

The Rise and Fall of Mercury Methylation in an Experimental Reservoir[†]

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For the past 9 years, we experimentally flooded a wetland complex (peatland surrounding an open water pond) at the Experimental Lakes Area (ELA), northwestern Ontario, Canada, to examine the biogeochemical cycling of methyl mercury (MeHg) in reservoirs. Using input–output budgets, we found that prior to flooding, the wetland complex was a net source of approximately 1.7 mg MeHg ha⁻¹ yr⁻¹ to downstream ecosystems. In the first year of flooding, net yields of MeHg from the reservoir increased 40-fold to approximately 70 mg MeHg ha⁻¹ yr⁻¹. Subsequently, annual net yields of MeHg from the reservoir declined (10–50 mg MeHg ha⁻¹ yr⁻¹) but have remained well above natural levels. The magnitude and timing of Hg methylation in the flooded peat portion of the wetland reservoir were very different than in the open water region of the reservoir. In terms of magnitude, net Hg methylation rates in the peat in the first 2 years of flooding were 2700 mg ha⁻¹ yr⁻¹, constituting over 97% of the MeHg produced at the whole-ecosystem level. But in the following 3 years, there was a large decrease in the mass of MeHg in the flooded peat due to microbial demethylation. In contrast, concentrations of MeHg in the open water region and in zooplankton, and body burdens of Hg in cyprinid fish, remained high for the full 9 years of this study. Microbial activity in the open water region also remained high, as evidenced by continued high concentrations of dissolved CO₂ and CH₄. Thus, the large short-term accumulation of MeHg mass in the peat appeared to have only a small influence on concentrations of MeHg in the biota; rather MeHg accumulation in biota was sustained by the comparatively small ongoing net methylation of Hg in the flooded pond where microbial activity

remained high. In large reservoirs, where the effects of wind and fetch are greater than in the small experimental reservoir we constructed, differences can occur in the timing and extent of peat and soil erosion, effecting either transport of MeHg to the food chain or the fueling of microbial activity in open water sediments, both of which could have important long-term implications for MeHg concentrations in predatory fish.

Introduction

Reservoirs are created for various purposes including the production of hydroelectricity, irrigation, flood control, fisheries production, and recreation (1). Reservoir creation has many environmental impacts, including the production and bioaccumulation of methyl mercury (MeHg) into fish. When a landscape is inundated to create a reservoir, the flooded organic carbon in soils and plants decompose. Linked to the decomposition of flooded organic matter is the microbial methylation of inorganic Hg (Hg(II)) to MeHg (CH₃Hg⁺) (2, 3). It is generally believed that most methylation occurs in anoxic environments (such as those found immediately following reservoir creation (4)) and that the primary methylating organisms are sulfate-reducing bacteria (5, 6). From a toxicological perspective, MeHg is the most important form of Hg because it bioaccumulates in food chains and is a strong neurotoxin for humans and wildlife. In almost all reservoirs created to date, MeHg concentrations in top predatory fish have exceeded those allowed for marketing and human consumption (e.g., 0.5 μg g⁻¹ in Canada and 0.3 μg g⁻¹ in the United States). These fish have often remained contaminated for up to 30 years following reservoir creation (7, 8). It was recently estimated that there are now over 1.5 million km² of reservoir surface area globally (9), making this a widespread environmental and socioeconomic problem for populations or individuals that rely on reservoir fisheries for subsistence and fish production.

In 1990/1991 we began a unique multidisciplinary whole-ecosystem experiment at the Experimental Lakes Area (ELA) in northwestern Ontario, Canada, which was designed to examine the environmental impacts of reservoir creation (10). The ELA Reservoir Project (ELARP) had two major objectives: (1) to improve our understanding of the biogeochemical cycling of Hg in reservoirs and (2) to determine if reservoirs are significant sources of the atmospheric greenhouse gases (GHGs) carbon dioxide (CO₂) and methane (CH₄) due to the decomposition of the flooded organic matter. The ELARP experimentally flooded a wetland complex (i.e., a peatland surrounding a central pond) because they are typically found low-lying on landscapes and are the first feature to be flooded when reservoirs are created. Also, a wetland provided what was thought to be a worst-case scenario for long-term decomposition and MeHg production due to the large stores of organic carbon held in peat (4). During the first 2 years following flooding, there were very large increases in concentrations of MeHg, CO₂, and CH₄ in the reservoir compared to the wetland pond prior to flooding (10). Although the wetland complex as a whole had been a source of MeHg even prior to flooding (11, 12), it became a much greater source (40-fold) after flooding (10). Flooding also caused the wetland to change from being a carbon sink of 6.6 g C m⁻² yr⁻¹ to a large source of 130 g C m⁻² yr⁻¹ in the form of CO₂ and CH₄ emitted to the atmosphere (10).

Research presented in this paper examines the longer-term (9 year) effects of flooding. We expand the scope of the

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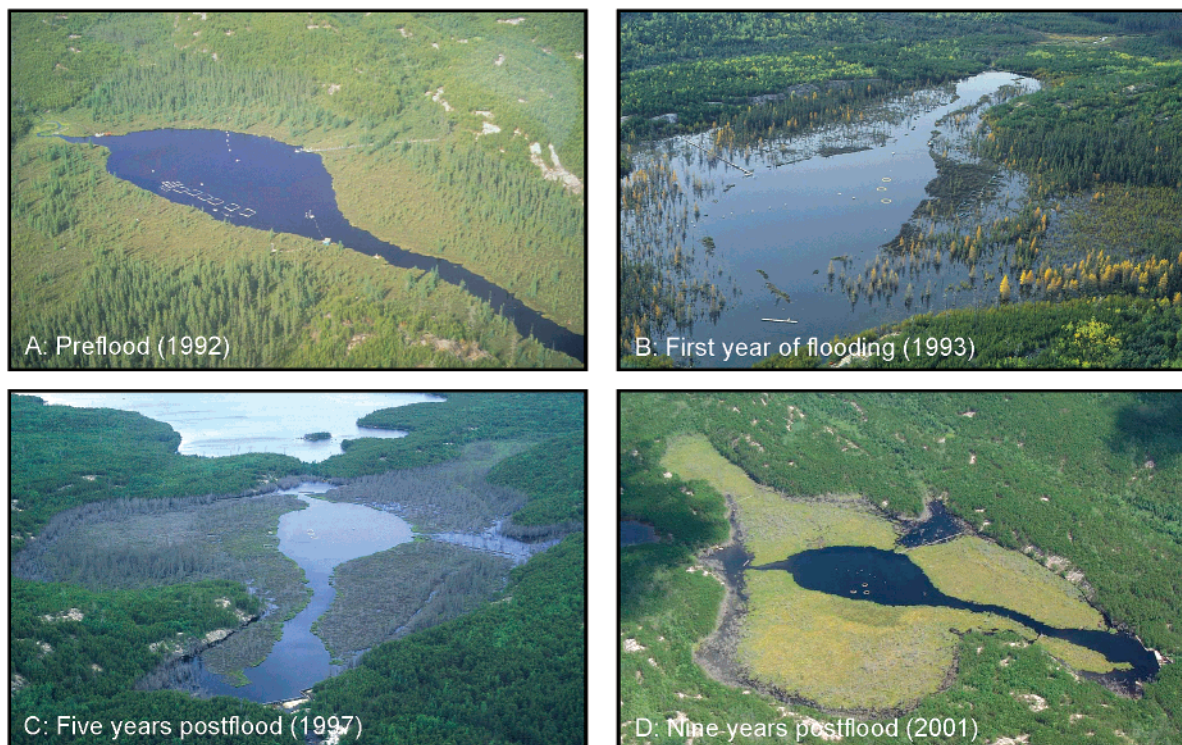


FIGURE 1. Aerial photographs of the wetland complex (peatland surrounding an open water pond) prior to flooding (1992; A), and the reservoir the first (1993; B), fifth (1997; C), and ninth (2001; D) years of flooding. Most of the inundated surface peat floated in the reservoir by 1996. By 2001, vegetation was regrowing on most of the floating peat surfaces. Photo credits: B. D. Hall (A) and V. L. St.Louis (B–D).

