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Impacts of Reservoir Creation on the Biogeochemical Cycling of Methyl Mercury and Total Mercury in Boreal Upland Forests

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Abstract

The FLooded Upland Dynamics Experiment (FLUDEX) at the Experimental Lakes Area (ELA) in northwest Ontario was designed to test the hypothesis that methylmercury (MeHg) production in reservoirs is related to the amount, and subsequent decomposition, of flooded organic matter. Three upland forest sites that varied in the amounts of organic carbon stored in vegetation and soils (Low C, 30,870 kg C ha^{-1}; Medium C, 34,930 kg C ha^{-1}; and High C, 45,860 kg C ha^{-1}) were flooded annually from May to September with low-organic carbon, low-MeHg water pumped from a nearby lake. Within five weeks of flooding, MeHg concentrations in the reservoir outflows exceeded those in reservoir inflows and remained elevated for the duration of the experiment, peaking at 1.60 ng L^{-1} in the Medium C reservoir. We estimated the net production of MeHg in each reservoir by calculating annual changes in pools of MeHg stored in flooded soils, periphyton, zooplankton, and fish. Overall, there was an initial pulse of MeHg production (range = 120–1590 ng m^{-2} day^{-1}) in all FLUDEX reservoirs that lasted for 2 years, after which time net demethylation (range = 360–1230 ng MeHg degraded m^{-2} day^{-1}) began to reduce the pools of MeHg in the reservoirs, but not back to levels found prior to flooding. Rates of MeHg production were generally related to the total amount of organic carbon flooded to create the reservoirs. Large increases in MeHg stores in soils compared to those in water and biota indicate that flooded soils were the main sites of MeHg production. This study should assist hydroelectric utilities and government agencies in making informed decisions about selecting sites for future reservoir development to reduce MeHg contamination of the reservoir fisheries.

Key words: methylmercury; mercury; MeHg production; reservoirs; Experimental Lakes Area.

Introduction

An important environmental consequence of flooding landscapes and creating reservoirs is the bioaccumulation of methylmercury (CH_3Hg^+; MeHg), a strong vertebrate neurotoxin, through the food web into fish. The health of people

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depending on reservoir fisheries for food is of concern, because human consumption of fish with sufficiently high concentrations of MeHg may cause teratogenic effects and irreversible neurological damage (Kurland and others 1960; Myers and others 2000; Rosenberg and others 1997). For example, MeHg concentrations in predatory fish harvested from northern boreal reservoirs in Manitoba (Bodaly and others 1984; Hecky and others 1991), Québec (Brouard and others 1994; Schetagne and Verdon 1999), and Newfoundland (Scruton and others 1994), Canada, as well as in Finland (Lodenius and others 1983), often exceed Canadian marketing limits of 0.5 μg g^{-1} wet mass for more than 20 years after initial flooding. It is therefore imperative that stakeholders consider MeHg contamination of fisheries when planning the construction of new reservoirs.

The decomposition of organic carbon (OC) in flooded vegetation and soils in reservoirs fuels the microbial methylation of inorganic mercury (HgII; IHg) to MeHg (Compeau and Bartha 1984; Hecky and others 1991; Kelly and others 1997; Hall and others 2004), as well as the production of the carbon greenhouse gases (GHGs) carbon dioxide (CO_2) and methane (CH_4), both of which are the direct byproducts of OC mineralization. The extent to which flooded OC is mineralized in reservoirs and the amount of MeHg produced may depend on the amount and type of OC flooded (Kelly and others 1997). For example, the quantity of easily decomposed labile OC flooded may be important to short-term decomposition processes fueling MeHg and GHG production, whereas the total quantity of OC flooded may affect the long-term duration of production.

To begin examining the link between OC mineralization and Hg methylation in reservoirs, a whole-ecosystem experiment was initiated at the Experimental Lakes Area (ELA) in northwestern Ontario in 1990/91 (Kelly and others 1997). The ELA Reservoir Project (ELARP) flooded a wetland complex because it was thought to provide the worst-case scenario for MeHg and GHG production due to the large stores of OC in peat available for decomposition over the long term. Within three weeks of flooding, yields of MeHg and carbon GHGs from the reservoir increased dramatically (Kelly and others 1997). Continued background monitoring of dissolved MeHg, CO_2 and CH_4 in the wetland reservoir showed that rates of MeHg and GHG production were well above preflood levels nine years after the initial inundation of the wetland (St. Louis and others 2004).

The main objective of the research presented here was to determine if flooding smaller quantities of OC compared to the ELARP would result in less MeHg and GHG production in reservoirs. We addressed this objective by initiating a new whole-ecosystem flooding experiment at the ELA in 1997. The FLooded Upland Dynamics Experiment (FLUDEX) flooded three upland boreal forest sites that varied in amounts of OC stored in soils and vegetation. The three upland reservoirs (Low C, Medium C, and High C), with OC storage of between 30,900 and 45,900 kg C ha^{-1}, contained between 60 and 27 times less OC than stored in the ELARP wetland reservoir (1.26×10^6 kg C ha^{-1}). Here we calculated Hg input–output budgets for three seasons of flooding (1999–2001) to determine net MeHg and total Hg (THg, an analytical term used to describe all forms of Hg) yields from the three FLUDEX reservoirs. We also estimated the net production of MeHg in each reservoir by calculating annual changes in pools of MeHg stored in flooded soils, periphyton, zooplankton, and fish. The resulting MeHg production rates in the FLUDEX upland reservoirs were compared to MeHg production rates observed in the ELARP wetland reservoir.

Methods

Description of FLUDEX Reservoir Sites

The ELA camp is located 50 km southeast of Kenora, Ontario, on the Precambrian Shield. The ELA experiences a cold temperate continental climate with 32-year mean July and January temperatures of 18.5 and −17.3°C, respectively. Mean annual wet deposition from 1969 to 2001 was 699 mm, with approximately 25% of this wet deposition falling as snow. Upland areas at the ELA ranged from open lichen-covered granite/gneiss rocks to shallow nutrient-poor acidic soils supporting jack pine (*Pinus banksiana*), black spruce (*Picea mariana*), and paper birch (*Betula papyrifera*) forest communities.

Three 17-year-old fire-regenerated upland forest sites differing in amounts of OC stored in vegetation and soils were chosen in 1997 to be experimentally flooded. The High C site had 45,900 kg C ha^{-1}, the majority of which was stored in trees (57%) and the fungal/humic (FH) layer of the soils (34%; Table 1). The 0.74 ha High C site had rapid but imperfect drainage, occasionally resulting in pools of standing water. There were two basic vegetation communities in the High C site: (1) a jack pine (*Pinus banksiana*) dominated forest with an understory of

Table 1. Carbon Stores (kg C ha^{-1})in the FLUDEX Sites Prior to Flooding[a]

	High C site	Medium C site	Low C site
Dominant vegetation (percent coverage)	*Pinus/Ledum/Sphagnum* (53%) *Pinus/Polytrichum* (47%)	*Pinus/Betula* (100%)	*Pinus/Vaccinium* (73%) *Polytrichum/Cladina* (22%) Organic pillows (5%)
Range of soil depth (cm)[b]	6.3–105.0	15.6–90.6	0–69.0
Range of forest floor depth (cm)[b,c]	1.0–37.0	3.5–13.0	2.0–7.5
Carbon in trees	26,210	27,600	19,570
in foliage[d]	1970	2730	1770
in bark[d]	2440	3760	1970
in wood[d]	21,800	21,110	15,830
Carbon in shrubs, herbs, and mosses[d]	1350	130	200
Carbon in litter and fungal/humic layer[c]	15,400	5700	8700
Carbon mineral layer[b]	2900	1500	2400
Total soil carbon (including litter)[b]	18,300	7200	11,100
Total carbon in above ground vegetation[d]	27,560	27,730	19,770
Total carbon (kg C ha^{-1})	45,860	34,930	30,870

[a] *All carbon amounts are in kg C ha^{-1}.*
[b] *Unpublished data: J. Venkiteswaran and S. Schiff, University of Waterloo, Waterloo, ON.*
[c] *Where forest floor exists.*
[d] *Matthews and others (2005)*

wetland plants such as Labrador tea (*Ledum groenlandicum*), *Sphagnum* spp. mosses, and leatherleaf (*Chamaedaphne calyculata*) shrubs growing in low-lying, wet soils, and (2) a drier upland area dominated by jack pine and *Polytrichum* spp. mosses (Table 1).

The 0.5 ha Medium C site had better drainage than the High C site and relatively complete coverage of dry soils ranging from 15 to 90 cm in depth (Table 1). A dense jack pine forest with tall birch (*Betula papyrifera*) and alder (*Alnus* spp.) shrubs, an understory of blueberry (*Vaccinium* spp.) shrubs, and an extensive groundcover of various mosses and herbs dominated the site. Approximately 80% of the total OC (34,900 kg C ha^{-1}) was stored in trees, whereas 16% was stored in the FH layer of soils (Table 1).

The 0.63 ha Low C site was located on a dry ridge-top. Approximately 73% of the site had shallow soils supporting sparse stands of jack pine and birch with a blueberry shrub-dominated understory. Twenty-two percent of the site had areas of thin glacial till with lichens, mosses, blueberry shrubs, and exposed bedrock. Five percent of the area was covered with lichens (*Cladina* spp.), mosses (*Polytrichum* spp., *Racomitrium microcarpon*), and grasses (*Poa* spp.) overlying less than 10 cm of organic deposits. The Low C site contained 30,900 kg C ha^{-1}, with 64% and 28% stored in trees and the FH soil layer, respectively (Table 1).

