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Increases in Fluxes of Greenhouse Gases and Methyl Mercury following Flooding of an Experimental Reservoir†

C. A. KELLY,*‡ J. W. M. RUDD,§
 R. A. BODALY,§ N. P. ROULET,||
 V. L. ST. LOUIS,‡ A. HEYES,||
 T. R. MOORE,|| S. SCHIFF,⊥ R. ARAVENA,⊥
 K. J. SCOTT,‡ B. DYCK,○ R. HARRIS,▽
 B. WARNER,△ AND G. EDWARDS◇

Department of Microbiology, University of Manitoba, Winnipeg, Manitoba, R3T 2N2 Canada, Freshwater Institute, Department of Fisheries and Oceans, 501 University Crescent, Winnipeg, Manitoba, R3T 2N6 Canada, Department of Geography, McGill University, Montreal, Quebec, H3A 2K6 Canada, Institute of Ground Water Research, University of Waterloo, Waterloo, Ontario, N2L 3G1 Canada, Department of Botany, University of Manitoba, Winnipeg, Manitoba, R3T 2N2 Canada, Tetra Tech Incorporated, 180 Forestwood Drive, Oakville, Ontario, L6J 4E6 Canada, Department of Geography, University of Waterloo, Waterloo, Ontario, N2L 3G1 Canada, and Department of Land Resource Science, University of Guelph, Guelph, Ontario, N1G 2W1 Canada

Experimental flooding of a boreal forest wetland caused the wetland to change from being a small, natural carbon sink, with respect to the atmosphere, of $-6.6 \text{ g of C m}^{-2} \text{ yr}^{-1}$ to a large source of $+130 \text{ g of C m}^{-2} \text{ yr}^{-1}$. This change was caused by the death of the vegetation, which eliminated the photosynthetic CO_2 sink and stimulated the microbial production of CO_2 and CH_4 from decomposition of plant tissues and peat. Another type of microbial activity that increased was the methylation of inorganic mercury to the much more toxic methyl mercury (MeHg) form. The wetland was a source of MeHg prior to flooding and became an even larger source (39 fold) after flooding. MeHg concentrations in the water sometimes exceeded 2 ng L^{-1} , with the average being 0.9 ng L^{-1} in the first 2 years after flooding. MeHg also increased in the flooded vegetation and peat, in lower food chain organisms, and in fish. Two recommendations, which should minimize both greenhouse gas production and MeHg production in reservoirs, can be made: (1) minimize the total area of land flooded (i.e., avoid flooding areas of low relief) and (2) minimize the flooding of wetlands, which contain larger quantities of organic carbon than uplands and are sites of intense production of MeHg.

Introduction

Many environmental and socio-economic consequences result from reservoir development (1). For instance, fish in

newly created reservoirs almost always accumulate high concentrations of methyl mercury (2-5), which are toxic to the fish consumer (6). Methyl mercury (MeHg) is produced from inorganic mercury by bacterial activity, which is enhanced by the decomposition of flooded vegetation and organic carbon in soils (4). Another emerging concern is the loss from reservoirs to the atmosphere of carbon dioxide (CO_2) and methane (CH_4), which are greenhouse gases. They are the major end products of the microbial decomposition of flooded organic material. It is well known that organic carbon decomposition causes oxygen depletion in newly flooded reservoirs. However, until the last few years, little attention was paid to the possibility that reservoirs might emit significant amounts of CO_2 and CH_4 to the atmosphere (7).

Recent studies of CO_2 and CH_4 fluxes from existing reservoirs (8, 9) have demonstrated that reservoirs are sources of these gases to the atmosphere, but this type of postflood study by itself does not answer the question "what is the net effect of reservoir creation on greenhouse gases in the atmosphere?". To answer this question, both pre- and postflood gas flux measurements are needed because there is no net effect on the atmosphere if the postflood fluxes are the same as the fluxes were from the terrestrial and natural water surfaces prior to flooding.

In contrast to the few studies done on greenhouse gas fluxes in reservoirs, there have been many studies on mercury in reservoirs (for example, ref 10). It is well known that reservoirs have mercury contamination problems in their fisheries that last for several decades after flooding (3, 10). Past studies, however, were limited by the lack of low-level analytical methods for MeHg and total Hg in water. This prevented quantitative studies of MeHg production and its movement into fish.

In order to take advantage of newly developed low-level mercury methods (11, 12) and to quantify the changes in both mercury and carbon cycling due to flooding, we began a whole ecosystem flooding experiment at the Experimental Lakes Area in northwestern Ontario 5 years ago. We chose an experimental site that was predominately peatland for three reasons: (1) many reservoirs in northern countries include peatland areas, and flooding of peatlands is becoming more common after the more favourable "canyon" configurations have been developed; (2) natural peatlands have been shown to be important sources of MeHg to downstream boreal ecosystems (13, 14), and flooding was expected to further enhance this production of MeHg; and (3) there is a large store of organic carbon in peat deposits, and if it decomposes after flooding it will contribute a large quantity of CO_2 and CH_4 to the atmosphere.

The Experimental Lakes Area Reservoir Project (ELARP) was undertaken with two objectives: (1) to quantify the change in greenhouse gas fluxes to the atmosphere as a result of flooding and to understand the mechanisms causing these changes and (2) to understand the processes leading to high MeHg concentrations in fish so that predictive models can be developed and mitigative measures designed to help minimize this problem in future reservoirs. These objectives are interrelated because production of CO_2 , methanogenesis, and mercury methylation are all microbial activities supported by decomposition of flooded organic material.

Methods

The experimental site was a 16.66 ha, boreal forest wetland located at the Experimental Lakes Area, northwestern Ontario. Before flooding, it was composed of a 2.39 ha central pond (Lake 979), which was surrounded by 14.4 ha of peatland (Figures 1A and 2). On June 23, 1993, after 2 years of pre-flood

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* Corresponding author telephone: 204-474-6831; fax: 204-275-7615.

‡ Department of Microbiology, University of Manitoba.

§ Freshwater Institute.

|| McGill University.

⊥ Institute of Ground Water Research, University of Waterloo.

○ Department of Botany, University of Manitoba.

▽ Tetra Tech Incorporated.

△ Department of Geography, University of Waterloo.

◇ University of Guelph.



FIGURE 1. Aerial view of the 979 wetland prior to flooding (A, top; photograph by B. Hall) and after flooding (B, bottom; photograph by A. Heyes). Water flowed from the top to the bottom of the photographs and the dam was located at the bottom of panel B. Panel B was taken during the second summer of flooding, and floating peat islands can be seen at the inundated shoreline of the former pond.

study, the wetland was flooded to a depth of 1.3 m above the previous pond level by damming the outflow. The flooding inundated the surrounding peatland (Figure 1B) and increased the surface area of the pond by a factor of 3 and the water volume by a factor of 6. Each year the reservoir was drained to pre-flood levels in late fall to simulate the winter drawdown of many northern hydroelectric reservoirs. In 1993, the drawdown date was October 5. In 1994, flooding began on May 26, and drawdown began on October 3.

Plant Biomass, Peat Mass, and Plant Decomposition Rates. In July 1992, the pre-flood, above-ground plant biomass

(excluding tree boles and branches) was estimated for each of the six vegetation community types identified in the experimental wetland (Figure 2). The above-ground biomass of non-vascular plants, herbs, and low shrubs was estimated by harvesting this material from 196 quadrats (0.5 m × 0.5 m). Tall shrub and tree foliage biomass was estimated from trunk diameter measurements using regression equations (15). Subsamples of the oven-dried biomass of each species were analyzed for C content (16). Leaf, branch, and stem tissues of woody species were analyzed separately.