Kelly et al. (10) study to include estimated whole-ecosystem net methylation and demethylation rates. We show that an initial pulse of Hg methylation in the flooded peat during the first 2–3 years after flooding accounted for more than 97% of the MeHg produced in the entire reservoir. Since that time, there has been a rapid net demethylation in the peat, returning the MeHg concentrations to near pre-flood levels. However, concentrations of MeHg in the open water regions of the reservoir and food chain organisms decreased very little over the entire 9-year period of flooding presumably because of continued methylation there. Thus, while a large stimulation of methylation in the peat came and went in the first few years of flooding, decomposition and methylation in the open water regions of the reservoir has continued to support high MeHg concentrations in biota for at least 9 years.

Methods

Site Description. We experimentally flooded a boreal wetland at the ELA (Figures 1 and 2). Prior to flooding, the wetland consisted of a 2.4 ha central pond, which was surrounded by 14.4 ha of peatland. Predominant wetland plants were *Sphagnum angustifolium/falax* and *S. magellanicum*, with an overstory of primarily black spruce (*Picea mariana*), tamarack (*Larix laricina*), Labrador tea (*Ledum groenlandicum*), and leatherleaf (*Chamedaphne calyculata*).

The predominant inflow into the wetland was from the upstream Lake 240 with a watershed area of 723 ha (Figure 2). Twenty-six ha of upland forest drained directly into the peatland (Figure 2). The upland areas of this catchment were burned in 1980, and forest regeneration was mainly jack pine (*Pinus banksiana*) and paper birch (*Betula papyrifera*). A 55.3 ha subcatchment (the east subcatchment), which contained a valley-bottom wetland, also drained into the wetland (Figure 2). The valley-bottom wetland areas of the east subcatchment were dominated by *Sphagnum* spp. with an overstory of alder (*Alnus* spp.) and black spruce, which did not burn in 1980.

Direct runoff from the uplands and from the east subcatchment into the wetland area were episodic from May to October depending on rainfall and antecedent moisture conditions. In November, this runoff diminished and remained near zero throughout the winter. Snow accumulated until it melted in late March or April.

After 2 years of pre-flood study, on June 23, 1993 we began raising the water level in the wetland 1.3 m by damming the outflow. The flooding inundated the peatland surrounding the pond, increasing the surface area of open water by three, and the water volume behind the outflow by six (10). Each October the reservoir was drained to just above pre-flood levels to simulate the winter drawdown of many northern hydroelectric reservoirs. Over the next 9 years, increasing amounts of the inundated peat floated, with almost all of the previously submerged peat floating by 2001 (Figure 1).

General Hg and Water Chemistry Sampling Methods, Frequency, and Analytical Techniques. All hydrological inputs and outputs to the wetland or reservoir were sampled in 1990/1991 to 1997/1998 and then again in 2001 (Table 1, Figure 2). Duplicate samples for MeHg and total Hg (all forms of Hg; THg) were taken in Teflon bottles weekly following spring melt, biweekly during the summer and fall, or during episodic runoff events as described in St.Louis et al. (12) and Kelly et al. (10). MeHg samples were frozen until analysis, whereas THg samples were preserved with a volume of concentrated trace metal grade HCl equivalent to 0.2% of the sample volume. Flett Research Ltd. (Winnipeg, Manitoba) analyzed samples for MeHg and THg using cold vapor atomic fluorescence spectrophotometry (CVAFS) (13–15). MeHg could be detected at concentrations above 0.01–0.02 ng L⁻¹ and at a blank level of 0.05–0.1 ng L⁻¹. The detection limit for THg was 0.2–0.3 ng L⁻¹ at a blank level of 0.3–0.4 ng L⁻¹. Concentrations used in this study were averages of the duplicate samples.

Coincidentally with Hg sampling, we collected water samples in Nalgene polypropylene bottles for analyses of DOC

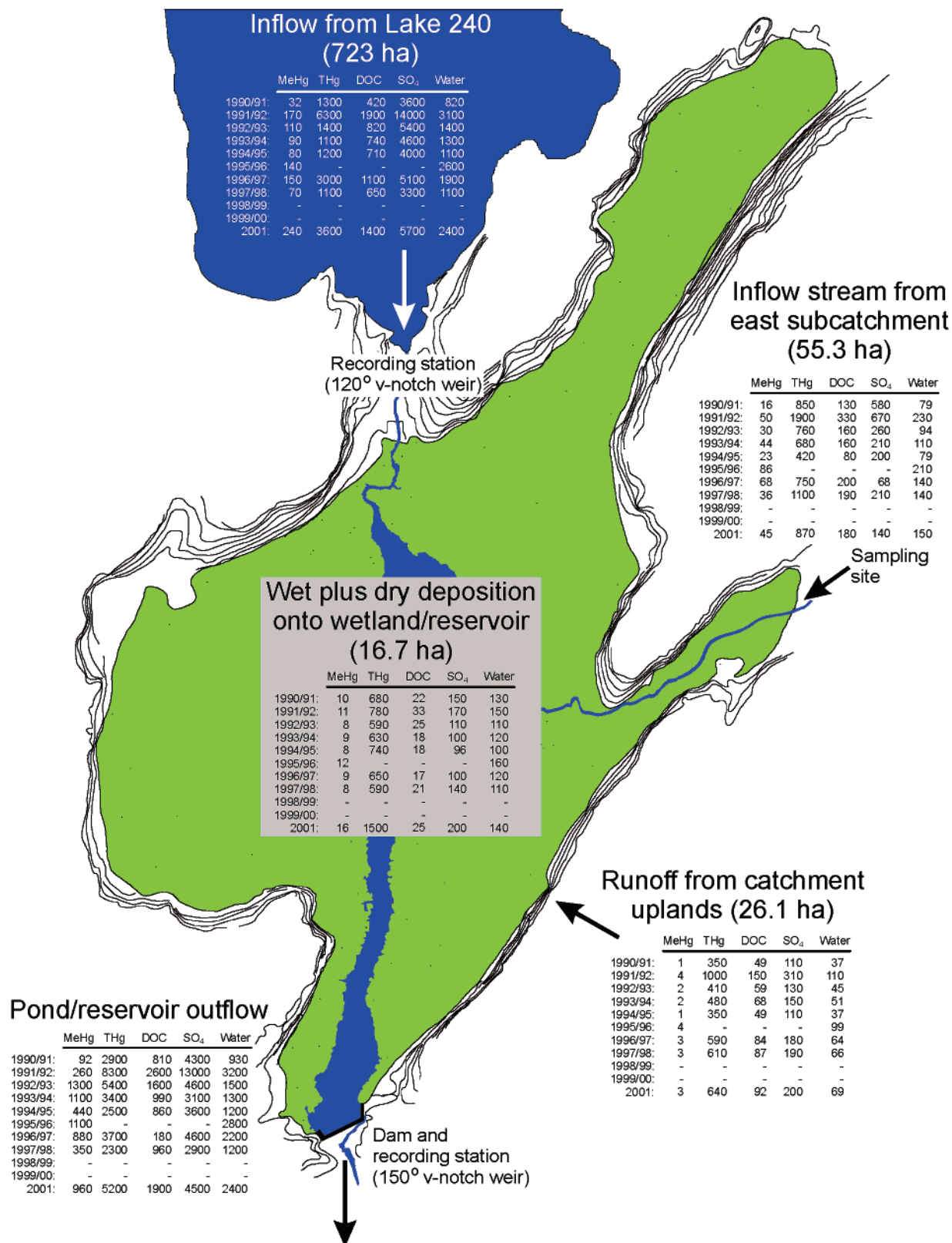


FIGURE 2. Mass inputs and outputs of MeHg, THg, DOC, SO₄, and water from the wetland prior to flooding in June 1993 and the reservoir postflood. Masses are annual totals for the water budget period of November 1 to October 31.

and SO₄. Following appropriate pretreatment and preservation, samples were analyzed as described by Stainton et al. (16).

