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Assessment of mercury bioaccumulation within the pelagic food web of lakes in the western Great Lakes region

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Abstract While mercury is a health hazard to humans and wildlife, the biogeochemical processes responsible for its bioaccumulation in pelagic food webs are still being examined. Previous studies have indicated both "bottom-up" control of piscivorous fish Hg content through methylmercury.(MeHg) supply, as well as site-specific trophic factors. We evaluated ten studies from the western Great Lakes region to examine the similarity of MeHg trophic transfer efficiency within the pelagic food web, and assessed regional-scale spatial variability. Analyses of bioaccumulation and biomagnification factors between water, seston, zooplankton, and preyfish indicated that the largest increases in MeHg occurred at the base of the food web, and that the relative extent of trophic transfer was similar between sites. Positive correlations were observed between aqueous unfiltered MeHg, total Hg, and dissolved organic carbon, and measures of the efficiency of MeHg trophic transfer were consistent across widely disparate systems (both natural and experimentally manipulated) throughout North America. Such similarity suggests that the aqueous supply of MeHg is largely controlling bioaccumulation in pelagic food webs, while local, lake-specific variability can result from an array of trophic (biological) factors.

Keywords Mercury · Methylmercury · Bioaccumulation · Food web · Trophic transfer

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Introduction

Contamination of aquatic systems by mercury (Hg) has led to potentially unsafe exposures to humans and wildlife, principally through dietary intake (Wiener et al. 2003; Mergler et al. 2007; Scheuhammer et al. 2007). Such exposures have led to the issuance of fish consumption advisories in lakes, rivers, and coastal zones in North America, including statewide advisories in many of the Great Lakes states (USEPA 2009). Methylmercury (MeHg), the most bioaccumulating form, is synthesized from inorganic mercury [Hg(II)] by aquatic bacteria at oxic/anoxic boundaries such as the sediment–water interface of lakes and rivers (Hurley et al. 1995; Marvin-DiPasquale et al. 2009).

The degree to which an aquatic system is impacted by MeHg contamination is a function of a number of factors, including the rate of supply of atmospherically derived Hg(II), net rate of mercury methylation by aquatic microbes, efficiency of transport and uptake of MeHg to suspended particles, and efficiency of trophic transfer (Wiener et al. 2006; Chasar et al. 2009). The efficiency of MeHg transfer within the aquatic food web is in turn influenced by trophic (biological) factors, most notably the

number of trophic positions involved, feeding and growth rates, dietary constraints, behavior, cannibalism, and organism condition (Wong et al. 1997; Gorski et al. 2003; Wiener et al. 2003; Dittman and Driscoll 2009). For e.g., Wong et al. (1997) observed higher MeHg concentrations in benthic invertebrates in an Ontario lake where stunted benthivorous fish had too small of a gape to eat larger individuals, thus selecting for collection and measurement of larger, MeHg-laden organisms.

Studies in both freshwater and marine systems have demonstrated that the greatest degree of pelagic Hg bioaccumulation occurred between water and suspended particles, and to lesser extents between subsequent trophic levels (Herrin et al. 1998; Watras et al. 1998; Hammerschmidt and Fitzgerald 2006). The fraction of Hg present as MeHg also increases markedly with trophic position, due to the ability of MeHg to move easily across biological membranes and its preferential retention in tissues compared to inorganic forms. Recent studies in National Parks of the upper Midwest U.S. indicated that while less than 10% of the Hg in water was present as MeHg, zooplankton and benthic macroinvertebrates ranged from 20 to 100% MeHg (K. Rolfhus, unpublished data). Behavior and feeding guild traits can affect MeHg content as well; for example, predaceous dragonfly larvae from the Midwest US National Parks exhibited a higher range of percent MeHg (50–100%) than did herbivorous mayflies (10–20% MeHg). Preyfish and piscivorous fish typically range between 90 and 100% MeHg (Bloom 1992).

Despite the inherent complexity of these systems, environmental scientists and managers strive to model the factors that lead to elevated Hg content of fish in order to evaluate exposure and risk to consumers. One of the persistent questions posed in food web studies is the extent to which Hg bioaccumulation is a "bottom-up" process, forced by the production/availability of aqueous MeHg, relative to one that depends largely upon the trophic factors mentioned above that are unique to each system. In Voyageurs National Park (MN), lakes with some of the highest- and lowest-fish Hg content in the state of Minnesota lie within just kilometers of each other, having received a nearly identical supply of atmospheric Hg(II) to their watersheds areally (Wiener et al. 2006). This suggests that certain lake-specific traits must exist that differentiate these systems from each other.

It is well documented that lakes that have low pH, elevated dissolved organic matter and sulfate concentrations, large watershed area/lake volume ratios, and greater connectivity to wetlands generally have elevated MeHg in their food webs (Wiener et al. 2006). Low pH, low alkalinity lakes typically have elevated Hg in predatory fish (Wiener et al. 2003), and the mechanism(s) of control is unclear. Low pH may co-vary with MeHg and organic acids derived from adjacent wetlands, which are important sources of MeHg (Sellers et al. 2001). Similarly, low pH may alter Hg and MeHg speciation and mobility across biological membranes, either passively or actively (Kelly et al. 2003). Dissolved organic carbon (DOC) can influence MeHg production, transport, and uptake in a number of ways as well—DOC ligands can mediate transport from source areas to zones of biological productivity, strongly bind Hg(II) and/or MeHg so that it is unavailable or unable to cross biological membranes, compete with particles for the metal, decrease photo-demethylation rates of MeHg in surface waters, and even stimulate microbial activity as a carbon food source. Positive correlations between biota MeHg and DOC are often observed in drainage lakes, where elevated DOC is a tracer of wetland influence (Wiener et al. 2006).

