Effects of burning before flooding on methyl mercury and greenhouse gas concentrations

by

Mariah Mailman

A Thesis Submitted to the
Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
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GENERAL ABSTRACT

Flooding terrestrial plants and soil causes decomposition of organic matter, which stimulates microbial methyl mercury (MeHg) production. Burning before flooding was tested as a method for mitigating MeHg contamination in reservoirs in a controlled, replicated field experiment at the Experimental Lakes Area (ELA), northwestern Ontario. Combinations of unburned and burned vegetation and soil were added to limnocorrals to simulate flooded ecosystems. Vegetation and soil were burned in a controlled manner with propane torches. In fresh plant samples, the mean total mercury (THg) concentrations ranged from 4 to 52 $ng \cdot g^{-1}$ dry weight (d. w.). Bryophytes contained high THg concentrations, and trees and shrubs contained relatively low concentrations. Mean concentrations of MeHg in fresh plants ranged from 0.1 to 1.3 $ng \cdot g^{-1}$ (d. w.). Fresh upland soil had higher THg concentrations (162 +/- 76 $ng \cdot g^{-1}$ d. w.) than any species of plant, and moderate MeHg concentrations (0.6 +/- 0.6 $ng \cdot g^{-1}$). After burning, vegetation lost a mean of 96.3% (92.6 to 98.7) of the mass, 97.8% (94.7 to 99.5) of the carbon, 96.6% (84.5 to 99.5) of the THg, and 94.2% (63.1 to 100.0) of the MeHg. Loss of THg and MeHg in vegetation correlated significantly with the loss of vegetation mass using Spearman's rank correlation procedure ($r=0.73$, $p<0.01$), but not with the loss of carbon. Of the original mass, carbon, THg, and MeHg in upland soil at ELA, 27.3, 94.8, 78.8, and 81.8% was lost. Vegetation and soil were added to limnocorrals in the following combinations: unburned vegetation and soil (Fresh treatments), burned vegetation and unburned soil (Partial Burn treatments), and burned vegetation and burned soil (Complete Burn treatments). Controls had no added vegetation or soil. Burning before flooding

lowered THg and MeHg concentrations in water. Concentrations of MeHg in zooplankton, Chironomid larvae, and emerging insects did not follow aqueous concentrations, but they were consistent among treatments. On the final sample date, MeHg concentrations in biota of Controls and Partial Burn Treatments were greater than in Complete Burn and Fresh Treatments. The lack of relationship between MeHg in biota and MeHg in water may have been due to modification of the bioavailability of MeHg by dissolved organic carbon (DOC). The bioaccumulation factors ($[MeHg]_{biota}/[MeHg]_{water}$) of MeHg in zooplankton, Chironomid larvae, and emerging insects were inversely correlated with DOC ($r^2 = 0.52$, 0.72, and 0.89, respectively). Although burning before flooding decreased MeHg concentrations in the water, it did not ameliorate MeHg accumulation in the lower food web. Burning before flooding lowered the partial pressure of carbon dioxide and methane by 40 and 97%, respectively, relative to Controls. Even though a significant proportion of the carbon decomposition after flooding would be released as methane, a stronger greenhouse gas than carbon dioxide, than if vegetation was burned before flooding, burning would mineralize much more carbon than decomposition and, thus, would probably not lessen greenhouse gas emissions from reservoirs.

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CHAPTER 1: MERCURY CYCLING AND CONTAMINATION IN FLOODED ECOSYSTEMS

General Introduction

Reservoir creation causes elevated MeHg concentrations in fish. Flooding terrestrial plants and soil enhances methyl mercury (MeHg) production and accumulation in aquatic organisms (Bodaly *et al.* 1984). Decomposition of flooded organic carbon stimulates microbial metabolism. Decomposition of flooded organic matter also releases mercury (Hg) from organic complexes. Hg is converted to MeHg by sulphate reducing bacteria (SRB). MeHg is the most available form of Hg to organisms. It accumulates in organisms mainly through dietary exposure. MeHg accumulates rapidly in aquatic organisms and biomagnifies through the food web. Elevated concentrations of MeHg in predatory fish are of great concern because fish are the main source of MeHg to humans (Richardson *et al.* 1995). High concentrations of MeHg in fish from boreal reservoirs may persist for 6 to 30 years after flooding.