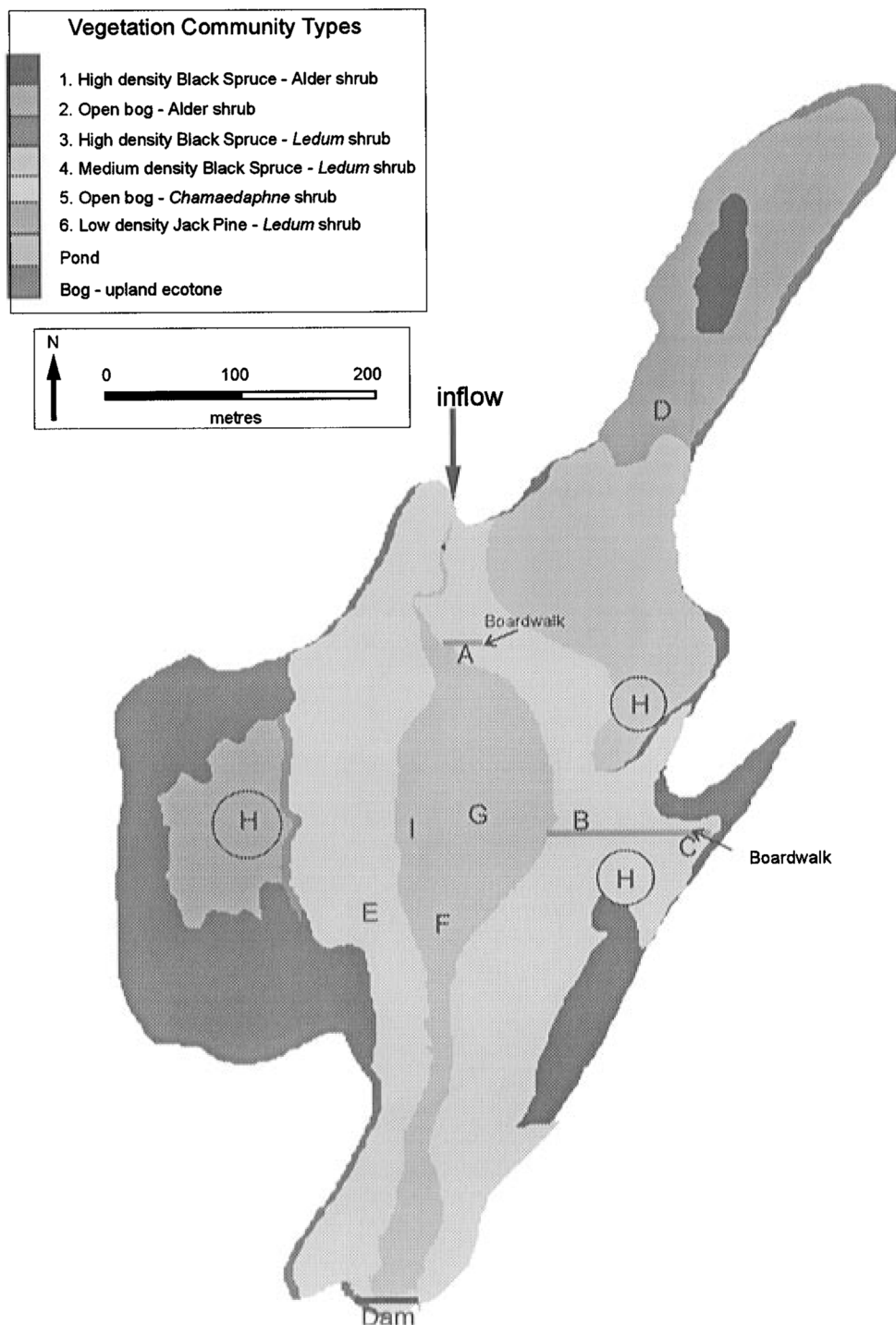


FIGURE 2. Map of experimental wetland, showing location of six vegetation communities and location of boardwalks, static chamber sites (A–D), flux-gradient towers (E and F), and general area of floating chamber sites (H). TBL samples, wind speed, and water temperature measurements were taken at the pond center (G). Fish cages were located at site I.

Peat thickness was determined along 20 transects by insertion of a metal rod until mineral substrate or gyttja were reached. Peat cores were taken to a depth of 1 m at 29 sites and characterized visually. At eight sites, which were selected to represent the major variations in peat profiles in the catchment, 10-cm increments of the cores were further analyzed for bulk density, water content, and loss on ignition.

Annual loss of vegetation carbon after flooding was measured in plant tissues enclosed in litterbags placed onto the peatland surface just prior to flooding (17). Eight tissue types, ranging from easily decomposed leaves to resistant wood blocks and *Sphagnum* sp. were enclosed in 2-mm fiberglass mesh bags and placed at four sites in October 1992.

The plant tissues tested were as follows: *Chamaedaphne calyculata* (leaves), *Chamaedaphne calyculata* (shoots), *Betula papyrifera* (leaves), *Sphagnum fuscum*, *Sphagnum angustifolium*, *Picea mariana* (needles), *Carex oligosperma* (sedge culms), and Douglas fir wood.

Carbon Flux Measurements. Several methods were used to measure gas fluxes between the various wetland surfaces and the atmosphere. Diffusive CO_2 and CH_4 fluxes from the pond surface were estimated by the thin boundary layer (TBL) method, using dissolved gas concentrations and wind speed (18, 19). In addition to measurement of diffusive fluxes, bubble traps (0.25 m in diameter) were also used. The volume of bubbles released from sediments each week was measured

by water displacement. The concentrations of CH₄ and CO₂ in the bubbles were determined using bubbles captured immediately after disturbance of surface sediments (because gas concentrations in trapped bubbles change with time). Bubble fluxes of CH₄ were sometimes as much as 20% of diffusive fluxes, but bubble CO₂ fluxes were always less than 1–2% of diffusive fluxes. Where TBL fluxes are reported, they include both diffusive and bubble fluxes.

In both 1991 and 1992, CH₄ release from the unflooded peatland was estimated using static chambers (SC, 24 cm in diameter; 20) at four sites with three chambers at each site (Figure 2). After flooding, floating chambers (FC, 24 cm in diameter) were used at seven sites (Figure 2) to estimate release of CH₄ and CO₂ from both the open areas and also from the treed areas of the flooded peatland where the TBL and flux-gradient (FG) methods (see below) could not be used.

During 1992 (unflooded) and 1993 (flooded), releases of CO₂ from the pond surface and to/from the open peat surface were estimated by the FG technique (21) using a wind profile corrected for stability (22). Air CO₂ concentrations were measured using a Licor 6250 IR detector. Prior to flooding, the FG technique was also used for a short time period to measure CH₄ flux from the open peat surface. CH₄ concentrations in air were measured using a tuneable diode laser detector.

Detailed comparison of the TBL, FG, and FC methods showed that the three methods agreed well when used simultaneously (Edwards et al., in preparation). For 15 intercomparisons of CO₂ fluxes, the TBL-determined flux averaged 94% of the FG-determined flux ($r^2 = 0.61$). For eight intercomparisons of CO₂ fluxes, the TBL-determined flux averaged 102% of the chamber-determined flux ($r^2 = 0.88$). For eight intercomparisons of CH₄ fluxes, the TBL-determined flux averaged 92% of the chamber-determined flux ($r^2 = 0.62$).

The long-term average incorporation of CO₂ into peat carbon was estimated from ¹⁴C profiles at three sites (23, 24).