Input–Output Budget Calculations. Input–output calculations were done as described in St. Louis et al. (11, 12) and for the first 2 years of this wetland flooding study (10).

The basic equation used for input–output budget calculations for the wetland was

$$Net_{(MeHg, THg, DOC, SO_4, Water)} = O_{(MeHg, THg, DOC, SO_4, Water)} - \sum I_{(MeHg, THg, DOC, SO_4, Water)}$$

TABLE 1. Summary of Inputs and Output of Water, MeHg, THg, DOC, and SO₄ to the Wetland Area of the Experimental Site

parameter	comments
Inputs to Wetland Areas Only	
deposition	concentrations measured in wet, wet plus dry, or bulk deposition
inflow from lake 240	concentrations measured; water volume measured at weir
inflow from valley-bottom wetland subcatchment	concentrations measured; water volume estimated on an areal basis from a nearby gauged lake 239 valley-bottom subcatchment
runoff from uplands	concentrations measured in runoff from a purely upland catchment (Lake 114 inflow); water volume estimated on an areal basis from the nearby gauged lake 239 valley-bottom subcatchment
Output	
outflow	concentrations measured; water volume measured at weir

where for MeHg, THg, DOC, SO₄, or water, $\sum I_{(MeHg, THg, DOC, SO_4, Water)}$ was the annual sum of all inputs to the entire wetland, and $O_{(MeHg, THg, DOC, SO_4, Water)}$ was the annual output from the wetland outflow (Table 1). Hydrological inputs to the wetland originated in stream inflows from Lake 240 and the valley-bottom wetland subcatchment and direct runoff from the uplands. Atmospheric inputs to the wetland included wet deposition of MeHg, wet plus dry deposition of THg, and bulk deposition of DOC or SO₄. The "Hg outputs" term in our mass balance does not include loss of Hg⁰ from the water to the atmosphere, because concentrations of dissolved gaseous Hg were at or below detection limits on the occasions when measured (unpublished data and G. Gill, Texas A&M University-Galveston, personal communication), most likely due to high concentrations of DOC (annual means ranging from 790 to 1260 $\mu\text{mol L}^{-1}$ in outflow water) diminishing the photoreduction of Hg to Hg⁰ (17). We therefore assumed a negligible flux of Hg⁰ from the water surface to the atmosphere.

For almost all years, annual budgets were calculated for the period November 1–October 31 because snowfall following freeze up in early November contributed to runoff in the subsequent spring. In the year 2001, however, the annual budget was calculated for the period January 1–December 31 because that was when chemical and hydrological monitoring occurred. A negative value for $\text{Net}_{(MeHg, THg, DOC, SO_4, Water)}$ indicates that the wetland or reservoir was a net sink, while a positive value indicates the wetland or reservoir was a net source of MeHg, THg, DOC, SO₄, or water.

Input–output budgets were also calculated each year for the time interval of June 15 to August 31. This shorter time interval was chosen because it was the warmest time of year and therefore the most active season for MeHg production and bioaccumulation.

Two small differences from methodology or calculations described in St. Louis et al. (11, 12) and Kelly et al. (10) were used here: (1) *Wet deposition*: In 2001 we collected wet deposition for analysis of THg and MeHg concentrations using an automated collector that opened only during rain events. Concentrations of THg were similar to those measured in previous years (1992–1994 and 1998–1999) with Teflon collectors only set out following the start of precipitation events ((18, 19) also see results). However, concentrations of MeHg in wet deposition collected in 2001 were unreliable due to preservation problems. Therefore, MeHg concentrations in wet deposition for 2001 were estimated as the volume-weighted concentrations measured in previous years (19). (2) *Dry deposition*: A recent study found that dry deposition of THg in the ELA region (estimated from both net throughfall and reactive gaseous Hg measurements) was approximately 13% of that found in wet deposition (19), and therefore this dry deposition rate was applied to the surface of the whole wetland complex. This was lower than the value of 50% derived from studies in the United States and used in previous publications (10–12).

Hg Stores in Unflooded and Flooded Peat. We collected cores from the peatland prior to and after flooding to determine stores of MeHg and THg in peat. Cores were taken when the upper 15–40 cm of the peatland was still frozen in March–April using a Teflon lined 10-cm barrel ice corer. During this spring period, the reservoir was still at its winter drawdown level, so the peat was close to its pre-flood configuration because the porewater in the floating peat had drained out. The cores were sectioned into 2 cm intervals while still frozen using a cleaned stainless steel knife. Below the frostline, samples were taken at measured depths by gloved hand. Cores were collected from spatially diverse sites 1 year prior to flooding in 1992 ($n = 6$) and 2 (1995; $n = 8$), 5 (1998; $n = 8$), and 8 years (2001; $n = 7$) after flooding.

Approximately 0.2–0.3 g of peat sample was analyzed wet for MeHg and THg, while another portion was dried to determine percent water. All peat samples were analyzed by Flett Research Ltd. MeHg concentrations were determined by distillation extraction, aqueous phase ethylation, and CVAFS detection (modification of ref 15) following a digestion overnight at room temperature in a mixture of 25 mL of deionized water and 600 μL of 9 molar H₂SO₄ saturated with KCl. Triplicates were analyzed in 10% of samples, with a mean coefficient of variation of 18%. MeHg spike recoveries averaged $100 \pm 25\%$ for 13 spiked samples. Method detection limits were 0.1–0.5 ng gdw^{-1} (g dry weight) of peat. THg was determined using CVAFS detection following a 6 h digestion at 150 °C in 5 mL of 7:3 HNO₃:H₂SO₄. Method detection limits were 0.2–0.4 ng gdw^{-1} . Spike and reference material recoveries typically were $100 \pm 10\%$.

Although the average depth of peat in the peatland was 1.7 m (20), we conservatively estimated Hg stores in the top 0.6 m of peat only because that was the average length of our cores. Mean concentrations of MeHg and THg in peat were multiplied by the mass of the top 0.6 m of peat. Average bulk density for the top meter of peat was 0.095 g cm^{-3} (20).

Organic Carbon Decomposition. In addition to quantifying net DOC production in the wetland reservoir using input–output budgets, we also measured dissolved concentrations of CO₂ and CH₄ in surface waters of the wetland pond prior to flooding, and the open water region of the reservoir after flooding, as an indicator of rates of decomposition of flooded organic matter during the ice-free season. Dissolved gas samples were collected and analyzed essentially as described in Hamilton et al. (21) and Kelly et al. (10), using preevacuated serum bottles with a KCl preservative and headspace analysis using flame ionization gas chromatography.