MeHg is a toxic compound that generates concern for environmental and food consumption regulators. The lowest water concentrations of MeHg that cause the following effects are indicated as reviewed by Wiener and Spry (1996). In fish, MeHg causes incoordination (1.2 $\mu g \cdot L^{-1}$), growth (0.8 $\mu g \cdot L^{-1}$), histology (0.15 $\mu g \cdot L^{-1}$), physiology (1.2 $\mu g \cdot L^{-1}$), reproduction (0.1 $\mu g \cdot L^{-1}$), development (1.0 $\mu g \cdot L^{-1}$), and survival (0.2 $\mu g \cdot L^{-1}$). The lowest Hg concentrations in human hair that caused the following effects are given as reviewed in Clarkson (1992). In humans, MeHg causes loss of sensation in skin (62.5 $\mu g \cdot g^{-1}$), loss of coordination of the muscles, especially in the

extremities (125 $\mu g \cdot g^{-1}$), disorders in articulation (300 $\mu g \cdot g^{-1}$), deafness (600 $\mu g \cdot g^{-1}$), death (780 $\mu g \cdot g^{-1}$), and effects to offspring (100 $\mu g \cdot g^{-1}$) (Clarkson 1990).

Research is being conducted to test hypotheses that may lead to a method to ameliorate MeHg in flooded ecosystems. The central objective of this research was to determine if burning terrestrial plants and soil before flooding would decrease MeHg contamination. This chapter is a general review of the biogeochemical cycle of Hg. The second chapter is a comprehensive review of MeHg mitigation options that have been considered for aquatic ecosystems. The main objective of the research presented in chapter three was to experimentally test if burning released Hg from plants and soil. Results of experimental burning of plants and soil were reported. We burned plants and soil with propane torches, analyzed THg and MeHg in fresh and burned samples and calculated, by difference, the amount of Hg released during burning. The main objective of the research presented in chapter four was to determine if burning plants and soil before adding them to limnocorrals affected MeHg accumulation in aquatic organisms. A secondary objective was to determine if charcoal was able to sequester Hg. This was a controlled, replicated field experiment. Four treatments were applied to limnocorrals in triplicate. They were fresh plants and fresh soil, burned plants and fresh soil, burned plants and burned soil, and controls to which no plants or soil were added.

A REVIEW OF THE BIOGEOCHEMICAL CYCLING OF MERCURY IN NATURAL AND FLOODED ECOSYSTEMS

Mercury in the atmosphere

Human activity has altered the natural biogeochemical cycle of Hg. Natural sources of Hg in the atmosphere are volatilization of Hg from water bodies and enriched geological deposits, emissions from wildfires, and wind-borne particulate matter (reviewed in Nriagu 1989). Hg also fluxes to the atmosphere from volcanic degassing. Combustion of fossil fuels, industrial, and municipal waste are sources of atmospheric Hg pollution. Atmospheric deposition of anthropogenic Hg exceeds natural sources (Lindberg *et al.* 1991; Lindberg *et al.* 1992). Human activities may account for up to 50% of the average global Hg emissions (Nriagu 1989).

The residence time of Hg in the atmosphere depends on the chemical form of Hg present. In the atmosphere, elemental Hg (Hg^0) can travel long distances and deposit far from the original source. Hg^0 can oxidize to ionic Hg (Hg^{2+}) (reviewed in Mason *et al.* 1994). Hg^{2+} may fall quickly to the surface of Earth as dry deposition or dissolved in atmospheric precipitation.

Mercury in terrestrial ecosystems

During dry and wet deposition over land, Hg may adsorb to foliage or organic-rich soil. Possible mechanisms of dry Hg deposition include deposition of particulate bound Hg, adsorption of Hg^{2+} onto plant surfaces, or oxidation of Hg^0 to Hg^{2+} and subsequent adsorption. When atmospheric Hg concentrations are high, stomata may assimilate Hg^0 directly from the atmosphere (Lindberg *et al.* 1992). Foliage that falls to

the ground is an important source of Hg and MeHg to the forest floor (Iverfeldt 1991; Kudo and Mortimer 1979; Munthe *et al.* 1995; Schwesig and Matzner 2001). However, atmospheric Hg is mainly deposited with precipitation (Lindqvist *et al.* 1991). Precipitation may wash dry deposits of Hg from foliage surfaces (Iverfeldt 1991; Rea *et al.* 2001).