For comparison with the FLUDEX reservoirs, the ELARP wetland reservoir consisted of a 2.4 ha center pond surrounded by a 14.4 ha peatland, dominated by black spruce (*Picea mariana*), larch (*Larix laricina*), *Sphagnum* spp., and Labrador tea and leatherleaf shrubs (Dyck and Shay 1999). The vast majority of OC in the site was stored as peat (1.26×10^6 kg C ha^{-1}). Less than 2% of the OC stored in the peatland was living vegetation and/or litter.

Upland Reservoir Construction

Upland reservoirs were constructed by building dikes along low-lying contours of the sites followed by flooding with water pumped from a nearby oligotrophic lake. In areas where flooding would not exceed 1 m depth, gravel dikes embedded with plastic sheeting were constructed. Wooden structural walls were constructed in areas where impoundment levels were to be greater than 1 m in depth. Sealing was achieved by incorporating a plywood–plastic–plywood ''sandwich'' technique on the walls and a plastic and concrete grout seal at the base. Areas of sites exceeding the height of inundation were not diked, creating ''riparian zones'' that were open to 4.7, 0.7, and 0.09 ha of upland above the High C, Medium C, and Low C reservoirs, respectively.

Beginning in 1999 (Table 2), water was pumped with a diesel pump into each reservoir from nearby oligotrophic Roddy Lake (L468) through aluminum

Table 2. Physical Properties of the FLUDEX Upland Reservoirs

	High C reservoir			Medium C reservoir			Low C reservoir		
Surface area (m^2)	7358			4966			6271		
Direct runoff area (m^2)	47,842			7334			929		
Reservoir watershed area (m^2)	55,200			12,300			7200		
Volume (m^3) above flooded soils	6870			4270			7120		
Volume (m^3) in flooded soils	1810			1810			800		
	1999[a]	2000[b]	2001[c]	1999[a]	2000[b]	2001[c]	1999[a]	2000[b]	2001[c]
Water renewal time (days)	11	8	9	10	6	6	8	7	7
Reservoir turnovers	9	14	11	10	17	18	11	14	15
Days of weir outflow	96	105	103	95	104	108	91	100	100
Days to fill	8	10	13	9	11	9	13	15	17

[a]*1999: Start of flooding: 22 Jun; start of drawdown: 04 Oct; days water pumped: 104.*
[b]*2000: Start of flooding: 30 May; start of drawdown: 21 Sep; days water pumped: 115.*
[c]*2001: Start of flooding: 29 May; start of drawdown: 24 Sep; days water pumped: 117.*

irrigation pipes (Figure 1). The reservoirs took between 8 and 17 days to fill to a maximum depth of 2 m and average depth of 1 m (Table 2). Water exited the reservoirs over v-notch weirs. In September/October, the reservoirs were emptied through gate valves installed at the bottom of the wooden walls to simulate drawdown in the shallow zones of northern hydroelectric reservoirs in the winter. Water volume and surface area of each reservoir was calculated using topographical maps determined from aerial photographs taken in 1982 and 1991.

Stores of MeHg and THg in the Upland Forest Sites Prior to Flooding

Estimates of MeHg and THg stored in foliage, shrubs, ground cover, wood, and soils were calculated to determine the total mass of MeHg and THg in each reservoir prior to flooding. MeHg concentrations in foliage (birch and alder leaves and pine needles), shrubs (blueberry and Labrador tea leaves), mosses, lichens, and wood collected at the ELA in each site prior to flooding (Hall 2003) were determined using cold vapor atomic fluorescence spectrometry (CVAFS) after overnight digestion in 25% KOH in methanol (Horvat and others 1993) and aqueous phase ethylation (Bloom 1989). THg concentrations were determined using CVAFS after digestion in 7:3 (vol:vol) nitric:sulfuric acid, as described by Bloom and Fitzgerald (1988). National Research Council reference materials (lobster hepatopancreas and marine sediment) were regularly run on both the MeHg and THg analytical systems, the results generally indicating between 80% and 110% recovery of certified values. Flett Research Ltd. (Winnipeg, Manitoba, Canada) analyzed plant tissues samples.

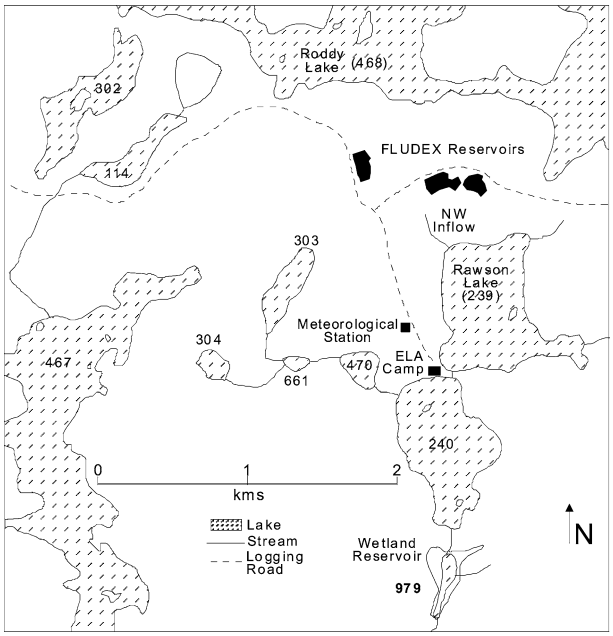

Figure 1. Location of study sites in relation to the Experimental Lakes Area (ELA) field camp.

The amount of foliage mass in the forest canopy in each reservoir was determined by weighing litterfall samples collected in duplicate at three sites within each reservoir (Matthews and others 2005). Two plastic containers (17 cm × 17 cm) were nested together; the bottom of the top container was removed, and a piece of 250 μm nitex mesh was wedged between them. Holes drilled in the bottom container allowed water to drain from the collectors. Collectors were attached to trees just above the water level and litter was collected from the containers monthly. Estimates of MeHg and THg

stored in the canopy were calculated by multiplying MeHg and THg concentrations in foliage by the total dry weight of litterfall in year 2 when the forests in the reservoirs lost all foliage. MeHg and THg concentrations in other plant tissues were multiplied by the total dry weight of each tissue in shrubs, ground cover, and wood (Matthews and others 2005).

Storage of MeHg and THg in upland forest soils was calculated using concentrations measured in soil cores taken from random locations in each site in October 1998 (13, 14, and 11 cores in the High C, Medium C, and Low C sites, respectively). Cores were collected using a stainless-steel barrel corer lined with plastic sleeves and were typically 8–15 cm long. Cores were sectioned into surficial litter/FH (the top 3–5 cm) and mineral layers, stored in acid-cleaned polypropylene cups, and immediately frozen. Cores were then lyophilized at −45°C and homogenized using an acid-cleaned mortar and pestle. THg and MeHg concentrations were determined at the University of Wisconsin–Madison and La Crosse Mercury Laboratories. MeHg samples were analyzed by CVAFS after distillation (Horvat and others 1993; Olson and others 1997) and aqueous phase ethylation (Bloom 1989). The aerial mass of MeHg and THg stored in each soil layer was calculated by multiplying the MeHg or THg concentrations by a mean soil bulk density determined by drying the soils at 60°C (surficial FH density = 1.0, 0.5, and 0.5 g cm^{-2} and mineral soil density = 2.5, 3.0, and 2.0 g cm^{-2} in the High C, Medium C, and Low C sites).

Upland Reservoir Mercury Input–Output Budgets

To calculate the *net* amount of MeHg or THg yielded from each experimental reservoir, quantities of MeHg and THg entering each reservoir were subtracted from quantities exiting (see St. Louis and others 1996; Kelly and others 1997). Input–output budgets were calculated for the period beginning on the first day that pumping began until the end of the drawdown (14–18 weeks each year; Table 2).

General Hg and Water Chemistry Sampling Methods and Analytical Techniques. All water samples taken to calculate MeHg and THg input–output budgets were collected in Teflon bottles using the clean-hands–dirty-hands sampling protocol (St. Louis and others 1996). MeHg water samples were frozen until analyzed. THg water samples were preserved using trace-metal-grade concentrated HCl to 1% of total sample volume. Twenty percent of all samples were taken in duplicate. MeHg in water was analyzed by CVAFS after distillation (Horvat and others 1993) and aqueous phase ethylation (Bloom 1989) (detection limits = 0.01–0.02 ng L^{-1} at a blank level of 0.05–0.1 ng L^{-1}). Total Hg in water was analyzed using CVAFS as described by Bloom and others (1988) with detection at 0.2–0.3 ng L^{-1} at a blank level of 0.3–0.4 ng L^{-1}. Flett Research Ltd. analyzed all water samples for MeHg and THg, with the exception of bottom water samples which were analyzed at the University of Wisconsin Mercury Laboratories. Spike recoveries for MeHg and THg were generally greater than 80% and greater than 90%, respectively.

Surface water samples were taken concurrently with Hg water samples in Nalgene polypropylene bottles and analyzed at the ELA water chemistry laboratory for dissolved organic carbon (DOC) as in Stainton and others (1977). Oxygen concentrations and temperature in each reservoir were monitored weekly using an YSI oxygen/temperature probe. Temperatures were also measured continually in 2001 using Onset Hobo data loggers.