The stable isotope ratio of CH₄ emitted from the peat surface, the natural pond surface, and the reservoir surface was measured. Samples were taken using 150-mL evacuated serum bottles from the static chambers placed on peat prior to flooding and from the floating chambers after flooding. ¹³C analyses were carried out at the Environmental Isotope Laboratory (EIL), University of Waterloo. CH₄ was converted to CO₂ by passing the gas with a helium oxygen mixture through copper oxide heated to 850 °C.

Mercury Concentrations and Mass Balances. MeHg inputs to the wetland included atmospheric deposition, direct local runoff, and gauged stream inflows from an upstream lake (Lake 240) and a terrestrial catchment (13, 14). The only outflow was at the dam site (Figures 1 and 2). Water samples to be analyzed for mercury concentrations were taken in acid-washed Teflon bottles using the clean-hands/dirty-hands technique (13). MeHg concentrations were determined by atomic fluorescence after aqueous phase ethylation of MeHg (11). Total mercury in water samples was reduced to Hg⁰, collected on gold traps, and analyzed by atomic fluorescence (12). Analytical precision was ±5% for THg and ±0.015 ng L⁻¹ for MeHg (Flett Research Ltd. (25)). These values were within 9% and 12% of a consensus value obtained in a recent international interlab comparison for THg and MeHg, respectively (26). Concentration measurements were combined with hydrologic measurements to obtain masses of MeHg entering and leaving the wetland. The annual net flux of MeHg out of the wetland before and after flooding was calculated by subtracting the annual masses in the output from the sum of the annual inputs (14).

MeHg concentrations in vegetation and peat were measured prior to and after flooding. Before flooding, samples of *S. fuscum*, black spruce needles, and peat were collected

and placed in 2-mm mesh fiberglass bags. The mesh bags were acid-washed prior to use. Twice a year, replicate bags were retrieved for determination of mass loss (17) and MeHg concentrations in the plant tissues (27).

Fish Mercury Uptake. Average net uptake of MeHg into finescale dace (*Semotilus margarita*) was measured by holding fish in open mesh pens, which allowed the fish to feed at all depths of water and at the sediment–water interface. The increase in body burden of mercury in the fish was calculated from the average growth rate and the increase in MeHg concentration over a 3-month period during each summer of the experiment. MeHg concentration in whole fish was determined by atomic absorption (28).

Results

Preflood Biomass, Peat Mass, and Plant Decomposition Rates. Prior to flooding, the peatland had a ground cover of *Sphagnum* mosses with an overstory of shrubs, primarily leather leaf (*C. calyculata* (L.) Moench) and Labrador tea (*Ledum groenlandicum*), and 36% tree cover composed mainly of black spruce (*P. mariana* (Mill) BSP). Six different vegetation communities were identified (Figure 2). The average biomass in each of the vegetation communities (excluding tree boles and roots) ranged from 404 to 1505 g of C m⁻², with an overall peatland average of 800 g of C m⁻². In the first 2 years after flooding, the loss of vegetation biomass estimated from the litterbag decomposition rates and the distribution of species prior to flooding was 230 g of C m⁻² or 115 g C m⁻² yr⁻¹. The largest preflood carbon pool was in the peat, which averaged 1×10^5 g of C m⁻² before flooding.

Carbon Fluxes. The effects of flooding on the pond and the peatland areas were different, and they will be examined separately.

In the pond, in its natural preflood state, concentrations of both CO₂ and CH₄ were above atmospheric equilibrium (Figure 3), and so the pond was a natural source of both gases to the atmosphere. During the first 2 years following flooding, average concentrations of these gases measured at the same site (the center of the original pond area) increased an average of 3 times for CO₂ and 6 times for CH₄ (Figure 3). Preflood CO₂ concentrations averaged 48 μM L⁻¹ with a median value of 41 μM L⁻¹; after flooding, these values increased to 141 and 138 μM L⁻¹, respectively. Preflood CH₄ concentrations averaged 1.1 μM L⁻¹ with a median value of 0.98 μM L⁻¹; after flooding, these values increased to 6.8 and 3.8 μM L⁻¹, respectively.

Gas fluxes from water surfaces are directly related to concentrations, and fluxes of both CO₂ and CH₄ from the pond to the atmosphere increased after flooding on both a daily (Table 1) and annual (Table 2; Figure 4) basis. CO₂ and CH₄ fluxes from the pre- and postflood water surfaces are naturally quite variable over time, due to day-to-day fluctuations in wind speed and seasonal changes in biological activities. In order to determine if there was a true change in gas fluxes after flooding, we collected 2 years of preflood and 2 years of postflood data, and we used several independent methods. Both the mean and median values obtained by all of these flux methods showed substantial increases after flooding (Table 1).

The natural variability of gas fluxes means that the number and time period of measurements is an important factor in obtaining an accurate long-term average (29). Thus, even though the three different flux measurement methods used for the water surfaces (FC, FG, TBL; Table 1) agreed well when used over the same time periods (see Methods), there were sometimes differences in the seasonally averaged daily values obtained by the different methods (Table 1) because of differences in the time periods of measurement (e.g., FG 108 days, TBL 23 days preflood; Table 1).

Prior to flooding, the CO₂ flux from the pond surface averaged 740 mg of CO₂ m⁻² d⁻¹ for 1991 and 1992, as

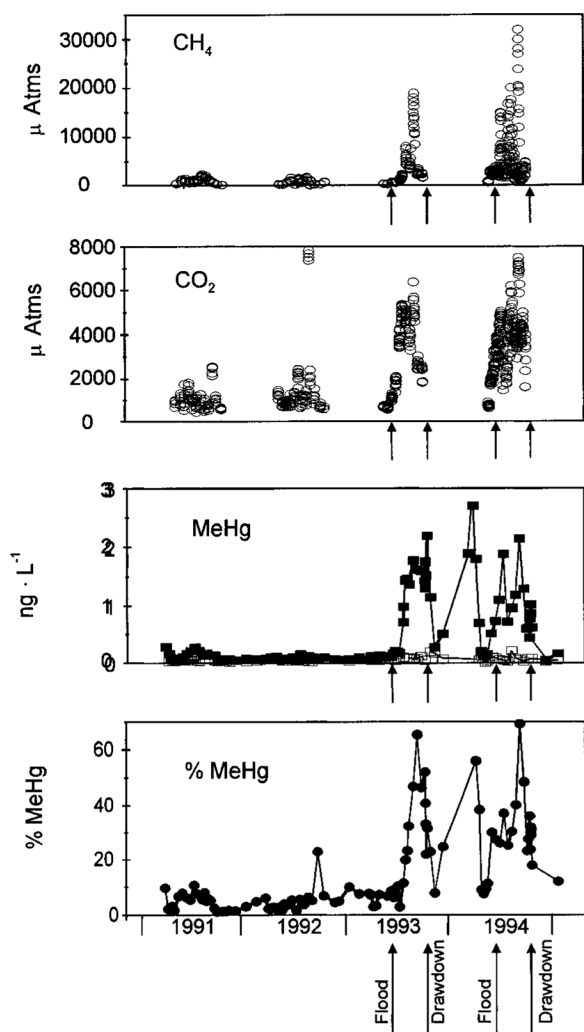


FIGURE 3. CO_2 , CH_4 , and MeHg concentrations and the ratio of MeHg to total mercury in the surface water of the central pond of the experimental wetland for 2 years prior and 2 years after flooding. CO_2 and CH_4 samples were taken throughout the ice-free season. MeHg was sampled year-round at the outflow (closed squares) and at the inflow of the wetland from Lake 240 (open squares). The unit for CO_2 and CH_4 (μatm) is the partial pressure that the dissolved gas would have if it were in equilibrium with the overlying atmosphere. All concentrations were above atmospheric equilibrium, which is $2 \mu\text{atm}$ for CH_4 and $365 \mu\text{atm}$ for CO_2 .

measured by the thin boundary layer (TBL) method (Table 1). The FG average, in 1992, was $1600 \text{ mg of CO}_2 \text{ m}^{-2} \text{ d}^{-1}$. After flooding, the TBL-measured flux increased to an average of $3700 \text{ mg of CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ (Table 1, 1993 and 1994), and the FG measurement increased to $3600 \text{ mg m}^{-2} \text{ d}^{-1}$. This increase was obviously a departure from the year to year natural variability observed in Lake 979 pre-flood (Figure 6), or in a reference wetland pond (Lake 632), where CO_2 fluxes averaged $1000 \text{ mg of CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ over a 4-year period and ranged from 480 to $1500 \text{ mg of CO}_2 \text{ m}^{-2} \text{ d}^{-1}$. CH_4 flux from the flooded pond area (TBL method) increased from an average of $17 \text{ mg of CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (1991 and 1992) to $88 \text{ mg of CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ after flooding (Table 1).