This paper assessed the similarity in extent of trophic transfer within the pelagic food webs of lakes in the western Great Lakes region. We evaluated the degree of spatial variability in measures of trophic transfer, and examined the evidence for "bottom-up" control of MeHg bioaccumulation by aqueous MeHg. Our work focused specifically on bioaccumulation of MeHg within pelagic food webs due to the limited supply of benthic data in the literature. The efficiency of trophic transfer of MeHg was quantified in two ways—by concentration ratios between adjacent food web components, and by "biomagnification rates" as defined by δ^{15}N signatures of trophic position (also termed "biomagnification power"; Kidd et al. 1995; Atwell et al. 1998; Wyn et al. 2009). The concentration ratio metrics were expressed as logarithms of bioaccumulation factors (BAFs) and biomagnification factors (BMFs), where:

$$\mathrm{BAF} = \frac{\text{seston or zooplankton Hg } \left(\text{ng kg}^{-1}\text{dry weight}\right)}{\text{aqueous Hg } \left(\text{ng l}^{-1}\right)} \quad \left(\text{unit l kg}^{-1}\right)$$

and

$$\mathrm{BMF} = \frac{\text{particulate food web component Hg } \left(\text{ng g}^{-1}\text{ dry weight}\right)}{\text{diet Hg } \left(\text{ng g}^{-1}\text{ dry weight}\right)} \quad (\text{unitless})$$

Biomagnification factors are typically defined as the concentration of mercury in a given food web component, such as zooplankton, relative to that of its diet. For reporting purposes, we have assumed that food web components and water were at or near a steady state with each other despite the potential for temporal variation.

Our study is relevant because the majority of Hg bioaccumulation is observed in the lower food web, yet we lack an examination of the extent of regional variability and mechanisms of MeHg trophic transfer in the pelagic food web of lakes; similar studies have recently evaluated lotic systems (Brigham et al. 2009; Chasar et al. 2009).

Historically, Hg bioaccumulation studies have focused on the relations between water and piscivores, ignoring the lower food web components where most of the biomagnification occurs. A survey of older literature indicated that lower food web MeHg data were scarce (aside from water), and tended to focus on total Hg content (THg, defined by strong chemical oxidation). However, it is apparent that MeHg is the more relevant species with regards to dietary uptake, and MeHg data are becoming more abundant. We present data from ten unique mercury studies across the western Great Lakes region. This effort is part of the Great Lakes atmospheric deposition (GLAD) Program's "Integrating Multimedia Measurements of Mercury in the Great Lakes Region" Project, which strives to produce meaningful answers to important Hg cycling questions through creation of a cooperative database. Such a strategy has been successfully employed in the northeast U.S. (Evers and Clair 2005; Evers et al. 2007).

Study sites and datasets

The studies and data sets for lakes employed in this study, while in close proximity, are quite different in size, watershed area, trophic structure, eutrophy, Hg concentration, organic matter content, and hydrology (Fig. 1). Table 1 summarizes the data sets and citations utilized in this analysis. Criteria for site selection included MeHg in water, seston (suspended particles), and/or zooplankton (some studies included a variety of small preyfish), limiting the number of comprehensive data sources available. Several data sets originated from published literature, while others were contributed by our co-authors.

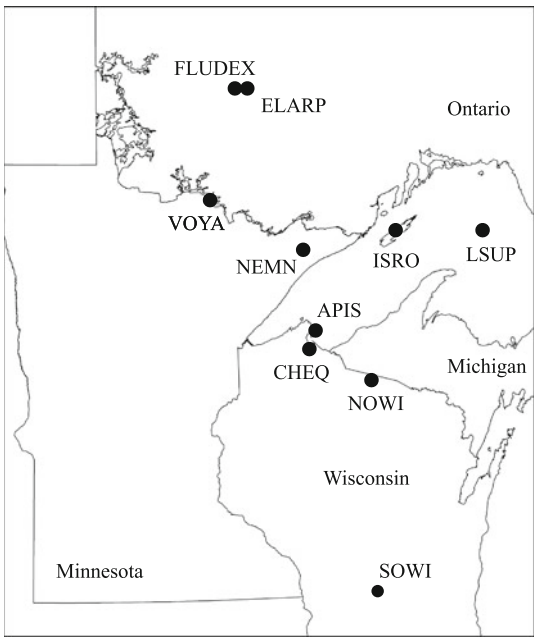

Fig. 1 Map indicating the location and acronyms of ten study sites in the western Great Lakes region

Of the ten study sites, eight were "natural" and two were experimentally manipulated systems. The experimental projects were conducted at the experimental lakes area (ELA) in northwestern Ontario in order to study the effects of inundation on mercury methylation, greenhouse gas emissions, and subsequent food web response. These projects consisted of flooding an existing boreal forest wetland (experimental lakes area reservoir project lake 979, "ELARP"; Kelly et al. 1997; St. Louis et al. 2004) and the inundation of a gradient of flooded upland soils (flooded uplands dynamics experiment, "FLUDEX"; Bodaly et al. 2004). Flooding represents a "worst-case scenario" in terms of MeHg production, as atmospherically derived legacy Hg is mobilized and methylated by microbes that suddenly have a large food supply (Bodaly and Fudge 1999). Both studies flooded experimental systems during the summer months and drew down water levels during cold months, somewhat mimicking hydroelectric reservoir hydrology. The ELARP reservoir was a 16 ha peatland complex with a 2 ha central pond. During flooding with water from an upstream lake, water levels were raised by 1.3 m to a post-flood maximum depth of 2.3 m. The FLUDEX study consisted of three shallow flow-through reservoirs (<1 ha, maximum depth ~2 m) exhibiting a gradient of soil/vegetation carbon content (31–46 Mg C ha^{-1}). Preyfish (finescale dace; *Phoxinus neogaeus*) were added to these systems after the initial flooding event and collected each fall, whereas water and plankton assemblages originated from source water from a nearby oligotrophic lake. In addition to the ELA studies, one of the 15 systems from the northern Wisconsin study (Little Rock Lake Treatment Basin) was experimentally acidified to note changes in mercury biogeochemistry and ecosystem response over time (Brezonik et al. 1993).

The natural systems included span a wide range of productivity, size, and hydrology. Open waters of lake superior ("LSUP") were the most oligotrophic, and the lake has one of the largest surface area/watershed area ratios of the study systems. Samples were collected during the early spring and late summer of 2000 from the *R/V Lake Guardian* using techniques adapted for oceanic collections (Rolfhus et al. 2003). Stations were well distributed spatially, and samples were collected from approximately10 m depth. Chequamegon Bay (WI; "CHEQ") is a southern embayment of Lake Superior that was sampled to determine the contribution of riverine inputs and marginal wetlands to the lake. Sites with and without tributary and wetland influence were examined to contrast Hg content in lower food web components. The preyfish data included from this project were age-1 yellow