Mercury Bioaccumulation in the Food Chain. Zooplankton were collected every 1–2 weeks during the ice-free season by horizontally towing an 80 μm net through the open water region of the reservoir. Samples were immediately frozen in whirl-pak bags. Microscopic inspection of all samples confirmed that zooplankton made up more than

TABLE 2. Average Annual Percentage Input (\pm SD) from Each Source and Average Annual Total Inputs to the Wetland/Reservoir

	average annual total inputs	average annual % of total inputs from each source			
		precipitation	lake 240	east subcatchment	direct runoff
MeHg	160 \pm 68 mg	7 \pm 4.2	64 \pm 7.5	27 \pm 5.9	2 \pm 0.5
THg	4300 \pm 2600 mg	18 \pm 6.5	46 \pm 11	22 \pm 6.1	13 \pm 2.9
DOC	14000 \pm 7200 kg	2 \pm 0.8	76 \pm 5.7	16 \pm 4.0	7 \pm 1.3
SO ₄	6300 \pm 3800 kg	2 \pm 0.9	89 \pm 4.4	5 \pm 3.7	3 \pm 1.0
water	2000 \pm 900 (*10 ³) m ³	7 \pm 2.4	83 \pm 3.5	7 \pm 1.3	3 \pm 0.6

TABLE 3. Net Yields of MeHg, THg, DOC, SO₄, and Water from the Wetland Area Preflood (1991 and 1992) and the Reservoir Postflood (1993–2001)

year	MeHg yield		THg yield		IHg yield		DOC yield		SO ₄ yield		water yield	
	mg ha ⁻¹	% of inputs	mg ha ⁻¹	% of inputs	mg ha ⁻¹	% of inputs	mol ha ⁻¹	% of inputs	kg ha ⁻¹	% of inputs	m ³ ha ⁻¹	% of inputs
Preflood												
1990/1991	1.9	150	-16	92	-18	90	11000	130	-4.6	98	-7700	88
1991/1992	1.6	110	-99	83	-100	83	7700	110	-91	90	-21000	90
Postflood												
1992/1993	70	860	130	170	61	130	29000	150	-82	77	-7900	92
1993/1994	54	730	35	120	-20	88	26000	140	-120	61	-15000	84
1994/1995	20	400	3.1	100	-17	88	24000	150	-50	81	-6000	92
1995/1996	50	450									-17000	91
1996/1997	38	370	-80	73	-120	59	23000	130	-52	84	-5100	96
1997/1998	14	300	-64	69	-77	61	8100	110	-56	75	-17000	81
1998/1999												
1999/2000												
2001	36	320	-85	79	-120	67	12000	110	-100	73	-20000	88

95% of the biomass. Prior to 1997, freeze-dried samples were analyzed in the Freshwater Institute Hg Laboratory (Winnipeg, Manitoba) for organic Hg using cold vapor atomic adsorption spectrophotometry (CVAAS) as described by Armstrong and Uthe (22) and Malley et al. (23). After 1997, freeze-dried samples were analyzed by Flett Research Ltd. specifically for MeHg using CVAAS as described by Watras and Bloom (24). Several intercomparison studies indicated that the organic Hg and MeHg determinations were equivalent for zooplankton ((25) also M. J. Paterson, unpublished data).

Finescale dace (*Phoxinus neogaeus*) were introduced into pens placed in the pond of the wetland prior to flooding in early summer of 1991 and 1992 and the central open water region of the reservoir in 1993–1995, 1998, and 2001 (26). Pens were large (19.6 or 38.5 m²), had open mesh (0.6 or 1.2 cm) walls, and were open to the bottom sediments of the reservoir to allow fish to feed on naturally available food (see ref 26 for a summary of feeding by finescale dace before and after flooding). Finescale dace were obtained from a local bait supplier. Initial stocking densities were 3.7–9.7 g m². Fish were sampled prior to introduction into the pens in May/June and then again in early October. Body burdens of THg were determined for whole fish, excluding the digestive tract and its contents, using two methods. For the first method, THg concentrations were determined for the whole body of the fish in the Freshwater Institute Hg Laboratory using CVAAS as described by Hendzel and Jamieson (27). Fresh weight of each fish was used to calculate total body burdens of Hg. For the second method, concentrations of THg were measured on muscle tissue only, and body burdens calculated using a conversion factor from a subsample of finescale dace for which both muscle and whole body determinations were performed. MeHg comprised 70–90% of the THg in the whole bodies of finescale dace (26). Standardized changes in body burdens of THg in finescale dace were calculated each year by subtracting the mean body burden of Hg in dace introduced to the pens from the mean

body burden of THg in dace in October and then dividing by the number of days the dace were held in the pens.

Results and Discussion

Hydrology of the Wetland and Reservoir. The largest annual input of water (83 \pm 3.5%) to the wetland prior to flooding and the reservoir after came from upstream Lake 240 and its 723 ha watershed (Table 2, Figure 2). Wet deposition onto the wetland accounted for on average only 7 \pm 2.4% of the total inputs of water to the wetland or reservoir (Table 2, Figure 2). The east subcatchment also supplied on average 7 \pm 1.3% of the water, whereas we estimated that 3 \pm 0.6% of the water was derived from direct upland runoff to the wetland or reservoir. On average, 89 \pm 4.5% of the water entering the wetland or reservoirs was exported annually (Table 3). There was no discernible increase or decrease in water yield due to flooding in 1993 (Table 3).

Average annual wet deposition at the ELA was 741 \pm 110 mm, ranging between 607 mm in 1994/1995 to 956 mm in 1995/1996. Although percent annual water yields remained fairly constant among years, there were large variations in annual water residence times (or m³ water yielded per ha) of the wetland and reservoir (Table 3). These differences in annual flushing rates had a direct effect on concentrations of Hg and other chemical species irrespective of biogeochemical processes occurring there. As a result, concentrations were not directly comparable among years.

THg Concentrations and Input–Output Budgets. Concentrations of THg in wet deposition collected between 1992 and 1998 ranged between 0.94 and 26 ng L⁻¹ with an overall volume-weighted average of 4.78 ng L⁻¹ (n = 26). Concentrations of THg in wet deposition collected in the summer and fall of 2001 were within the range of those measured earlier, but there was a greater frequency of high concentration events, and so the volume-weighted average for 2001 was higher (9.54 ng L⁻¹, n = 8). Wet and estimated dry deposition of THg onto the wetland ranged between 3.5 and 6.0 mg ha⁻¹ yr⁻¹ (Figure 2) and contributed on average 18 \pm

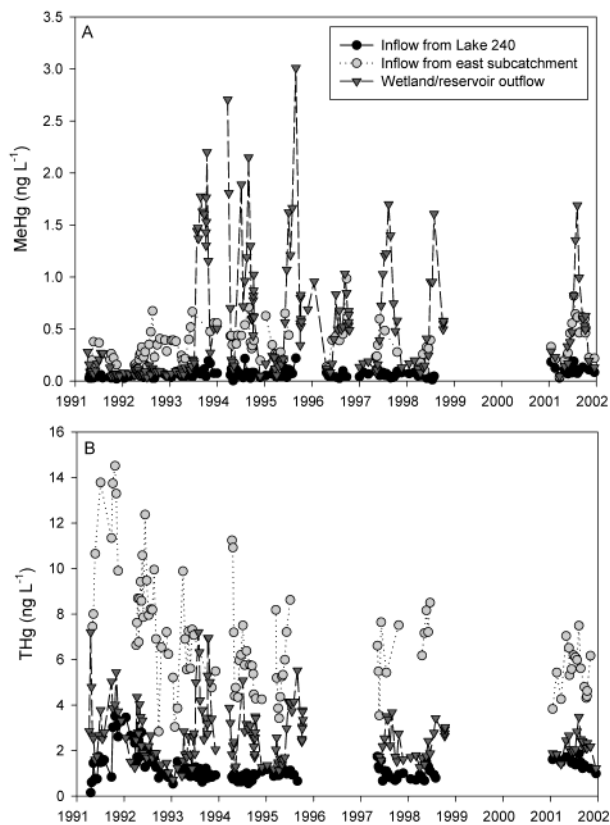


FIGURE 3. Concentrations of MeHg (A) and THg (B) in water entering the wetland/reservoir from Lake 240 and the east subcatchment and water exiting out the outflow. The wetland was flooded in mid-June 1993.

7% of the total THg inputs to the wetland or reservoir annually (Table 2, Figure 2).

