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Fluxes of methylmercury to the water column of a drainage lake: The relative importance of internal and external sources

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Abstract

We studied fluxes of methylmercury (MeHg) through a Precambrian Shield lake using a mass balance approach. The primary goal of the study was to determine the importance of various sources of MeHg to the water column of the lake. The relative importance of all sources was: in-lake production >>> inflow from a brown-water lake with riparian wetlands >>> wet deposition > inflow from an upstream oligotrophic lake > direct inflow from uplands surrounding the lake. MeHg accumulated in the hypolimnion of Lake 240 when oxygen was present. Water-column sinks for MeHg included photodegradation of MeHg, which was about 3.5 times greater than the loss of MeHg through outflow. At present, there are few studies available on mass balance fluxes of MeHg in lakes, and this is the first study that includes losses of MeHg by photodegradation. The inclusion of photodegradation in this study results in a clear demonstration that in-lake production of MeHg is very important. In drainage lakes, the relative importance of in-lake production versus inflow of MeHg from wetlands will vary according to the extent of wetlands in the drainage basin, as well as the volume of precipitation, which produces runoff and transports MeHg from wetlands to downstream lakes.

Methylmercury (MeHg) is a common contaminant of fish flesh in North American lakes, and concentrations in piscivorous fish are usually about 10^6 times greater than in lake water (Wiener and Spry 1996). An ongoing question in mercury research is, Where does the MeHg in lakes come from? This question is difficult to answer because of methodological limitations that have prevented researchers from quantifying all the possible sources of MeHg to lakes and to their food chains.

One source is the production of MeHg within the lake itself, formed by bacterial methylation of inorganic mercury in sediments. Another group of sources is externally formed MeHg, which enters the lake from streams, direct runoff (DRO), or direct atmospheric deposition. The relative importance of internal versus external sources is expected to depend on the rate of in-lake MeHg production, the concentrations of MeHg in atmospheric deposition, the size of the terrestrial catchment, and the percentage of surface in the catchment that contains wetland areas (Hurley et al. 1995; Rudd 1995). The percentage wetland in catchments is of consequence because wetlands are important sites of MeHg production and important sources to downstream lakes (St. Louis et al. 1994, 1996; Hurley et al. 1995; Babiarz et al. 1998; Lee et al. 1998). There are also several sinks of MeHg in lakes. It is lost by microbial demethylation in sediments (Ramlal et al. 1986; Oremland et al. 1991), long-term sediment burial (Henry et al. 1995), outflow, and abiotic photodegradation in surface waters (Sellers et al. 1996).

The measurement of internal MeHg production is much more difficult than the measurement of external sources. One reason is that it is not possible to quantitatively assay rates of either mercury methylation or demethylation in lakes and wetlands (Rudd 1995). State-of-the-art isotopic methods continue to be limited by the inability to determine the fraction of the added labeled substrate that is available to the methylating or demethylating bacteria (Hintelmann et al. 1995).

To date, there have been only a few studies of MeHg fluxes in whole-lake ecosystems (Hultberg et al. 1994; Watras et al. 1994; Henry et al. 1995). Photodegradation of MeHg in lakes (Sellers et al. 1996) was unknown at the time of these studies. It appears to be an important sink for MeHg, which changes the view of the relative importance of several internal and external fluxes of MeHg. The study presented here is the first in which photodegradation of MeHg was measured at the same time as inflows and outflows. We also estimated fluxes from the lake sediments during the summer months when methylation is known to be most active in Precambrian Shield lakes (Ramlal et al. 1993; Krabbenhoft et al. 1998). It should be noted that flux from the sediments to the water column is not necessarily equivalent to production in the sediments, because not all of the MeHg produced will enter the water column. The inclusion of photodegradation measurements in this study, however, allows a much

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Table 1. Characteristics of the study lakes.

Parameter	Lake 239	Lake 240	Lake 470
Mean depth (m)	10.5*	6.1*	0.8†
Maximum depth (m)	30.4*	13.1*	n.a.
Surface area (h)	56.1*	44.1*	4.24†
Residence time (yr)	7.4‡	1.5‡	0.072§
pH‖	6.68–7.45	6.48–7.31	6.05–6.57
DOC (μmol L^{-1})‖	440–620	550–640	840–1,010

* From Brunskill and Schindler 1971.
† From Beaty and Lyng 1989.
‡ 1970–1994 annual mean; Beaty and Lyng unpubl. data.
§ 1970–1990 annual mean; Beaty and Lyng unpubl. data.
‖ n = 18, 12, and 4 during 1995 for Lake 239, Lake 240, and Lake 470, respectively.
n.a. = not available.

more accurate determination of flux to the water column than was possible in the past.

The objectives of our study were (1) to compare the relative importance of MeHg photodegradation to other MeHg fluxes to and from the water column of a Precambrian Shield lake, and (2) to make the best possible determination of the relative importance of external versus internal sources of MeHg in this lake.

Methods

Study site—Lake 240 is an oligotrophic drainage lake situated in the boreal forest of the Precambrian Shield of northwestern Ontario at the Experimental Lakes Area (ELA; Johnson and Vallentyne 1971). Lake 240 is part of a 723-ha watershed characterized by wetlands, six upstream lakes, and upland forests that are dominated by immature jackpine (St. Louis et al. 1994). There are no wetland areas that drain directly into Lake 240. The lake has one outflow and receives water directly from two lakes, Lake 239 and Lake 470, which are connected to Lake 240 by short streams. Lake 239 is also oligotrophic, but it is larger and deeper and has a much longer water residence time than Lake 240 (Table 1). Lake 470 is a much smaller, brown-water lake that has a short water residence time and extensive areas of wetlands upstream.

