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Mercury content and speciation in the plankton and benthos of Lake Superior

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Abstract

As part of a study to assess the importance of watersheds in controlling sources, transport, fate, and bioavailability of monomethyl mercury (MeHg) in Lake Superior, biotic samples were collected and analyzed to determine total mercury (HgT) and MeHg content, and to examine size, species, trophic and geographic trends. Plankton was collected in two ways: vertical tows of non-metallic, 153 μm mesh net (bulk zooplankton), and by passively filtering near-surface water through stacked Nitex sieves, generating size-fractionated seston (<35, 35–63, 63–112, and > 112 μm). Benthos was sampled using a Ponar grab to collect sediment, and a non-metallic sieve to separate biota from substrate. Samples were processed to quantify dry weights, HgT and MeHg. Results for bulk zooplankton sampled offshore showed a range of approximately from 35 to 50 ng MeHg/gram dry weight (gdw) and from 80 to 130 ng HgT/gdw during April, and from 15 to 25 ng MeHg/gdw and from 20 to 70 ng HgT/gdw during August. Results from sieved, near-surface water from offshore sites in April showed a dominance by the <35 μm size fraction both in total mass and mass of MeHg compared to other size fractions. On a dry weight basis, however, we found little difference between the size fractions in April (MeHg ranges from 2 to 10 ng/gdw). During the summer cruise, we found similar concentrations in the <35 μm fraction, but higher in the 112–243 μm size fraction (MeHg 14–16 ng/gdw). The MeHg concentration in *Mysis relicta* ranged from 33 to 54 ng/gdw throughout the lake. Chironomid larvae were 8 ng MeHg/gdw and amphipods were 32 ng MeHg/gdw.

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1. Introduction

Mercury in freshwater systems continues to attract attention of researchers because of its bioac-

cumulation in food webs, which can lead to health impairments in wildlife and human populations (Clarkson, 1990). The biomagnification of methylmercury (MeHg) at each trophic transfer often results in contamination of predatory fish in excess of consumption limits for human populations. Resulting fish consumption advisories are regularly

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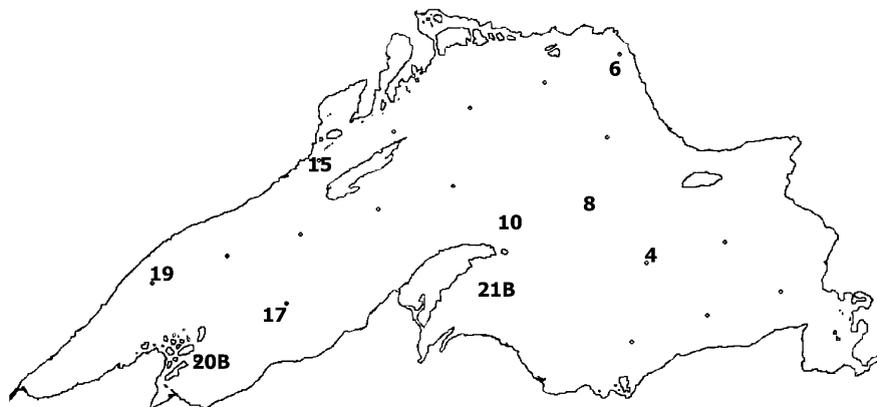


Fig. 1. Lake Superior stations sampled for this study during the Spring (April) and/or Summer (August) 2000 synoptic cruises of the US EPA's *R/V Lake Guardian*.

posted for lakes remote from point sources of mercury pollution, and point to the potential for watersheds to transform low concentrations of inorganic mercury to the more available organic form, which is readily concentrated in biota. The ultimate accumulation of mercury in biota is influenced by many variables including watershed soil and vegetation characteristics, ground and surface water chemistry, and food web structure (Babiarz et al., 1998; Hurley et al., 1995; St. Louis et al., 1994; Watras et al., 1998).

As part of a larger study to examine watershed influences on the bioavailability of such mercury inputs to Lake Superior, the current study examined total mercury (HgT) and MeHg in biota and seston from offshore sites during April and August of 2000. We collected and analyzed a variety of samples for both HgT and MeHg in an attempt to characterize the lower food web of both the pelagic and profundal zones.

