hg for NIST 2976 were 11.4% and 10.9%, respectively. The method detection limits (based on 3 standard deviations of 11 blank extracts) were 18 pg and 0.43 ng and the average blank values were 12 pg and 0.59 ng for MeHg and inorganic Hg, respectively. All sample values for MeHg were above blank + 3 standard deviations. For inorganic Hg, all sample values were above the mean blank value.

2.2. Lake-wide comparison

In 2009, we sampled water, seston, and zooplankton at 12 stations representing the full range of trophic conditions in the lake (Fig. 1). Samples were collected between August 7 and September 11, 2009 during scheduled sampling of designated water quality monitoring stations conducted by the VTANR-LCMP (Vermont Department of Environmental Conservation, 2009). Water quality sampling included measurements of chlorophyll *a*, secchi depth, temperature, alkalinity, nutrients (TN and TP), chloride, and dissolved oxygen. The methods for this sampling are described elsewhere (Vermont Department of Environmental Conservation, 2009).

Sampling for Hg speciation analysis, seston mass, and DOC was conducted in triplicate. Samples were collected off the windward bow rail of a fiberglass research vessel. Water grab samples for Hg speciation were collected at ~20 cm depth in the epilimnion with the EPA "clean hands/dirty hands" method directly into pristine 2-L PTEG sampling vessels (see Jackson et al., 2009). Samples were triple bagged and placed immediately in the dark on ice in a cooler for shipment to the laboratory. Separate 2-L grab samples were collected in PTEG bottles for gravimetric analysis of seston mass. These samples were also stored in the dark on ice. Filtered samples were collected from the filtrate of the VTDEC chlorophyll *a* sampling apparatus (0.2-μm Teflon filter; see Vermont Department of Environmental Conservation, 2009) into pre-combusted 60-ml amber glass bottles and stored in the dark on ice for later measurement of DOC.

Field sampling personnel transported samples on ice directly to the Dartmouth College Trace Element Analytical Facility laboratory within 48 h of collection. Previous work (Jackson et al., 2009) identified a 48-h hold time as acceptable to maintain mercury speciation in Lake Champlain waters. The 2-L water samples were immediately filtered with pre-combusted Whatman GF/F filters to operationally