Hydrology measurements—Stream outflow and inflow volumes were measured continuously throughout the study. Stream flows were monitored using a trapezoidal cut-throat flume, a 12-in. Parshall flume, and a 120-degree v-notch weir for Lake 470 and 239 inflows and for Lake 240 outflow, respectively (Beaty unpubl. data.). Rainfall was measured twice a day with a standard Type B rain gauge (Meteorological Service of Canada) located within the Lake 240 watershed.

Sample collection and analyses—The 1-yr study began in mid-March 1995 and ended in mid-March 1996. During high spring flow (16 Mar–3 May 1995), whole-water samples for analyses of MeHg concentration were taken weekly at the two inflows and outflow of Lake 240. Biweekly samples were taken after the spring runoff period (17 May–6 Sep). During ice cover until the end of the study period (9 Nov 95–15 Mar 96), samples were collected monthly. Samples were collected in duplicate, and the results reported are the average concentration of the two samples. Lake 240 profile samples were collected every 4 weeks between 8 May 1995 and 4 October 1995. Water was pumped from depth using a peristaltic pump equipped with platinum-cured silicone tubing (Cole-Parmer) that had been prewashed with 0.1% HCl. Samples were collected in perfluoralkoxy (PFA) Teflon® bottles (125 or 250 ml) that had been washed in hot concentrated nitric and stored in 0.1% hydrochloric acid. To prevent contamination, ultraclean sampling protocol that included gloved hands and Ziploc® bags was used (St. Louis et al. 1994).

Lake-water profile samples were also collected for dissolved sulfate and oxygen analyses using the same peristaltic pump system. Sulfate and oxygen concentrations were analyzed as described in Stainton et al. (1977).

Unchannelized DRO samples from bedrock outcrop areas were collected using V-shaped collectors constructed of plywood boards (~2.5 cm × 20 cm × 200 cm), which were secured to bedrock with fiber-glass cloth and resin and painted with epoxy paint. The bedrock area within the walls of each was ~2 m^2. The outflows from these two collectors were ~5 m from the lake's edge. As a precaution against contamination from catchment construction material, sample collection did not begin until the walls had been first washed by an intensive rain event. One collector was sampled three times during the study, and the other was sampled twice.

Stream inflow, outflow, epilimnetic, and catchment samples were frozen until they were analyzed for MeHg concentration. Samples were analyzed within 1 month of collection using methods described by Horvat et al. (1993). The detection limit, determined as two times the standard deviation of the mean of long-term average of blank concentrations, was 0.02 ng L^{-1} at a blank concentration range of 0.002–0.026 ng L^{-1}. When the concentration of MeHg was below the detection limit, it was designated as one-half of this value, i.e., 0.01 ng L^{-1}.

Measurement of relative photodegradation rates—There is a linear relationship between MeHg concentrations and photodegradation rates (PRs) in lake water under the same light exposure (Sellers et al. 1996). Because concentrations of MeHg in Lake 240 surface waters approached the limit of detection, we used low-level additions of MeHg (1–3 ng L^{-1}) to measure relative rates of MeHg photodegradation. Lake 240 surface water was filtered through a 0.45-μM cellulose acetate filter. Filtration does not affect PRs (Sellers et al. 1996), but it does reduce analytical variability caused by the presence of particles. On each sampling day, a bulk surface-water sample was collected from Lake 240 and kept in the dark during transportation back to the laboratory, where it was quickly processed under indoor light. In the lab, MeHg was mixed into the surface-water sample, which was then distributed into several 125-ml PFA-Teflon® bottles, each of which was sealed into two Ziploc® bags and placed in a dark container for immediate transport back to the lake. It should be noted that MeHg is photodegraded primarily by ultraviolet (UV) light but also by visible light (Sellers 1997).

One-liter Teflon® bottles transmit 100% of visible but only 66 and 78% of UVB and UVA, respectively (Amyot pers. comm.). Although the thinner walled 125-ml bottles may transmit more light than 1-liter bottles, our estimates of PRs are likely underestimates of the true rates (Sellers 1997).

Bottles were incubated on the surface of the lake for 2–5 d and below the surface for 7–11 d. Two bottles were used for each depth. One bottle was frozen immediately and kept in the dark to prevent photodegradation. The second bottle was frozen at the end of the in situ incubation period. In this way, all analyses for MeHg concentration could be done on the same day, which eliminated day-to-day analytical variability. Duplicate analyses were performed on each bottle. In addition, several dark bottles were wrapped in foil and incubated on the lake surface for 3–4 d and deeper depths of the incubation for 6–7 d. The PRs calculated from these bottles served as controls for the light-incubated bottles.

During the incubations of the water samples, incident photosynthetically active radiation (PAR) ranged from 5 to 37 μE m^{-2} d^{-1} and averaged 23 μE m^{-2} d^{-1}, which is close to the mean daily average for the entire ice-free season (25 μE m^{-2} d^{-1}). Thus, the light levels during incubation were a good representation of the seasonal range of in situ conditions.

The fraction of MeHg in the incubation bottles that was photodegraded was determined from the difference in MeHg concentrations between time-zero bottles and bottles incubated in situ for 2–11 d. This relative rate was calculated as follows:

$$F = \left(\frac{\Delta C - \Delta B}{C}\right) \times 100 \quad (1)$$

where F is the percentage of MeHg lost per day, ΔC is the change in MeHg concentration between the time-zero and the in situ-incubated bottles (ng L^{-1} d^{-1}), ΔB is the average dark value of MeHg loss (ng L^{-1} d^{-1}), and C is the initial MeHg concentration (ng L^{-1}). Previous tests had shown that no loss to the walls of the bottles occurred during these incubations (Sellers et al. 1996).