Hg deposited in soil may flux back into the atmosphere (Johnson and Lindberg 1995; Kim and Lindberg 1995). Hg emissions from soil to the atmosphere appear to be temperature dependent (Lindberg *et al.* 1991; Xiao *et al.* 1991b; Zhang *et al.* 2001). Variations in Hg flux from soils of the Tahquamenon River watershed, Michigan, were influenced by temperature; open field sites had higher mean Hg fluxes than shaded forest sites (Zhang *et al.* 2001). Simulated rain events also increased the flux of Hg from soil to the atmosphere. Precipitation may cause Hg to flux out of the soil by these mechanisms: displacing gases in soil pore spaces, desorption of Hg^{2+} by water molecules, or desorption of Hg^{2+} and subsequent reduction in solution (Lindberg *et al.* 1999; Zhang and Lindberg 1999). It is not likely that translocation of Hg from soil pore water to foliage is a significant mechanism by which Hg could flux out of soil (Bishop *et al.* 1998; J. Graydon pers. comm.; Xiao *et al.* 1991a).

Hg binds with dissolved organic carbon (DOC) and adsorbs to solid particles in soil. Soil is therefore very efficient at retaining Hg. Hg has a higher affinity for humic substances than inorganic ions. Partitioning of Hg in organic-rich soil is a function of dissolved versus particulate fractions of organic matter. Adsorption to inorganic surfaces controls the behaviour of Hg in inorganic mineral soils (Schuster 1991; Xu and Allard 1991). Hg accumulation in soil correlated positively with carbon content (Grondin *et al.*

1995). The redox state of iron affects Hg penetration in soil. In tropical soils, Hg concentrations were related to the quality of organic matter, specifically the humic and fulvic breakdown products, and its penetration and progressive adsorption onto iron oxides (Roulet and Lucotte 1995). Hg forms highly soluble complexes with aqueous hydroxide and chloride to form $Hg(OH)_2$ and $HgCl_2$, respectfully, that can bind directly to iron oxides (Campbell and Stokes 1985). The presence of fulvic acid can also enhance adsorption of Hg to iron at a range of pH conditions (2.5-9.5) (Xu and Allard 1991). Water percolating through litter and soil can dissolve humic matter. Humic matter can adsorb Hg and transport it, generally downward, into mineral soil horizons. (Schwesig and Matzner 2001) found 60 and 19% of THg and MeHg, respectfully, that was deposited from the atmosphere moved downward into mineral soil. Soil profiles had opposing gradients of THg and MeHg (Schwesig and Matzner 2001). Organic soils retained MeHg. THg moved downward into mineral soil. Leaching rates of Hg from soil are low in runoff (Branfireun *et al.* 1998; Krabbenhoft and Babiarz 1992; Lindqvist *et al.* 1991; Mierle and Ingram 1991; Schuster 1991). However, In flooded soil, Hg is redistributed toward the sediment-water interface (Grondin *et al.* 1995; Morrison and Thérien 1991).

Even though soils retain Hg, they are significant sources of Hg and MeHg to watersheds. Hg from soil is transported in runoff from upland catchment areas to lower lying areas (Branfireun *et al.* 1998; Bishop *et al.* 1995; Hurley *et al.* 1995; St. Louis *et al.* 1994). The transport of THg and MeHg via runoff is controlled by dissolved organic complexes (Lee and Iverfeldt 1991; Mierle and Ingram 1991; Caldwell *et al.* 2000; Matilainen *et al.* 2001). Hg concentrations in lake sediment correlate significantly with the ratio of watershed area to lake area (WA:LA), and WA:LA correlates with the colour

of lake water (French *et al.* 1999). Since colour reflects the concentration of dissolved organic acids, this suggests that proportionally larger drainage basins deliver greater amounts of Hg adsorbed to organic matter into lakes. In addition, Grondin *et al.* (1995) found lower Hg concentrations in upland soils than in low lying wetland soils and attributed this to leaching of Hg from upland sites and transportation and accumulation in poorly drained soils. Runoff is a significant mode of Hg transportation.

