Increases in Total and Methylmercury in Zooplankton following Flooding of a Peatland Reservoir[§]

MICHAEL J. PATERSON,*.[†] JOHN W. M. RUDD,[†] AND VINCENT ST. LOUIS[‡]

Department of Fisheries and Oceans, Freshwater Institute, 501 University Crescent, Winnipeg, Manitoba, Canada R3T 2N6, and Department of Biological Sciences, CW 405 Biological Sciences Centre, University of Alberta, Edmonton, Alberta, Canada T6G 2E9

Fish from new reservoirs often have elevated concentrations of methylmercury (MeHg) that they primarily accumulate from food such as zooplankton. The objectives of this research were (i) to determine the effect of reservoir creation on total mercury (THg) and MeHg in zooplankton and (ii) to examine how variations in community structure and water chemistry affect MeHg bioaccumulation by zooplankton. Beginning in June 1992, we measured concentrations of THg and MeHg in zooplankton from an experimental reservoir (L979) and an unmanipulated reference pond (L632). After flooding of L979 in June 1993, mean concentrations of MeHq in zooplankton increased from 32 to >300 ng g⁻¹ dw and THg increased from 87 to $>500 \text{ ng g}^{-1} \text{ dw}$. Annual fluxes of MeHg through the zooplankton community increased 10–100× after impoundment. MeHg concentrations in zooplankton, seston, and water were strongly correlated with each other (r > 0.92). Bioaccumulation factors relating MeHg in zooplankton to MeHg in water or seston did not change after impoundment, despite large changes in water chemistry and zooplankton community structure. Concentrations of Hg in zooplankton from Lake 632 did not change dramatically over the 4 years of study.

Introduction

One of the most important environmental problems affecting new reservoirs is the contamination of fish with methylmercury (MeHg) (1). Decomposition of flooded terrestrial vegetation and soil carbon stimulates bacterial methylation that converts inorganic Hg to more toxic MeHg that accumulates and biomagnifies in aquatic food webs (2, 3). Concern about human consumption of fish contaminated with MeHg has led to the closure of subsistence, sport, and commercial fisheries in many reservoirs with resultant social upheaval and economic loss (4). High concentrations of MeHg have also been found in fish from many natural lakes.

Under most conditions, fish obtain MeHg almost exclusively from their diet (5). Zooplankton are consumed by many adult and juvenile fish and, consequently, are an important source of MeHg in most freshwater food webs. Information is limited on changes in zooplankton MeHg concentrations following the creation of new reservoirs (1, 6, 7), and factors affecting bioaccumulation of MeHg by zooplankton are poorly understood. The creation of new reservoirs typically results in large changes in water chemistry and plankton community structure (8), and the effects of these variations on MeHg accumulation by zooplankton are unclear. It is well-known that concentrations of MeHg in fish vary with water chemistry, fish community composition, and diet (9-11). Variations in water chemistry and plankton community structure may also affect MeHg accumulation by zooplankton (12, 13). For example, changes in dissolved organic carbon (DOC), pH, temperature, and trophic conditions may affect MeHg accumulation by zooplankton (14-17). Because diet is the main route of uptake by fish, any factors that strongly affect MeHg concentrations in zooplankton are also likely to affect MeHg uptake by fish.

This study examines changes in Hg accumulation by zooplankton collected before and after the creation of a small experimental reservoir in a boreal wetland. The objectives of this research were (i) to determine the effect of reservoir creation on total mercury (THg) and MeHg concentrations and fluxes in the zooplankton community and (ii) to examine how changes in plankton community structure and water chemistry affected MeHg bioaccumulation by zooplankton. We focus mostly on MeHg because this is the most toxic form of Hg and because it predominates in fish.

Site Description and Methods

Lake 979 (L979) is surrounded by peatland and is immediately downstream of lake 240 at the Experimental Lakes Area (ELA) in northwestern Ontario [see figures in Kelly et al. (*3*) and Paterson et al. (*8*)]. After 1 year of pre-impoundment study of zooplankton, the water level of L979 was raised 1.3 m between June 28 and July 5, 1993, by closing a dam constructed at the outflow. Flooding inundated the surrounding peatland, increased the maximum depth from 1.2 to 2.5 m, increased the lake area from 2.4 to 16 ha, and led to a $9 \times$ increase in lake volume. Each year the water level was drawn down 1 m in late September–early October to mimic water regimes in many northern hydroelectric reservoirs. In May of each year the pond was reflooded.

L979 was oligotrophic prior to impoundment, with low biomasses of bacteria, phytoplankton, and zooplankton similar to other ELA lakes (Table 1). The oligotrophic nature of L979 was partly a result of rapid flushing of the pond by water from upstream L240 (8). Impoundment of L979 resulted in elevated concentrations of phosphorus, DOC, and other nutrients especially over flooded peat (8). After impoundment, oxygen concentrations in water overlying flooded areas often declined to $<1 \text{ mg L}^{-1}$, and pH decreased from a pre-impoundment mean of 6.6 to as low as 5.3 at the center buoy.