Even though concentrations of THg in upland runoff water were high ($9.72 \pm 2.85 \text{ ng L}^{-1}$ (12)), because of the small area of direct upland runoff (26 ha), annual inputs of THg from upland areas only accounted for $13 \pm 3\%$ of the THg inputs (Table 2, Figure 2). Concentrations of THg were also high in water entering the wetland and reservoir from the east subcatchment containing riparian wetlands along the valley-bottom stream (Figure 3), but the east subcatchment provided on average $22 \pm 6\%$ of the THg entering the wetland or reservoir annually (Table 2, Figure 2). THg concentrations in water entering from Lake 240 were much lower (Figure 3), but because of the volume of water entering from the large watershed drainage area (723 ha) of this source, it provided on average $46 \pm 11\%$ of all THg inputs to the wetland or reservoir (Table 2).

Following flooding, there was a progressive decrease in concentrations of THg in the reservoir, declining from on average 3.2 to 2.2 ng L^{-1} (Figure 3). Prior to flooding, the wetland was a net sink of between 16 and $99 \text{ mg THg ha}^{-1} \text{ yr}^{-1}$, yielding approximately 90% of the THg that entered the wetland (Table 3). This percent net retention of THg is common for undisturbed boreal wetlands (12). In the first year after flooding, the reservoir became a large net source of THg to downstream lakes ($130 \text{ mg THg ha}^{-1} \text{ yr}^{-1}$, or 170% of inputs; Table 3). In the next 2 years, it was still a source, but a much smaller one, yielding only 35 and $3 \text{ mg THg ha}^{-1} \text{ yr}^{-1}$. A large portion of the increased THg export in 1993 was actually MeHg export (see below), suggesting that methylation was an important factor in increasing the mobility of Hg in the wetland. The reservoir was only a net source of inorganic Hg (IHg; or THg minus MeHg) during the first year after flooding (Table 3). In subsequent years, the reservoir

returned to being a sink for THg of similar size as that of the wetland prior to flooding (Table 3). For IHg, however, the postflood sink in later years was smaller than prior to flooding because of sustained high methylation of Hg(II) within the wetland and the subsequent export of the methylated form (see below).

MeHg Concentrations and Input–Output Budgets. The volume-weighted mean concentration of MeHg in wet deposition was 0.077 ng L^{-1} ($n = 26$). Annual wet deposition of MeHg onto the wetland ranged between 0.48 and $0.96 \text{ mg ha}^{-1} \text{ yr}^{-1}$ (Figure 2) and contributed on average $7 \pm 4.2\%$ of the total MeHg inputs ($162 \pm 4.2 \text{ mg}$) to the wetland or reservoir annually (Table 2).

Concentrations of MeHg in direct upland runoff to the reservoir were very low ($0.04 \pm 0.032 \text{ ng L}^{-1}$ (12)). As seen for THg, because of the small area of direct upland runoff to the wetland or reservoir, annual inputs of MeHg from this source accounted for on average of only $2 \pm 0.5\%$ of the total MeHg inputs (Table 2, Figure 2). Concentrations of MeHg in water entering the wetland from upstream Lake 240 were also very low throughout the study period, with annual averages ranging between 0.04 and 0.09 ng L^{-1} (Figure 3). However, with respect to mass input of MeHg, Lake 240 was the largest external source of MeHg to the wetland or reservoir ($64 \pm 8\%$ of all inputs) because of its large watershed drainage area (Table 2, Figure 2).

Inputs from the east subcatchment had the highest concentrations of MeHg (0.25 – 0.42 ng L^{-1} ; Figure 3). This subcatchment contained riparian wetlands along the valley-bottom stream, which has been shown in the past to be a net source of MeHg (11, 12). Although the watershed area of the east subcatchment was only 55.3 ha, it provided on average $27 \pm 6\%$ of the MeHg entering the wetland or reservoir annually (Table 2, Figure 2).

In the 2 years prior to flooding, concentrations of MeHg in water in the wetland pond were on average 0.15 and 0.08 ng L^{-1} (Figure 3). These are higher concentrations than for upland runoff and lake surface water but lower than for water flowing from the riparian wetland of the east subcatchment because of dilution in the wetland pond with water from upstream Lake 240.

Approximately 3 weeks after flooding, MeHg concentrations in the reservoir jumped 7-fold (Figure 3), coinciding with increases in concentrations of dissolved CH_4 (indicative of increased anaerobic decomposition (10) and below). On one occasion in the summer of 1995, when there was low inflow from Lake 240, MeHg concentrations reached levels of approximately 3 ng L^{-1} (Figure 3). MeHg concentrations in the open water region of the reservoir decreased after the first 2 years of flooding to on average between 0.46 and 0.65 ng L^{-1} annually but still remained much higher than those in the wetland pond prior to flooding (Figure 3). These high concentrations occurred even though we added no Hg(II) to the reservoir, and atmospheric inputs at the ELA were low (19), demonstrating that Hg(II) stored in the flooded peat and vegetation was methylated after flooding. Similarly high concentrations of MeHg were also observed in the few other reservoirs that were sampled in the early stages of flooding (8, 27). **These reservoir surface water concentrations are much higher than those for unflooded wetlands or lakes (e.g., refs 11 and 12) and are among the highest MeHg concentrations recorded for any ecosystems, including those that have been polluted by point sources of Hg(II) (28–30).**

The percentage of THg that is MeHg (%MeHg) is a good relative indicator of MeHg production rates in ecosystems (31, 32, 12). Prior to flooding, the THg in the pond was 5–10% MeHg (Figure 4), which is similar to other unperturbed wetlands (12, 33, 34). After flooding, the %MeHg increased to 60–80% (Figure 4), demonstrating that very intense Hg methylation had occurred following flooding. Peaks in