Interactions between the peat surface and the atmosphere prior to flooding were quite different from the pond. Measurements using the flux gradient method showed that in 1992 the undisturbed peatland was a small net sink [$-67 \text{ mg of CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ (Table 1) or $-4 \text{ g of C m}^{-2} \text{ yr}^{-1}$ (Table 2)] for CO_2 in 1992, due to CO_2 fixation activity of the vegetation and net accumulation of this fixed carbon as peat. On a longer time scale (over the last 2000 years), net accumulation of carbon in the peatland averaged $20\text{--}30 \text{ g of C m}^{-2} \text{ yr}^{-1}$

(measured by ^{14}C profiles in the peat). The fact that the 1992 CO_2 uptake by the plant community was less than 20% of the long-term average sink rate was probably due to the very cool and cloudy weather conditions during the summer of that year.

After flooding and the death of the vegetation, the water-covered peat surface changed from being a small sink to a large source of CO_2 to the atmosphere. The most unambiguous evidence for this change comes from the flux-gradient measurements, in which the same measurement method was used over the open peatland surface both before and after flooding, in 1992 (preflood) and 1993 (postflood). The net change in flux of CO_2 over the open peat surface measured by this method was $+70 \text{ g of C m}^{-2} \text{ yr}^{-1}$ (Figure 4A).

The part of the peatland further back from the original pond area had tree cover and thus was not amenable to use of the FG method. Combining measurements made by the FCs (Table 1) in the treed areas (50% of the peatland) and by the FG method (Table 1) in the open areas (50%), the average flux from the peatland area for the first 2 years after flooding was estimated at $+1800 \text{ mg of CO}_2 \text{ m}^{-2} \text{ d}^{-1}$. On an annual basis, this was equal to a carbon flux of $+105 \text{ g of CO}_2\text{-C m}^{-2} \text{ yr}^{-1}$, compared to a preflood carbon flux of $-4 \text{ g of CO}_2\text{-C m}^{-2} \text{ yr}^{-1}$ in 1992 and -20 to $-30 \text{ g of CO}_2\text{-C m}^{-2} \text{ yr}^{-1}$ on the long term (Table 2).

For CH_4 , overall the peat surface was a small source to the atmosphere prior to flooding (Table 1), even though one small area, near the inflowing stream (site A), was naturally flooded and had high fluxes (Table 1). Almost all of the peatland was much drier (as at sites B–D, Figure 2), with the average water table being 10–20 cm below the peat surface. Fluxes at these three drier sites were low (Table 1), averaging $0.8 \text{ mg of CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. The predominance of these low fluxes in the peatland as a whole was confirmed during a 6-week period in the summer of 1992 by FG measurements that showed that the average flux was $0 \pm 2 \text{ mg of CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ for the open peatland area. After flooding, the average CH_4 flux to the atmosphere from the peatland increased greatly to $48 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (Table 1). On an annual basis, the $\text{CH}_4\text{-C}$ flux increased from $0.13 \text{ g of CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$ to $7.9 \text{ g of CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$ (Table 2; Figure 4B).

CH_4 fluxes from the pond surface were higher than from the peat surface prior to flooding (Tables 1 and 2). After flooding, the net change in CH_4 flux from the pond surface ($+12 \text{ g of CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$; Figure 4B) was somewhat larger than from the peat surface ($+7.7 \text{ g of CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$; Figure 4B).

Some of the flooded organic carbon and/or its decomposition products moved from the peatland area into the pond area, and so it is appropriate to combine these two areas and to look at the net change in fluxes for the whole wetland. When this is done (Table 2), the entire wetland (pond and peatland) prior to flooding was a small net source of CO_2 in 1992 ($+6.6 \text{ g of C m}^{-2} \text{ yr}^{-1}$), and a small net sink on the long term (-7.1 to $-16 \text{ g of C m}^{-2} \text{ yr}^{-1}$). After flooding, the combined peatland and pond area was a large source of CO_2 ($+120 \text{ g of C m}^{-2} \text{ yr}^{-1}$, Table 2). For CH_4 , the entire wetland was a small source prior to flooding ($+0.52 \text{ g of C m}^{-2} \text{ yr}^{-1}$, Table 2). CH_4 flux increased 18-fold to $+8.9 \text{ g of C m}^{-2} \text{ yr}^{-1}$ (Table 2).

Mercury Concentrations and Mass Balances. Natural wetlands are sites of net MeHg production (13, 14), and this was the case for the experimental wetland in its preflood state. Prior to flooding, MeHg concentrations in the central pond averaged 0.1 ng L^{-1} (Figures 3 and 5), which was about one-third higher than in the lake water flowing into the wetland (Lake 240 outflow, Figures 3 and 5). After flooding, the average MeHg concentration in the new reservoir was about 10-fold higher (0.9 ng L^{-1} , Figure 5), with some values over 2 ng L^{-1} (Figure 3). Reservoir drawdown in the fall of 1993 and 1994 returned MeHg concentrations in the pond to

TABLE 1. Daily Fluxes of CO₂ and CH₄ from Vegetated and Water Surfaces of the Experimental Wetland Measured by Several Different Methods for 2 Years before (1991 and 1992) and after Flooding (1993 and 1994)^a

	method ^b	location ^c	no. of sites	no. of days ^d	preflood		postflood		
					CH ₄ mean (median)	CO ₂ mean (median)	no. of days	CH ₄ mean (median)	CO ₂ mean (median)
peat area	SC	A	3	26	176 (163)				
		B	3	25	2.4 (2.8)				
		C	3	21	-0.06 (-0.07)				
		D	3	14	0.11 (0.12)				
	FC	H	10-16				24	48 (30)	2400 (1700)
pond area	FG	E	1	108 ^e		-67 (-160)	246 ^f	1100 (2900)	
	FG	F	1	108 ^e		1600 (2300)	246 ^f	3600 (3100)	
	TBL	G	1	23 ^d	17 (11)	740 (460)	76	88 (43)	3700 (2400)

^a CH₄ fluxes are in mg of CH₄ m⁻² d⁻¹ and CO₂ fluxes are in mg of CO₂ m⁻² d⁻¹. ^b SC, static chamber method; FG, flux-gradient method; TBL, thin boundary layer method; FC, floating chamber method. ^c Site locations are shown on Figure 2. ^d Number of days on which measurements were made. ^e 1992 only. ^f 1993 only.