Impoundment of L979 strongly affected plankton community structure [summarized in Paterson et al. (8)]. Mean zooplankton biomass increased by more than $10 \times$ from 27 μ g L⁻¹ dry weight (dw) before impoundment to approximately 300μ g L⁻¹ dw after flooding in 1993 and 1994 (Table 1). During the third summer of flooding (1995), mean zooplankton biomass declined to 82 μ g L⁻¹ dw. The pre-impoundment zooplankton community was composed primarily of small species (<500 μ m in length), such as *Bosmina longirostris* (Müller). After flooding, zooplankton biomass was dominated by a single species of Cladocera, *Daphnia rosea* Sars, which had a mean length >500 μ m. Bacterial biomass also

^{*} To whom inquiries should be addressed. E-mail: patersonm@ dfo-mpo.gc.ca; phone: (204)984-4508; fax: (204)984-2404.

[†] Freshwater Institute.

[‡] University of Alberta.

 $[\]ensuremath{{}^{\$}}$ Experimental Lakes Area Reservoir Project (ELARP) Contribution No. 49.

TABLE 1. Means and Ranges (in Parentheses) for Water Chemistry, Bacteria, and Plankton in Lakes 979 and 632, 1992–1995

. . . .

flood -1993 2-1.0) 0.14	po 1993 (0.1-0.4) 0.	0st-impoundment 1994	1995 80 (0.7. 14 E)	L632 1992–1995
- 1993 2-1.0) 0.14	1993 (0.1–0.4) 0.	1994	1995 80 (0 7 14 5)	1992-1995
2-1.0) 0.14	(0.1-0.4) 0.	(61 (0 2 2 2) /	00 (0 7 1 / F)	
$\begin{array}{cccc} 4-0.8) & 0.44 \\ 1-1.3) & 1.30 \\ 10) & 12.2 \\ 0-1170) & 1031 \\ -6.9) & 6.1 (\\ 116) & 297 \\ -4) & 4.9 (\end{array}$	(0.3-0.7) 0. (0.7-3.0) 0. (11-18) 1! (830-1210) 9 5.9-6.6) 6. (130-550) 32 2.3-8.4) 6.	$\begin{array}{c} 1.01 \\ 0.56 \\ 0.4-0.8) \\ 1.43 \\ 0.2-0.7) \\ 0.57 \\ (7-24) \\ 0.57 \\ (660-1540) \\ 1.5 \\ 0.4 \\ (6.0-6.9) \\ 6.26 \\ (23-511) \\ 0.4 \\ (1.0-12.7) \\ 3 \end{array}$	$\begin{array}{c}$	0.34 (0.06-3.01) 0.62 (0.3-1.5) nd 7.9 (4-20) 1032 (160-1700) 6.0 (5.1-6.4) 152 (15-495) 3.2 (0.4-12.4)
	1-1.3) 1.30 10) 12.2 0-1170) 1031 -6.9) 6.1 (16) 297 -4) 4.9 (awdown, nd, no	1-1.3) 1.30 (0.7-3.0) 0 10) 12.2 (11-18) 1 0-1170) 1031 (830-1210) 9 -6.9) 6.1 (5.9-6.6) 6 16) 297 (130-550) 3 -4) 4.9 (2.3-8.4) 6 awdown, nd, not determined; wy	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

increased dramatically from 0.14 mg L⁻¹ wet weight (ww) in 1992 to >1 mg L⁻¹ ww in 1993 (Table 1). In 1994 and 1995, bacterial biomass decreased but was still 4–6× greater than in pre-impoundment years. Despite increases in nutrient concentrations after flooding, mean phytoplankton biomass decreased from 0.5 mg L⁻¹ ww in 1992 to 0.14 mg L⁻¹ ww in 1993, presumably as a result of increased grazing by zooplankton. In 1994 and 1995, phytoplankton biomass was elevated above pre-impoundment levels, with mean concentrations of 0.6 and 4.8 mg L⁻¹ ww, respectively.

Lake 632 (L632; maximum depth = 1.2 m; surface area = 0.86 ha) was the reference system for this study and is surrounded by a headwater wetland dominated by Sphagnum spp., leatherleaf (Chamaedaphne calyculata L. Moench), and black spruce (Picea mariana Mill. BSP) (18). L632 is oligotrophic (Table 1) and was unmanipulated, except for the inadvertent introduction of finescale dace (Chrosomus neogaeus Cope) in 1992. The zooplankton community was predominantly composed of Daphnia pulex Leydig, B. longirostris, Diaptomus leptopus Forbes, and Mesocylops edax Forbes in 1992 and 1993. In July 1994, D. pulex and D. leptopus almost disappeared from the pond, presumably as a result of increased planktivory by dace. After this time, the zooplankton community was almost exclusively made up of B. longirostris and M. edax. Mean annual zooplankton biomass did not change substantially over the 4 years of study.

Sample Collection. Zooplankton samples for Hg analysis were collected weekly during the ice-free season from June 1992 to October 1995 using horizontal tows of 80- and 400- μ m nets. We focus on results obtained from the 80- μ m samples because these are most representative of the zooplankton community as a whole. On many occasions, we were unable to obtain sufficient biomass for Hg analyses with the 400- μ m net.