Table 1 Summary of datasets evaluated in this study

Location	Citation	# Lakes	*n*	Collection year(s)	Aq. MeHg (ng l^{-1})[a]	Seston MeHg (ng g^{-1} dw)	Zooplankton MeHg (ng g^{-1} dw)	Preyfish THg (ng g^{-1} dry wt)
Apostle Islands, WI (APIS)	K. Rolfhus, unpublished	2	2	2005	1.94 (1.34–2.53)	51.6 (25.1–78.2)	375 (269–481)	525 (350–965)
Northern WI (NOWI)	Watras et al. (1998)	15	15	1994	0.28 (0.04–0.83)	33.3[e] (13–94)	57 (6–161)	485
Southern WI (SOWI)	Herrin et al. (1998)	1	2	1994–1995	0.29 (0.07–0.52)	9.4 (9.1–9.6)	143 (100–186)	385 (287–483)
Voyageurs NP, MN (VOYA)	Knights et al. (in prep.), Wiener et al. (2006)	13	23	2000–2004	0.17 (0.04–0.28)	9.1 (0.7–33.7)	120 (7–279)	483 (205–909)
Chequamegon Bay, WI (CHEQ)	K. Rolfhus, unpublished	7	7	2004	0.13 (0.05–0.18)	5.6 (1.8–11.4)	43 (22–67)	94 (61–156)
Northeast Minnesota (NEMN)	Monson and Brezonik (1998)	12	12	1992	0.11 (0.06–0.15)	–	106 (28–199)	–
Isle Royale, MI (ISRO)	Gorski et al. (2003)	2	2	1998–1999	0.08[b] (0.06–0.09)	13.4 (12.5–14.3)	53 (50–55)	105[c] (100–110)
Open Lake Superior (LSUP)	Rolfhus et al. (2003), Back et al. (2003)	1	2	2000	0.006	3.9 (3.0–4.8)	30 (18–41)	–
ELA Flooded Uplands (FLUDEX)	Hall et al. (2005), Hall et al. (2009)	3	15	1999–2003	0.45 (0.09–0.79)	61.2[d] (37.1–84.7)	275 (145–469)	1,472[c] (1,115–2,540)
ELA Flooded Wetland (ELARP)	Paterson et al. (1997, 1998)	1	2	1993–1994	0.98 (0.87–1.09)	–	423 (305–540)	1,288[c] (1,119–1,457)

[a] Unfiltered sample

[b] 0.45 μm filtered sample

[c] Dry weight MeHg concentration calculated from wet weight THg concentration using 80% water content, assuming 100% MeHg

[d] Measured during years 2 and 3 of inundation only (2000–2001)

[e] Estimated from Fig. 4b of Watras et al. (1998)

Mercury species are reported as mean (range). Location abbreviations are used throughout the paper and figures

perch (*Perca flavescens*). A second southern Lake Superior location, the apostle islands national lakeshore ("APIS"), consisted of two very shallow ($\sim$2 m) lagoons on Stockton and Outer Islands. The lagoons contained high levels of dissolved organic matter and productivity. Preyfish were collected only from Stockton Island Lagoon (northern redbelly dace, *Phoxinus eos*).

Data from a second northern Wisconsin study ("NOWI"; Watras et al. 1998) included the Little Rock Lake acidification project, which had both a reference and treatment (acidified) basin. The majority of the 15 lakes were seepage, and were the location of some of the first reliable trace-level Hg data obtained for freshwater lakes world-wide in the 1980s. The northeastern Minnesota lakes ("NEMN"; Monson and Brezonik 1998) are similar to the northern Wisconsin lakes in size, geology, and hydrology. Both the NOWI and NEMN sites are considered to be semi-remote and their Hg principally supplied by non-point atmospheric deposition. The southern Wisconsin site ("SOWI") was located at Devils Lake near the Madison, WI metro area (Herrin et al. 1998), where the entire pelagic food web was evaluated over a 2-year period. The preyfish measured in this study were mimic shiners (*Notropis volucellus*).

Data sets from two U.S. National Parks, Voyageurs (MN, "VOYA") and Isle Royale (MI; "ISRO"), were also included. Lakes from the ISRO site (northeastern Lake Superior), while considered remote, are just due east of the Thunder Bay, ON Canada urban area. The lakes vary in eutrophy, hydrology, and elevation on the island (Gorski et al. 2003). Voyageurs National Park is located along the US–Canadian border, and contains a gradient of lakes varying in productivity, size, and fish Hg content (Sorenson et al. 2005; Wiener et al. 2006). Ryan and Mukooda Lakes,

for e.g., exhibited some of the highest and lowest Hg concentrations in northern pike (*Esox lucius*), respectively, in the state of Minnesota (Minnesota Fish Contaminant Database, Minnesota Pollution Control Agency, St. Paul, MN).

Sample collection and analyses

Methods and analytical details for the majority of sites can be found in the citations within Table 1. Samples collected from APIS, CHEQ, and VOYA were analyzed for MeHg in water, seston, and bulk zooplankton, and for THg in preyfish and northern pike. Water samples were collected using standard clean techniques with a peristaltic pump from $\sim$1.0 m depth, promptly acidified, and stored cold in the dark until analysis. Seston were collected by filtering a known volume of water from 1.0 m depth through an ashed, quartz-fiber filter housed in a Teflon filter pack, and were stored frozen until analysis. A corresponding sample for suspended particulate material was collected and filtered onto a pre-weighed quartz-fiber filter to determine mercury concentrations on a per-unit-of-mass basis. Bulk zooplankton were obtained by towing an acid-cleaned, 142-μm Nitex plankton net horizontally between 1 and 4 m depth, and samples immediately frozen until processing and analysis.

Methylmercury content in water, seston filters, and bulk zooplankton were determined by distillation, derivitization with an ethylating reagent, thermal decomposition, GC separation, and analysis by cold vapor atomic fluorescence spectrophotometry (Horvat et al. 1993; Olson et al. 1997). Methods for THg analyses were adapted from Hammerschmidt et al. (1999), utilizing a strong acid digestion technique and cold vapor atomic fluorescence spectrophotometry. Detection limits for these procedures were 0.03 ng l^{-1} for aqueous MeHg and 0.8 ng g^{-1} dry weight for MeHg in solids. To verify method performance, we analyzed the standard reference material TORT-2 (National Research Council of Canada lobster hepatopancreas), assessed recoveries on standard additions, and measured precision by measuring 10% of samples in triplicate. The mean recovery of standard additions was 99.0%, while analysis of the TORT-2 standard reference material averaged 144 ng g^{-1} dry weight (the accepted 95% CI was 152 $\pm$ 13 ng g^{-1} dry weight). The mean coefficient of variation from triplicate analyses was 10.7%. Lower food web components were analyzed for $\delta^{15}N$ fractionation at the South Dakota State University Plant Science Department (Brookings, SD) with a mass spectrometer as described by Vander Zanden et al. (2000). Isotope fractionation was reported as per mil (‰) relative to an atmospheric nitrogen standard, $\delta^{15}N = (([^{15}N/^{14}N]_{sample}/([^{15}N/^{14}N]_{standard}) - 1) \times 1000$.