Inputs. Inputs of MeHg and THg to the upland reservoirs included water pumped from Roddy Lake, wet deposition in open areas, throughfall through the forest canopy, and direct runoff from the ungauged terrestrial areas above each reservoir (Hall 2003).

Pumped inflow. Volume of water pumped into the reservoirs was regulated and monitored by means of control valves and inline flow meters. Daily readings and adjustments were made in an attempt to equalize water residence times among the reservoirs (Table 2).

Water at the end of the inflow pipe was sampled weekly for concentrations of MeHg and THg for the first month after flooding and then biweekly until reservoir drawdown. Average MeHg and THg concentrations in water pumped into each reservoir on two consecutive sampling dates were multiplied by the volume of water that entered each reservoir between the two dates to calculate mass inputs for that period. For each year of flooding, total inputs of MeHg and THg were calculated by summing the inputs for each sampling period.

Wet deposition in the open and throughfall. Standard recording gauges at the ELA meteorological site were used to determine wet deposition volume in open areas. Wet deposition during the May–September study period was 13% (425 mm), 54% (580 mm), and 16% (399 mm) above the 32-year average (377 mm) in 1999, 2000, and 2001, respectively. The volume of throughfall was determined using standard rain gauges placed under the

forest canopy in the Medium C and Low C reservoirs. The areas of the reservoirs that received either direct wet deposition or throughfall were calculated from the % canopy cover at each site.

Wet deposition in the open was collected for MeHg and THg analysis at the ELA meteorological site in 1998–1999 into ultraclean wide-mouth Teflon jars placed on acid-washed plexiglass trays secured to wooden posts (St. Louis and others 2001). In 2000, wet deposition samples were collected in automated collectors installed on a cliff in the Lake 658 watershed approximately 7 km from the FLUDEX sites. Duplicate throughfall collectors, 1 m in length, were set up at the sites by attaching wooden eavestrough holders to the trunks of trees. Within 15 minutes of the beginning of a precipitation event, acid-washed Teflon-lined eavestroughing (12.5 cm wide by 0.75 m long) was set out on the holders. Throughfall drained into 1 L acid-washed wide-mouth Teflon jars through an acid-washed nitex screen to remove large particles (St. Louis and others 2001). Throughfall was collected from all three sites prior to flooding in 1998, and after flooding from the Medium C reservoir in 1999 and from the Low C reservoir in 2000 and 2001. There was no significant difference in MeHg and THg concentrations in throughfall among upland reservoirs when sampled concurrently in 1998 (ANOVA; $p = 0.92$ and 0.93; $n = 34$ and 20 for MeHg and THg, respectively; Hall 2003).

Wet deposition inputs of MeHg and THg (mg ha^{-1}) were estimated by multiplying the volume-weighted concentrations for each season by the total volume of either wet deposition in the open or in throughfall in the period that the reservoirs were flooded. Concentrations of MeHg in wet deposition in the open were not measured in 2001, so the volume-weighted concentrations from 2000 were used to estimate input for 2001.

Direct runoff. The volume of water entering each reservoir in direct runoff through undiked areas was estimated on an aerial basis using a nearby gauged subcatchment with similar soils and vegetation (NW inflow to Rawson Lake, 56.4 ha; Figure 1). However, because the NW inflow to Rawson Lake contained approximately 3% wetland and the presence of wetlands in catchments has been shown to affect concentrations of MeHg in runoff (St. Louis and others 1994), samples used to determine MeHg and THg concentrations in direct runoff were taken from the Lake 114 inflow ungauged weir site. The Lake 114 catchment contained no wetlands and was dominated by purely upland stands of jack pine and paper birch of similar post fire age as the forests in and above the reservoirs. Runoff from the Lake 114 catchment was episodic during the summer months depending on rainfall intensity and antecedent moisture conditions. Samples were therefore taken opportunistically from May to September when there was runoff from this catchment. Inputs of MeHg and THg from direct runoff into the upland reservoirs were calculated by multiplying the estimated runoff water volume from the NW inflow by the average concentrations measured at the Lake 114 inflow weir.

Outputs. Mercury exited the upland reservoirs in water flowing over the weirs or out the drains during drawdown, in seepage, and as gaseous elemental Hg (Hg^0) fluxing off the surfaces of the reservoirs (Hall 2003).

Weir outflow. Samples were collected for MeHg and THg analysis from above the reservoir outflow weirs weekly during the first month of flooding, and then biweekly until autumn drawdown. Average MeHg and THg concentrations in water exiting the reservoirs over the v-notch weirs on two consecutive sampling dates were multiplied by the volume of water that exited each reservoir between the two dates to calculate mass outputs for that period. For each year of flooding, total outputs of MeHg and THg were calculated by summing the outputs for each sampling period.

Seepage. Seepage was estimated in the water balance as the residual term and verified by independent seepage measurement surveys performed periodically during the study period. To estimate Hg loss due to seepage, we multiplied the seepage water volume by the concentration of MeHg and THg measured at the weir. Surface water concentrations were used because we could not confirm the origin of the seepage water and we assumed that Hg concentrations in the water flowing over the weir were representative of concentrations in the reservoir.

Drawdown. The drawdown water volume was separated into two components: (1) surface waters estimated as 95% of the total water column volume and (2) bottom waters (1.5 cm from soil–water interface) estimated as 5% of total water column volume. To calculate the mass of MeHg and THg exiting through the drawdown pipe, the volume of surface water was multiplied by MeHg and THg concentrations in samples taken at the weir just prior to the beginning of drawdown, whereas the volume of bottom water was multiplied by average bottom water concentrations measured in samples taken 1–2 weeks prior to drawdown.

Hg^0 fluxes from reservoir surfaces. An important loss of Hg out of aquatic ecosystems may be the flux of Hg^0 from the water surface to the atmosphere. Hg^0 can be formed as a result of the photoreduction of MeHg and HgII in the water column (Amyot and others 1994; Sellers and others 2001). Although we did not directly measure fluxes of Hg^0 from the reservoir surfaces, we determined the upper limits of dissolved Hg^0 concentrations in the water column. In 2001, samples for dissolved Hg^0 analysis were collected by completely filling a 2.5 L acid-washed glass bottle with reservoir surface water. In the laboratory, 250 mL of water was removed from each bottle to create a headspace. Bottles were fitted with caps containing an inlet consisting of one piece of 5 mm Teflon tubing that extended to the bottom of the bottle and an outlet attached to a gold-coated-bead Hg^0 trap. UHP nitrogen was then bubbled through the sample at a rate of approximately 5 L min^{-1} for between 2 and 6 h in the dark, forcing dissolved Hg^0 out of solution and onto the gold traps. Quantification of Hg^0 collected on the gold traps was performed in the ELA Hg clean laboratory with a Tekran Model 2500 Mercury Vapour Detector (see Lindberg and others 2000), using dual gold-coated-bead amalgamation with a detection limit of 0.5 pg.

Sources of Error in Input-Output Budgets and Statistical Analysis. The two main sources of error in our input–output budget were associated with the analyses of samples for MeHg and THg, and the estimation of water volumes used in our calculations. Analytical error was less than 10% for both MeHg and THg samples. These values were within 19% and 10% of a consensus value obtained in a recent interlab comparison. Standard procedures and equipment were used for the measurement of precipitation, flow (v-notch weirs and calibrated flow meters), and water levels (precision recorders and data loggers). Evaporation was measured directly with Class A evaporation pans placed in shallow areas of the reservoirs. Although it is difficult to independently assess error associated with each of these parameters, errors generally accepted are 5% for precipitation, weir flow, and water levels, approximately 15% for evaporation, and about 18% when applying gauged runoff to similar ungauged areas (Winter 1981). By far, the major component of the water balance is the inflow by pumping where the associated errors were 5%.

The FLUDEX could not replicate experimental units due to the difficulty replicating whole-ecosystem experiments (Schindler 1998). However, data trends, as well as pre- and postflood comparisons, convincingly demonstrate effects of flooding on changes in MeHg and THg concentrations among the reservoirs. Inferential statistics are used to emphasize results, acknowledging the implication of pseudoreplication (Hurlbert 1984).

Pools of MeHg Stored in Upland Forest Reservoirs

To estimate the total net production of MeHg in the reservoirs at the end of each flooding season (September), MeHg stored in soils and food web organisms was calculated and added to the net loss of MeHg out of the outflow calculated using the input–output budgets. For each year, these total stores of MeHg were then subtracted from stores calculated the previous September.

Soils. MeHg stored in soils in September was estimated from MeHg concentrations measured in cores collected using an acid-cleaned acrylic tube sampler (one core from three sites located in each reservoir). Cores were sectioned into surficial litter/FH and mineral layers, stored in acid-cleaned polypropylene cups, and immediately frozen. MeHg pools were obtained by multiplying the MeHg concentration by a mean soil bulk density determined by drying the soils at 60°C (see section on MeHg and THg storage in unflooded upland forest sites).