Our interest in the lower food web derives from the tremendous bioconcentration that occurs between water and small particles (e.g. phytoplankton), and the general paucity of information available on these organisms from the Great Lakes (Mason and Sullivan, 1997). Armed with such information, researchers will better be able to quantify mercury cycling in Lake Superior, and modeling efforts will more realistically simulate

these systems and predict responses to natural and anthropogenic perturbations.

2. Methods

Samples were collected during the Spring (April) and Summer (August) 2000 synoptic cruises of the USEPA *R/V Lake Guardian* on Lake Superior. Of the 23 stations visited by the ship during 2000, 9 were sampled for plankton and benthos. Of those 9 (circled in Fig. 1), 4 were sampled during both cruises for size-fractionated seston, and 5 for bulk zooplankton.

Zooplankton was collected by vertical tows of a 153 μm mesh, non-metallic net from near bottom to the surface. Sample was drained directly from the cod-end bucket into 1-l Teflon bottles, double bagged, and immediately frozen. Upon returning to the lab, zooplankton samples were thawed, quantitatively subsampled for mercury and total mass using a clean, wide-bore, borosilicate glass syringe. Subsamples were then filtered onto a muffled quartz fiber filters for mercury determination, or onto a membrane filter for dry mass determination.

Seston was sieved into four size classes (>112 , 63–112, 35–63 and <35 μm) by pumping large volumes of near-surface water (5-m depth) through stacked acrylic sieves. Volumes sieved ranged from

450 to 1950 l, and allowed quantitative recovery of size-fractionated material for mercury and total dry mass determinations. Samples were resuspended in $<35 \mu\text{m}$ water, and subsamples filtered onto quartz fiber filters for mercury determinations, nylon $0.4 \mu\text{m}$ for pigment analysis, and polycarbonate $0.4 \mu\text{m}$ filters for dry mass determinations.

Bottom dwelling organisms were collected using a Ponar grab to collect sediment, which was then rinsed through a ship-board 'elutriator' to concentrate animals. Individual animals were sorted and grouped by taxon, rinsed with deionized water and immediately frozen in small volume (7–25 ml) Teflon vials. Upon returning to the lab, benthos samples were freeze-dried, homogenized, and subsampled for mercury and dry mass determinations.

Samples for HgT analysis (filters or benthos homogenate) were placed into 125-ml Teflon containers with approximately 75 ml of deionized water and 6 ml BrCl. The containers were then heated (60°C) overnight in an oven. Sample aliquots were then analyzed by CVAAS after SnCl_2 reduction and gold amalgamation (Hurley et al., 1998). Samples for MeHg analysis that had been processed onto quartz fiber filters were distilled and quantified by CVAAS after GC ethylation (Hurley et al., 1998). Benthic animals for MeHg analysis were sonicated for 8 h and extracted in warm (60°C) KOH/MeOH overnight before analysis (Bloom, 1992).

To determine if seasonal, size, or species-related differences in mercury concentrations were significant, the Shapiro–Wilk test was applied at the $P < 0.05$ level using univariate procedures in SAS (Version 6.12, SAS Institute, Inc.) first to determine if data were normally distributed. For normally distributed data, the t -test was used (Microsoft Excel 2000) to compare means between two groups. For non-normal data, the Wilcoxon Signed Rank test was used to compare two sample groups, and Kruskal–Wallis (SAS) for more than two sample groups.

A primary consideration in studies such as this is the reliability of reported results. Standard laboratory procedures at the UW clean lab included analyzing certified reference material (TORT-2), lobster hepatopancreas from the National Research Council (Canada) within each batch of samples

processed, as well as sample replicates (taken through processing and analysis) and analytical duplicates of samples. Results of TORT-2 analysis were always within the certified range (HgT concentration = 270 ± 60 ng/gram dry weight (gdw), MeHg concentration = 152 ± 13 ng/gdw). Replicated zooplankton samples taken separately through the digestion and analysis were typically within 10% for MeHg and 20% for HgT. Analytical duplicates of a given sample were much more consistent, typically within 5% for both MeHg and HgT analyses.