Consistency of methods and data

The data sets presented here have been collated from studies conducted over two decades and distances of hundreds of miles, and therefore several assumptions must be considered in data interpretation. Over time, collection and analytical methods evolve, and operationally defined Hg fractions may differ between research groups. The aqueous MeHg determinations may have been filtered or unfiltered (noted in Table 1). A variety of filter types and pore sizes were employed to collect seston, typically a glass/quartz-fiber filter or polymer membrane filter. Zooplankton samples were generally collected in bulk tows using hoop nets with Teflon jars attached to the end, but mesh sizes may have varied by research group (generally 35–300 μm; Back et al. 2003; Monson and Brezonik 1998), as well as vertical/horizontal towing technique. The degree of sample washing and handling may vary, which may include non-zooplankton particulate material that would generally decrease MeHg concentration. Preyfish taxa varied by site, but the datasets consistently sampled small cyprinid minnows or age-1 yellow perch. These perch have been shown to be reliable indicators and integrators of MeHg exposure via planktonic diet, constrained by gape size during the first year (Wiener et al. 2003); see individual citations listed in Table 1 for detailed methods used in each study.

Results and discussion

Table 2 presents a summary of the log BAF, log BMF (mean $\pm$ SE), and number of lakes reporting data within each site. It is apparent that, despite the diversity of sites, the lower food web BAFs and BMFs were similar in magnitude. The seston:water BAFs reflected the largest increase in MeHg within the pelagic food web (mean log BAF = 4.97), which was consistent with values presented in prior literature for Wisconsin lakes (4.6–6.8; Back and Watras 1995) and marine systems (4.2–5.1; Baeyens et al. 2003; Hammerschmidt and Fitzgerald 2006).

There may be merit to excluding Lake Superior (LSUP) from the analysis; the measured aqueous MeHg value employed a direct ethylation technique, where a "reactive" sub-fraction was measured by adding sodium tetraethylborate directly to the sample. This technique was used due to the extremely low MeHg concentrations in the water, and the inability to steam-distill large enough volumes of water while in the field. Thus, the measured "total" MeHg value

Table 2 Summary of log BAF and log BMF values evaluated in this study

Site	Seston:water		Zooplankton:water		Zooplankton:seston		Preyfish:zooplankton	
	log BAF (l kg^{-1})	*n*	log BAF (l kg^{-1})	*n*	log BMF	*n*	BMF	*n*
VOYA	4.60 ± 0.16^{a}	13	5.78 ± 0.07^{ab}	13	1.18 ± 0.19^{a}	13	0.69 ± 0.10^{ab}	5
ISRO	5.26^{ab}	2	5.85^{ab}	2	0.59^{ab}	2	0.30^{a}	2
APIS	4.38^{ab}	2	5.29^{ab}	2	0.91^{ab}	2	0.29	1
NEMN	–		5.95 ± 0.09^{a}	12	–		–	
LSUP	5.82	1	6.67	1	0.86	1	–	
CHEQ	4.61 ± 0.22^{ab}	5	5.63 ± 0.06^{ab}	4	0.81 ± 0.24^{ab}	3	0.32 ± 0.10^{a}	4
SOWI	4.69	1	5.85	1	1.16	1	0.44	1
NOWI	5.30 ± 0.10^{b}	13	5.40 ± 0.15^{b}	15	0.19 ± 0.11^{b}	13	0.93 ± 0.10^{b}	15
ELARP	–		5.62	1	–		0.50	1
FLUDEX	5.08 ± 0.12^{ab}	3	5.39 ± 0.04^{ab}	3	0.70 ± 0.06^{ab}	3	0.75 ± 0.04^{b}	3

n Number of lakes within each study site where paired data component was available

Superscripts refer to statistical similarity of sites based upon Tukey's multiple-comparison post-hoc test

The NOWI preyfish:zooplankton BMF mean and standard error were estimated using a mean preyfish value of 485 ng g^{-1} dry weight reported in Watras et al. (1998)

was likely an under-estimate of the true value. Underestimates of aqueous MeHg would have served to artificially increase BAF values. With Lake Superior omitted, the log seston:water BAFs were more tightly grouped (mean 4.85). A statistical comparison of seston:water log BAFs from the six sites where paired data were available from multiple lakes indicated a significant difference only between VOYA and NOWI (One-way ANOVA, SPSS Software, df = 5.32; F = 4.184, $P = 0.005$; Tukey's multi-comparison test; 38 individual lakes). While there was only weak correlation between seston:water BAF and unfiltered aqueous MeHg concentration ($r^2 = 0.12$), a stronger negative relation was observed with aqueous DOC ($r^2 = 0.40$, $r^2 = 0.46$ with APIS outlier removed; Fig. 2a). While these data were consistent with the simple diffusion of MeHg into the solid phase, speciation-related active transport may play an important role in cellular uptake to phytoplankton and bacteria (Mason et al. 1996; Watras et al. 1998).

Zooplankton:water BAFs for MeHg were also similar among the study sites (mean log BAF = 5.74; Table 2). Omission of LSUP from the analysis (for the same analytical reasons explained above) resulted in a mean log BAF of 5.64. Statistical analysis of zooplankton:water log BAFs from the seven sites where paired data were available from multiple lakes indicated a significant difference only between NEMN and NOWI (One-way ANOVA, df = 6.44; F = 2.828, $P = 0.020$; Tukey's multi-comparison test; 51 individual lakes). Zooplankton:seston and preyfish:zooplankton log BMF values were far lower than corresponding seston:water and zooplankton:water BAFs (Table 2), reflecting the importance of the lowest portions of the food web to MeHg trophic transfer. The mean log