Food Web. Periphyton was collected from 2 m-long × 2 cm-diameter fir dowels that were hung among the trees at five stations within each reservoir (Hall 2003) prior to flooding in years 2 and 3 (2000–2001). Each September, periphyton was rinsed from two dowels at each station into plastic bags and immediately frozen. Periphyton was analyzed for MeHg at Flett Research Ltd. using the same analytical methods as for plant samples (see above section on MeHg stores in plants). The mass of MeHg in the periphyton community was calculated by multiplying MeHg concentrations with the total mass of periphyton (unpublished data, D. Findlay, Freshwater Institute, Winnipeg, MB and J. Venkiteswaran and S. Schiff, University of Waterloo, Waterloo, ON) in each reservoir. Dowels were not installed in the first year of flooding (1999), but grab samples of periphyton attached to trees in each reservoir were collected in September and analyzed for MeHg concentrations. Because quantitative estimates of periphyton biomass were not available, year 1 periphyton MeHg mass was calculated by multiplying the concentration of grab samples taken in 1999 with the estimate of biomass in year 2 (2000).

Zooplankton were collected for MeHg analysis using a 150 μm sweep net from the open regions of each reservoir and immediately frozen in whirl-pak

Table 3. Average concentrations (ng g^{-1}) and Stores of (mg ha^{-1}) of Methylmercury (MeHg) and Total Mercury (THg) in the FLUDEX Sites Prior to Flooding

	High C reservoir				Medium C reservoir				Low C reservoir			
	MeHg		THg		MeHg		THg		MeHg		THg	
	ng g^{-1}	mg ha^{-1}	ng g^{-1}	mg ha^{-1}	ng g^{-1}	mg ha^{-1}	ng g^{-1}	mg ha^{-1}	ng g^{-1}	mg ha^{-1}	ng g^{-1}	mg ha^{-1}
Aboveground												
Wood and bark	0.23	21	3.6	330	0.23	15	3.6	230	0.23	13	3.6	210
shrubs and ground cover	0.50	2	37.8	290	0.49	<1	43.5	10	0.62	<1	49.4	20
foliage	0.12	1	11.3	100	0.12	1	11.3	90	0.12	1	11.3	70
Fungal/humic soil	1.13	113	89.1	8960	0.20	10	44.2	4450	0.52	16	39.2	2360
Mineral soil layer	0.17	41	51.8	5200	0.04	11	96.0	9670	0.08	9	81.0	4920
Total		*178*		*14,880*		*37*		*14,450*		*39*		*7580*

bags (Paterson and others 1998). Flett Research Ltd. analyzed zooplankton for MeHg using the same methods outlined for plants and periphyton. Zooplankton biomass was determined by collecting samples at 10–12 stations within each reservoir using a quantitative tube sampler (Paterson and others 1997; Peech Cherewyk 2002). MeHg pools were obtained by multiplying aerial zooplankton biomass in each reservoir by the MeHg concentrations in zooplankton. Biomass and MeHg concentrations in benthic organisms were not measured.

Fine-scale dace (*Phoxinus neogaeus*) were introduced annually into the reservoirs at densities between 0.35 and 0.44 fish m^{-2}. Fish were caught each September with either minnow traps (1999) or small mesh gill nets (2000 and 2001). Approximately 0.2 g of white epaxial muscle were analyzed for THg using cold vapor atomic absorption spectrometry (Hendzel and Jamieson 1976) in the Freshwater Institute Mercury Laboratory (Winnipeg, MB). The majority of THg in fish is MeHg (Hall and others 1997; Bodaly and Fudge 1999). Muscle THg concentrations are approximately 30% higher than whole-body concentrations, therefore a conversion factor of 0.7 was applied to muscle THg concentrations to calculate total body burdens (Bodaly and Fudge 1999; St. Louis and others 2004; unpublished data, R.A. Bodaly and A. Majewski, Freshwater Institute, Winnipeg, MB). To determine THg stored in fish in each reservoir, average body burdens at the beginning of each season were subtracted from final average body burdens and multiplied by an estimate of fish biomass.

Determination of MeHg Production and MeHg Degradation Rates. Whole-reservoir rates of MeHg production or MeHg degradation were estimated by dividing net changes in total MeHg stores from the end of one flooding season to the end of the next by the number of days that reservoirs were flooded each year. For the first year of flooding, we subtracted the MeHg stored in vegetation and soils prior to flooding from the total MeHg stored in the reservoirs in September 1999.

Results and Discussion

MeHg and THg Storage in Unflooded Upland Forest Sites

Prior to flooding, average MeHg concentrations in plants and soils ranged from 0.12 to 1.13 ng g^{-1} (Table 3). Average THg concentrations were between 3.6 and 96.0 ng g^{-1}. MeHg stores prior to flooding in the High C site (178 mg ha^{-1}) were 5–6-fold greater than in the Medium C and Low C sites (37 and 39 mg ha^{-1}, respectively; Table 3). THg stored in vegetation and soils in the High C and Medium C sites (14,900 and 14,500 mg ha^{-1}) were similar, and about 2-fold greater than in the Low C site (7580 mg ha^{-1}; Table 3). For all sites, MeHg and THg were predominantly stored in soils (81%–95% and 95%–98%, respectively). MeHg was primarily found in the FH layer of soils in the High C and Low C sites, whereas MeHg mass was split evenly between the FH and mineral layers of soils in the Medium C site (Table 3). In the Medium C and Low C sites, THg masses were 2 times higher in the mineral layers than in the overlying FH layer. In the High C site, storage of THg in the FH layer was greater than the mineral layer.

The large difference between stores of MeHg and THg at our sites is most likely due to the higher deposition of THg than MeHg to ELA forests over the 18 years of fire regeneration (St. Louis and

Table 4. Water Inputs and Outputs (m^3) to and from the FLUDEX Upland Reservoirs in 1999, 2000, and 2001

	High C reservoir			Medium C reservoir			Low C reservoir		
	Year 1	Year 2	Year 3	Year1	Year 2	Year 3	Year 1	Year 2	Year 3
Inputs									
Inflow	78,600	93,300	84,800	76,700	69,600	74,700	96,900	108,600	106,900
Wet deposition in the open	1220	1790	1310	820	1200	880	1140	1680	1230
Throughfall	710	990	1300	480	670	880	560	780	1020
Direct run off	4680	12,220	4950	710	1850	780	60	150	90
Total water input	*85,210*	*108,300*	*92,360*	*78,710*	*73,320*	*77,240*	*98,660*	*111,210*	*109,240*
Outputs									
Weir	60,200	80,200	64,000	60,800	57,200	63,700	33,500	42,500	51,500
Seepage	16,000	15,900	13,000	15,400	13,900	14,500	23,100	19,100	12,200
Bedrock fracture							36,900	43,400	40,800
Outflow pipe (total)									
Surface water	6530	6530	6530	4050	4050	4050	6760	6760	6760
Bottom water	340	340	340	210	210	210	360	360	360
Evaporation	1620	1800	1900	1350	1300	1350	1380	1650	1570
Canopy interception	840	1280	370	570	870	250	660	1000	290
Total water output	*85,530*	*106,050*	*86,140*	*82,380*	*77,530*	*84,060*	*102,660*	*114,770*	*113,480*

others 2001). The amount of THg present as MeHg (%MeHg) in the sites prior to flooding was greater in the High C site (1.1%) compared to the Medium C and Low C sites (0.2% and 0.4%, respectively), likely because of the presence of pockets of saturated *Sphagnum* soils in the High C site, where MeHg production is known to occur (St. Louis and others 1994; Branfireun and others 1998). Over the long term, litterfall represents an important input of both OC and Hg to soils under growing forests (St. Louis and others 2001). However, in the FLUDEX reservoirs, litterfall represented a one-time pulse of OC and Hg from the canopy into our reservoirs. This OC addition provided additional substrates for decomposition in the second year of flooding after the trees had died (Matthews and others 2005). However, despite the large flux of litterfall into the reservoirs in 2000, the input of litterfall MeHg (1.1–1.7 mg ha^{-1} $season^{-1}$) was very low due to extremely low concentrations of MeHg in litter. THg inputs ranged from 65 to 422 mg ha^{-1}.

Water and Mercury Budgets

Inputs. Pumped input. Concentrations of Hg in water entering each reservoir were always between 0.01 and 0.15 ng MeHg L^{-1} and between 0.8 and 2.3 ng THg L^{-1}. Pumped inflow over the course of each season contributed on average 95 ± 1% of total water inputs to all three upland reservoirs (Table 4). Inflow water contributed between 3 and 9 mg MeHg (Table 5) and 77 and 147 mg THg (Table 6) among reservoirs over the three-year study. This input was equivalent to between 87% and 98% of total MeHg inputs and between 47% and 91% of all THg inputs to the upland reservoirs.

Wet deposition and throughfall. Concentrations of Hg in wet deposition collected in the open in 1998–2000 ranged between 0.01 and 0.23 ng MeHg L^{-1} and between 0.2 and 25.6 ng THg L^{-1} (Hall 2003). Concentrations of Hg in throughfall ranged from 0.062 to 0.344 ng MeHg L^{-1} and from 3.10 to 33.36 ng THg L^{-1}. Volume-weighted seasonal averages of MeHg and THg in wet deposition in the open (0.07 ± 0.02 to 0.13 ± 0.02 and 3.9 ± 0.7 to 13.2 ± 2.7 ng L^{-1} for MeHg and THg, respectively) were always lower than those in throughfall (0.15 ± 0.04 to 0.3 ± 0.02 and 7.7 ± 2.5 to 24.7 ± 4.8 ng L^{-1}; Hall 2003).