Methylation of mercury

MeHg is the predominant methylated Hg compound in freshwaters. It occurs at high concentrations in low oxygen environments (Bloom *et al.* 1991). For example, in five pristine lakes in Wisconsin at pH 4.6 to 7.2, the volume weighted mean concentration of THg was about 1 $ng \cdot L^{-1}$ of which MeHg constituted seven to 25% in the oxic epilimnion and 50 to 90% in the anoxic hypolimnion. The predominant sources of MeHg include direct atmospheric deposition, precipitation, wetland runoff, stream inflow, and in-lake methylation (reviewed in Rudd 1995). Sinks for MeHg in lakes includes the outflow, long-term sediment burial, microbial demethylation (Ramlal *et al.* 1986) and photodegredation (Sellers *et al.* 1996).

The largest reservoir of Hg in freshwater systems is in lake sediments. Uncontaminated lake sediments usually contain 0.02 to 0.1 $\mu g g^{-1}$ of Hg with MeHg constituting about one percent. Pore waters are usually enriched with MeHg relative to the overlying water column (Gagnon *et al.* 1996). The degree to which sediments bind MeHg depends on the properties of the sediment, pH, and dissolved oxygen concentrations. Generally, oxic conditions favour uptake of Hg by sediment, and anoxic

conditions yield Hg to the water. In natural fresh waters the three main processes that affect Hg cycling are methylation, sorption to suspended particulate, matter and demethylation.

Although abiotic Hg methylation does occur, microbially mediated methylation of Hg is much more significant (Jensen and Jernelov 1969). In anoxic and weakly sulphidic lacustrine sediment MeHg is synthesized by certain species of SRB (Compeau and Bartha 1985; Gilmour and Henry 1991). Inhibiting SRB activity prevents methylation. In-lake production of MeHg by sulphate reducing bacteria (SRB) is the most important source of MeHg (Sellers *et al.* 2001). Only net methylation rates were attainable before isotopic studies were developed. New methods that use stable isotopes of Hg allow determination of MeHg formation and degradation (Gilmour and Henry 1991). Isotopic assays have allowed for the identification of environmental conditions that are most important to the methylation process. The factors that affect methylation are the presence of SRB, their growth phase and rate of metabolism, the organic content of the substrate, temperature, redox conditions and pH, and the availability of Hg, which is governed by the concentration of DOC and redox conditions.

Mercury uptake mechanisms in microorganisms

SRB may acquire Hg through passive diffusion (Benoit *et al.* 2001; Mason *et al.* 1996), or by protein facilitated transport reactions (Hudson *et al.* 1994). In passive diffusion the availability of Hg to microorganisms mainly depends on the concentration of neutral dissolved Hg complexes, rather than the ionic or total dissolved inorganic Hg, because bacterial membranes are more permeable to uncharged molecules (Gutknecht

1981). Neutral HgS (HgS^0), mercuric bisulphide ($Hg(SH)_2^0$), and mercuric polysufide (HgS_n^0) are the dominant neutral complexes available to microorganisms in anoxic pore waters (Benoit *et al.* 1999a). In oxic environments mercuric chloride is the predominant species, and diffusion of ionic Hg through the lipid bilayer of the cell membranes depends only on Cl^- concentration (Morel *et al.* 1998). However, at true Hg concentrations facilitated Hg uptake is the most significant transport mechanism (Hudson *et al.* 1994). The bioavailability of Hg in protein facilitated uptake reactions is not determined solely by the bulk solution chemistry, such as the concentration of neutral sulphide compounds, as it is for passive diffusion. Rather, one or more proteins are involved in transporting Hg into the cell. The species of Hg required differ depending on the proteins that are present at the time of facilitated transport. In this case, sulphate is not required for methylation, but high sulphide concentrations can still affect this uptake mechanism negatively by binding of Hg^{2+}.