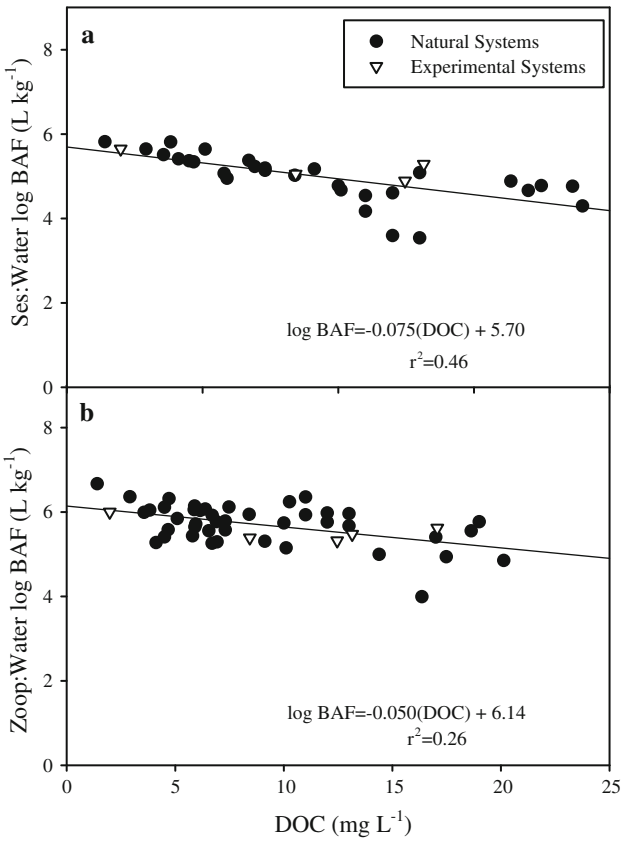

Fig. 2 **a** Relationship of seston:water log BAF (l kg^{-1}) to aqueous dissolved organic carbon (mg l^{-1}) in the western Great Lakes study sites, **b** relationship of zooplankton:water log BAF (l kg^{-1}) to aqueous dissolved organic carbon

zooplankton:seston BMF was 0.80. Statistical analysis of zooplankton:seston log BMFs from the 6 sites where paired data were available from multiple lakes indicated a

significant difference only between VOYA and NOWI (One-way ANOVA, df = 5.30; F = 5.006, $P = 0.002$; Tukey's multi-comparison test; 36 individual lakes). The mean preyfish-zooplankton log BMF for MeHg was 0.53 (Table 2), indicating that efficiency of MeHg biomagnification was slowing with trophic position. Statistical analysis of preyfish:zooplankton log BMFs from the five sites where paired data were available from multiple lakes uncovered more complexity: ISRO and CHEQ were statistically different than FLUDEX and NOWI, and all sites were not different than VOYA (One-way ANOVA, df = 4.24; F = 5.006, $P = 6.436$; Tukey's multi-comparison test; 29 individual lakes). It was apparent that trophic transfer in the lowest portions of the food web was not markedly different between sites, especially if the NOWI data were excluded. The majority of the statistically significant differences were due to the combination of high seston and low zooplankton MeHg concentrations at NOWI compared to other sites (Table 1), which may be related to region- or lake-specific plankton assemblages, timing of collection, type of sample filtration, or a methodological difference.

The observed similarity of MeHg BAFs and BMFs extended to the experimentally flooded FLUDEX and ELARP systems as well, which exhibited their highest concentrations in water, seston, and zooplankton in the first two years after inundation. In both of these cases, rapid "pulses" of newly methylated Hg were incorporated into the ecosystem from decomposing vegetation and O/A-Horizon soil organic matter, and thus behaved much differently than the stable natural systems encountered elsewhere (Hall et al. 2005, 2009). The three FLUDEX experimental reservoirs varied in soil and vegetation carbon content by 1.5-fold (Hall et al. 2005). Despite a 40-fold range in aqueous MeHg throughout the study period (0.040–1.6 ng l^{-1}), log BAFs for seston:water varied by only one unit temporally over 5 years of inundation, and only by 0.4 log units between reservoirs within a given year. Zooplankton:water BAFs declined steadily after initial flooding (log BAF year 1 post-flood: 5.93, and by year 5: 4.74). The highest concentrations in FLUDEX preyfish (finescale dace) were delayed to the second year of flooding, but showed the same subsequent pattern of decline. Similarly, the ELARP flooded wetland zooplankton:water log BAFs varied by only 0.5 units between repeated years of inundation and drawdown, despite 58-fold increases in aqueous MeHg (0.038–2.2 ng l^{-1}) and 10-fold increases in zooplankton MeHg relative to pre-flood conditions (Bodaly and Fudge 1999). Fish in the ELARP reservoir (finescale dace) increased in MeHg concentration by nearly threefold over 2 years of inundation, yet not to the extent that zooplankton did (Bodaly and Fudge 1999); corresponding preyfish–zooplankton log BMFs decreased over time. A more involved description of the plankton dynamics in these experimental reservoirs may be found in Hall et al. (2009).

Variation due to seasonality was observed in natural systems as well. Back et al. (2003) observed twofold decreases in Lake Superior seston and zooplankton MeHg concentrations between spring and summer sampling, with the authors suggesting growth dilution of both phytoplankton and zooplankton as a plausible mechanism. In contrast, increases in MeHg were observed in zooplankton between spring and summer in lakes of northeastern Minnesota (Monson and Brezonik 1998). Seasonality was also observed in Devil's Lake, WI, where MeHg building up in the hypolimnion from the summer's in situ production was released by fall mixis and rapidly scavenged by particles into the food web (Herrin et al. 1998). Observations of MeHg in edible versus inedible portions of the seston in their study suggested that MeHg diffused into particles rather than via sorption to particle surfaces.

Despite the contrasts between the ten studies, the similarity of BAF and BMF values suggests a bottom-up forcing of Hg content in the food web in the western Great Lakes region. This was supported by a common trend in aqueous unfiltered THg and MeHg versus DOC among our sites (Fig. 3). Positive correlations between both THg and MeHg and DOC were observed, with a somewhat stronger relationship between THg and DOC ($r^2 = 0.89$) than with MeHg ($r^2 = 0.69$). Strong positive correlations between MeHg and DOC were also observed by Watras et al. (1998) in the NOWI lakes and Hall et al. (2009) in the FLUDEX and ELARP systems. It is worth noting that while the experimentally modified sites were consistent with "natural" lakes with regards to THg, they tended to be elevated in MeHg. Flooding and acidification are both known to enhance MeHg content in lakes under certain circumstances.