In the first two years of flooding, throughfall volume was 46% and 44% of wet deposition. By the third year of flooding, when most foliage had fallen off the dead trees, 78% of wet deposition made it through the canopy. Water inputs from wet deposition in the open and throughfall accounted for only between 1% and 2% of total water inputs (Table 4). MeHg inputs from wet deposition in the open and throughfall were low (<0.5 mg), constituting between 4% and 8% of total MeHg inputs (Table 5), whereas THg inputs in wet deposition and throughfall ranged between 4.6 and 25 mg, contributing between 6% and 23% of all THg inputs (Table 6).

Table 5. Inputs and Outputs of Methylmercury (mg MeHg) and MeHg Exports (mg ha^{-1}) to and from FLUDEX Upland Reservoirs

	High C reservoir			Medium C reservoir			Low C reservoir		
	Year 1	Year 2	Year 3	Year 1	Year 2	Year 3	Year 1	Year 2	Year 3
Inputs									
Inflow	3.4	4.3	7.2	3.4	3.0	6.0	4.1	5.1	9.1
Wet deposition in the open	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Throughfall	0.2	0.2	0.4	0.1	0.1	0.3	0.1	0.1	0.3
Direct runoff	0.2	0.3	0.5	<0.1	0.1	0.1	<0.1	<0.1	<0.1
Total MeHg input	*3.9*	*4.9*	*8.2*	*3.6*	*3.2*	*6.6*	*4.4*	*5.2*	*9.4*
Outputs									
Weir	39.4	48.5	31.4	52.0	49.1	40.0	14.9	18.1	13.2
Seepage	9.3	9.2	6.3	11.6	11.8	9.0	9.7	7.4	3.4
Bedrock fracture							15.5	16.7	11.2
Outflow pipe									
Surface water	3.1	2.9	2.7	2.6	7.3	1.4	1.7	1.4	1.3
Bottom water	0.6	0.9	0.2	0.2	0.1	0.1	0.2	0.1	0.1
Total MeHg output	*52.4*	*61.5*	*40.6*	*66.4*	*68.3*	*50.4*	*42.0*	*43.6*	*29.2*
MeHg output–MeHg input	48.5	56.6	32.4	62.8	65.1	43.8	37.6	38.4	19.7
MeHg yield[a] (mg MeHg ha^{-1})	**65.9**	**77.0**	**44.0**	**126.0**	**131.0**	**88.2**	**59.9**	**61.2**	**31.5**

[a]*MeHg yield = MeHg output - MeHg input / reservoir area (see Table 2).*

Table 6. Inputs and Outputs of Total Mercury (mg THg) and THg Exports (mg ha^{-1}) to and from the FLUDEX Upland Reservoirs

	High C reservoir			Medium C reservoir			Low C reservoir		
	Year 1	Year 2	Year 3	Year 1	Year 2	Year 3	Year 1	Year 2	Year 3
Inputs									
Inflow	78.2	125.4	89.8	76.6	92.1	79.0	96.3	147.1	113.0
Wet deposition in the open	16.1	6.9	12.1	10.8	4.6	8.1	15.1	6.5	11.4
Throughfall	17.6	7.7	24.9	12.0	5.2	16.9	13.8	6.0	19.5
Direct runoff	42.6	124.8	41.4	6.4	18.7	6.5	0.5	1.6	0.8
Total THg input	*155*	*265*	*168*	*106*	*121*	*111*	*126*	*161*	*145*
Outputs									
Weir	186	256	181	258	196	159	87.1	91.0	86.4
Seepage	48.0	53.3	37.2	74.6	53.4	37.2	76.6	44.0	22.6
Bedrock fracture							123	101	74.7
Outflow pipe									
Surface water	14.4	21.4	11.8	7.9	10.2	5.7	9.5	13.1	7.2
Bottom water	4.6	0.9	0.9	0.7	0.4	0.4	1.2	0.8	0.4
Total THg output	*253*	*332*	*230*	*341*	*260*	*203*	*297*	*250*	*191*
THg output–THg input	*97.9*	*67.1*	*62.2*	*235*	*139*	*92.0*	*171*	*88.7*	*46.6*
THg yield[a] (mg THg ha^{-1})	**133**	**91.2**	**84.5**	**474**	**280**	**185**	**273**	**141**	**74.3**

[a]*THg yield = THg output - THg input / reservoir area (see Table 2).*

Direct runoff. Concentrations of Hg in runoff from the Lake 114 upland catchment ranged between 0.01 and 0.13 ng MeHg L^{-1} and 6.6 and 14.9 ng THg L^{-1} (Hall 2003). The volume of water entering the High C reservoir in runoff was estimated to vary between 5% and 11% of the total water inputs among years (Table 4). MeHg inputs due to runoff into the High C reservoir were less than 0.5 mg for the flooding season, or between 5% and 6% of total MeHg inputs (Table 5). THg

inputs to the High C reservoir from direct runoff ranged from 41 to 125 mg and contributed up to 47% of all THg inputs (Table 6). Total runoff water inputs to the Medium C and Low C reservoirs were less than 3% of total water inputs, delivering less than 3% of the total MeHg inputs. Direct runoff contributed from less than 1% to 16% of all THg inputs to the Medium C and Low C reservoirs (Table 6).

Outputs. Weir outflow. Average MeHg concentrations in outflow waters from all three upland reservoirs were about 3.4 times greater than concentrations in inflow water within the first week of flooding. Concentrations of MeHg in outflow water from all reservoirs remained elevated for the duration of the experiment, peaking at 1.60 ng L^{-1} in year 2 in the Medium C reservoir (Figure 2A). MeHg concentrations in the Medium C reservoir were almost always higher than in the High C and Low C reservoirs until just prior to drawdown (Figure 2A). Concentrations of THg in water exiting over the reservoir weirs were much higher than in inflow water (Figure 2B). Concentrations of THg in outflow water tended to decrease throughout each season, and average annual mean THg concentrations in all reservoirs decreased over the first three years of flooding.

As in the FLUDEX upland reservoirs, concentrations of MeHg in the outflow waters of the ELARP wetland reservoir increased within the first month of flooding and remained elevated over the course of the three-year period, reaching a maximum outflow concentration of 3.2 ng L^{-1} in year 3 postflood (Figure 2A). Average annual MeHg concentrations in the wetland reservoir increased over the first three years of flooding, while THg concentrations stayed relatively constant.

The % MeHg in FLUDEX reservoir outflows began to increase after the third week of flooding and continued to increase, peaking at over 45% MeHg midway through the second flooding season (Figure 2C). The Medium C reservoir had higher % MeHg values than the two other upland reservoirs. The % MeHg decreased by the end of the second season of flooding but began to increase again in the latter part of the third year of flooding. The % MeHg was generally higher in water exiting the ELARP wetland reservoir than in water exiting the FLUDEX upland reservoirs.

Although water concentrations are important in determining MeHg accumulation in aquatic organisms (Paterson and others 1998), they cannot be used to examine relative rates of MeHg production because the flushing rates were different among reservoirs. Water yields (measured outflow/

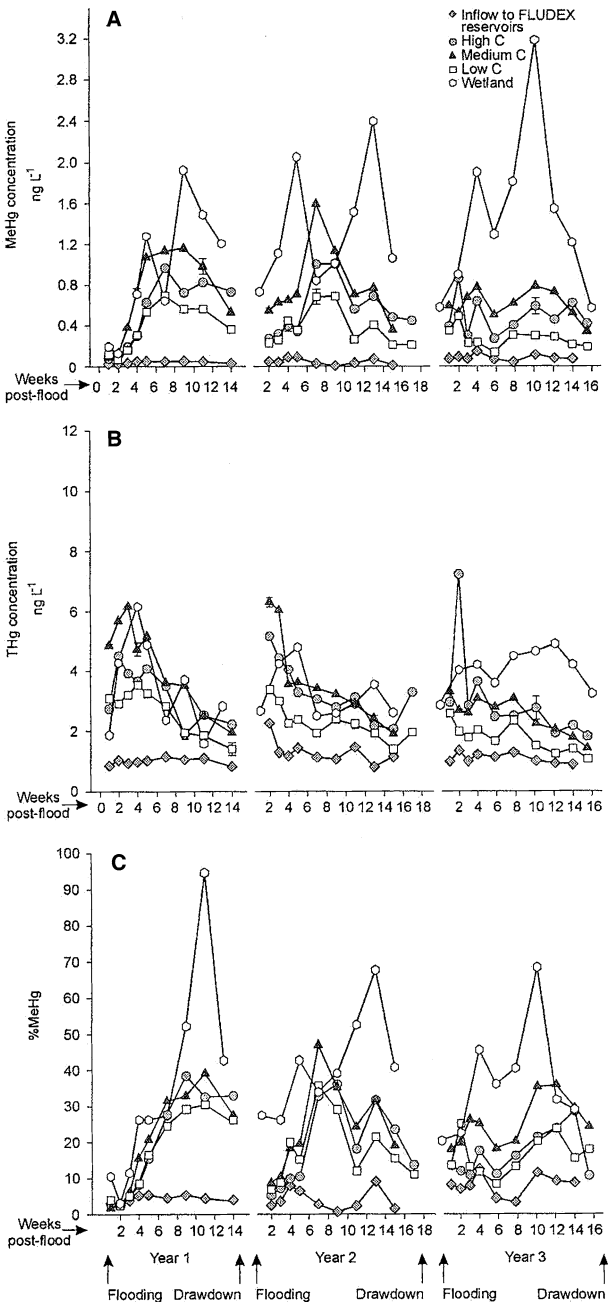

Figure 2. A Concentrations of methylmercury (MeHg) in water flowing over the outflow weirs. **B** Concentrations of total mercury (THg) in water flowing over the outflow weirs. **C** The proportion of THg present as MeHg in the upland and wetland reservoirs (%MeHg). For **A, B**, and **C**, error bars represent one standard error in duplicate samples. Differences in concentrations cannot be directly compared due to differences in reservoir flushing rates.

total inflow) averaged 71%, 79%, and 40% for the High C, Medium C, and Low C reservoirs, respectively (Table 4). The lower water yields for the Low C reservoir were due to uncontrolled flow through

a subsurface bedrock fracture (see section on seepage). The mass of MeHg and THg in water exiting the Medium C outflow weir (range = 40–52 mg MeHg and 159–258 mg THg) exceeded that leaving the High C and Low C reservoir outflow weirs (range = 13–49 mg MeHg and 86–256 mg THg) over the three-year period. Between 29% and 79% of the total mass of MeHg and THg exiting the reservoirs went over the weirs (Tables 5 and 6).