After collection, net contents were stored and frozen in plastic whirl-pak bags. A small subsample from each net tow was preserved in 3% sugar-formalin for determination of the relative biomass of different species using techniques described in Paterson et al. (8). On three occasions in 1995, we measured concentrations of MeHg in *Chaoborus* spp., an insect predator on zooplankton. *Chaoborus* samples were collected with a 150- μ m net, at least 1 h after sunset. Animals were picked from samples using acid-cleaned forceps and frozen. *Chaoborus* were not identified to species, but *C. flavicans* and *C. trivittatus* occurred in emergence samples collected from L979 in 1994 (19).

Water samples for THg and MeHg determinations were collected at least every 2 weeks at the center buoy or outflow of lakes 979 and 632 using the "clean hands, dirty hands" technique (*20*). MeHg concentrations in water were not available for L632 in 1995. On 31 occasions, samples from

L979 were passed through a 0.45- μ m filter to distinguish operationally defined particulate and dissolved fractions. Particulate concentrations were normalized (ng g⁻¹ dw) to total suspended solid concentrations (TSS) measured on samples collected at the same time. On 14 of the 31 occasions, TSS was not directly determined but was estimated using suspended C concentrations and a regression equation developed from L979. Particulate and dissolved MeHg were not measured in L632. Water chemistry (nutrients, pH, oxygen) and biomasses of phytoplankton, bacteria, and zooplankton were determined using methods described in Stainton et al. (*21*) and Paterson et al. (*8*).

Hg Determinations. Zooplankton were freeze-dried, ground with an acid-washed glass mortar and pestle, subsampled, and weighed. MeHg in zooplankton was measured as organic Hg, which we found to be equivalent to MeHg (see below). THg and organic Hg were determined with cold-vapor atomic absorption spectrophotometry (CV-AAS) using the methods of Armstrong and Uthe (*22*) and Malley et al. (*23*). Determinations of THg and organic Hg were made in duplicate whenever sufficient biomass was available. The average coefficient of variation (CV) for organic Hg measures in 50 replicated samples was 17%, comparable to CVs reported in other studies using gas chromatography and cold-vapor atomic fluorescence spectroscopy (GC–CVAFS) (*16, 17*). All zooplankton Hg concentrations are expressed as ng g^{-1} dry weight.

Organic Hg and MeHg concentrations were compared in subsamples from eight zooplankton collections from lakes 979 and 632. MeHg concentrations were determined by Flett Research Ltd., Winnipeg, MB, using GC-CVAFS after aqueous phase ethylation (15). The resulting organic Hg and MeHg concentrations were found to be statistically equivalent (paired *t*-test; p > 0.2), within the power of the test. With the type I error rate set at 0.05, we could detect a 15% difference in Hg concentrations with a power of approximately 0.75 (24). Organic Hg concentrations were highly correlated with MeHg determinations ($r^2 = 0.97$; p < 0.001), and the y-intercept and slope of the resulting regression line were not statistically different from 0 and 1, respectively (ttests; p < 0.01). Certified reference materials from the National Research Council of Canada (DORM-1, DOLT-2) were also analyzed for THg and organic Hg along with each group of samples. In all cases, THg and organic Hg concentrations for reference materials fell within certified ranges for THg and MeHg. Taken together, these results indicate that the organic Hg and MeHg measures were equivalent.

Concentrations of Hg in water and seston samples were determined using GC–CVAFS (*25, 26*). Larger zooplankton were removed from water samples with a pipet before Hg analyses. For both water and zooplankton, inorganic Hg

was determined as the difference between THg and MeHg determinations. Net MeHg fluxes through the zooplankton community were estimated as the product of MeHg concentrations in zooplankton and daily productivity estimates for zooplankton. Zooplankton productivity was determined using techniques outlined in Paterson et al. (8).

Bioaccumulation and Biomagnification. Traditionally, bioaccumulation of Hg has been estimated using a bioaccumulation factor (BAF_{diss}), defined as the ratio of the concentration of MeHg in seston or zooplankton (ng g $^{-1}$ dw) and the concentration of MeHg in the dissolved phase (ng mL⁻¹). For zooplankton, we also estimated BAF_{unfilt}, using MeHg concentrations in unfiltered water samples, to extend the size of our data set. In all cases, interpretations based on BAF_{diss} and BAF_{unfilt} were identical. The ratio of MeHg in zooplankton (ng g^{-1} dw) to MeHg in seston (ng g^{-1} dw) was used as a measure of biomagnification (BMF) within the planktonic food chain. BAFs are ratios and, consequently, have many undesirable properties for statistical analysis (27). Below, we depict changes in BAFs graphically for ease of interpretation and to facilitate comparisons with other studies. For statistical analyses, we used the residuals from regressions relating concentrations of MeHg in zooplankton or seston to MeHg concentrations in water. We used model II regression (28) because the independent and dependent variables were probably measured with comparable error. Overall, interpretations based on regression residuals or BAFs were similar.

Results and Discussion

HgConcentrations in Zooplankton. Prior to impoundment, concentrations of MeHg in zooplankton collected with the 80- μ m net varied between 11 and 54 ng g⁻¹ (mean = 32), and THg concentrations were between 60 and 238 ng g⁻¹ (mean = 87) (Figure 1; Table 2). Within 6 weeks of flooding, average MeHg concentrations increased $10 \times$ and often exceeded 300 ng g^{-1} . THg concentrations increased 5× to >500 ng g^{-1} . Hg concentrations in zooplankton remained elevated through the first 3 years of impoundment. MeHg concentrations in zooplankton were strongly correlated with instantaneous hydrologic flushing rates (r = -0.8; p < 0.0001) because water and zooplankton were diluted by inflows with low MeHg concentrations from upstream L240. In each year, concentrations of MeHg were low in spring because of high flushing rates following snowmelt and low methylation rates associated with colder water temperatures.