Estimation of in situ, absolute PRs—Depth profiles of relative PRs (in % d^{-1}) were determined 10 times during the 1995 ice-free season. For each depth and sampling date, the in situ PR (ng L^{-1} d^{-1}) was calculated by

$$PR = \left(\frac{F}{100}\right) \times C \quad (2)$$

where C is the in situ MeHg concentration (ng L^{-1}) measured closest to the date when water was collected for incubations (within 2 weeks for half the incubations and the same day for the other half), and F is from Eq. 1.

For the top 0.5 m of the water column, the mass of MeHg photodegraded in the lake during the ice-free period (191 d) was calculated using the following equation:

$$M = PR_{av} \times V \times 191 \text{ d} \quad (3)$$

where M is the mass of MeHg photodegraded (ng), PR_{av} is the depth-integrated PR (ng L^{-1} d^{-1}) averaged for the 10 incubations during the ice-free period, and V is the volume of water (liters) in the first 0.5 m of Lake 240. Because light extinction follows an exponential decrease with depth, PR_{av} was calculated by extrapolating surface rates to 0.5 m along an exponential decay curve and at 0.1-m intervals. The model used 1% of surface rates at 0.5 m.

MeHg in inflows and outflows—The annual masses of MeHg in the inflows and outflow of Lake 240 were calculated as follows:

$$M = \sum (C_i \times V_i) \quad (4)$$

where M is the mass of MeHg (ng), C_i is the mean concentration of MeHg (ng L^{-1}) in the inflows or outflow for period i, and V_i is the volume of inflow or outflow (liters) for the same period. The lengths of the periods were 1 week during spring flow, 2 weeks during the remainder of the ice-free season, and monthly during the winter. Water samples were taken at the beginning and end of periods, i.

DRO from the terrestrial catchment of Lake 24 was sampled for MeHg five times during the open-water season. DRO volume was estimated by prorating the average water discharge from two nearby hydrologically monitored catchments (Lake 239NW inflow and Lake 239NE inflow; Beaty unpubl. data) to the DRO area of Lake 240 (118 ha, or 16% of the total 723 ha).

For estimation of the mass of direct atmospheric precipitation of MeHg onto the lake surface, we used average MeHg concentrations given in St. Louis et al. (1994) for 1992 and measured rainwater volumes from the nearby ELA meteorological site for March 1995–March 1996.

Errors associated with our budget calculations are as follows. The instrument error of the rain gauges is 1–5% (Winter 1981). The error associated with the hydrological structures used to monitor stream flow is considered to be <5% (Winter 1981). Scheider et al. (1978) evaluated the error associated with prorating measured discharge to estimate ungauged DRO discharge and found that the long-term DRO estimate had a mean error of 18%. We expect ours to be much less than this because the monitored catchments from which DRO discharge was estimated are within the Lake 240 watershed. Only 13% of the water entering Lake 240 was ungauged DRO. The analytical error for MeHg was always within 20%, and, on average, it was 9%.

Calculation of net MeHg accumulation during stratification—The amount of MeHg that accumulated in Lake 240 during the stratification period was calculated from the concentration profiles taken at the beginning and end of summer stratification (8 Jun–4 Oct 95) and from the lake bathymetry as follows:

$$M = \left(\frac{C_1 + C_2}{2}\right) \times V \quad (5)$$

where C_1 and C_2 are the concentrations of MeHg at the top and bottom of a 1-m interval (or fraction thereof), and V is the volume of water in the depth interval.

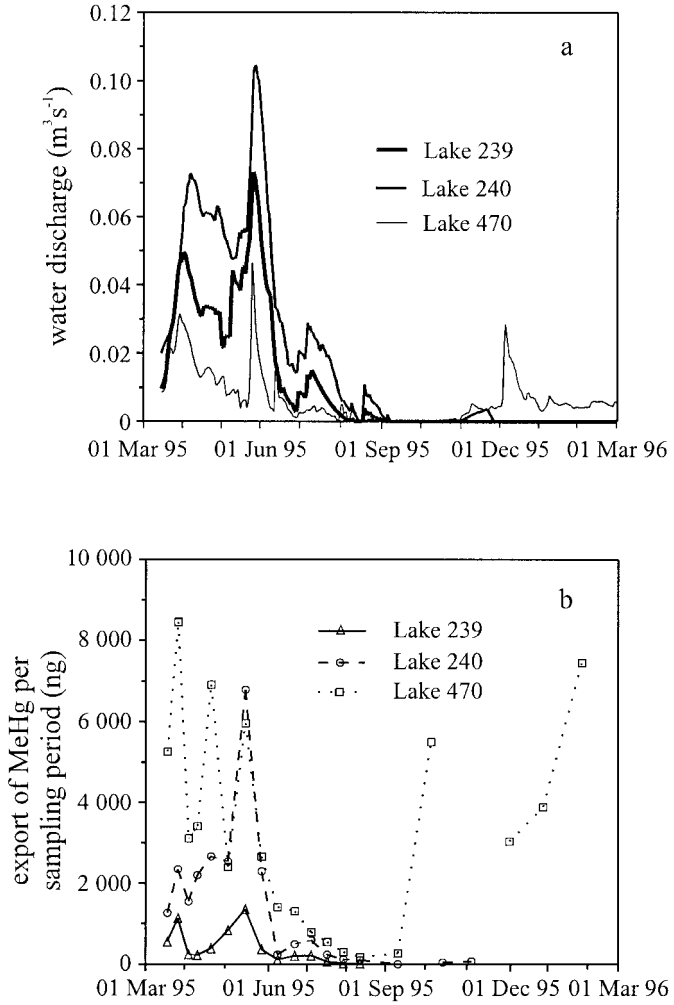

Fig. 1. (a) Water discharge, and (b) MeHg export from the study lakes, 1995–1996.