Seepage. Between 11% and 23% of the water inputs to the reservoirs seeped through the wooden and gravel dikes at the soil–bedrock interface. Seepage losses were similar among all reservoirs and study seasons. Seepage also occurred from a bedrock fracture in the Low C reservoir (~36% of total water inputs). Seepage rates decreased over time as dikes and wooden walls swelled and self-sealed. The total mass of MeHg and THg in seepage from the upland reservoirs was greatest in the Low C reservoir in the first year of flooding (2.5 mg MeHg and 199 mg THg; Tables 5 and 6) because dike seepage volumes were highest in the Low C reservoir (Table 4) compared to the other upland reservoirs. Mass loss from seepage in the High C and Medium C reservoirs ranged from 6 to 12 mg MeHg and from 37 to 75 mg THg over the three-year study.

Drawdown. The average volume of water exiting the upland reservoirs through the drawdown pipe in autumn accounted for 6 ± 0.4% of total water losses (Table 4). Concentrations of MeHg and THg in bottom waters ranged between 0.19 and 2.66 ng MeHg L^{-1} and 1.1 and 13.3 ng THg L^{-1} in all reservoirs over the three-year study (Hall 2003). The outputs of MeHg and THg through the drawdown pipes were similar among the upland reservoirs in all years, ranging from 3% to 11% of total MeHg outputs and from 3% to 8% of all THg outputs.

Hg^0 fluxes from reservoir surfaces. Average dissolved Hg^0 concentrations in year 3 were higher in the Low C reservoir (65 ± 10 pg L^{-1}) than the Medium C and High C reservoirs (36 ± 8 and 22 ± 6 pg L^{-1}, respectively). These concentrations constituted 3.7%, 1.5%, and less than 1% of average seasonal THg concentrations in water in the Low C, Medium C, and High C reservoirs, respectively. Average dissolved Hg^0 concentrations were negatively correlated with average DOC concentrations (r^2 = 0.9997; Figure 3A) and this negative relationship likely reflected less reduction of HgII to Hg^0 due to DOC screening of photoreducing UV energy (Scully and Lean 1994; Amyot and others 1997). It is also possible that increased DOC concentrations contributed to HgII stabilization, for example, by complexation, making it unavailable for reduction and therefore reducing Hg^0 production and subsequent evasion to the atmosphere (Rolfhus and Fitzgerald 2001; unpublished data, K. Rolfhus). Concentrations of dissolved Hg^0 were measured in only year 3 when the annual average DOC concentrations were at their lowest (Figure 3B), resulting in decreased UV screening compared to the first two years of flooding when average DOC concentrations were higher. Therefore, we expect that dissolved Hg^0 concentrations were very low in years 1 and 2. Due to the very small proportion of dissolved Hg^0 compared to water THg concentrations, dissolved Hg^0 fluxes from the upland reservoirs were assumed to be insignificant and were not included in the mercury input–output budgets.

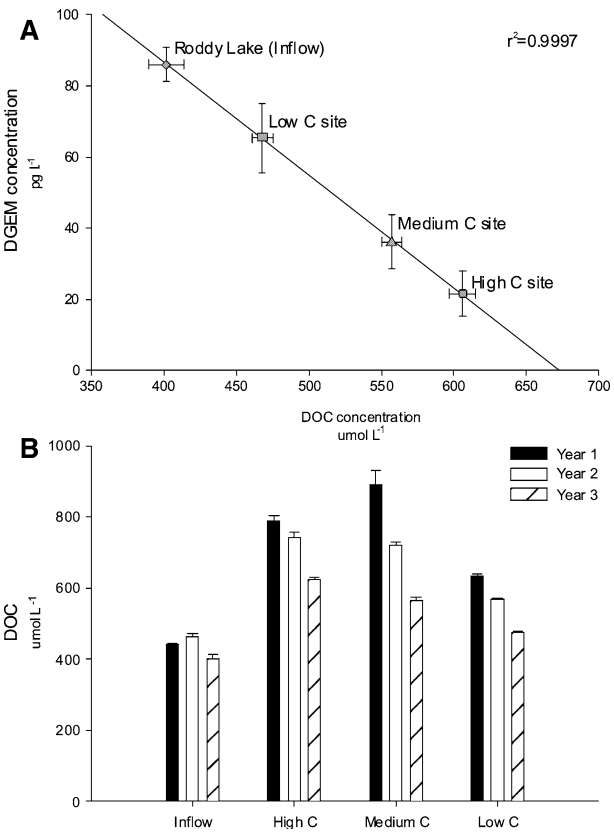

Figure 3. A Year 3 concentrations of dissolved gaseous elemental mercury (DGEM) in relation to concentrations of dissolved organic carbon (DOC) in the reservoirs and source lake, **B** Average seasonal DOC (μmol L^{-1}) concentrations in upland reservoirs.

Mercury Yields. Net yields of MeHg and THg could not be calculated for the upland sites prior to flooding because the sites were not hydrologically gauged. However, a previous study at the ELA examined net yields of MeHg and THg from

Table 7. Net yields of Methylmercury (MeHg) and Total Mercury (THg) from Unflooded Upland Forested and Wetland Catchments and Upland and Wetland Reservoirs at the Experimental Lakes Area

	MeHg yield		THg yield		Reference
	mg ha^{-1} y^{-1}	mg ha^{-1} day^{-1}	Mg ha^{-1} y^{-1}	mg ha^{-1} day^{-1}	
Upland forests	−0.3	−0.0008	−30	−0.8	St. Louis and others (1996)
Catchments containing wetlands	−0.6	−0.002	−25	−0.07	St. Louis and others (1996)
Oligotrophic lake (L240)	0.04 0.06	0.0001 0.002	3.1	0.008	Sellers and others (2001) St. Louis and others (1996)
Upland reservoirs (FLUDEX)	NA[a]	0.27–1.22	NA[a]	0.6–4.55	This study
Wetland reservoir (first 3 years of flooding)	19.9–69.8	0.05–0.15	3.1–130.3	0.008–0.36	St. Louis and others (2004)

Negative values represent Hg sinks, positive values represent Hg sources. na = not available.
[a]*Exports from upland reservoirs were measured ony from May/June to September/October each year.*

unflooded upland forested and wetland catchments over a three-year period (1990–1993; St. Louis and others 1996). The purely upland catchment (Lake 114 inflow) retained both MeHg and THg (0.3 and 30 mg ha^{-1} y^{-1} for MeHg and THg respectively; Table 7), and, as a result, we assumed that the FLUDEX upland sites were also sinks for atmospheric inputs of MeHg and THg prior to flooding.

The hydrological control over the FLUDEX reservoir inflow and outflow rates enabled us to account for 98% of the water volumes over the three-year period (Table 4). All three upland reservoirs exported MeHg and THg during the three years of flooding. Net seasonal losses of MeHg from the Medium C reservoir exceeded those from the other upland reservoirs in all years, ranging from 0.58 to 1.22 mg MeHg ha^{-1} day^{-1} (Table 5 and Figure 4). Exports of MeHg from the High C and Low C reservoirs ranged from 0.27 to 0.67 mg ha day^{-1} (Figure 4). THg yields were also highest from the Medium C reservoir (1.58–4.55 mg ha^{-1} day^{-1}). THg exports from the High C and Low C reservoirs ranged between 0.63 and 2.63 mg THg ha^{-1} day^{-1} (Figure 4). Net yields of MeHg, however, were highest in the first two years of flooding and decreased substantially in year 3, whereas THg yields decreased after year 1.