Post-impoundment concentrations of THg and MeHg in zooplankton far exceeded observations from unpolluted, unimpounded lakes both in the ELA and the literature. In July of 1993 and 1996, the mean MeHg concentration in zooplankton collected from 31 ELA lakes was 57.4 ng g⁻¹ (range 4–126 ng g⁻¹) (*29*). Concentrations of MeHg and THg in preimpoundment L979 and L632 were also similar to those reported from other pristine lakes in North America (*6*, *7*, *13*, *17*, *30–32*). No large changes in zooplankton Hg concentrations similar to those observed in L979 were seen in L632 (Figure 1).

Our study is the first to document changes in concentrations of Hg in zooplankton collected both before and after the creation of a new reservoir. The results from L979 parallel previous findings of elevated concentrations of MeHg in water, fish, and macroinvertebrates collected from new reservoirs (e.g., *1* and *33*). Zooplankton collected from new reservoirs in northern Quebec and Finland have also been found to have elevated concentrations of MeHg as compared to zooplankton from nearby lakes (*6*, *7*, *34*). Maximum concentrations of MeHg in zooplankton from Quebec reservoirs were >400 ng g⁻¹ dw, similar to maximum concentrations observed in L979 (*6*, *7*). Hg concentrations in zooplankton from the pelagic zone of older reservoirs (>20



FIGURE 1. Changes in concentrations of THg and MeHg in zooplankton collected with the 80- μ m net in lakes 979 and 632. Open squares indicate MeHg concentrations in *Chaoborus* spp. collected from L979 in 1995.

years after impoundment) are usually similar to unimpounded lakes (1, 7, 29).

MeHg/THg Ratios in Zooplankton. The MeHg/THg ratio in zooplankton from L979 increased from a pre-impoundment mean of 24% to 54% after flooding (Table 2). MeHg/ THg ratios also increased in water samples collected after impoundment (*35*). Despite the increases observed in L979, the post-impoundment MeHg/THg ratio for zooplankton was similar to that observed in L632 (42%). Possibly, higher MeHg/THg ratios are related to high DOC concentrations found in L632 and post-impoundment L979. Our findings confirm previous observations that MeHg/THg ratios may vary considerably in zooplankton (*6, 12, 15*).

Storage and Fluxes of MeHg in the Zooplankton Community. Because both zooplankton biomass and MeHg concentrations increased after impoundment of L979, the total amount of MeHg stored in zooplankton per liter of water increased nearly 100× from 0.001 ng L^{-1} in 1992 to 0.09 ng L^{-1} in 1993 and 1994 (Table 3). Mean concentrations of MeHg per liter in zooplankton were even higher (on average, $6\times$) over flooded peat, where zooplankton populations flourished (8). MeHg in zooplankton was <1% of MeHg concentrations in unfiltered water before impoundment (Table 3), similar to other unimpounded lakes and L632 (31, 36). After flooding in 1993 and 1994, MeHg in zooplankton from L979 made up>5% of unfiltered MeHg values. By 1995, mean zooplankton biomass and the pool of MeHg stored in zooplankton decreased by >50%, but the size of this pool was still $40 \times$ larger than in 1992.

Net fluxes of MeHg through the zooplankton community represent an upper limit on the amount available to fish from zooplankton. In L979, MeHg fluxes increased approximately $60 \times$ after impoundment in 1993 and 1994 (Table

TABLE 2. Time-Weighted Mean Concentrations (ng g^{-1} dw) of MeHg, THg, and MeHg/THg Ratios in Zooplankton and Water Collected from Lakes 979 and 632

	L979					
	pre-flood 1992–1993		post-impoundment		L632	
		1993	1994	1995	1992-1995	
zooplankton MeHg (80 μ m)	32 (11-54)	346 (79–692) 410 (126–658)	319 (37–615) 520 (68–1002)	300(29-664)	102 (7–293) 102 (17–224)	
zooplankton THg ($400 \ \mu$ m)	122 (60–191)	578 (238–730)	619 (171–957)	502 (270-1173)	222 (45-504) 235 (32-490)	
zooplankton % MeHg ($400 \ \mu$ m) zooplankton % MeHg ($400 \ \mu$ m)	24 (16–39)	48 (38–49)	49 (22–68)	62 (52-94)	42 (13-70) 47 (24-78)	
water % MeHg	7 (2–23)	35 (12–58)	32 (8–67)	34 (8–68)	10 (5-21)	
⁸ Averages do not include data colleg	tod after drawdown	THawas not moasur	od in 400 um samplos	from 1 070 bocauso of ir	sufficient biomas	

^a Averages do not include data collected after drawdown. THg was not measured in 400 μm samples from L979 because of insufficient biomass. Ranges are in parentheses.