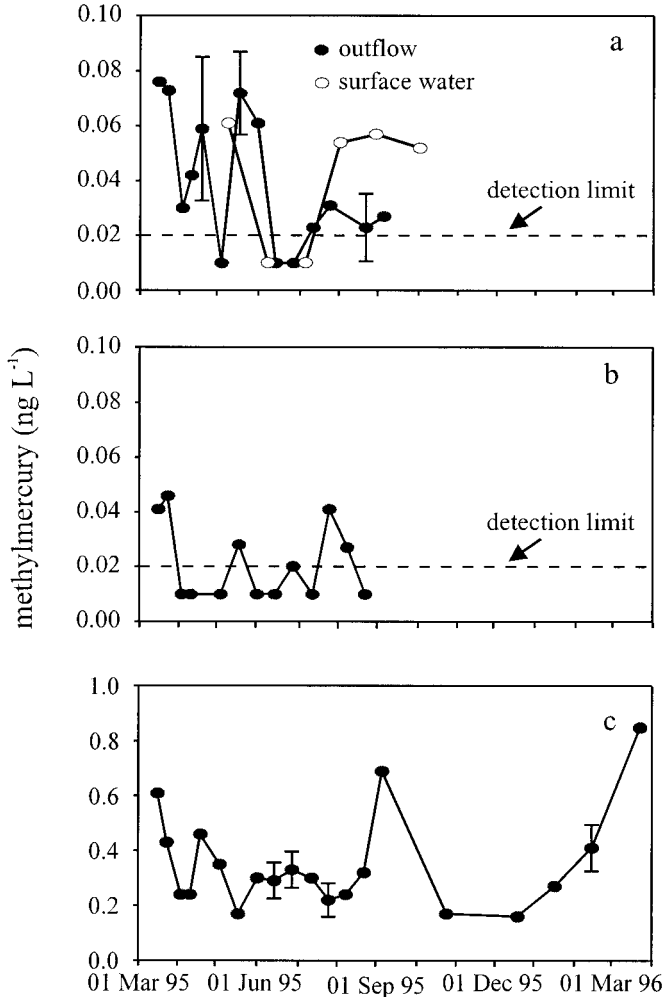

Fig. 2. MeHg concentration in whole-water samples of (a) Lake 240, (b) Lake 239 outflow, and (c) Lake 470 outflow (bottom panel), March 1995–March 1996. Symbols represent the average concentration of duplicate analyses. Range bars between single analyses are shown if single measurements deviate from the average measurement >15%.

Results

Hydrology—Flow rates at the stream inflows and the lake outflow peaked during spring melt and were low or nonexistent during summer and for most of the winter (Fig. 1a). The winter of 1995–1996 was marked by low water flow in general, and there was no outflow from Lake 240 during the winter (Fig. 1a). For the study period, Lake 240 received 38% of its water from Lake 239, 24% from Lake 470, and 25% from precipitation onto the lake surface (Table 1). The remaining input, 13%, was from direct overland runoff from the adjacent forested uplands. About 65% of the annual water loss was through the lake outflow, with the remainder leaving by evaporation from the lake surface (Table 1). Groundwater flux into and out of Lake 240 was insignificant (Beaty pers. comm.).

Concentration of MeHg in Lake 240 and in its outflows and inflows—Surface-water concentrations at the center of the lake ranged from <0.02 to 0.061 ng L^{-1} (Fig. 2a). MeHg concentrations in the Lake 240 outflow ranged from <0.02 to 0.076 ng L^{-1} during the open-water season of 1995 (Fig. 2a). In the first part of the summer, the concentrations in the lake center and the outflow were similar, but later in the season, the concentrations tended to be higher at the center (Fig. 2a). In general, concentrations at both sites were lower during the early summer months than during late summer, fall, and winter (Fig. 2a).

The inflow from Lake 239 functioned as a diluent of MeHg in Lake 240, as MeHg concentrations in the inflow from Lake 239 (Fig. 2b) were lower than in the surface water of Lake 240 (Fig. 2a) and were often below the detection limit, ranging from <0.02 to 0.046 ng L^{-1}. No seasonal pattern in MeHg concentration was discernible for the Lake 239 outflow (Fig. 2b), and there was no outflow from Lake 239 during the winter.

MeHg concentrations were about 10 times higher in the inflow from Lake 470 (Fig. 2c) than in the inflow from Lake 239 or in Lake 240 itself, ranging from 0.17 to 0.85 ng L^{-1}.

Table 2. Water and methylmercury (MeHg) inputs to/losses from Lake 240 for a 1-yr period (March 1995–March 1996).

	Drainage area*	Water discharge (m)†	% of total water input	Average MeHg (ng L^{-1})	Mass of MeHg to or from Lake 240 (mg)
Inputs					
Lake 239	393	326,454	38	0.02	6
Lake 470	168	205,831	24	0.31	63
Direct runoff	118	108,770	13	0.03	3
Wet deposition	—	211,592	25	0.04	9
Total					81
Losses					
Outflow	—	553,141		0.04	24
Photodegradation	—	—			86
Total					110

* Total drainage area of the Lake 240 watershed is 723 ha; Beaty and Lyng unpubl. data.