Measures of seston:water log BAFs and zooplankton:water log BAFs regressed against DOC (Fig. 2) indicated slight negative trends that were similar in magnitude to that found among seston:water partition coefficients (K_d) by Watras et al. (1998) in the 15 NOWI lakes (seston:water log $K_d = -0.08[DOC] + 6.04$; $r^2 = 0.22$) and that observed in the FLUDEX and ELARP systems (Hall et al. 2009). Two extremely high-DOC outlier data points have been removed from Fig. 2b—Stockton Island Lagoon (APIS; which is a shallow, extremely productive lagoon with abundant epiphyton and periphyton) and Lake 979 (ELARP; an experimentally flooded wetland pond); the Stockton Lagoon outlier was also removed from Fig. 2a. The APIS lagoons produced some of the highest aqueous water column MeHg concentrations that we have observed in a semi-remote temperate forest ecosystem. Despite the extreme nature of the sites, the two outliers appeared to continue the trends of the lower-DOC sites. The negative trend supports the idea

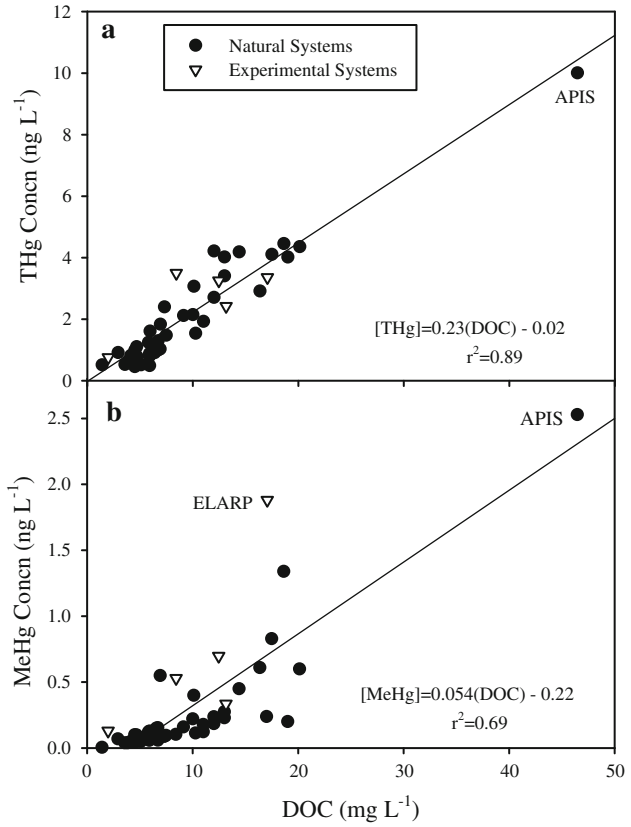

Fig. 3 **a** Relationship of unfiltered aqueous total Hg (ng l^{-1}) to dissolved organic carbon (mg l^{-1}) in the western Great Lakes study sites, **b** relationship of unfiltered aqueous MeHg (ng l^{-1}) to dissolved organic carbon

Table 3 Summary of linear regression coefficients of log(MeHg) (ng g^{-1} dry weight) versus $\delta^{15}N$ for food web components including bulk zooplankton, age-1 yellow perch, and northern pike, ranked by slope

Lake	*n*	Slope	Intercept	r^2
Ek	16	0.119[a]	2.01	0.75
Brown	16	0.125[a]	2.19	0.51
Jorgens	17	0.133[a]	1.99	0.54
Richie (ISRO)	3	0.142[a]	1.19	0.71
Tooth	18	0.143[a]	2.28	0.64
Fishmouth	14	0.182[ab]	1.48	0.91
Oslo	16	0.182[ab]	1.83	0.64
O'Leary	12	0.191[ab]	1.14	0.96
Sargent (ISRO)	3	0.204[ab]	0.80	0.66
Mukooda	19	0.206[ab]	0.82	0.80
Ryan	20	0.231[ab]	1.75	0.93
Peary	15	0.261[ab]	0.84	0.80
Locator	15	0.282[ab]	0.89	0.92
Agnes	17	0.298[ab]	0.84	0.89
Little trout	16	0.314[ab]	0.74	0.95
Net	28	0.381[b]	0.02	0.82

All lakes are from VOYA with the exception of Sargent and Richie (ISRO)—data for northern pike from these two lakes were normalized to a standard 55-cm length

Superscripts refer to statistical similarity of sites based upon comparison of 95% confidence intervals for each slope estimate

that dissolved organic matter competitively binds Hg species relative to particles at elevated DOC concentrations. Dissolved organic carbon is often linked to the Hg methylation process, as a proxy for wetland influence or as an indicator of elevated productivity that supports microbial methylation (Wiener et al. 2006). It also has been implicated as a mechanism for increased solubilization from particles, leading to the possible increase in bioavailability of inorganic Hg to methylating organisms (Aiken et al. 2003; Hall et al. 2008). Measures of pH did not yield clear trends with aqueous THg and MeHg among our study systems.

Table 3 presents a summary of MeHg biomagnification rates in the food webs of two of the study sites where stable isotope and MeHg data were available: the US National Parks VOYA and ISRO (Gorski et al. 2003). The rate is defined as the slope of a plot of tissue log[MeHg] (ng g^{-1} dry weight) versus $\delta^{15}N$ (‰). The fractionation of stable isotopes of nitrogen ($\delta^{15}N$) has been used to establish trophic position in aquatic food webs in terms of intervals of $\delta^{15}N = 3.4‰$ (Stewart et al. 2008). Northern pike and yellow perch were presented as THg concentration (assuming 100% as MeHg, and converted from wet-weight to dry weight using 80% water content), and zooplankton as actual measured MeHg values. Northern pike concentrations at VOYA were raw data, while the ISRO northern pike were normalized by linear regression to a concentration at a common 55-cm length. As expected, MeHg concentrations increased with increasing trophic position. While the VOYA data were not synoptic (northern pike and age-1 yellow perch data were collected in 2001–2002, zooplankton in 2002–2003), slopes observed for VOYA lakes (mean ± SE: 0.22 ± 0.02) and ISRO (mean 0.17; Gorski et al. 2003), were similar to values reported in the literature in acidic and mining-impacted lakes (0.19–0.23; Stewart et al. 2008; Wyn et al. 2009), streams (0.14–0.27; Chasar et al. 2009) and marine environments (0.16–0.28; Atwell et al. 1998; Senn et al. 2010). Statistical comparison of the regression slopes indicated that individual lakes were significantly different in terms of MeHg trophic transfer efficiency (ANCOVA, df = 15.213; F = 6.571, $P < 0.001$). These findings suggest that while food webs are transferring MeHg in a fairly consistent manner regionally, trophic factors such as organism growth rate and feeding behavior appear to have lake-specific influence within a given site.