3. Results

MeHg in zooplankton ranged from 32 to 46 ng/gdw during April, and from 15 to 25 ng/gdw during August (Fig. 2a). April MeHg concentrations (mean = 40.9, S.D. = 4.9, $n = 5$) were significantly higher ($P < 0.01$, t -test, $t = 8.89$) than August MeHg concentrations (mean = 18.3, S.D. = 3.7, $n = 9$). At stations sampled during both cruises, the observed decline in MeHg concentration ranged from 48 to 69%. HgT in bulk zooplankton ranged from 78 to 133 ng/gdw during April, and from 22 to 67 ng/gdw during August (Fig. 2b). April HgT concentrations (mean = 101.0, S.D. = 23.1, $n = 6$) were also significantly higher ($P < 0.01$, t -test, $t = 5.33$) than August HgT concentrations (mean = 44.5, S.D. = 14.5, $n = 9$). At stations sampled during both cruises, the decline in HgT concentration ranged from 39 to 76%. Overall, zooplankton MeHg generally ranged from 30 to 56% of HgT, with the exception of Station 10, off the Keweenaw Peninsula, at which we found MeHg to be 77% of HgT during the August cruise.

MeHg concentrations in size-fractionated seston were generally low, and showed the importance of the $<35 \mu\text{m}$ fraction during the spring (Fig. 3a) and the $>112 \mu\text{m}$ fraction during the summer (Fig. 3b). Within the April data, there were significant differences among the size fractions ($P < 0.01$, Kruskal–Wallis, $\chi^2 \cong 13.55$). The $<35 \mu\text{m}$ fractions (mean = 6.9, S.D. = 1.8, $n = 6$) were significantly higher ($P < 0.01$, Wilcoxon, $Z = 2.84$) than all other fractions. Also, the $35 \mu\text{m}$ fractions (mean = 0.7, S.D. = 0.5, $n = 6$) were significantly

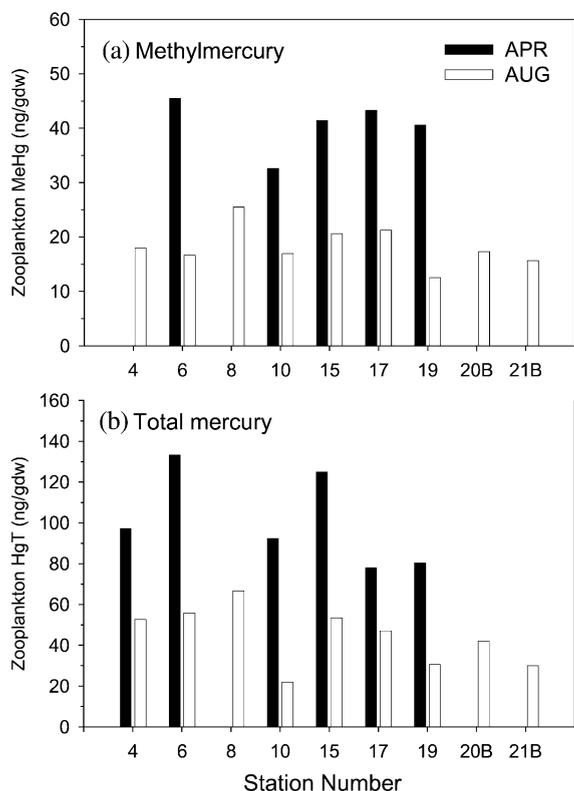


Fig. 2. Concentrations of MeHg (a) and HgT (b) in bulk zooplankton samples from Lake Superior stations sampled during Spring (April) and Summer (August) 2000 cruises. Concentrations are reported as ng per gram dry weight of composite zooplankton.

lower than other fractions ($P < 0.01$, Wilcoxon, $Z = 3.13$), with the 63 μm fractions being statistically similar to the 112 μm fractions ($P > 0.05$, t -test, $t = 0.67$).