† Calculated from water discharge data presented here, not from measured concentrations.

There are extensive areas of riparian wetlands upstream of Lake 470; wetlands are known to be sites of MeHg production (St. Louis et al. 1994, 1996; Hurley et al. 1995; Babiarz et al. 1998; Lee et al. 1998). The outflow from Lake 470 had two peaks in concentration (Fig. 2c): one in late summer (at the beginning of September) and another in the winter (Jan–Mar 96). The winter peak in concentration occurred at a time of very low flow rate from Lake 470 and when both Lake 470 and the stream leading down to the weir where samples were collected were covered with snow.

Masses of MeHg entering and leaving Lake 240—Lake 240 received 85% of its externally supplied MeHg from the two stream inflows: 78% from Lake 470 and 7% from Lake 239 (Table 2). Most of the mass input from Lake 239 occurred during the spring flow (Fig. 1b). Inputs decreased to very low levels for the remainder of the year. There were five peaks of MeHg input from Lake 470. The first three occurred during the spring and early summer of 1995 (end of March to mid-May). The fourth occurred in the fall, beginning in October. The fifth occurred at the beginning of February of the following winter, when the volume of water flowing was quite low (Fig. 1a) but concentrations were high (Fig. 2c).

We estimate that about 11% of the external inputs of MeHg to Lake 240 was from direct wet precipitation onto the lake surface, which was surprisingly high, considering that this site is in a remote area. There was an additional small input from the DRO area of Lake 240 (4%; Table 2), which contains no wetland areas.

Over the 1-yr period, loss of MeHg by the lake outflow (24 mg; Table 2) was 30% of total inputs (81 mg) from external sources. Thus, if one considers only external inputs and losses, the lake would be calculated a net sink for MeHg (57 mg).

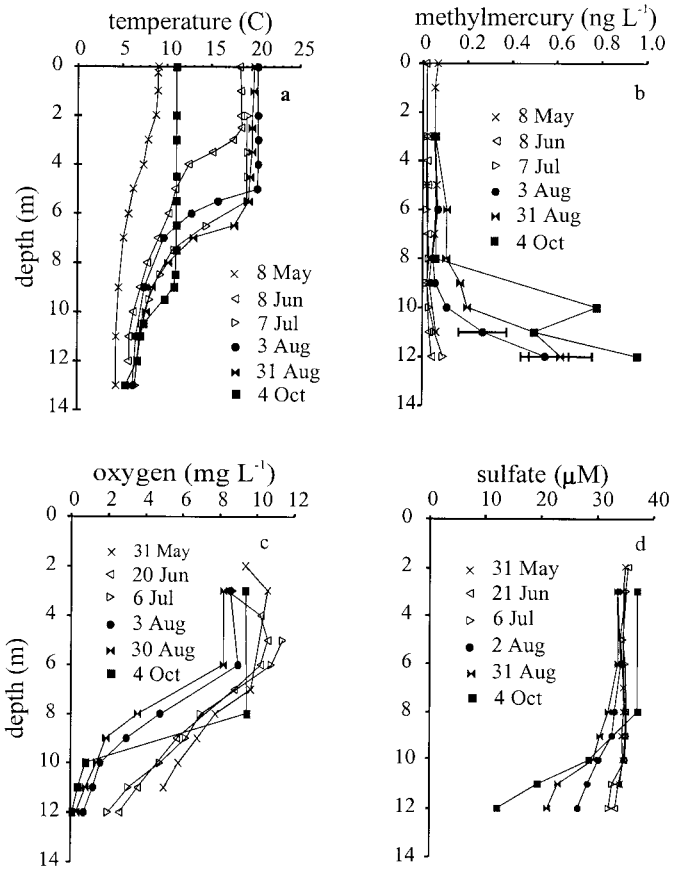

Fig. 3. (a) Temperature, (b) MeHg, (c) oxygen, and (d) sulfate concentrations in whole-water samples of Lake 240, 1995. For (b), range bars between single analyses are shown if single measurements deviate from the average measurement >15%.

Water-column chemistry—Lake 240 was thermally stratified by 8 June, at which time the epilimnion was 3 m, and the top of the hypolimnion was at 8 m below the lake surface (Fig. 3a). The hypolimnion remained at this depth at least until 31 August. There was a partial circulation of the lake on 4 October to a depth of 9 m (Fig. 3a,c).

During the stratification period, hypolimnetic concentrations of MeHg increased progressively, with the deepest water increasing from 0.04 to 0.95 ng L^{-1} (Fig. 3b), while oxygen and sulfate were decreasing (Fig. 3c,d). MeHg concentration increased in the hypolimnion (Fig. 3b), even though some oxygen remained present throughout the water column for the entire stratification period (Fig. 3c). The highest MeHg concentrations in the hypolimnion observed on the last sampling date (4 Oct) were coincident with the presence of phytoplankton particles (visual observation of whole-water samples) in these water samples. There was loss of sulfate from the hypolimnion with time as it diffused into the hypolimnetic sediments and was reduced (Fig. 3d).