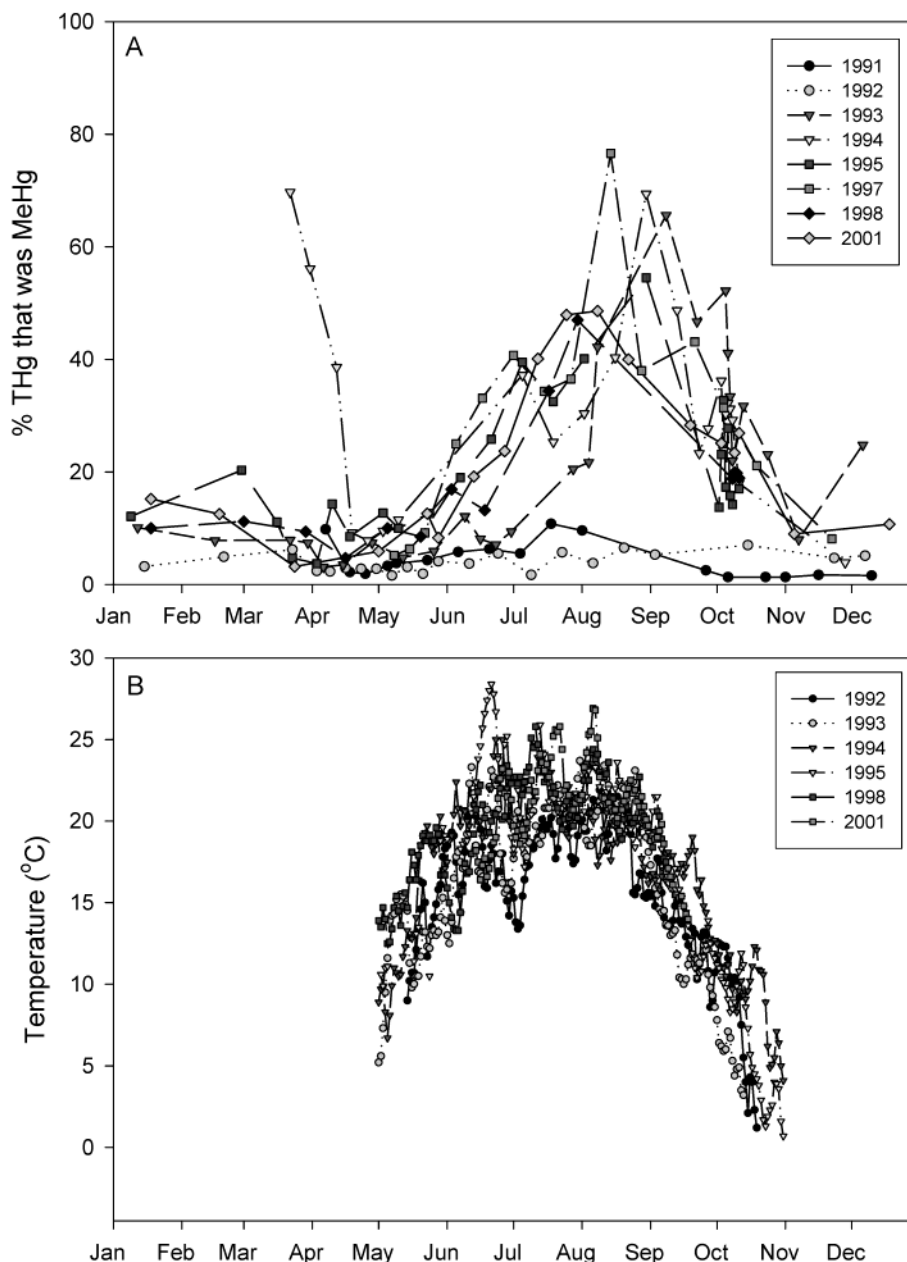


FIGURE 4. Seasonal patterns in the % of the THg that was methylated (A) and surface water temperatures (B) in the water of the wetland prior to flooding in June 1993 and the reservoir postflood.

%MeHg in reservoir water always lagged the summer maximum temperature by about a month (Figure 4), except in spring 1994 following a winter in which the open water region went totally anoxic because water flow from upstream Lake 240 stopped. This pattern of elevated %MeHg during the summer period persisted 9 years after flooding, although the amplitude of the peak became somewhat muted as time passed.

Prior to flooding, the wetland was a net source of ~ 1.7 mg MeHg $\text{ha}^{-1} \text{yr}^{-1}$ to downstream ecosystems, yielding $\sim 130\%$ of the amount of MeHg that entered the wetland (Table 3). In the first year of flooding, net export of MeHg from the reservoir increased 40-fold to approximately 70 mg MeHg $\text{ha}^{-1} \text{yr}^{-1}$, yielding over 860% of MeHg inputs (Table 3). Subsequently, annual net yields of MeHg from the reservoir have declined but still remained well above natural levels 9 years postflood ($10\text{--}50$ mg MeHg $\text{ha}^{-1} \text{yr}^{-1}$) (Table 3).

Mercury Bioaccumulation in the Food Chain. Impoundment of the wetland resulted in large increases in MeHg

concentrations in zooplankton. Mean annual concentrations of MeHg in zooplankton were 7–10 times higher in 1993–1995, and 14–30 times higher in 1996–2001, than in pre-flood years (Figure 5), indicating that there were no signs that MeHg concentrations in the reservoir zooplankton were returning to those observed prior to impoundment. To a large extent, increases in MeHg in zooplankton followed increases in MeHg concentrations measured in the reservoir water (Figure 3). There were no corresponding increases in zooplankton MeHg concentrations in neighboring lakes during the same time period ((25) M. J. Paterson, unpublished data).

Seasonal changes in body burdens of Hg in finescale dace were on average much higher after flooding (7.3 ± 2.0 ng Hg $\text{fish}^{-1} \text{d}^{-1}$) than prior to flooding (1.8 ± 3.8 ng Hg $\text{fish}^{-1} \text{d}^{-1}$) (Figure 5). Bodaly and Fudge (26) originally concluded that there was a tentative slowing of Hg uptake by dace over the first 3 years of flooding. However, this conclusion has not borne out over the longer term. Subsequent sampling showed that seasonal changes in body burdens of Hg were still

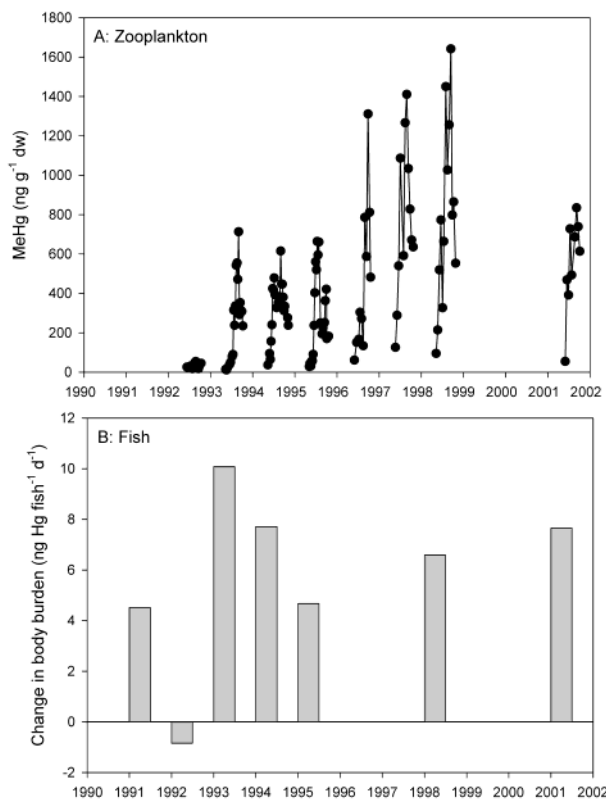


FIGURE 5. Concentrations of MeHg in zooplankton collected from the wetland pond prior to flooding in June 1993 and the reservoir postflood (A). Rates of MeHg accumulation in finescale dace annually introduced into mesh pens in the wetland pond and reservoir during the open water season (B). The wetland was flooded in mid-June 1993.

elevated 6 and 9 years postflood, and that these changes were within the range of those observed in the first 3 years of flooding (Figure 5). Patterns of Hg accumulation in finescale dace did not mirror patterns of MeHg concentrations in zooplankton (Figure 5), suggesting that dace were consuming benthic invertebrates, for which we have no long-term Hg data. In fact, only 19% of the stomach contents before flooding, and 24% of the stomach contents after flooding, were zooplankton, whereas 74% and 63% of the stomach contents before and after flooding, respectively, were benthic invertebrates such as chironomids, odonates, hemipterans, and tricoptera (26). Because the benthic invertebrates were much larger in mass than the zooplankton and were numerically dominant in the experimental reservoir, they constituted the greater majority of food biomass for the finescale dace. Concentrations of MeHg in benthic invertebrates and emerging chironomids in the experimental reservoir also increased in the first 2–3 years of flooding (35, 36), a trend also observed in hydroelectric reservoirs in northern Quebec (37).

Sulfate Reduction. Sulfate-reducing bacteria active in anaerobic environments are thought to be the primary Hg methylating organisms (6). Prior to flooding, between 90 and 98% of the SO_4 that entered the wetland in all inputs exited out the outflow annually (Table 3). After flooding, the reservoir only yielded between 61 and 84% of the annual SO_4 inputs (Table 3). This suggests an increase in SO_4 reduction in the reservoir due to flooding. To examine this quantitatively, we calculated mass transfer coefficients for SO_4 removal (S_s ; m yr^{-1}) during the warm summer months of each year when microbial activity was at its peak (June 15–August 31). This calculation takes into account that SO_4 removal from the water flowing through the wetland or reservoir by SO_4

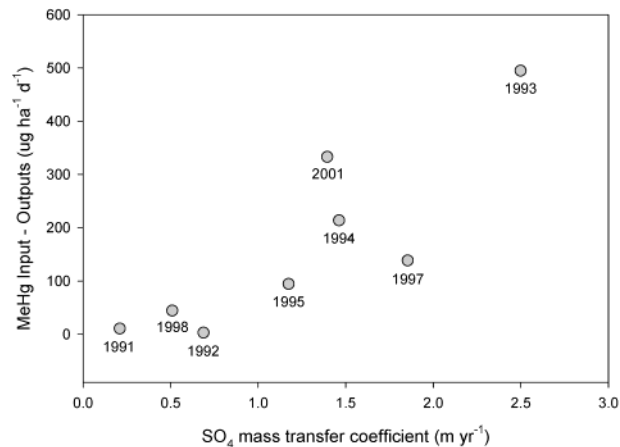


FIGURE 6. The relationship between summer (June 15–August 31) SO_4 reduction rates (measured as a mass transfer coefficient) and the net mass of MeHg yielded (inputs–outputs) from the wetland/reservoir for the same time period. The wetland was flooded in June 1993.

reduction in sediments is affected by both SO_4 reduction rate and water residence time (38)

$$S_s = R_s * q_a / (1 - R_s)$$

where R_s = fraction of SO_4 retained in wetland ((outputs–inputs)/inputs), and q_a = areal outflow of water (m yr^{-1}).