Methyl transfer process in microorganisms

Once inorganic Hg has entered the microorganisms, it is methylated by a two-step process. Within the bacterium *Desulfovibrio desulphuricans*, the methyl transfer sequence requires two steps of which the second reaction is enzymatically-catalyzed. The sequence of methyl transfer is from methyl tetrahydrofolate (THF) to the corrinoid protein, methylcobalamine (Me-Co-Protein), to Hg^{2+} (Choi *et al.* 1994).

1) $\text{Me-THF} + \text{Co-protein} \rightarrow \text{THF} + \text{Me-Co-Protein}$

2) $\text{Me-Co-Protein} + Hg^{2+} \rightarrow \text{Co-protein} + MeHg^+$

In the second reaction, Me-Co-Protein is the in vivo methyl donor. This protein has never been isolated, but an increase in the rate of the reaction by 600 fold in its presence indicates that it is important in this reaction. When mercuric ions are in excess, the formation of MeHg depends on the concentration of the Me-Co-Protein (Choi *et al.* 1994).

Growth phase of microorganisms during methylation

The rate at which methylation occurs may be dependent on the growth phase of the microorganisms. Hg methylation rates may be greatest during certain phases of bacterial growth. Ramamoorthy *et al.* (1982) found that growing cells produce elemental Hg, non-growing but living cells demethylate Hg, and dead cells produce MeHg. However, Hg methylation has also been observed during periods of exponential bacterial growth (Ebinghaus *et al.* 1994). Studies should be done to elucidate the effect of the bacterial growth phase on MeHg production. The seasonal production and decline of MeHg may be due to changes in the microbial species present, or their growth phase as indicated above, or by variations in the organic content of the substrate.

Location of methylation in freshwater lakes and reservoirs

SRB have the greatest potential to methylate Hg when organic substrates are abundant. High nutrient concentrations enhance the metabolic activity of the microorganisms. Therefore high carbon sites host microbial communities with higher Hg methylation activity per unit of microbial biomass. As a result, the amount of organic matter in the sediment correlates positively with Hg methylation rates (Compeau and

Bartha 1985; Choi and Bartha 1994). The greatest MeHg concentrations are found on the upper sediment layers. In Clear Lake, California, a Hg-polluted eutrophic lake, Macalady *et al.* (2000) found a strong positive relationship between the sediment organic carbon content and the microbial community structure, and also with the Hg methylation potential. In the anaerobic sediment of an acidified oligotrophic lake, high Hg methylation and demethylation rates also correlated positively with the concentrations of organic matter (Pak and Bartha 1998). Organic substrates provide a nutrient-rich habitat for SRB, but their activity may be affected by additional environmental conditions such as temperature and dissolved oxygen concentrations.

Temperature effects on methylation

The most significant site of MeHg production is the epilimnetic sediment, and rates of Hg methylation appear to be controlled, in part, by temperature (Bodaly *et al.* 1993; Ramlal *et al.* 1993; Krabbenhoft *et al.* 1998). Temperature accounts for approximately 30% of the variability in Hg methylation rates (Korthals and Winfrey 1987). In support of this, an extended period of high temperatures during the summer months stimulated Hg methylation activity in Precambrian Shield lake sediments (Ramlal *et al.* 1993). Additionally, the rate of methylation in warmer epilimnetic sediments of several remote Canadian Shield lakes was 20 to 40 times faster than in cooler hypolimnetic sediments (Ramlal *et al.* 1993). Sometimes peak MeHg concentrations are observed during early spring, which could be a result of MeHg transport from the catchment area in the runoff of melting snow. Temperature is an important variable in

determining the location of methylation within a lake because it affects the rate of bacterial respiration and, therefore the redox conditions.

Temperature also affects demethylation of MeHg. MeHg demethylation rate is inversely related to temperature (Ramlal *et al.* 1993; Bodaly *et al.* 1993; Winfrey and Rudd 1990). Demethylation rates were highest in the cooler hypolimnetic sediments in summer, and increased in epilimnetic sediment as temperatures dropped (Ramlal *et al.* 1993).