Lake MeHg accumulation—The mass of MeHg in the water column of Lake 240, calculated from concentration profiles (Fig. 3b), was least during the early summer months and greater in spring and fall (Fig. 4). During the stratifi-

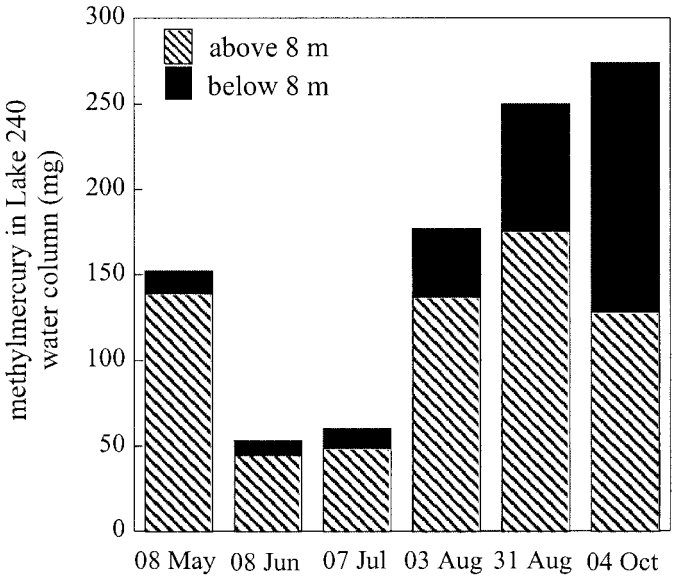

Fig. 4. Mass of MeHg in the water column of Lake 240 during the ice-free season, 1995.

cation period (8 Jun–4 Oct), there was a fivefold increase in the mass of MeHg in the lake water column from 53 to 274 mg, representing a total accumulation of about 220 mg (Fig. 4). The proportion of this MeHg found below 8 m also increased during this time, so that by the end of this period, it accounted for one-half of the MeHg in the lake (Fig. 4). This change in MeHg mass in the hypolimnion, which represents 11% of the lake volume, was an 18-fold increase over the prestratified value. Above 8 m, the mass of MeHg increased threefold during the same period (Fig. 4).

Relative PRs—Only bottles incubated between 0 and 0.5 m below the lake surface exhibited rates of MeHg degradation that were considered to be different from the dark bottles. The average dark value was -0.6% d^{-1} (± 1.68, $n = 6$) for surface-incubated samples, and 2.5% d^{-1} (± 1.59, $n = 6$) for subsurface (0.25–0.5 m) incubations. The rates of MeHg photodegradation calculated for 0–0.5 m (Eq. 1) ranged from -3 to 27% d^{-1} (Fig. 5). The highest rates were found in bottles incubated on the surface of the lake. Rates were much lower at 0.25-m depth (Fig. 5). At 0.5-m depth and at all of the deeper depths, rates were either slightly negative or positive (Fig. 5). From these data, we concluded that photodegradation activity was highly exponential, following the pattern of light extinction, and limited to the first 0.5 of the water column. We also confirmed our previous results indicating that there was no measurable MeHg degradation in the absence of light (Sellers et al. 1996).

Absolute PRs—Measured relative MeHg PRs (in % d^{-1}) on specific dates (Fig. 5) were applied to in situ MeHg concentrations (Eq. 2) to estimate in situ absolute rates during the ice-free season. These were done for the surface of the lake and for the 0–0.5-m depth interval. The depth-integrated in situ rates were multiplied by the volume of water in the upper 0.5 m. The seasonal pattern of relative rates (Fig. 6a) was different from the seasonal pattern of surface and whole-lake absolute rates (Fig. 6b). Relative rates at the surface were highest in mid-May, early July, and mid-August, with the lowest rates measured at the end of September (Fig. 6a). Absolute rates were at a minimum during June 1995, then increased progressively until the beginning of September before declining again to low levels in the late fall (Fig. 6b). The higher absolute rates in the late summer and early fall occurred because of an increase in MeHg concentrations in the surface waters during that time (Fig. 2), which demonstrates that PRs were more influenced by changes in concentration than in light. Previous experiments have shown a direct positive relationship between the MeHg concentration in lake water and the rate of MeHg photodegradation (Sellers 1997).

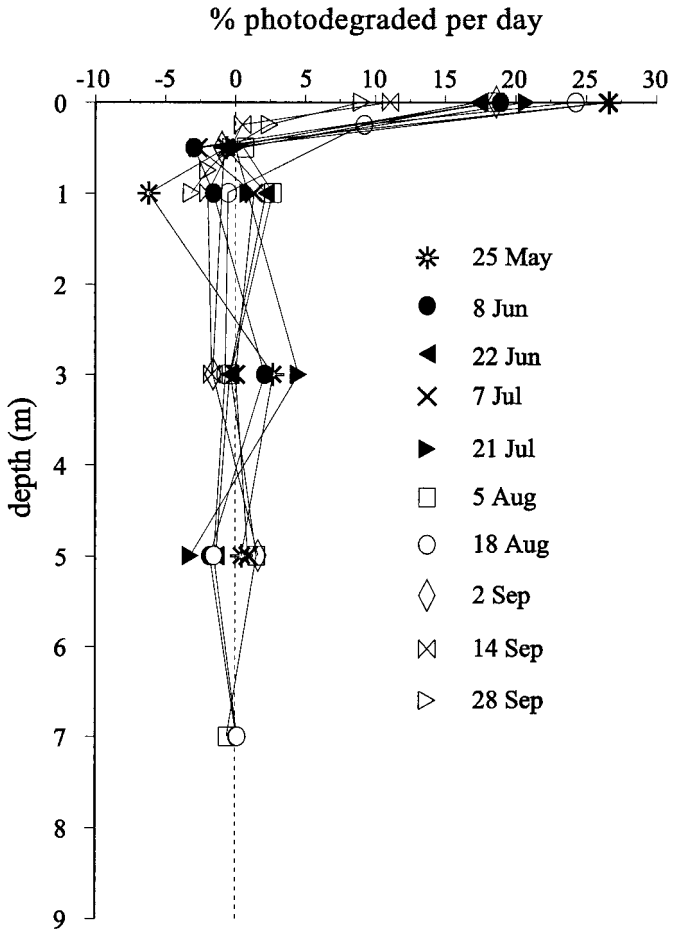

Fig. 5. Depth profiles of MeHg PRs in bottles incubated in Lake 240, 1995.