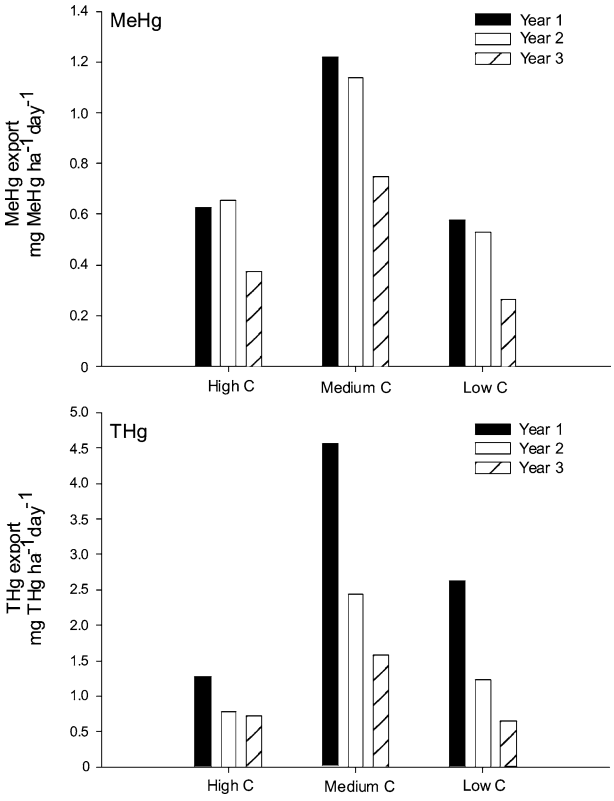

Figure 4. Export yields of methylmercury (mg MeHg ha^{-1} day^{-1}) and total mercury (mg THg ha^{-1} day^{-1} from the upland reservoirs.

Pools of MeHg Stored in the Reservoirs

Soils. Between 79% and 97% of the total MeHg stores in the reservoirs after inundation were found in the litter/FH and mineral soils (Table 8). Post-flood MeHg stores were generally higher in the litter/FH layer of soils (between 200 and 1700 mg ha^{-1}) than in the mineral soils (between 30 and 1500 mg ha^{-1}). Total MeHg stores in both the litter/FH and mineral layers combined were always highest in the High C reservoir and lowest in the Low C reservoir (Table 8). In all FLUDEX upland reservoirs, flooding resulted in a large increase in MeHg mass stored in soils. MeHg stores in soils over three years of flooding increased 9–21, 37–70, and

Table 8. Methylmercury Stored (mg MeHg ha^{-1}) in Soil, Vegetation, and Biota in Upland Forest Reservoirs and Exported over the Weir

	Soils		Food web			Yield	Total	% of total		
Reservoir	Fungal/humic	Mineral	Periphyton[a]	Zooplankton	Fish	over weir	MeHg	MeHg in soils	MeHg in Food web	MeHg yielded
High C										
Year 1 (1999)	807	621	6	0.4	13	66	1510	94	1	4
Year 2 (2000)	1751	1514	10	<0.1	26	77	3440	97	1	2
Year 3 (2001)	1008	807	16	0.1	32	44	1910	95	2	2
Medium C										
Year 1	487	704	20	5.1	19	127	1360	87	3	9
Year 2	817	658	9	<0.1	35	131	1650	89	3	8
Year 3	685	85	24	0.2	50	88	932	83	8	9
Low C										
Year 1	266	219	17	5.9	20	60	588	83	7	10
Year 2	564	51	11	<0.1	33	61	721	85	6	9
Year 3	202	29	7	1.3	26	32	297	78	11	11

[a]*Because quantitative periphyton biomass was not obtained in year 1, year 2 MeHg biomass data were used to calculate year 1 MeHg pools (see text).*

9–25 times those found in soils prior to flooding in the High C, Medium C, and Low C reservoirs, respectively (Tables 3 and 8). These large increases in MeHg stores in soils postflood suggest that flooded soils were the main sites of MeHg production. The biomethylation of inorganic Hg depends on the metabolism of the methylating organisms (most likely sulfate-reducing bacteria) (Compeau and Bartha 1985) and anoxic flooded soils would likely provide a favorable environment for growth of these organisms (Gilmour and Henry 1991). MeHg pools in soils decreased in the third year of flooding, but not to levels seen prior to inundation (Figure 5). Similar conclusions were reached in the first three years of flooding the ELARP wetland reservoir (Kelly and others 1997; St. Louis and others 2004).

Food Web. The periphyton, zooplankton, and fish communities represented the smallest MeHg pools in the upland reservoirs at the end of each flooding season, accounting for 1%–10% of total MeHg stores (Table 8). MeHg stores were less than 24 and 6 mg ha^{-1} in periphyton and zooplankton, respectively, and between 13 and 50 mg ha^{-1} in fish. Pools of MeHg in food web organisms generally did not differ among reservoirs. Stores of Hg in fish generally increased over time each year of flooding (Table 8), whereas MeHg stores in zooplankton decreased after the first season of flooding. There were no temporal patterns observed in MeHg pools in periphyton.

Total MeHg Production in Upland Forest Reservoirs

The total storage of MeHg in our upland reservoirs ranged from 290 mg ha^{-1} to over 3300 mg ha^{-1} (Table 8). Within each year, MeHg storage in the High C reservoir (1510–3340 mg ha^{-1}) was up to 2 times higher than storage in the Medium C reservoir (930–1650 mg ha^{-1}) and 3–6.5 times higher than in the Low C reservoir (300–720 mg ha^{-1}). MeHg stores within each reservoir were highest at the end of the second season of flooding and then declined dramatically by the end of the third flooding season. However, total stores of MeHg in the reservoirs never approached the low levels observed prior to flooding (Figure 5). Year 3 storage in the High C, Medium C, and Low C reservoirs were 12, 35, and 19 times higher than preflood storage, respectively (Figure 5).

Overall, there was an initial pulse of MeHg production in all three reservoirs that lasted for 2 years, after which net MeHg degradation began to

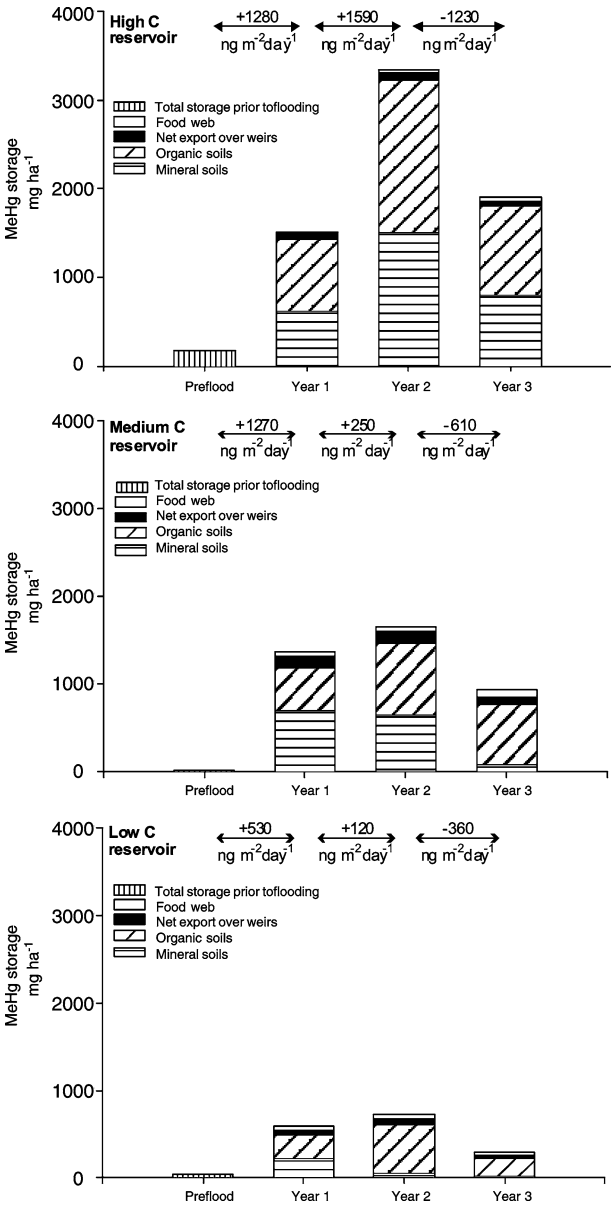

Figure 5. Methylmercury stores (mg MeHg ha^{-1}) in upland reservoirs. MeHg production and demethylation rates are shown at the top of each panel; positive values represent net MeHg production and negative values represent net demethylation

reduce the pools of MeHg in all of our upland reservoirs. Rates of MeHg production and MeHg degradation were generally related to the amount of total C stored in the reservoirs prior to flooding (Figure 6). Rates of MeHg production were highest in the High C reservoir, producing 1280 and 1590 ng m^{-2} day^{-1} in the first and second years of flooding, respectively (Figure 6). The rate of MeHg production in the Medium C reservoir in the first year of flooding (1270 ng m^{-2} day^{-1}) was very similar to that observed in the High C reservoir. The MeHg production rate in the Low C reservoir in the first year of flooding (530 ng m^{-2} day^{-1}) was more than 2.4 times lower than rates observed in the High C and Medium C reservoirs (Figure 6). By the end of the second year of flooding, MeHg stores and rates of net MeHg production in the High C reservoir exceeded those in the Medium C (250 ng m^{-2} day^{-1}) and Low C (120 ng m^{-2} day^{-1}) reservoirs.

Net MeHg degradation was observed in all three reservoirs in the third year of flooding (Figure 6). Rates of net MeHg degradation in the High C reservoir (1230 ng m^{-2} day^{-1}) exceeded those in the Medium C and Low C reservoirs (Figure 6). Compared to the High C reservoir, net MeHg degradation was 2 times lower in the Medium C reservoir (610 ng m^{-2} day^{-1}) and almost 3.4 times lower in the Low C reservoir (360 ng m^{-2} day^{-1}). We conclude that the destruction of MeHg was microbial because photodegradation of MeHg in the water column was likely to be minimal (see above), and the largest decreases in MeHg pools were observed in the litter/FH and mineral soil layers (Table 8), where the microbial demethylators would be expected to be most active (Robinson and Tuovinen 1984; Ullrich and others 2001).