TABLE 3. Changes in Mean Storage and Fluxes of MeHg in the Zooplankton Community in the Original Pond Area of L979

	1992	1993	1994	1995
zooplankton MeHg in water (ng L ⁻¹)	0.001	0.089	0.094	0.043
zooplankton MeHg as % of unfiltered water concn	0.8	7.0	7.8	2.4
net MeHg flux through the zooplankton community (µg m ² yr ⁻¹)	0.02	1.38	1.13	0.37
net MeHg flux through the fish community (µg m ² yr ⁻¹)	-0.02	0.08	0.20	0.14

3). Although MeHg concentrations in zooplankton remained high in 1995, fluxes declined from >1 to 0.37 mg m⁻² yr⁻¹ because zooplankton productivity decreased from >15 mg of C m⁻² d⁻¹ in 1993–1994 to 6.5 mg of C m⁻² d⁻¹ in 1995 (29). It is unclear whether this decline is indicative of a trend toward lower MeHg fluxes with aging of the reservoir. In 1995, MeHg fluxes were still $20 \times$ higher than in 1992. Concentrations of MeHg increased in both macroinvertebrates and fish from L979 (37, 38), indicating that increases in MeHg at the base of the food chain (zooplankton and seston) were passed on to higher trophic levels. Fluxes of MeHg through the zooplankton community exceeded uptake by fish 3 to $17 \times (3, 37)$ and remained comparatively high in 1995 (Table 3). Because MeHg concentrations remained high in zooplankton, MeHg uptake by fish would be expected to decline only if consumption of zooplankton also decreased.

Relationships between MeHg Concentrations in Water, Seston, and Zooplankton from L979. Within 6 weeks of flooding, MeHg concentrations in unfiltered and filtered water samples increased from a pre-impoundment mean of 0.1 to >1 ng L⁻¹ (Figure 2). These changes are described in detail by Kelly et al. (*3*). Mean concentrations of particulate MeHg increased from a pre-flooding average of 32 to >300 ng g⁻¹ dw after impoundment.

MeHg concentrations in zooplankton were highly significantly correlated (r > 0.9) with MeHg in unfiltered water, in filtered water, and on particles (Figure 3). Correlations between MeHg in filtered water and on particles were not as strong as for zooplankton but were still significant (r =0.71; p < 0.01). In contrast to MeHg, concentrations of THg in water did not increase substantially after impoundment (3). Concentrations of THg and inorganic Hg in unfiltered water and zooplankton were not significantly correlated with each other.

Although several studies indicate that fish and macroinvertebrates accumulate MeHg mostly from their diet (*5*, *39*, *40*), the dominant pathway of MeHg uptake by zooplankton is less certain. Because zooplankton have high surface area to volume ratios, considerable uptake from water may be possible. Unfortunately, it is not possible to determine the relative importance of MeHg uptake by zooplankton from food versus water with the L979 data because of the close correspondence of changes in concen-



FIGURE 2. Changes in concentrations of MeHg in unfiltered water samples, in filtered water samples (dissolved fraction), and on particulate matter in L979.

trations of MeHg in filtered water, seston, and zooplankton. Our data suggest, however, that transfers among these phases occurred rapidly and within the biweekly sampling interval of our study. There were no indications of lagged responses of zooplankton MeHg concentrations to changes in MeHg in either seston or water. The residuals of the zooplankton unfiltered water regression were not significantly autocorrelated at a lag of 14 days within any study year. Laboratory studies have also found rapid uptake and depuration of MeHg by zooplankton and phytoplankton (41-43).

MeHg Bioaccumulation by Zooplankton. Many laboratory and synoptic surveys indicate that bioaccumulation of



FIGURE 3. Model II regressions relating concentrations of MeHg in zooplankton (MeHg_{zoo}), unfiltered water (MeHg_{unfilt}), filtered water (MeHg_{diss}), and seston (MeHg_{part}). Only samples collected within 3 days of each other were used in the regressions.

MeHg by zooplankton and seston may be affected by variations in water chemistry and plankton community structure. For example, MeHg bioaccumulation can vary with DOC, pH, temperature, and trophic conditions (14-17) or among different zooplankton taxa (13, 44). One objective of our study was to examine whether MeHg accumulation by zooplankton was affected by the large changes in water chemistry and food web structure that followed impoundment of lake 979.

There was no indication that MeHg accumulation by zooplankton changed with MeHg availability in the physicalchemical environment of L979. Relationships between MeHg concentrations in zooplankton, water, and seston were determined using model II regression (Figure 3), and in all cases, the slopes of the regression lines were not significantly (p > 0.2) different from 1 [test of Clarke (45) as modified by McArdle (46)]. A slope of 1 in a log-log regression indicates that the relationships between MeHg concentrations in water, seston, and zooplankton remained proportionally constant throughout the range of values encountered.

Zooplankton BAFs in lakes 979 and 632 also did not change dramatically despite large variations in water chemistry and food web structure (Table 1, Figure 4). BAFunfilt values in L979 ranged between 5.2 and 5.7 before flooding and between 5.2 and 5.9 after flooding. BAFs were similar in both L979 and L632. $BAF_{diss}\xspace$ values in L979 showed no strong trends over time. After correction for multiple comparisons (Bonferroni correction), residuals from the zooplankton-water and seston-water regressions from lakes 979 and 632 were not significantly correlated with plankton community structure (phytoplankton biomass, ¹⁴C primary production, bacterial biomass, % Daphnia, zooplankton biomass), zooplankton population attributes (Daphnia birth rate), or physical-chemical factors (suspended C, particulate C:N, DOC, pH, temperature, flushing rates). No r² exceeded 0.5.