TABLE 2. Annual Fluxes of CO₂ and CH₄ from Peatland Surface, Pond Surface, and Entire Experimental Wetland^a

	peatland (14.4 ha)	pond (2.39 ha)	entire wetland (16.66 ha)
CO ₂ before (long term)	-20 to -30 ^b	+70 (est) ^c	-7 to -16
CO ₂ before (short term)	-4.0 ^d	+70 ^c	+6.6 ^e
CO ₂ after (1993 and 94)	+105 ^f	+220 ^g	+120
CH ₄ before	+0.13 ^h	+2.8 ⁱ	+0.52
CH ₄ after	+7.9 ^j	+15 ⁱ	+8.9
CO ₂ + CH ₄ before (long term)	-20 to -30	+73	-7 to -16
CO ₂ + CH ₄ after	+112	+235	+130

^a All values are in g of C m⁻² yr⁻¹, with 1 year equal to 220 ice-free days. ^b Estimated by ¹⁴C dating of peat cores. ^c Average of the TBL (1991 and 1992) and FG (1992) measurements, see Table 1. ^d 1992 FG measurement. ^e Calculated using long-term peatland CO₂ flux and 1991 and 1992 pond fluxes. ^f Average of the FC (1993 and 1994) and FG (1993) measurements, see Table 1. ^g Average of the TBL (1993 and 1994) and FG (1993) measurements, see Table 1. ^h Average of the SC measurements (1991 and 1992), see Table 1. ⁱ Average of the TBL measurements before flood (1991-1992) and after flood (1993-1994), see Table 1. ^j Average of the FC measurements (1993 and 1994), see Table 1.

near preflood values (Figure 3). During the winter of 1993-1994, the central pond became completely anoxic under the ice, and MeHg concentrations reached their highest level (2.8 ng L⁻¹). These high concentrations may have been due to the anoxia (30) or to movement of MeHg-rich peat porewater (0.5-3 ng of MeHg L⁻¹) into the pond area due to the pressure of ice and snow on the peat (5).

In contrast to MeHg, flooding had very little effect on THg concentrations. Average THg concentrations after flooding were only slightly higher than preflood concentrations (Figure 5). Both pre- and postflood THg concentrations were similar to an undisturbed reference wetland pond (Lake 632, Figure 5).

Flooding caused an increase in the percent of THg in the water that was MeHg, from about 4% to as high as 73% (Figure 3). The average postflood percent of MeHg (32%) was about 7 times higher than preflood (Figure 5). It was also about 7 times higher than in Lake 240, a clear-water lake (Figure 5). Natural brown-water wetland ponds at ELA, e.g., Lake 632 (Figure 5), have a higher percent of MeHg than lakes (25), but the percent of MeHg in Lake 632 was only about one-third of the average postflood percent in the experimental reservoir (Figure 5).

On a mass balance basis, the wetland was a source of MeHg prior to flooding. After flooding, it became a much larger source (39-fold, Figure 6). The mass of MeHg in the flooded vegetation also increased, because the increase in MeHg concentration in the flooded vegetation was much larger than the loss of tissue mass from the plants (Table 3).

Fish Mercury Uptake. MeHg uptake by fish increased after flooding. The average concentration in the yearling finescale dace prior to flooding was 0.10 ng g⁻¹ and was 0.32 ng g⁻¹ after flooding. The average summer uptake by these fish prior to flooding ranged between -0.08 μg of MeHg per fish during the very cool summer of 1992 and +0.27 μg of

MeHg per fish during the warm summer of 1991. Summer uptake after flooding increased to 0.73 and 0.63 μg of MeHg per fish in 2 years of average summer temperatures. The fact that these postflood rates were greater than in either of the two preflood years showed that the effect of flooding on fish mercury uptake was much greater than the effects of natural annual weather variation.

In order to put the uptake of MeHg into fish into perspective with other MeHg fluxes, the individual fish uptake rates were used to estimate the total MeHg uptake by a hypothetical (natural density) population of fish in the pond prior to flooding and in the reservoir after flooding. The total MeHg uptake estimated for this population was then divided by the area of the entire wetland in order to transform fish uptake into the same units as used for the MeHg mass balance budgets (μg of MeHg m⁻² yr⁻¹). Before flooding, uptake into the fish population was estimated to be +0.08 and -0.03 μg of MeHg m⁻² yr⁻¹, compared to a net flux (outflow - inputs) of MeHg from the wetland of 0.21 and 0.18 μg m⁻² yr⁻¹ in 1991 and 1992 (Figure 6). After flooding, fish uptake was estimated to be 0.23 and 0.20 μg m⁻² yr⁻¹, while the net MeHg flux from the wetland was 7.0 and 8.5 μg m⁻² yr⁻¹ (Figure 6).

Discussion

Flooding caused profound changes in both MeHg and carbon cycling in the experimental wetland. One of the biggest effects was that the wetland changed from being a small net carbon sink to a large net source of carbon to the atmosphere (Table 2). The change in CO₂ flux from negative to positive (Figures 4 and 6) was caused by a combination of (1) the death of most of the natural wetland vegetation and the loss of its CO₂ fixing capability and (2) the decomposition of the dead vegetation, which produced CO₂.

The increased CH₄ flux after flooding was caused by a combination of increased production resulting from anoxic

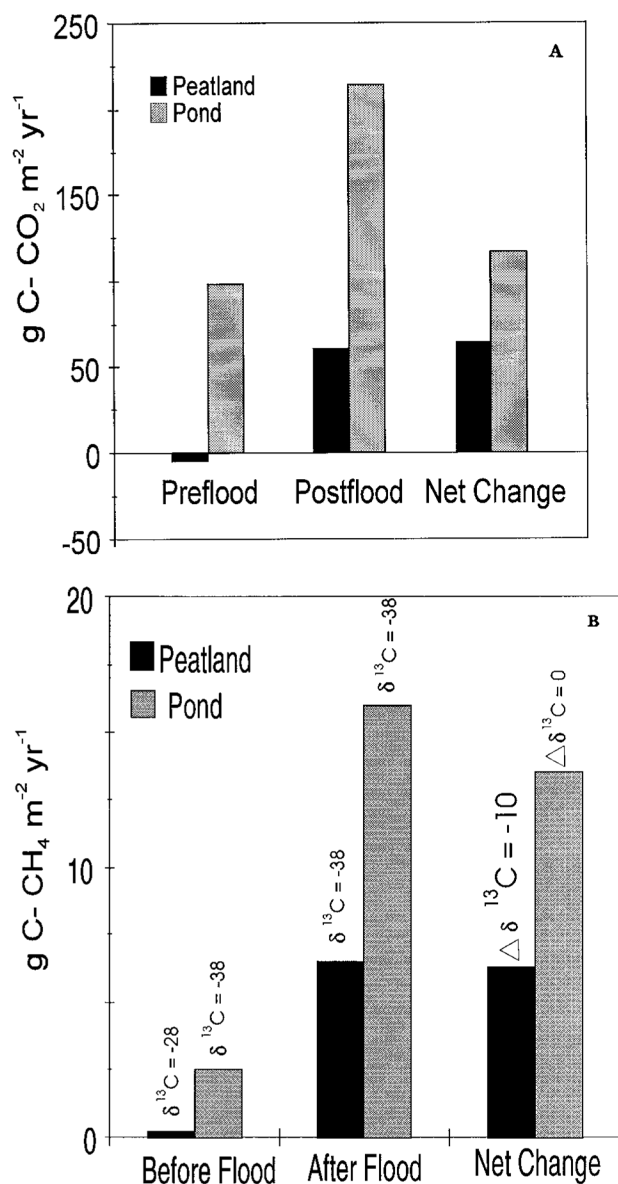


FIGURE 4. (A) Annual CO₂-C fluxes to/from the peatland and pond and the net changes in fluxes after flooding as measured by the flux-gradient (FG) method. (B) Annual CH₄-C fluxes from the peatland and pond areas and the net changes in fluxes after flooding. The average value δ¹³C of the CH₄ leaving these surfaces and the net change in δ¹³C is shown above the bars. Preflood fluxes from the peatland were measured by the static chamber method (SC), and postflood peatland fluxes were measured by the floating chamber method (FC). All pond fluxes were measured by the thin-boundary layer method (TBL).