S_s values, which are indicative of SO_4 reduction rates, increased after flooding (Figure 6) as might be expected from the high decomposition rates and low oxygen values in the reservoir (10). The fact that both SO_4 reduction and Hg methylation increased and remained high after 9 years of flooding (Table 3, Figures 5 and 7) is consistent with evidence from other ecosystems that SO_4 reducing bacteria are the primary Hg methylating bacteria (6), although it is possible that the sulfate-reducing bacteria that were stimulated by flooding were not the actual Hg methylators.

Production of DOC. Prior to flooding, the wetland yielded between 7700 and 11 000 $\text{mol DOC ha}^{-1} \text{ yr}^{-1}$ or 110–130% of the total DOC inputs (Table 3). In the first 3 years following flooding, yield of DOC from the reservoir increased 3-fold to between 24 000 and 29 000 $\text{mol DOC ha}^{-1} \text{ yr}^{-1}$ or approximately 145% of the annual DOC inputs (Table 3). The increase in DOC yields following flooding most likely resulted from the decomposition of flooded vegetation in the reservoir. Four to 5 years after flooding, the reservoir was again exporting only 110–130% of the total DOC inputs, similar to yields from the wetland prior to flooding (Table 3). As seen in other studies, there was a positive relationship between DOC exported and MeHg exported ($r^2 = 0.66$, $n = 8$).

Production and Demethylation of MeHg in Peat. Prior to flooding, there were no strong differences in peat MeHg concentration with depth (Figure 7). Concentrations of MeHg in the top 0.6 m of peat were on average $1.08 \pm 0.15 \text{ ng g dw}^{-1}$. However, there was a 10-fold increase in average MeHg concentration to $10.5 \pm 1.2 \text{ ng g dw}^{-1}$ 2 years after flooding (Figure 7). By 5 years postflood, the average concentration of MeHg in peat had dropped to $2.0 \pm 0.29 \text{ ng g dw}^{-1}$, and remained low, but still was elevated above pre-flood concentrations, 9 years after flooding at $3.5 \pm 0.85 \text{ ng g dw}^{-1}$.

Using the average concentration of MeHg in all depths for each coring date, and the bulk density of the peat, we estimated that the mass of MeHg in the top 0.6 m increased from 8.8 to 85 g during the first 2 years of flooding (Figure 8). This is probably a conservative estimate of MeHg production because peat cores were collected in the winter when microbial methylation would have been minimal.

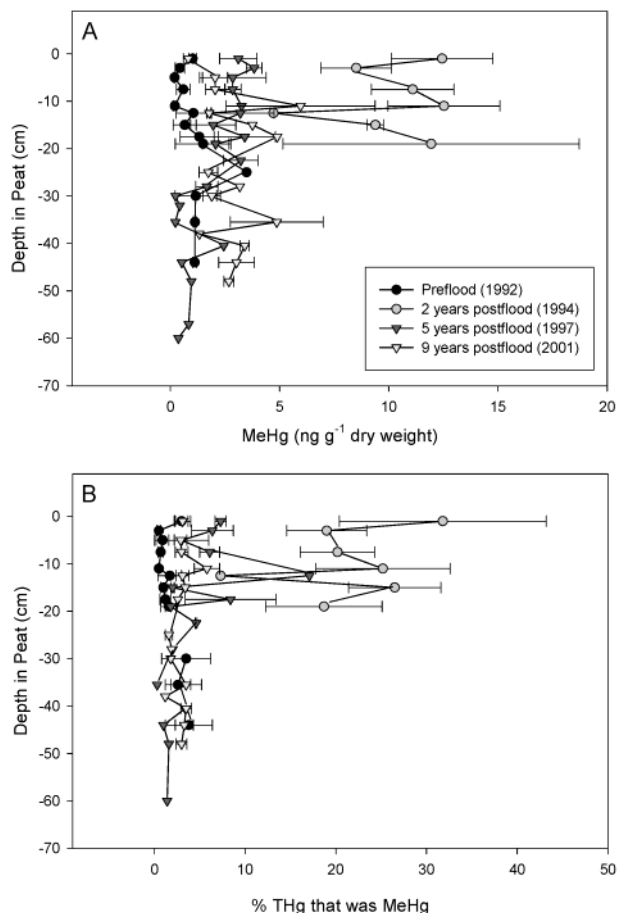


FIGURE 7. Concentrations of MeHg (A) and % THg that was MeHg (B) in peat collected from various depths prior to and after flooding in June 1993.

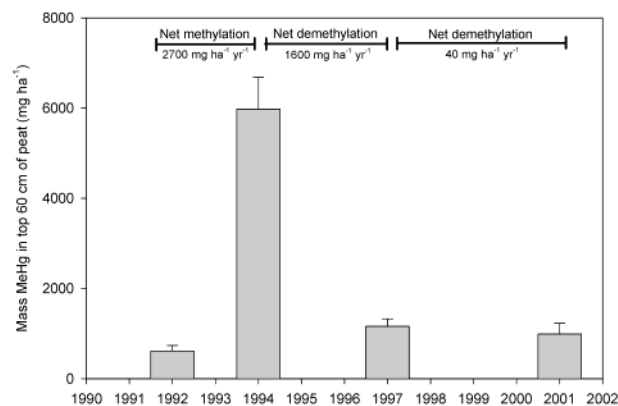


FIGURE 8. Mass of MeHg in the top 60 cm of peat prior to and after flooding in June 1993. Net methylation and demethylation rates were calculated from the difference in masses between the years the peatland was sampled, divided by the area of the peatland (14.3 ha) and the number of years between sampling.

During this same period, only 2.4 g of MeHg exited the reservoir outflow (Figure 2). At the whole-ecosystem level, at least 97% of the MeHg production occurred in the peat, whereas at most only 3% flowed out the outflow. This demonstrates that the flooded peat was the major site of Hg methylation, not the open water region of the reservoir. During this 2-year period, there was a net production of 2700 mg MeHg ha⁻¹ yr⁻¹ in the ecosystem (Figure 8).

During the subsequent 3 years of flooding, the mass of MeHg in the upper 0.6 m decreased from 85 to 16 g, at a net

loss rate of 1600 mg MeHg ha⁻¹ yr⁻¹ (Figure 8). There are three possible means by which MeHg could have been lost from the peat: (1) leaching and loss out the reservoir outflow, (2) photodegradation to either Hg(II) or Hg⁰, and/or (3) microbial demethylation. During this 3-year period, only about 2.6 g of MeHg exited the reservoir outflow (Figure 2). This input–output calculation clearly demonstrates that only a small fraction of the MeHg in the peat could have been lost via leaching. Furthermore, because this loss occurred in the peat in the dark (where photodegradation of MeHg was not possible), the loss must have occurred by microbial demethylation of MeHg. These data also suggest that there was likely a loss of Hg⁰ from the floating peat directly to the atmosphere, because Hg⁰ is commonly one of the products of microbial demethylation (39), although we did not attempt to measure this flux.