FIGURE 4. (a) Changes in zooplankton bioaccumulation factors (BAFs) for MeHg. (b) Changes in zooplankton biomagnification factors (BMFs) in L979. A BMF of 0 indicates no biomagnification from seston to zooplankton. (c) Changes in zooplankton BAFs in L632 calculated using MeHg concentrations in unfiltered water.

There was no evidence that species composition affected MeHg accumulation by zooplankton. Prior to flooding, 80- μ m net samples analyzed for Hg from L979 were dominated by Bosmina longirostris (a herbivore/detritivore) and Polyphemus pediculus Linné (a predaceous cladoceran) whereas 400- μ m samples contained mostly *P. pediculus* (Figure 5). After impoundment, both sample sets were dominated by Daphnia rosea, a herbivore/detrivore. Rotifers were generally rare, and no samples contained large amounts of detritus or phytoplankton. In general, changes in MeHg concentrations in zooplankton collected with the 400-µm net closely followed changes observed in the 80- μ m samples (Table 2). MeHg concentrations in 1992 and 1994 were significantly higher in 400- μ m samples than in 80- μ m samples (paired *t*-tests, *p* < 0.001). Hg concentrations in the 80- and 400- μ m fractions were not statistically different in L632. The reasons for higher concentrations of MeHg in 400- versus 80-µm samples collected from L979 in 1994 are unclear but may be related to different specific growth rates, Hg-depuration rates, or egg ratios in large versus small Daphnia. Higher concentrations of MeHg in 400- μ m samples collected in 1992 may have been related to the high proportion of the predacious species, P. pediculus, found in these samples (see below).

The absence of strong effects of changes in zooplankton species composition on Hg concentrations may partly reflect the limited dietary range of dominant zooplankton species in L979. Both before and after impoundment, the zooplankton community was primarily composed of cladocerans that are indiscriminate particle feeders. Paterson et al. (8) inferred that the predominant source of food for zooplankton in L979 shifted from phytoplankton prior to flooding to bacteria in 1993. This was because primary production by phytoplankton was insufficient to support zooplankton productivity at this time. In 1994 and especially 1995, phytoplankton productivity increased while zooplankton productivity declined slightly, and zooplankton probably



FIGURE 5. Changes in the relative biomass of different zooplankton taxa in samples used for L979 Hg analyses. (a) $80-\mu m$ net samples. (b) $400-\mu m$ net samples.

reverted to feeding on phytoplankton. Despite these apparent changes in the diet of Cladocera, there was no evidence for large changes in bioaccumulation of MeHg in L979.

Overall, our results suggest that changes in community structure and water chemistry in lakes 979 and 632 had a minimal effect on MeHg bioaccumulation by zooplankton despite the fact that ranges of variation for many measures often equaled or exceeded those reported in synoptic surveys. In general, zooplankton BAFs in L979 and L632 were similar to BAFs reported from other studies in a variety of aquatic habitats including small lakes (*13, 15, 31, 47*), a large lake (*48*), and an estuary (*49*) (range of BAFs = 5.2–6.4). For many purposes, modeling of Hg transfer in planktonic food webs may not require large amounts of information on zooplankton community composition or water chemistry.

Biomagnification of MeHg in the Planktonic Food Web. Several studies have found increasing MeHg concentrations from seston to zooplankton and from herbivore/detritivores to predators (*6*, *7*, *33*, *48*, *50*). In contrast, there was little biomagnification of MeHg from seston to zooplankton in L979, and BMFs did not change dramatically with impoundment (Figure 4). On average, concentrations of MeHg in zooplankton were only $1.4 \times$ MeHg concentrations in seston. Residuals from the zooplankton—seston regression were not significantly correlated with changes in water chemistry or zooplankton community structure.

There was also little evidence of biomagnification within the zooplankton community of L979. On three dates in 1995, MeHg concentrations in *Chaoborus* were lower than concentrations in their presumed zooplankton prey (Figure 1). Back et al. (*16*) and Parkman and Meili (*51*) have reported similar findings, and bioenergetic studies suggest that this is a result of exceptionally high growth rates and growth dilution of Hg by *Chaoborus (52)*. The other common predatory zooplankton species in L979, *P. pediculus*, was dominant only in 400- μ m samples collected in 1992. MeHg concentrations in these samples were, on average, $2 \times$ higher than in 80- μ m samples collected at the same time (composed primarily of *B. longirostris*) and may indicate biomagnification within the zooplankton community.