Over the ice-free period, we estimated that the total amount of MeHg photodegraded in Lake 240 (Eq. 3) was 86 mg. This was 3.5 times greater than the losses to lake outflow and about the same as total external inputs (Table 2). In total, losses (110 mg) were greater than external inputs (81 mg) by about 35%. Assuming no significant change in the mass, there must have been an in-lake flux of about 30 mg MeHg (produced in situ) from the sediments to the water column.

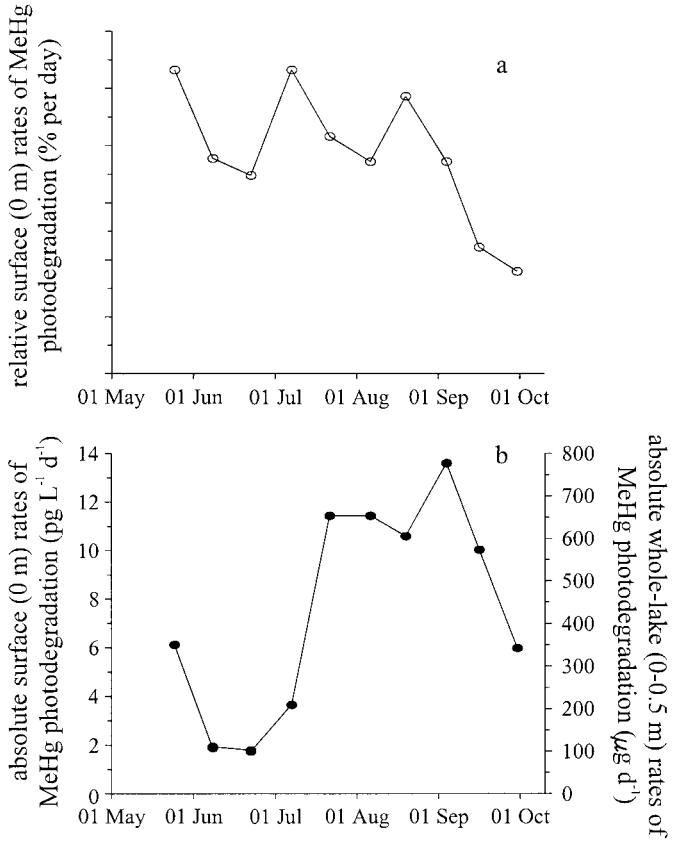

Fig. 6. (a) Measured relative rates of MeHg photodegradation at the surface of Lake 240, and (b) estimated absolute rates of MeHg photodegradation at the surface of Lake 240 and in the whole lake during the ice-free season, 1995.

Discussion

In this study, the order of importance for external sources of MeHg to Lake 240 for 1 yr were: Lake 470 >>> wet deposition > Lake 239 > DRO (Table 2). The predominance of Lake 470 in supplying MeHg over Lake 239 can be explained by the combined effect of wetlands and water residence time. Wetlands influence downstream lakes because they are important sources of MeHg and DOC, and Lake 470 has more upstream wetlands than Lake 239. Lake 470 also has a shorter residence time, which means that in-lake processes (e.g., MeHg photodegradation) are minimized compared to the larger Lake 239. Lake 239 also receives water from wetland areas, but its longer residence time (Table 1) means lower DOC concentrations (Rasmussen et al. 1989), increased water clarity (Francko 1990), and greater opportunity for MeHg photodegradation in the lake water before it flows out. Even though Lake 239 contributed 60% more water to Lake 240, it provided 90% less MeHg than did Lake 470. Thus, despite the larger surface and watershed area of Lake 239 (Table 1), it contributed even less MeHg than did direct wet deposition onto the smaller Lake 240 surface.

Our conclusion that photodegradation was restricted to the first ½ m of Lake 240 is consistent with more recent work by Krabbenhoft et al. (in press), who estimated photodegradation of MeHg in alpine lakes and also found it to be restricted to the first 1 m, with most occurring within the first 0.1 m. The importance of photodegradation as a loss mechanism of MeHg in Lake 240 (Tables 2, 3) refutes earlier claims that sunlight photodegradation is likely unimportant (e.g., Baughman et al. 1973). The estimated amount of photodegradation in Lake 240 during the 1995 ice-free season (86 mg) was less than the preliminary estimate for this lake (680 mg; Sellers et al. 1996). The first estimate of photodegradation (Sellers et al. 1996) was derived from a model using correlation curves of photodegradation versus light and photodegradation versus concentration. In this study, the amount of photodegradation was made from in situ measurements of rates and from more accurate measurements of MeHg concentration. Further, Sellers et al. (1996) modeled photodegradation to a depth of 4 m in Lake 240, whereas in this study, it was calculated for the top 0.5 m of the water column.

Table 3. External and internal fluxes of methylmercury for Lake 240 during the stratification period of 8 Jun–4 Oct 95.