Within the August data, there were also differences between the size fractions ($P < 0.01$, Kruskal–Wallis, $\chi^2 \cong 15.56$). The 112 μm fractions (mean = 10.3, S.D. = 4.6, $n = 6$) were significantly higher than all other fractions ($P < 0.01$, Wilcoxon, $Z = 3.11$). The $< 35 \mu\text{m}$ fractions (mean = 4.5, S.D. = 1.0, $n = 5$) were significantly lower than the 112 μm fractions ($P < 0.05$, t -test, $t = 3.00$), but significantly higher than the 35 μm and 63 μm fractions ($P < 0.01$, Wilcoxon, $Z = 2.69$), which were similar ($P > 0.05$, Wilcoxon, $Z = 1.04$).

The April $< 35 \mu\text{m}$ fractions were significantly higher than their August counterparts ($P < 0.05$, Wilcoxon, $Z = 2.10$). Following an opposite trend, the 112 μm fractions in August were significantly higher than they were in April ($P < 0.05$, t -test, $t = 2.88$). The high MeHg concentrations in the April $< 35 \mu\text{m}$ fractions were not statistically different than the high MeHg concentrations in the August 112 μm fractions ($P > 0.05$, Wilcoxon, $Z = 0.88$).

To normalize for difference in total volume sieved at each station, mass on each size fraction was summed and expressed per unit volume. Summed suspended particulate mass was also esti-

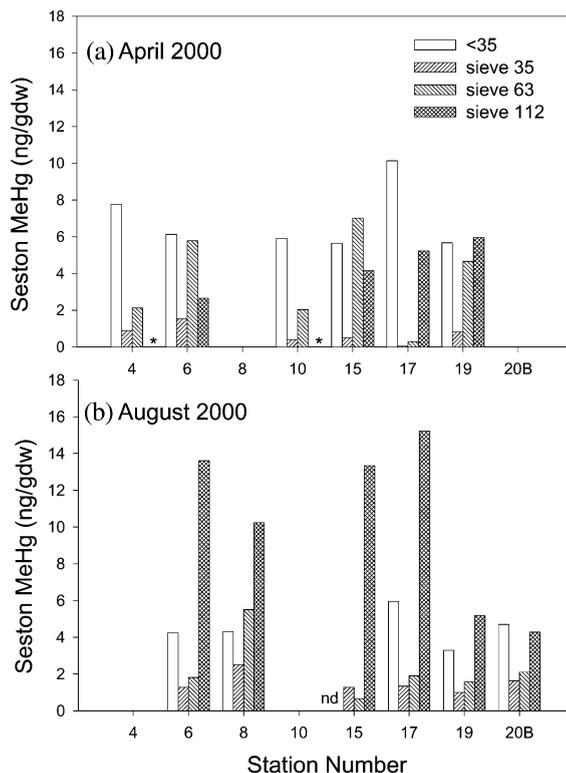


Fig. 3. Concentrations of MeHg in size-fractionated, near-surface particulate matter during April (a) and August (b) 2000 Lake Superior cruises. Concentrations are reported as ng per gram dry weight of seston collected from each of the stacked sieves (35, 63, 112 μm) or from sample which passed through the sieve array ($< 35 \mu\text{m}$). Samples which had insufficient mass for MeHg determinations are indicated with an (*), one sample for HgT was lost and not determined (nd).

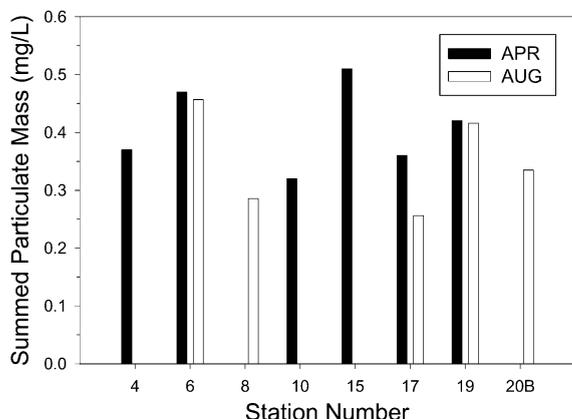


Fig. 4. Total suspended particulate mass estimated by summing size individual size fractions for stations sampled during the Spring (April) and Summer (August) 2000 Lake Superior cruises.

ated for all size fractions, ranged from 0.32 to 0.51 mg/l during April, and from 0.26 to 0.46 during August (Fig. 4), with no significant difference between the April and August samples ($P > 0.05$, Wilcoxon, $Z = 1.19$). Mercury concentration dynamics in these size fractions are not simply reflecting changes in particulate mass. Furthermore, for any given sample, particulate mass is predominantly found in the $< 35 \mu\text{m}$ fraction, ranging from 92 to 98% during the spring, and from 94 to 98% during the summer.