Comparison of Changes in MeHg Concentrations in Zooplankton and Benthic Macroinvertebrates from L979. There were some striking contrasts between changes in MeHg in zooplankton and in benthic macroinvertebrates collected from L979 by Hall et al. (38). Prior to impoundment, concentrations of MeHg in benthos were similar to or higher than concentrations in zooplankton. Predacious insects had a mean MeHg concentration of 189 ng g⁻¹, and collector/ shredders had a mean concentration of 72 ng g⁻¹ before flooding. After impoundment, concentrations of MeHg increased approximately 3× in macroinvertebrate predators and $<1-4\times$ in collector/shredders. These increases were much less than the $>10\times$ increase observed in the zooplankton community. Differences between zooplankton and benthic macroinvertebrates are unlikely to have been a consequence of the longer life spans of benthic macroinvertebrates because, by 1994, all invertebrates had probably completed at least one full generation in L979. Although the mechanisms are unclear, our results suggest that impoundment may affect MeHg concentrations in zooplankton more than benthic invertebrates. If the results from L979 hold true for other reservoirs, planktivorous fish may be at greater risk of increased exposure to MeHg than benthivorous fish. Strange et al. (53) reported that Hg concentrations in planktivorous cisco (Coregonus artedii Lesueur) were higher than concentrations in benthivorous whitefish (Coregonus clupeaformis Mitchell) collected from the Southern Indian Lake reservoir in northern Manitoba. Hence, an understanding of factors underlying differences in zooplankton and benthic invertebrate MeHg accumulation may help to explain variations in the response of Hg concentrations in fish from different reservoirs.

Acknowledgments

Manitoba Hydro and the Canadian Department of Fisheries and Oceans Habitat Action Plan funded this research. We thank all who assisted with the collection of samples including J. Embury, P. Gerrard, M. Lyng, and C. Magura. Zooplankton Hg analyses were completed by R. Omole. Water chemistry data were provided by the ELA and Freshwater Institute Chemical Analytical Laboratories under the supervision of M. Stainton and E. Schindler. Phytoplankton and bacteria data were provided by D. Findlay and zooplankton counts were completed by W. Findlay. R. Bodaly, B. Hall, R. Hecky, C. Kelly, and D. Rosenberg provided constructive criticism and support throughout the study. R. Bodaly, D. Rosenberg, N. Yan, and two anonymous reviewers kindly provided useful comments on earlier drafts of this manuscript.

Literature Cited

- (1) Bodaly, R. A.; St. Louis, V. L.; Paterson, M. J.; Fudge, R. J. P.; Hall, B. D.; Rosenberg, D. M.; Rudd, J. W. M. In *Mercury and Its Effects* on Environment and Biology; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 1997; pp 259–287.
- (2) Hecky, R. E.; Ramsey, D. J.; Bodaly, R. A.; Strange N. E. In Advances in Mercury Toxicology; Suzuki, T., Imura, N., Clarkson, T. W., Eds.; Plenum: New York, 1991; pp 33–52.
- (3) Kelly, C. A.; Rudd, J. W. M.; Bodaly, R. A.; Roulet, N. P.; St. Louis, V. L.; Heyes, A.; Moore, T. R.; Schiff, S.; Aravena, R.; Scott, K. J.; Dyck, B.; Harris, R.; Warner, B.; Edwards, G. *Environ. Sci. Technol.* **1997**, *31*, 1334–1344.
- (4) Rosenberg, D. M.; Berkes, F.; Bodaly, R. A.; Hecky, R. E.; Kelly, C. A.; Rudd, J. W. M. Environ. Rev. 1997, 5, 27–54.
- (5) Hall, B. D.; Bodaly R. A.; Fudge R. J. P.; Rudd, J. W. M.; Rosenberg, D. M. Water Air Soil Pollut. 1997, 100, 13–24.

- (6) Plourde, Y.; Lucotte, M.; Pichet P. Can J. Fish. Aquat. Sci. 1997, 54, 821–831.
- (7) Tremblay, A.; Lucotte, M.; Schetagne, R. Sci. Total Environ. 1998, 213, 307–315.
- (8) Paterson, M. J.; Findlay, D.; Beaty, K.; Findlay, W.; Schindler, E. U.; Stainton, M.; McCullough, G. *Can. J. Fish. Aquat. Sci.* **1997**, *54*, 1088–1102.
- (9) Grieb, T. M.; Driscoll, C. T.; Gloss, S. P.; Schofield, C. L.; Bowie, G. L.; Porcella, D. B. *Toxicol. Chem.* **1990**, *9*, 919–930.
- (10) Lindqvist, O.; Johansson, K.; Aastrup, M.; Andersson, A.; Bringmark, L.; Hovsenius, G.; Håkanson, L.; Iverfeldt, Å.; Meili, M.; Timm, B. *Water Air Soil Pollut.* **1991**, *55*, 131–157.
- (11) Lange, T. R.; Royals, H. E.; Conner, L. L. Trans. Am. Fish. Soc. 1993, 122, 74–84.
- (12) Meili, M. Ph.D. Thesis, Uppsala University, 1991.
- (13) Back, R. C.; Watras, C. J. *Water Air Soil Pollut.* **1995**, *80*, 931–938.
- (14) Boudou, A.; Ribeyre, F. Bull. Environ. Contam. Toxicol. 1981, 27, 624–629.
- (15) Watras, C. J.; Bloom, N. S. Limnol. Oceanogr. **1992**, *37*, 1313–1318.
- (16) Back, R. C.; Visman, V.; Watras, C. J. Can. J. Fish. Aquat. Sci. 1995, 52, 2470–2475.
- (17) Westcott, K.; Kalff, J. Can. J. Fish. Aquat. Sci. 1996, 53, 2221-2228.
- (18) St. Louis, V. L.; Rudd, J. W. M.; Kelly, C. A.; Beaty, K. G.; Flett, R. J.; Roulet, N. T. *Environ. Sci. Technol.* **1996**, *30*, 2719–2729.
- (19) Wiens, A. Department of Fisheries and Oceans, Winnipeg, unpublished results.
- (20) St. Louis, V. L.; Rudd, J. W. M.; Kelly, C. A.; Beaty, K. G.; Bloom, N. S.; Flett, R. J. Can. J. Fish. Aquat. Sci. 1994, 51, 1065–1076.
- (21) Stainton, M. P.; Capel, M. J.; Armstrong, F. A. J. Fish. Mar. Serv. Misc. Spec. Publ. 1977, No. 25, 166 pp.
- (22) Armstrong, F. A. J.; Uthe, J. F. At. Absorpt. Newsl. 1971, 10, 101– 103.
- (23) Malley, D. F.; Stewart, A. R.; Hall, B. D. Environ. Toxicol. Chem. 1996, 15, 928–936.
- (24) Cohen, J. Statistical Power Analysis for the Behavioral Sciences, 2nd ed.; Lawrence Erlbaum Associates: Hillsdale, NJ, 1988; p 567
- (25) Bloom, N. S.; Crecelius, E. A. Mar. Chem. 1983, 14, 49-59.
- (26) Bloom, N. S. Can. J. Fish. Aquat. Sci. 1989, 46, 1131-1140.
- (27) Berges, J. A. Limnol. Oceanogr. 1997, 42, 1006-1007.
- (28) Ricker, W. E. J. Fish. Res. Board Can. 1973, 30, 409-434.
- (29) Paterson, M. Department of Fisheries and Oceans, Winnipeg, unpublished data.
- (30) Sorensen, J. A.; Glass, G. E.; Schmidt, K. W.; Huber, J. K.; Rapp, G. R. Environ. Sci. Technol. 1990, 24, 1716–1726.
- (31) Monson, B. A.; Brezonik, P. L. *Biogeochemistry* **1998**, *40*, 147–162.