Flux	Methylmercury (mg)
Σ External inputs*	13
Outflow	3
Photodegradation	54
Water column accumulation	220
Flux from sediments†	264

* Includes stream inputs and wet deposition onto the surface of the lake.
† Calculated using Eq. 6.

There were two interesting features of the hypolimnetic profiles of MeHg measured during summer stratification (Fig. 3b): (1) their shape (increasing concentration with increasing depth), which suggests a sediment origin of the MeHg that accumulated during stratification; and (2) a peak on 4 October at 10 m, which was 2 m above the sediment surface.

An increase in MeHg in the entire hypolimnion (Figs. 3b, 4) has been observed in other lakes (Verta et al. 1994; Watras et al. 1994; Henry et al. 1995; Regnell et al. 1997; Herrin et al. 1998). The main difference between Lake 240 and these other lakes is that there was very little anoxia in the water column of Lake 240. The most extensive anoxia existed on 4 October below 12 m (Fig. 3c), a portion of the lake that represents 2% of the hypolimnetic volume. Late summer profiles (3 Aug and 31 Aug) strongly suggested that a flux of MeHg came from the hypolimnetic sediment to the water column rather than from the water column itself (Fig. 3b). This could be MeHg that was produced in the hypolimnetic sediments from methylation of inorganic mercury (Ramlal et al. 1993) and subsequently diffused across the sediment-water interface, or MeHg released from particles decomposing on the sediment surface (Hurley et al. 1994; Watras et al. 1996). Regardless of mechanism, water-column MeHg in the hypolimnion was likely from in-lake production because the total water-column accumulation (Table 3) was much greater than external inputs (Table 2).

New production of MeHg in Lake 240 is not restricted to

the hypolimnion. Two studies have shown that methylation is more important in epilimnetic sediments than in hypolimnetic sediments (Ramlal et al. 1993; Krabbenhoft et al. 1998). Ramlal et al. (1993) measured MeHg production rates in the epilimnetic sediments of nearby drainage lakes (Northwestern Ontario Size Series Lakes near Red Lake, Ontario) that were nine times higher than in the hypolimnetic sediments. Bodaly et al. (1993) also found that epilimnetic sediment methylation positively correlated with temperature in the same lakes. These lakes are very similar to ELA lakes (Fee and Hecky 1992); epilimnetic sediments are likely, therefore, to be significant sites of new production in Lake 240. After release from these sediments, MeHg could have become attached to particles, which settled and decomposed in the hypolimnion.

The accumulation of settling particles in the deep thermocline could explain the peak of MeHg in the water column at 10 m late in the season on 4 October (Fig. 3b), especially because hypolimnetic samples collected on this date contained abundant phytoplankton particles. Watras et al. (1996) also observed an MeHg maximum in their study lake, which was near the top of the anoxic hypolimnion and associated with a particle phase. They concluded that this was due to new MeHg production by methylating bacteria that thrive just below the oxic–anoxic interface. We favor particle accumulation as the explanation for the peak observed in Lake 240 because of the timing of the peak with thermocline erosion and the absence of extensive anoxia in the hypolimnion.

The accumulation of MeHg in the water column as a whole during the summer months (220 mg; Fig. 4) was several times greater than all external inputs (81 mg; Table 2). This demonstrates strongly that in-lake MeHg production made an important contribution to the mass of MeHg in the water column during this period. We used this accumulated mass to estimate the net flux of MeHg from the sediments to the water column during summer stratification. This is not the total amount of newly produced MeHg, because some of it must have accumulated or been demethylated in the sediments.

To estimate the flux from sediments, we include photodegradation, external inputs, change in mass, and outflow.

$$SF = \Delta M - \sum I + P + O \quad (6)$$

where SF is the flux of MeHg from the sediments to the water column, ΔM is the change in mass of MeHg in the lake (220 mg; Fig. 4), ΣI is the sum of all external inputs of MeHg, P is the mass photodegraded, and O is the mass of MeHg in the lake outflow. P was calculated as follows:

$$P = \sum (PR_{avi} \times V \times d_i) \quad (7)$$

where PR_{avi} is the depth-integrated PR during a sampling period i, and d_i is duration of the period in days. There were eight periods between 8 June and 4 October.

The estimated flux of MeHg from the sediments during summer stratification (264 mg; ~5 ng m^{-2} d^{-1}; Table 3) was about 3.5 times greater than the combined annual inputs to Lake 240 from external sources (Table 2), showing that in-lake production during the summer months is a very important source of MeHg to the water column on an annual cycle. Even if we did not include photodegradation losses in the calculation, the estimated sediment flux would have been 210 mg, which is still much larger than external inputs. Fish in Lake 240 might also have accumulated some MeHg during summer stratification (Watras et al. 1994), in which case MeHg sediment flux would be >264 mg.

Our study leads us to conclude that in-lake production was important in Lake 240. During the 1995 stratification period in Lake 240, it was at least one order of magnitude greater than external inputs and at least 30 times greater than atmospheric deposition. This conclusion differs from Hultberg et al. (1994), who found that there was sufficient MeHg entering Swedish lakes from terrestrial sources to account for all MeHg accumulation by fish and concluded that in-lake MeHg production was unlikely to be important. Hultberg et al. (1994), however, did not measure any in-lake fluxes of MeHg. Our conclusion that in-lake production is a very important source of MeHg to lake water and to aquatic food chains is consistent with that of Henry et al. (1995), Watras et al. (1996), and Krabbenhoft et al. (1998). Of course, during wetter years, when stream flow draining wetland areas is greater, external sources of MeHg would likely be more important.

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