Attempts to collect sufficient benthos mass for mercury detection were hampered due to the paucity of benthos in pelagic Lake Superior and their low Hg concentration. The few individuals collected in August were pooled across all stations sampled, and provided adequate material to measure MeHg concentrations in chironomid larvae (7.9 ng/gdw) and amphipods (31.9 ng/gdw) for lake-wide values. Samples of the migratory omnivore *Mysis relicta* sorted from vertical tows conducted at night in August, yielded MeHg concentrations ranging from 33 ng/gdw at Station 17 to 54.01 ng/gdw at Station 8 (Fig. 5).

4. Discussion

These results provide useful information regarding the bioaccumulation of mercury in the Lake

Superior food web. It has been well-established by previous studies in freshwater food webs that the major step in bioconcentration occurs at the initial uptake from the dissolved to particulate phase (Watras et al., 1994). We have attempted here to document such concentrations in size-fractionated seston and the zooplankton community. The results presented tend to be in the lower range of previously reported, comparable studies (Cleckner et al., in press), and mirror both the generally low concentrations of offshore mercury (both HgT and MeHg, Rolffhus et al., in press) as well as the oligotrophic nature of Lake Superior.

The decrease in both MeHg and HgT content of zooplankton observed at every station between spring and summer sampling is most probably due to the increase in zooplankton biomass without a concomitant pulse of mercury. While the summed particulate mass was similar during the two cruises, MeHg concentration in the $< 35 \mu\text{m}$ fraction, presumably food for the herbivorous zooplankton, tended to be lower during August sampling than during April. While we do not have simultaneous estimates of zooplankton standing biomass during our study, previous estimates along the same cruise tract do indicate approximately fourfold increase in zooplankton biomass during the growing season, i.e. between the April and August samples (Barbiero et al., 2001). This increase in biomass is clearly sufficient to account for the 50–70%

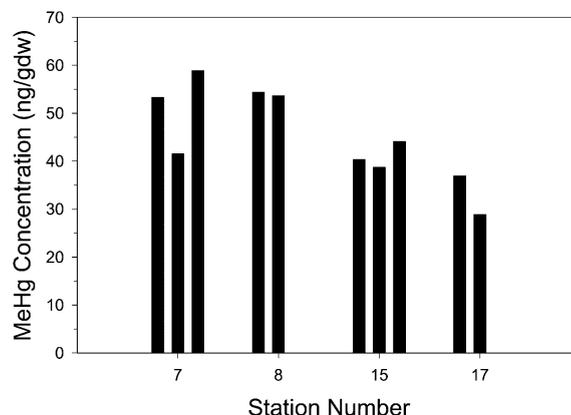


Fig. 5. Concentration of MeHg in *Mysis relicta* sampled from Lake Superior during the August 2000 cruise.

decrease in MeHg concentrations observed during this study. This is not to imply, however, that it is necessarily the zooplankton growth which is diluting the mercury; it may as well be the phytoplankton growth which supported the zooplankton biomass increase. We can assume that the zooplankton community composition changes little offshore between the spring and summer taxonomically, the real difference being ontogenetic changes (maturation) of the dominant copepod species during the growing season (Barbiero et al., 2001).

5. Conclusions

Mercury concentration and speciation in bulk zooplankton from offshore Lake Superior was found to be similar to other remote sites with communities dominated by calanoid copepods (Back and Watras, 1995). The decline in both MeHg and HgT observed at all stations strongly suggests dilution by increasing biomass during the summer growing season. This study also demonstrates the effectiveness of large volume sieving as a means of size-fractionating seston for MeHg determination, and illustrates the importance of the <35 μm fraction in terms of MeHg in seston. We also report some of the first, although limited, MeHg concentrations in benthos, including *Mysis*, from widely separated stations in Lake Superior.

Acknowledgments

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