Our findings utilizing two metrics of MeHg accumulation (BAF, BMF, and biomagnification rate) indicate that a widely disparate collection of aquatic systems spanning a

multi-state region and several years of collection have similar MeHg bioaccumulation traits within the pelagic food web. Stewart et al. (2008) came to the same conclusions in a mining-impacted reservoir in California, observing that bioaccumulation factors were consistent in both benthic and pelagic food webs. They further stated that MeHg concentrations at the base of the food web were the best predictor of piscivorous fish Hg content. Wiener et al. (2006) concluded that lower food web factors (a combination of pH, sulfate ion concentration, and degree of wetland connectivity) were the principal factors controlling Hg accumulation in predator fishes of VOYA. Both Chasar et al. (2009) and Brigham et al. (2009) stated that MeHg in fish and invertebrates from a broad array of US streams are strongly positively correlated with filtered fractions of aqueous MeHg, DOC, specific UV absorbance, and percent wetland in the watershed. Further, Wyn et al. (2009) concluded that MeHg uptake at the base of the food web was more important than trophic factors in low-pH lakes of Nova Scotia, Canada. Statistical analyses of our MeHg trophic transfer metrics indicated that while significant differences existed between sites (principally NOWI), they bioaccumulated MeHg in the lower portions of the pelagic food web to a similar extent. Within a given site, other lake-specific trophic (biological) factors may have contributed to variability (e.g., organism spatial/temporal distribution, behavior, feeding, metabolic constraints, life history, etc.). The importance of such trophic factors may be more pronounced in comparisons of aquatic systems that are similar geochemically and hydrologically. The similarity of our study sites to others in the literature suggest that the lake-specific traits that promote the production and mobilization of aqueous MeHg are controlling bioaccumulation in a "bottom-up" fashion within the aquatic food web. These factors include atmospheric deposition rate, extent of watershed and marginal wetland influence, sulfate content, pH, and organic matter supply.

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References

Aiken G, Haitzer M, Ryan JN, Nagy K (2003) Interactions between dissolved organic matter and mercury in the Florida Everglades. J Phys IV 107:29–32

Atwell L, Hobson KA, Welch HE (1998) Biomagnification and bioaccumulation of mercury in an arctic marine food web: insights from stable nitrogen isotope analysis. Can J Fish Aquat Sci 55:1114–1121

Back RC, Watras CJ (1995) Mercury in zooplankton of northern Wisconsin lakes: taxonomic and site-specific trends. Water Air Soil Pollut 80:931–938

Back RC, Gorski PR, Cleckner LB, Hurley JP (2003) Mercury content and speciation in the plankton and benthos of Lake Superior. Sci Tot Environ 304:349–354

Baeyens W, Leermakers M, Papina T, Saprykin A, Brion N, Noyen J, De Gieter M, Elskens M, Goeyens L (2003) Bioconcentration and biomagnification of mercury and methylmercury in North Sea and Scheldt Estuary fish. Arch Environ Contam Toxicol 45:498–508

Bloom NS (1992) On the chemical form of mercury in edible fish and marine invertebrate tissue. Can J Fish Aquat Sci 49:1010–1017

Bodaly RA, Fudge RJP (1999) Uptake of mercury by fish in an experimental boreal reservoir. Arch Environ Contam Toxicol 37:103–109

Bodaly RA, Beaty KG, Hendzel LH, Majewski AR, Paterson MJ, Rolfhus KR, Penn AF, St. Louis VL, Hall BD, Matthews CJD, Cherewyk KA, Mailman M, Hurley JP, Schiff SL, Venkiteswaran JJ (2004) Experimenting with hydroelectric reservoirs. Environ Sci Technol 38:347A–352A

Brezonik PL, Eaton JG, Frost TM et al (1993) Experimental acidification of Little Rock Lake, Wisconsin: chemical and biological changes over the pH range 6.1 to 4.7. Can J Fish Aquat Sci 50(5):1101–1121

Brigham ME, Wentz DA, Aiken GR, Krabbenhoft DP (2009) Mercury cycling in stream ecosystems. 1. Water column chemistry and transport. Environ Sci Technol 43:2720–2725

Chasar LC, Scudder BC, Stewart AR, Bell AH, Aiken GR (2009) Mercury cycling in stream ecosystems. 3. Trophic dynamics and methylmercury bioaccumulation. Environ Sci Technol 43:2733–2739

Dittman JA, Driscoll CT (2009) Factors influencing changes in mercury concentrations in lake water and yellow perch (*Perca flavescens*) in Adirondack lakes. Biogeochem 93:179–196

Evers DC, Clair TA (2005) Mercury in northeastern North America: a synthesis of existing databases. Ecotoxicology 14:7–14

Evers DC, Han YJ, Driscoll CT, Kamman NC, Goodale MW, Lambert KF, Holsen TM, Chen CY, Clair TA, Butler T (2007) Identification and evaluation of biological hotspots of mercury in the northeastern US and eastern Canada. Bioscience 57:29–43

Gorski PR, Cleckner LB, Hurley JP, Sierzen ME, Armstrong DE (2003) Factors affecting enhanced mercury bioaccumulation in inland lakes of Isle Royale National Park, USA. Sci Total Environ 304:327–348

Hall BD, St. Louis VL, Rolfhus KR, Bodaly RA, Beaty KG, Paterson MJ, Peech Cherewyk KA (2005) The impact of reservoir creation on the biogeochemical cycling of methyl and total mercury in boreal upland forests. Ecosystems 8:248–266

Hall BD, Aiken GR, Krabbenhoft DP, Marvin-Dipasquale M, Swarzenski CM (2008) Wetlands as principal zones of methylmercury production in southern Louisiana and the Gulf of Mexico region. Environ Pollt 154:124–134

Hall BD, Cherewyk KA, Paterson MJ, Bodaly RA (2009) Changes in methylmercury concentrations in zooplankton from four

experimental reservoirs with differing amounts of carbon in the flooded catchments. Can J Fish Aquat Sci 66:1910–1919

Hammerschmidt CR, Fitzgerald WF (2006) Bioaccumulation and trophic transfer of methylmercury in Long Island Sound. Arch Environ Contam Toxicol 51:416–424

Hammerschmidt CR, Wiener JG, Frazier BE, Rada RG (1999) Methylmercury content of eggs in yellow perch related to maternal exposure in four Wisconsin lakes. Environ Sci Technol 33:999–1003