decomposition of vegetation and a decrease in the consumption of CH₄ by CH₄-oxidizing bacteria. The decrease in CH₄ oxidation can be seen by the increase in the δ¹³C of CH₄ in the peatland area after flooding (Figure 4B). When CH₄ is produced by the methanogenic bacteria, it has a very negative δ¹³C value (-53 to -70‰ in the peat porewater at 20 cm depth). As it is oxidized, the value becomes more positive. ¹³C measurements on CH₄ samples collected from the static chambers on the peat surface prior to flooding showed that this CH₄ was highly oxidized (δ¹³C value of -28‰, Figure 4B) as it moved above the water table and through the upper 10–20 cm of unsaturated peat. After flooding, the CH₄ emitted from the submerged peat surface was not oxidized, but after passing through the overlying water column, some oxidation occurred (δ¹³C in CH₄ emitted to the atmosphere was -38‰) but not as much as in the unflooded peat. In the pond area, however, there was no

detectable change in the efficiency of CH₄ oxidation, with δ¹³C in emitted CH₄ averaging -38‰ both before and after flooding. While it is difficult to use δ¹³C data to calculate a percent change in CH₄ oxidation, it appears overall that the major reason for the increased CH₄ flux was not decreased oxidation but increased production due to increased anaerobic habitat.

Most of the gas flux after flooding must have come from decomposing vegetation (Table 2, Figure 6). However, because much more organic carbon is stored as peat than as vegetation in wetlands, it is important to ask whether decomposition of peat contributes to the greenhouse gas flux after flooding. The answer is most likely yes. Prior to flooding, the peatland contained 800 g of C m⁻² of plant material and 1 × 10⁵ g of C m⁻² of peat (Figure 6). During the first 2 years of flooding, litterbag experiments indicated that about 115 g of C m⁻² yr⁻¹ of plant material was degraded (Figure 6). The increase in CO₂ and CH₄ flux from the entire wetland area in the first 2 years after flooding was 130 g of C m⁻² yr⁻¹ (Table 2). If all of this increase is attributed to the peatland area, 150 g of C m⁻² yr⁻¹ was decomposing from both plant material and peat. Thus, peat decomposition likely contributed 30–40 g of C m⁻² yr⁻¹ to the total gas flux, and there would be sufficient peat in the experimental wetland to sustain this decomposition rate for 2000 yr. Under natural circumstances on the Hudson Bay Lowlands, decomposition of "old" peat (2000 years) occurs under water (130 g of C m⁻² yr⁻¹), and this has resulted in the formation of ponds as secondary features on the surface of the peatland and releases both CO₂ and CH₄ to the atmosphere (19). It remains to be seen whether peat decomposition in the reservoir changes as the vegetation disappears and the peat surface becomes more exposed.

During the second and third years of flooding, accumulation of gas bubbles in the peat was observed, and much of the peat in the wetland floated. These bubbles were not observed during the first year of flooding, which might suggest that the rate of peat decomposition increased in the following 2 years. However, incubations of peat under flooded and unflooded conditions indicate that while the decomposition rate may have increased somewhat due to higher temperatures in the flooded peat (Figure 7), a more significant change was that the ratio of CH₄ to CO₂ produced increased (V. St. Louis and C. Poschadel, unpublished data). This would lead to floating of the peat because CH₄ is much less soluble in water than is CO₂.

Floating peat islands are common features in our reservoir and in large reservoirs that flood peatlands. In our reservoir, flux of CH₄ from the surface of floating peat islands was much faster than from submerged peat or from the water surface (K. Scott, unpublished data). These fluxes were high because the CH₄ did not have to pass through the water column before reaching the atmosphere and thus was not oxidized, as shown by δ¹³C analyses (C. Poschadel, unpublished data). The importance of these islands will be considered more quantitatively in the future.

Not only did concentrations and fluxes of greenhouse gases increase after flooding, but concentrations and fluxes of MeHg also increased. In the flooded wetland, MeHg concentrations were much higher than observed in any of the natural lakes at the ELA, including brown-water lakes that are surrounded by peatlands (e.g., Figure 5). The average percentage of total mercury that was MeHg in the reservoir increased from 4% to 32% after flooding, which was much higher than the averages for other clear-water and brown-water lakes at the ELA (Figure 5) or for water draining ELA wetlands (25). During midsummer, when methylation rates are often high, percent of MeHg peaked at 73%, which is a higher percentage than the highest percentages observed in lakes elsewhere (e.g., refs 31 and 32).

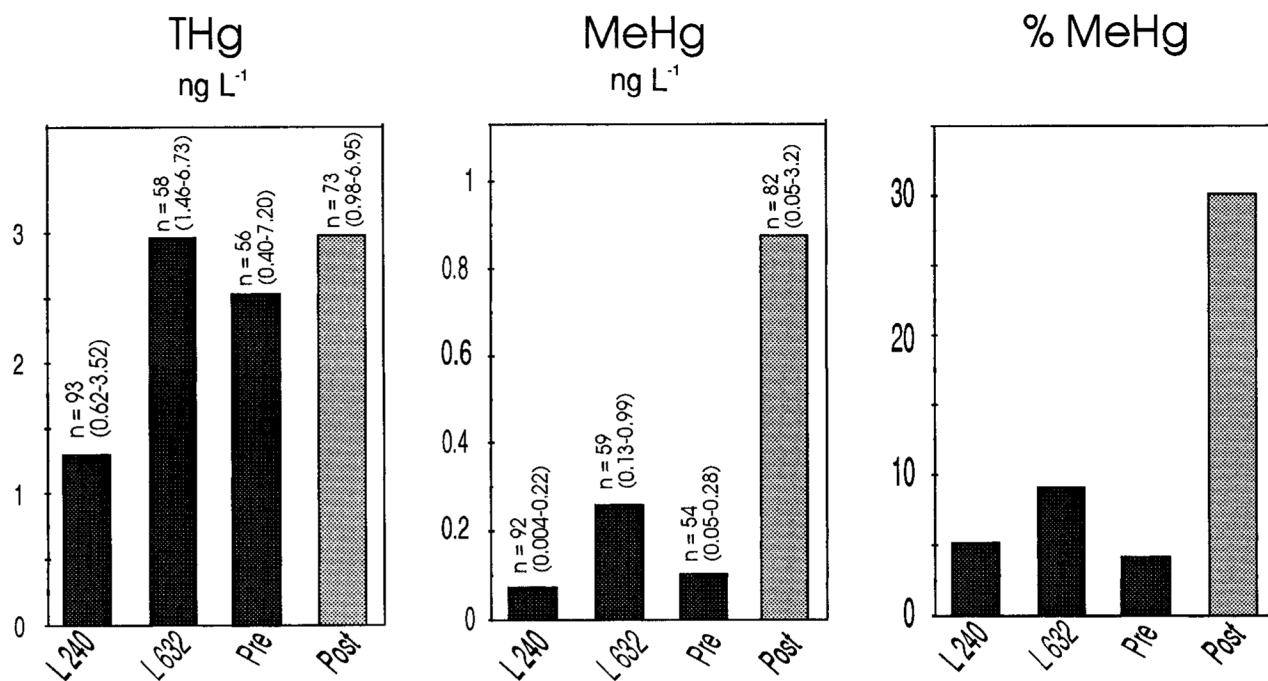


FIGURE 5. Average concentrations of THg and MeHg and the percent of THg that is MeHg in surface waters of Lake 240 (a clear-water lake) and Lake 632 (a brown-water wetland pond) and in the experimental reservoir before and after flooding.