MeHg production in the High C reservoir was similar or higher than MeHg production in the Medium C reservoir; however, MeHg concentrations in water were higher in the Medium C reservoir compared to the other upland reservoirs. This suggests that there was a disconnect in the movement of MeHg from the sites of production (soils) to the water column. Water concentrations are important in the bioaccumulation of MeHg in aquatic organisms (Paterson and others 1998), so this disconnect may have important implications in MeHg contamination of reservoir fisheries.

Comparisons of FLUDEX Upland and ELARP Wetland Reservoirs

To compare rates of MeHg production in the upland reservoirs with those in the wetland reservoir, we calculated similar rates of production for the first two years after flooding. Despite the ELARP wetland reservoir having 26 times more OC stores than the FLUDEX upland reservoirs, the rate of MeHg production in the wetland reservoir in the first two years of flooding (2700 mg ha^{-1} y^{-1}) was only 1.7 times higher than the rate in the High C reservoir (1580 mg ha^{-1} y^{-1}). Lower MeHg production rates were observed in the Medium C and Low C reservoirs at 810 and 340 mg ha^{-1} y^{-1},

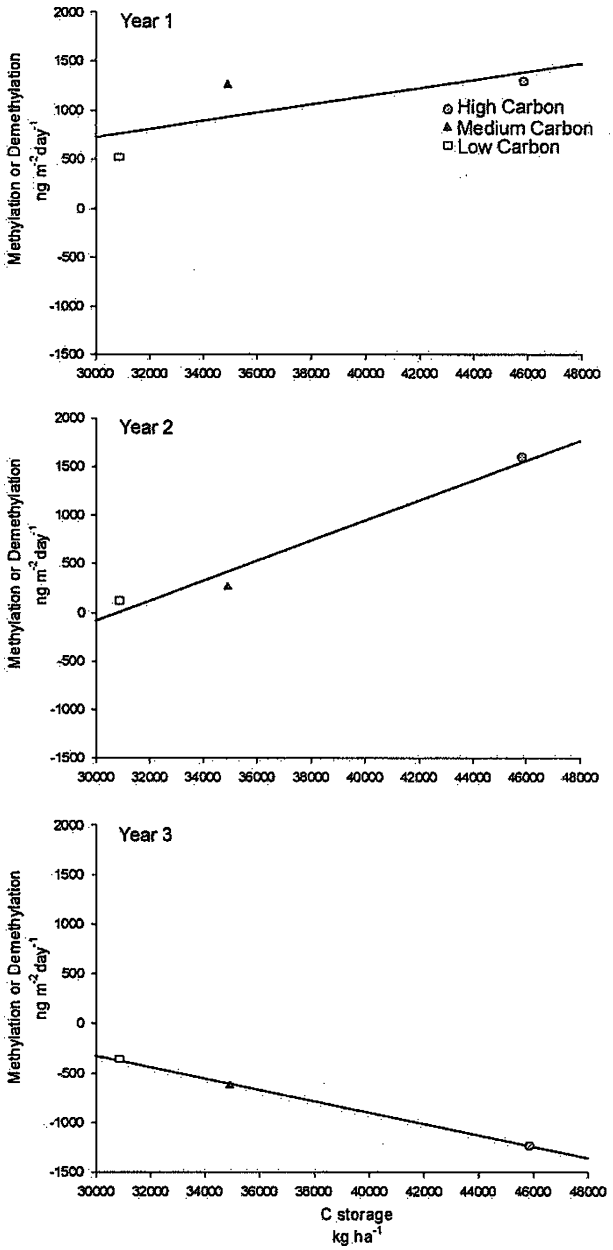

Figure 6. Methylmercury (MeHg) production and MeHg degradation rates (ng m^{-2} day^{-1}) in the upland reservoirs as a function of preflood carbon stores.

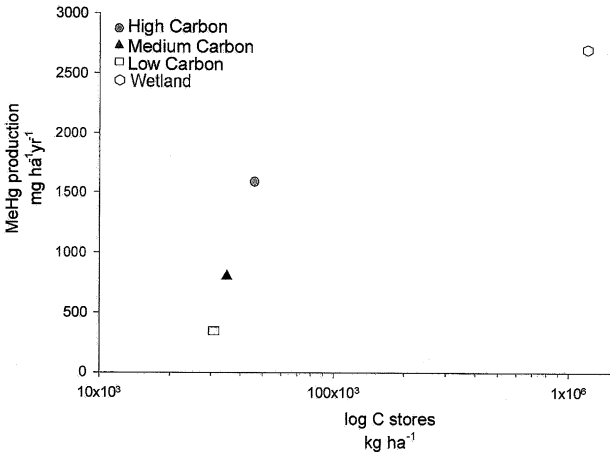

Figure 7. Methylmercury production (mg MeHg ha^{-1} y^{-1}) in the upland and wetland reservoirs as a function of log C storage (kg ha^{-1}).

respectively. Although the highest MeHg production rate was observed in the wetland reservoir, there was more MeHg produced per unit of flooded C in the upland reservoirs (Figure 7). This suggests that bacteria producing MeHg in the upland reservoirs were using OC more efficiently than microorganisms in the wetland reservoir, possibly because OC stored in peat over the long term is more recalcitrant than OC stored in the upland reservoir in the 18 years since the last fire. It is also possible that OC stored in peat may be more effective in complexing HgII, thereby decreasing its availability for methylation. Demethylation in the wetland reservoir was measured only in year 5. The demethylation rate in the wetland (1600 mg MeHg ha^{-1} y^{-1}) was greater than demethylation rates in the Medium C and Low C reservoirs (730 and 420 mg ha^{-1} y^{-1}, respectively), but similar to demethylation in the High C reservoir (1440 mg ha^{-1} y^{-1}; Figure 7).

Net MeHg production is dependent on many environmental factors (Ullrich and others 2001). Rates of production and destruction of MeHg by bacteria are affected by temperature, pH, and redox potential. However, similarities in rates of carbon GHG production in the upland reservoirs (Matthews and others 2005) suggest that the physiochemical environment did not significantly differ among the FLUDEX reservoirs, and that differences in MeHg production are likely not attributed to differences in anoxia and reducing conditions, temperature, and pH. Another important factor in the net production of MeHg is the ability of HgII to enter the cytoplasm of methylating organisms. This bioavailability could also be affected by environmental conditions, most notably the presence of inorganic and organic complexing agents (especially sulfides and DOC) that may prevent the transfer of HgII across cell membranes (Babiarz and others 2001, 2003; Benoit and others 2001). Differences in SO_4 concentrations can also affect MeHg production because the majority of MeHg is produced as a byproduct of metabolic SO_4 reduction. It is also possible that the bioavailability of HgII in our

reservoirs differed and this resulted in differences in net MeHg production.

Conclusions

Our results support our original hypothesis that the reservoir with the highest *amount* of stored OC would have the highest amount of MeHg production. However; MeHg production rates in our High C reservoir were not drastically different from those in the wetland reservoir. Greenhouse gas production did not differ among the upland reservoirs (Matthews and others 2005), which indicates that the amount of easily decomposable OC was similar among the upland reservoirs. However, our results suggest that once flooded, newer, more labile OC stored in upland forests promotes relatively higher rates of MeHg production compared to older, more recalcitrant OC stored in peatlands. One of the goals of the FLUDEX and ELARP reservoir projects at the ELA has been the development of computer models designed to predict MeHg increases in fish living in reservoirs. The relationship between MeHg production and total OC storage suggests that total OC stores flooded in the creation of reservoirs can be added to these models to help predict MeHg production rates in reservoirs. Predicted MeHg production rates in reservoirs may then be used to assess possible MeHg contamination in reservoir fisheries, depending on the movement of MeHg throughout the reservoir.

The majority of MeHg was produced in the soils and peat and was not transferred to the water column. Our research indicates that, unless other processes that enhance the movement of MeHg associated with flooded soils and peat particles to the water column are present (for example, erosion see Louchouarn and others 1993), flooding wetlands may not necessarily result in a worse-case scenario for MeHg contamination of reservoir fisheries because the majority of MeHg produced in the soils remains there and does not enter the water column and, thus, the food web. Reservoirs created over upland forests containing relatively low OC stores may result in contamination of reservoir fisheries equal to, or exceeding, those in reservoirs created over wetland areas with very large OC stores. However, the production of MeHg and the export of MeHg and THg in the upland and wetland reservoirs decreased over the first three years of flooding. This suggests that MeHg production rates in our reservoirs began to decrease early in the evolution of the reservoir. In fact, after only two years of flooding, there was net demethylation in the soils of the reservoirs. Regardless of declines in later years, modeling exercises have shown that 2–5 years of enhanced MeHg production can result in 20–30 years of elevated MeHg concentrations in predatory fish (R. Harris, Tetra Tech Inc., Oakville, ON, personal communication). Studies on the wetland reservoir at years 4–9 after flooding show that MeHg concentrations in the open water region of the reservoir are not decreasing as expected (St. Louis and others 2004). Additional studies of the FLUDEX and ELARP reservoirs in 2002 and 2003 will allow us to assess further decreases in MeHg production in our experimental reservoirs.

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