The percentage of THg that was methylated also demonstrated that both Hg methylation and MeHg demethylation occurred within the flooded peat (Figure 7). Two years after flooding, approximately 20% of the THg in peat had been methylated compared to only 1–2% prior to flooding (Figure 7). The %MeHg decreased to approximately 3.5% in the last 5 years of flooding (Figure 7).

Lack of Relationship between Methylation in the Open Water Regions of the Reservoir and the Flooded Peat. The extent and duration of Hg methylation was very different in the flooded peat compared to the open water regions of the reservoir. In the flooded peat, net Hg methylation had for the most part finished by 5 years after flooding, at which time MeHg concentrations returned to near pre-flood levels (Figure 7). In the open water regions of the reservoir, there was an immediate sustained increase in MeHg concentrations following flooding. We also saw a large increase in the net yield of MeHg from the reservoir as a whole using input–output budgets, but this net yield has only decreased slowly over the 9 years we have been monitoring the reservoir. Thus net Hg methylation has continued in the open water regions of the reservoir, while there was net MeHg demethylation in the flooded peat following a short period of net methylation.

When trying to understand the differences in methylation in the flooded peat and open water regions of the reservoir, it is important to examine the physical changes that have occurred in the reservoir over time due to flooding. Immediately after inundation in 1993, most of the flooded peat was submerged below the water surface of the reservoir (Figure 1). Over time, the peat progressively floated because of peat decomposition, bubble production, and increased buoyancy (40). By 1997, the peat had mostly floated (Figure 1), and the reservoir water was in contact with the edges and underside of the floating peat mats rather than the peat surface. This physical change most likely resulted in less mixing of water by wind over the flooded peat, isolating the open water region of the reservoir more than when the peatland was initially inundated and submerged. Furthermore, peat pieces sloughed off the edges of the floating peat into the open water region of the reservoir due to wave action where they fueled decomposition. While peat is generally considered to be recalcitrant and somewhat resistant to decomposition, peat dispersed into surface water is biodegradable (41), and both aerobic and anaerobic decomposition clearly have remained high in the open water regions of the reservoir as demonstrated by the continuing high concentrations of dissolved CO₂ and CH₄ there (Figure 9).

An intriguing question to ask is why did the net Hg methylation decrease in the flooded peat but not in the open water regions of the reservoir, even though decomposition rates have remained high in both the flooded pond and flooded peat (S. Schiff et al. University of Waterloo, Ontario, Canada; personal communication). We hypothesize that the explanation for this difference is related to the bioavailability

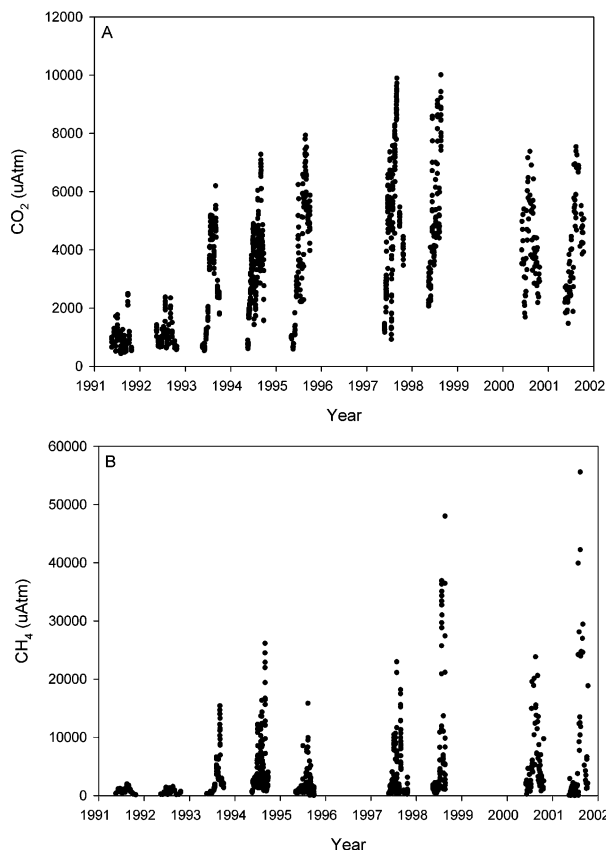


FIGURE 9. Concentrations of dissolved CO_2 and CH_4 in the surface waters of the wetland pond prior to flooding in June 1993 and the reservoir postflood.

of inorganic Hg for production of MeHg. The inputs of new Hg(II) each year from deposition and inflows to the pond are higher than the net yield of MeHg in the outflow (Figure 2). As this Hg flows through the reservoir each year, a portion of it could be available for ongoing Hg methylation. In the peat, however, much more Hg was methylated in the first 2 years than could have come from the annual inputs, and so Hg already present in the peat must have been utilized for the methylation. The very high rates of Hg methylation that occurred in the few years following inundation may have depleted the bioavailable Hg pool there.

The time course of MeHg concentrations in the zooplankton and fish (Figure 5) followed the course of MeHg concentrations in the reservoir water (Figure 3) much more closely than in the peat (Figure 7). This suggests that the biota concentrations are being maintained by the comparatively very small source of sustained Hg methylation in the open water regions of the reservoir. In contrast, the vast majority of MeHg produced in the experimental reservoir (97% of it in the flooded peat) appears to have made only a minor contribution to concentrations of MeHg in the food chain.

Implications of This Research with Respect to Large Reservoirs. We see this research contributing to the understanding of Hg cycling in reservoirs as follows. Early in the evolution of reservoirs, our study and other research (42) have demonstrated that there is a large production of MeHg in flooded soils and peat. Our study has also shown that because of microbial demethylation, the persistence of this very large mass of MeHg is relatively short-lived (2–3 years). The fate of MeHg produced in the soils and peat during this early time period could be very important in determining the long-term concentration of MeHg in predatory fish populations. We see two scenarios, both determined by the

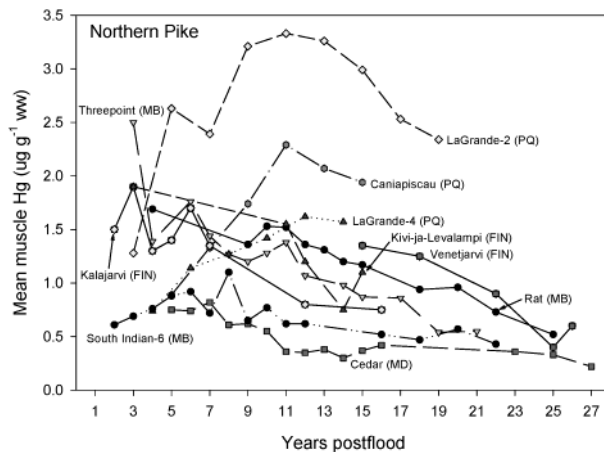


FIGURE 10. Concentrations of THg in the muscle tissue of northern pike (*Esox lucius*) in northern Canadian (Manitoba and Quebec) and Finnish reservoirs (8, 44, 45).

presence or absence of peat/soil erosion during the early years of flooding. In the first case, if there is not significant erosion during the early years the MeHg will be demethylated without contributing importantly to fish MeHg concentration. This was the case for our experimental reservoir where there was minimal peat erosion, and the fish MeHg concentration was elevated, but only by the relatively small MeHg production in the flooded pond. In the second case, if erosion is extensive during the first years of reservoir flooding, a large mass of MeHg would be transported to the open water regions of the reservoir and be bioaccumulated by the food chain and fish, resulting in even higher MeHg concentrations of fish. This latter mechanism has been proposed for the very large hydroelectric reservoirs in northern Quebec such as LaGrande-2, where erosion rates soon after flooding were very high (42, 43), and fish MeHg concentrations have been very high for several decades (Figure 10). Fish MeHg concentrations in these northern Quebec reservoirs are much higher than in other large hydroelectric reservoirs created in, for example, northern Manitoba and Finland (Figure 10), where erosion is more gradual and incomplete, as it was in our experimental reservoir.

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