The high percentage of MeHg was likely a sign of higher than natural rates of transformation of inorganic mercury into MeHg. For this and several other reasons (see below), we conclude that the large increases in MeHg concentrations (Figures 3 and 5) and net MeHg export from the flooded wetland (Figure 6) were a result of increased net production of MeHg rather than release of MeHg that was in the wetland prior to flooding. Equilibration of the reservoir water with MeHg in flooded plants and peat might have been important because MeHg concentrations are naturally high in both peat and in many wetland plant species (27). However there was a lag period of 2 weeks before MeHg concentrations increased in the flooded pond (Figure 3). This lag would not be expected if equilibration alone were the cause of the increase, because MeHg in water equilibrates almost immediately with MeHg in peat and vegetation (Heyes, unpublished data). Pre-existing MeHg might also have been released at a later date as the tissues decomposed, but the concentration and, more importantly, the mass of MeHg in the peat and vegetation increased rather than decreased during decomposition (Table 3). Thus, MeHg increased in the water, fish, food chain organisms (33; M. Paterson, personal communication), flooded vegetation, and peat. Therefore, there must have been a large increase in net MeHg production after flooding to account for the large changes in MeHg concentrations and net fluxes that we observed. It is also likely that some of the increase in net ecosystem mercury methylation rate was due to decreased rates of photodegradation of MeHg (34) because of increased color of the water after flooding (data not shown).

Increased MeHg production after flooding is consistent with three types of changes in microbial habitat conditions that are known to enhance methylation rates. First, the sudden death of the vegetation caused a large amount of organic carbon to become available for decomposition, and methylation rates are enhanced at higher decomposition rates even when no additional mercury is added to the system (35). Second, this high decomposition activity led to a greater dominance of anaerobic habitat, as shown by increased CH₄ concentrations and fluxes after flooding (Figure 3; Table 2). CH₄ concentrations increased 2 weeks after flooding, and this was when MeHg concentrations also increased (Figure 3). Anoxic conditions are known to promote methylation (30). Third, the mercury methylation process is stimulated

by increased temperature to a greater degree than is general microbial activity (36, 37), and the newly flooded peat was on average 1–4 °C warmer than the peat in its natural state (Figure 7).

It is informative to compare MeHg levels in the experimental reservoir with the English–Wabigoon River system, which is located nearby and was polluted by inorganic Hg inputs from a chloralkali plant (38). MeHg concentrations in this river system are about 1–2 ng L⁻¹ (38). This is very similar to the MeHg concentrations in the experimental reservoir, even though the only external input of Hg to this experimental wetland has been very low inputs of Hg from the atmosphere (30 mg ha⁻¹ yr⁻¹; 39). The percent of THg as MeHg in the two systems was however very different. In the English–Wabigoon system, it was 6% (38), which is within the range for natural systems (25), but was much lower than in the experimental reservoir (Figures 3 and 5). Thus, one of the main differences between reservoirs and other polluted and unpolluted water bodies is the efficiency with which Hg is methylated in reservoirs.

While the increase in surface water MeHg concentrations and net flux did not occur immediately, this increase did occur very early in the lifetime of the reservoir. This early increase has not been documented in other reservoirs because analytical methods were not available. MeHg increases also occurred rapidly after flooding in vegetation and peat (A. Heyes, unpublished data), benthic organisms (33), and zooplankton (M. Paterson, personal communication). One of the primary goals of the ELARP was to study the early stages of flooding when microbial rates are at their highest, because at this time a large quantity of MeHg could be produced and bioaccumulated by the food chain. It will be important to continue to observe the reservoir in the future to determine how important this early stage of MeHg production and bioaccumulation is as compared to the longer term.

This flooding experiment is the first to measure MeHg uptake by fish together with a mass balance budget of MeHg before and after flooding. Compared to the net flux of MeHg into the water and out the outflow, the estimated fish uptake was small (Figure 6). The largest flux was the accumulation of MeHg in the vegetation and peat (unpublished data).

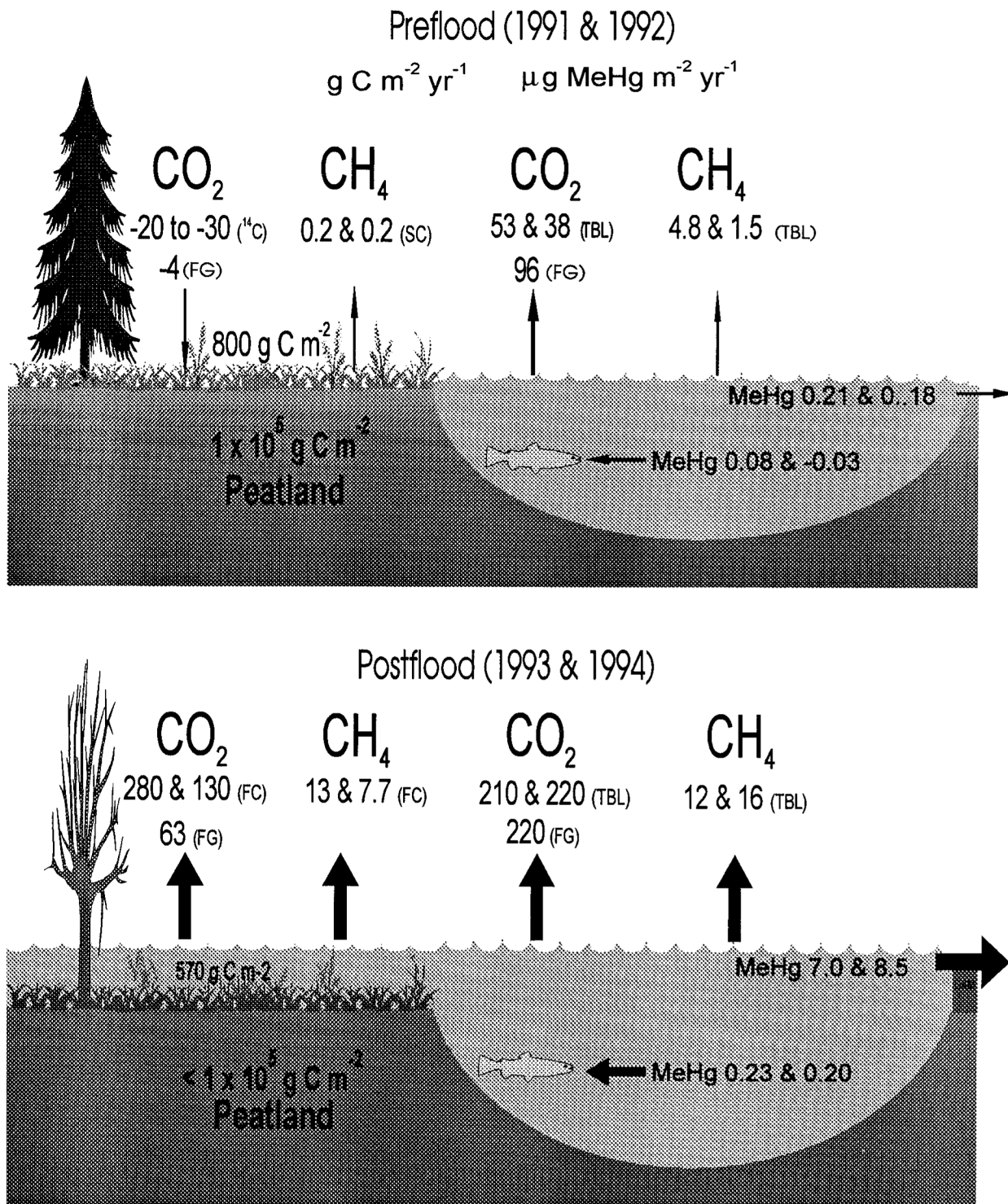


FIGURE 6. Annual downstream loss (mass output – mass input) of MeHg from the experimental wetlands annual fluxes of MeHg into fish for 2 years prior to and 2 years after flooding, and pre- and postflood fluxes of CH_4 and CO_2 from the peatland and pond surfaces of the wetland to the atmosphere. Methods used for measurement of the gas fluxes are shown in brackets: TBL, thin boundary layer method; FG, flux-gradient (1992 and 1993 only); ^{14}C , carbon accumulation rate by ^{14}C dating; FC, floating chambers; SC, static chambers on the peatland surface.