Herrin RT, Lathrop RC, Gorski PR, Andren AW (1998) Hypolimnetic methylmercury and its uptake by plankton during fall destratification: a key entry point of mercury into lake food chains? Limnol Oceanogr 43(7):1476–1486

Horvat M, Liang L, Bloom NS (1993) Comparison of distillation with other current isolation methods for the determination of methyl mercury-compounds in low-level environmental samples. 2. Water. Anal Chim Acta 282:153–168

Hurley JP, Benoit JM, Babiarz CL, Shafer MM, Andren AW, Sullivan JR, Hammond R, Webb DA (1995) Influences of watershed characteristics on mercury levels in Wisconsin rivers. Environ Sci Technol 29:1867–1875

Kelly CA, Rudd JWM, Bodaly RA, Roulet NT, St. Louis VL, Heyes A, Moore TR, Schiff S, Aravena R, Scott KJ, Dyck B, Harris R, Warner B, Edwards G (1997) Increases in fluxes of greenhouse gases and methyl mercury following flooding of an experimental reservoir. Environ Sci Technol 31:1334–1344

Kelly CA, Rudd JWM, Holoka MH (2003) Effect of pH on mercury uptake by an aquatic bacterium: implications for Hg cycling. Environ Sci Technol 37:2941–2946

Kidd KA, Hesslein RH, Fudge RJP, Hallard KA (1995) The influence of trophic level as measured by δ^{15}N on mercury concentration in freshwater organisms. Water Air Soil Pollut 80:1011–1015

Marvin-DiPasquale M, Lutz MA, Brigham ME, Krabbenhoft DP, Aiken GR, Orem WH, Hall BD (2009) Mercury cycling in stream ecosystems. 2. Benthic methylmercury production and bed sediment pore water partitioning. Environ Sci Technol 43: 2726–2732

Mason RP, Reinfelder JR, Morel FMM (1996) Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. Environ Sci Technol 30:1835

Mergler D, Anderson HA, Chan LHM, Mahaffey KR, Murray M, Sakamoto M, Stern AH (2007) Methylmercury exposure and health effects in humans: a worldwide concern. Ambio 36:3–11

Monson BA, Brezonik PL (1998) Seasonal patterns of mercury species in water and plankton from softwater lakes in Northeastern Minnesota. Biogeochemistry 40:147–162

Olson ML, Cleckner LB, Hurley JP, Krabbenhoft DP, Heelan TW (1997) Resolution of matrix effects on analyses of total and methyl mercury in aqueous samples from the Florida Everglades. Fres J Analyt Chem 358:392–396

Paterson MJ, Findlay D, Beaty KG, Findlay W, Schindler EU, Stainton MP, McCullough G (1997) Changes in the planktonic food web of a new experimental reservoir. Can J Fish Aquat Sci 54:1088–1102

Paterson MJ, Rudd JWM, St. Louis V (1998) Increases in total and methylmercury in zooplankton following flooding of a peatland reservoir. Environ Sci Technol 32:3868–3874

Rolfhus KR, Sakamoto HE, Cleckner LB, Stoor RW, Babiarz CL, Back RC, Manolopoulos H, Hurley JP (2003) The distribution and fluxes of total and methylmercury in Lake Superior. Environ Sci Technol 37:865–872

Scheuhammer AM, Meyer MW, Sandheinrich MB, Murray MW (2007) Effects of environmental methylmercury on the health of wild birds, mammals, and fish. Ambio 36:12–18

Sellers P, Kelly CA, Rudd JWM (2001) Fluxes of methylmercury to the water column of a drainage lake: the relative importance of internal and external sources. Limnol Oceanogr 46:623–631

Senn DB, Chesney EJ, Blum JD, Bank MS, Maage A, Shine JP (2010) Stable isotope (N, C, Hg) study of methylmercury sources and trophic transfer in the northern Gulf of Mexico. Environ Sci Technol 44:1630–1637

Sorenson JA, Kallemyn LW, Sydor M (2005) Relationship between mercury accumulation in young-of-the-year yellow perch and water-level fluctuations. Environ Sci Technol 39:9237–9243

St. Louis VL, Rudd JWM, Kelly CA, Bodaly RA, Harris R (2004) The rise and fall of mercury methylation in an experimental reservoir. Environ Sci Technol 38:1348–1358

Stewart AR, Saiki MK, Kuwabara JS, Alpers CN, Marvin-DiPasquale M, Krabbenhoft DP (2008) Influence of plankton mercury dynamics and trophic pathways on mercury concentrations of top predator fish of a mining-impacted reservoir. Can J Fish Aquat Sci 65:2351–2366

US Environmental Protection Agency (2009) Biennial national listing of fish advisories, 2008. Publication EPA-823-F-09-007

Vander Zanden MJ, Shuter BJ, Lester NP, Rasmussen JB (2000) Within- and among-population variation in the trophic position of a pelagic predator, lake trout (*Salvelinus namaycush*). Can J Fish Aquat Sci 57(4):725–731

Watras CJ, Back RC, Halvorsen S, Hudson RJM, Morrison KA, Wente SP (1998) Bioaccumulation of mercury in pelagic freshwater food webs. Sci Total Environ 219:183–208

Wiener JG, Krabbenhoft DP, Heinz GH, Scheuhammer AM (2003) Ecotoxicology of mercury. In: Hoffman DJ, Rattner BA, Burton GA Jr, Cairns J Jr (eds) Handbook of ecotoxicology, 2nd edn. CRC Press, Boca Raton, pp 409–463

Wiener JG, Knights BC, Sandheinrich MB, Jeremiason JD, Brigham ME, Engstrom DR, Woodruff LG, Cannon WF, Balogh SJ (2006) Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): importance of atmospheric deposition and ecosystem factors. Environ Sci Technol 40:6261–6268

Wong AHK, McQueen DJ, Williams DD, Demers E (1997) Transfer of mercury from benthic invertebrates to fishes in lakes with contrasting fish community structures. Can J Fish Aquat Sci 54: 1320–1330

Wyn B, Kidd KA, Burgess NM, Curry RA (2009) Mercury biomagnification in the food webs of acidic lakes in Kejimkujik National Park and National Historic Site, Nova Scotia. Can J Fish Aquat Sci 66:1532–1545

Knights BC, Jeremiason JD, Wiener JG, Sandheinrich MB, Rolfhus KR, Brigham ME and Kallemeyn LW (in preparation) The influence of trophic factors on mercury in northern pike from interior lakes in Voyageurs National Park, USA