- (32) Tremblay, A.; Lucotte, M.; Rowan, D. *Water Air Soil Pollut.* **1995**, *80*, 961–970.
- (33) Tremblay, A.; Lucotte, M. *Can. J. Fish. Aquat. Sci.* **1997**, *54*, 832–841.
- (34) Surma-Aho, K.; Paasivirta, J.; Rekolainen, S.; Verta, M. Publ. Water Environ. Res. Inst. 1986, 65, 59–71.
- (35) Kelly, C. A.; Rudd, J. W. M.; St. Louis, V.; Heyes, A. Water Air Soil Pollut. 1995, 80, 715–724.
- (36) Watras, C. J.; Morrison, K. A.; Back, R. C. In Global and Regional Mercury Cycles: Sources, Fluxes, and Mass Balances, Lewis: Chelsea, MI, 1996; pp 409–416.
- (37) Bodaly, D. Department of Fisheries and Oceans, Winnipeg, Manitoba, unpublished results.
- (38) Hall, B. D.; Rosenberg, D. M.; Wiens, A. Can. J. Fish. Aquat. Sci., in press.
- (39) Fowler, S. W.; Heyraud, M.; La Rosa, J. *Mar. Biol.* **1978**, *46*, 267–276.
- (40) Parks, J. W.; Sutton, J. A.; Hollinger, J. D.; Russell, D. D. Appl. Organomet. Chem. 1988, 2, 181–184.
- (41) Fujita, M.; Hashizume, K. Water Res. 1975, 9, 889-894.
- (42) Huckabee, J. W.; Elwood, J. W.; Hildebrand, S. G. In *The Biogeochemistry of Mercury in the Environment*; Nriagu, J., Ed.; Elsevier/North-Holland Biomedical: Amsterdam, 1979; pp 277–302.
- (43) Ribeyre, F.; Boudou, A. Int. J. Environ. Stud. 1982, 2, 35-40.
- (44) Rask, M.; Metsälä, T.-R.; Salonen, K. In *Mercury Pollution: Integration and Synthesis*; Watras, C. J., Huckabee, J. W., Eds.; Lewis: Chelsea, MI, 1994; pp 409–416.
- (45) Clarke, M. R. B. *Biometrika* **1980**, *67*, 441–446.
- (46) McArdle, B. H. Can. J. Zool. 1988, 66, 2329-2339.
- (47) Becker, D. S.; Bigham, G. N. Water Air Soil Pollut. 1995, 80, 563–571.
- (48) Mason, R. P.; Sullivan, K. A. Environ. Sci. Technol. 1997, 31, 942–947.
- (49) Rudd, J. W. M. Department of Fisheries and Oceans, Winnipeg, unpublished data.
- (50) Tremblay, A.; Lucotte, M.; Meili, M.; Cloutier, L.; Pichet. P. Water Qual. Res. J. Can. 1996, 31, 851–873.
- (51) Parkman, H.; Meili, M. Can. J. Fish. Aquat. Sci. 1993, 50, 521– 534.
- (52) Visman, V. M.Sc. Thesis, York University, Toronto, 1995.
- (53) Strange, N. E.; Bodaly, R. A.; Fudge, R. J. P. Can. Techn. Rep. Fish. Aquat. Sci. 1991, No. 1824, 36 pp.

Received for review April 6, 1998. Revised manuscript received September 28, 1998. Accepted September 30, 1998.

ES980343L