Another ELARP study, carried out at trace level MeHg concentrations, showed that almost all of the MeHg uptake by fish is from food rather than water (40). Because food is so important, we studied MeHg bioaccumulation at the lower level of the fish food chain by quantifying the flux of MeHg into forage fish (Figure 6), which are prey for larger predatory fish. The average 3-fold increase in forage-fish MeHg concentration after flooding (0.10 vs 0.32 ng g^{-1}) was not as large as the average 10-fold increase in MeHg concentrations in water. There are many factors that could explain the lower

(relative) bioaccumulation of MeHg in the fish after flooding. These include changes in the base of the food chain (e.g., different food organisms with different MeHg concentrations as compared to food value), different plankton and benthos growth rates, and changes in fish diet, food availability, and growth rates. There may also have been a change in the amount of time for the fish to come into equilibrium with the ecosystem. This is the reason that modeling is an important tool in understanding the cycling of a toxicant through ecosystems, and one of the goals of the ELARP was to develop

TABLE 3. Preflood MeHg Concentrations of Peat and Vegetation Samples Compared to Their Concentrations after 2 Years of Flooding^a

sample type	preflood MeHg (ng/g) ^b	postflood MeHg (ng/g) ^b	mass loss (%)
Sphagnum	2.5	8	20
spruce needles	0.2	2	60
peat	2	10	undetactable

^a The mass loss of the plant tissue after 2 years of flooding is also given. ^b Dry weight.

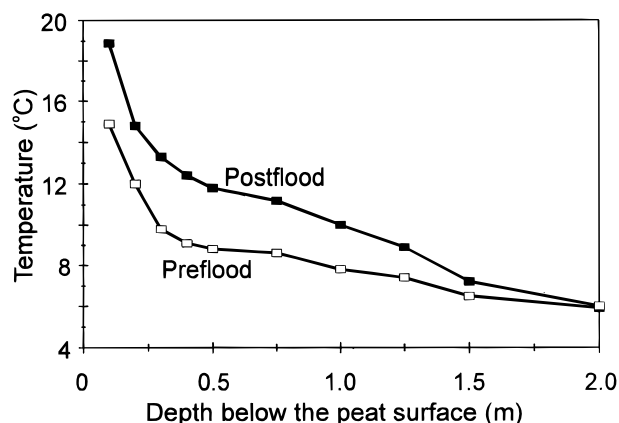


FIGURE 7. Mean summer (July 15–September 7) temperatures in peat, before and after flooding.

a mechanistic model of mercury cycling in reservoirs. All of the ELARP data on carbon cycling, water, vegetation, peat, benthos, zooplankton, and fish are being used to calibrate this model, which will predict mercury concentration in predatory fish in existing and future reservoirs.

In applying the results of this experimental flooding to larger reservoirs, an important question that must be answered is how typical are the results obtained in this experimental reservoir? With respect to CO₂ fluxes, the comparison with large northern reservoirs is good. In a study of northern Quebec reservoirs, the average time-weighted CO₂ fluxes were 1700 (shallow areas) and 2200 (deep areas) mg of CO₂ m⁻² d⁻¹ (9) as compared to 3600 mg of CO₂ m⁻² d⁻¹ in our experimental reservoir (Table 1). CO₂ flux is much greater than CH₄ flux in all of these reservoirs, and the fact that CO₂ flux is similar in both systems suggests that overall carbon cycling is also similar. These CO₂ fluxes are also similar to those predicted for biomass decomposition in boreal reservoirs (7) and support the hypothesis that some reservoirs could be significant sources of greenhouse gases. CH₄ fluxes were higher in the experimental wetland than in the Quebec reservoirs. The different CH₄ fluxes could be due to either different rates of production or oxidation of CH₄. Reservoirs in non-boreal locations, such as the tropics, likely have much different flux rates and patterns over time (8).

The percentage of carbon released as CH₄ from reservoirs is important because CH₄ has a higher global warming potential than CO₂ (41). This percentage is variable and may be much higher in tropical environments, so detailed studies of CH₄ fluxes on a variety of system types are needed in order to evaluate the total contribution of reservoirs to global CH₄ fluxes.

It is also interesting to compare the gas fluxes from the experimental reservoir to natural lakes. The postflood fluxes were greater than those observed in natural lakes (42) and from a nearby unflooded reference wetland pond at ELA (Lake 632, data not shown). However, they were within the range observed for natural wetland ponds on the Hudson Bay Lowlands (19). While reservoir fluxes are within the bounds

of some wetland ponds, it must be clearly understood that it is not the absolute value of the postflood fluxes but the net change in the fluxes of the flooded area that is relevant to the assessment of the possible importance of reservoirs as sources of gases to the atmosphere.

With respect to mercury cycling in reservoirs, comparison of ELARP data to larger systems cannot be done because comparable data on MeHg concentrations in water, MeHg mass balances, and annual MeHg in small fish and decomposing plants are not yet available for larger reservoirs. However, the situation is at least generally similar because fish mercury uptake, which is the end result of many steps involving the production and bioaccumulation of MeHg, increased in the experimental reservoir, just as it is known to increase in larger reservoirs (3, 10).

The initial results of this experiment lead to several recommendations concerning reservoir planning and construction:

(A) When choosing a reservoir site, the total area flooded should be considered. Obviously, the more area flooded, the greater will be the total CO₂ and CH₄ flux to the atmosphere. With respect to mercury, existing reservoir data indicate that fish MeHg levels are positively related to the amount of terrestrial area flooded (43). Thus, minimizing the area flooded is a desirable goal in reservoir site selection.

(B) The percentage of total area that is wetland should be considered. Natural wetlands are high sources of MeHg, for reasons that we are just beginning to understand (44). In this experiment, flooding a wetland area led to very high increases in MeHg in the water, peat, vegetation, and fish and to profound changes in greenhouse gas fluxes. Avoiding wetland areas should help to minimize the increase in fish mercury and greenhouse gas fluxes to the atmosphere (45). In order to complete our understanding, however, a companion experiment needs to be done in which an upland area is flooded so that the relative contribution of each type of area to gas fluxes and to MeHg fluxes can be predicted.

(C) In addition to the initial effects of flooding on the wetland, the time course of decomposition and methylation in later years needs to be considered. This is because peatlands contain large amounts of carbon, which could support decomposition activity for many years. Decomposition of flooded material is the common link between greenhouse gas flux and mercury methylation, and in the initial years after wetland flooding both processes were greatly increased. However, with time they could become less linked. Perhaps the bioavailable Hg is consumed before all of the organic carbon is decomposed, or the methylation process might follow a different time course than overall decomposition.

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