Effects of redox conditions on methylation

The primary site of methylation is at the oxic-anoxic interface (Gilmour and Henry 1991; Korthals and Winfrey 1987; Lemly 1999). Below this zone microbial activity decreases and high sulphide concentrations limit the availability of Hg for methylation in deep sediment layers (Gilmour and Henry 1991). In the oxygenated surface zone SRB metabolism diminishes and bacterial degradation of MeHg is the predominant process (Bubb *et al.* 1993). Lakes in northwestern Ontario had the greatest rates of methylation in the epilimnetic sediment below the oxic-anoxic interface, which was always below the sediment-water interface (Ramlal *et al.* 1993). It is necessary to measure the gradient of MeHg concentration in the sediment to determine the site of Hg methylation because MeHg may be released from the sediments to the water column resulting in high aqueous concentrations.

High MeHg concentrations in the hypolimnion are likely a result of MeHg being released from decomposing organic matter that deposited on the sediment surface (Huebert 2002; Watras *et al.* 1996). MeHg bound to organic matter was probably

produced in epilimnetic sediments, which was then transported to the hypolimnion and settled. This was supported by abundant seston particles in hypolimnetic water samples that contain high MeHg concentrations (Sellers *et al.* 2001). In Lake Hoare, Antarctica, whole water samples from the water column suggest that the predominant source of MeHg was in situ Hg methylation at the oxic-anoxic interface within the sediments, or at the sediment-water interface (Vandal *et al.* 1998). This was concluded because the difference in the percent total Hg as MeHg was approximately 30% below 22 m depth and only about 10% from 4 to 20 m depth. This stresses the importance of sampling MeHg in the sediment rather than in the water column.

Effects of dissolved organic carbon on methylation

The speciation and solubility of Hg is influenced by binding with DOC. Hg forms strong and highly stable complexes with DOC due to the presence of carboxylic groups. DOC can act as a reducing agent by intra-molecular electron transfer causing the reduction of Hg^{2+} to Hg^0, which fluxes out of the aquatic system (Allard and Arsenie 1991). Hg^0 production is enhanced by light, but decreases with increasing pH and chloride concentrations. Therefore Hg binding with DOC can decrease the pool of Hg in the system by reduction, but may inhibit precipitation of mercuric sulphide (HgS).

DOC increases the solubility of HgS, even though HgS is very insoluble under ambient conditions (Ravichandran *et al.* 1998). The degree to which DOC-Hg binding prevented HgS precipitation and aggregation in the Everglades depended on Hg concentrations (Ravichandran *et al.* 1999). At low Hg concentrations DOC prevented precipitation. At moderate Hg concentrations DOC inhibited aggregation of colloidal

HgS due to adsorption of DOC and electrostatic repulsion. At high Hg concentrations solid HgS formed (Ravichandran *et al.* 1999). High concentrations of humic and fulvic acids cause Hg to be released from HgS regardless of the redox conditions (Ravichandran *et al.* 1998). However, when calcium and other cations are present they inhibited dissolution of HgS by saturating the binding sites on the DOC.

Hg-DOC complexes affect the bioavailability of Hg. As DOC concentrations increase, the specific rate of net methylation decreases due to an increase in organic binding of Hg^{2+} (Miskimmin *et al.* 1992). Further evidence was observed using the bioindicator, a genetically altered microorganism that emits light when Hg enters the cell. The bioindicator revealed that Hg-DOC complexes reduce the availability of Hg^{2+} to methylating microorganisms, but not under low pH conditions (Barkay *et al.* 1997). Low pH decreases the Hg binding capability of DOC.

Effects of acidity on methylation

Effects of pH on Hg methylation are not clear, but pH affects Hg-DOC binding, Hg^0 formation, and possibly sorption to particulate matter and the composition of the microbial community. The number of binding sites on DOC decreases as pH decreases. Increasing acidity causes the charge on organic molecules to neutralize because anions are protonized; metals are desorbed and the aggregation and precipitation of DOC increases (reviewed in Davis *et al.* 1985). As a result, Hg bound to DOC decreases with acidity and results in the release of MeHg from sediments (Hintelmann *et al.* 1995). This stimulates Hg methylation because Hg binds directly to microbial cells (Winfrey and Rudd 1990). Therefore the rate of methylation is inversely related to pH (Bloom *et al.*

1991; Miskimmin *et al.* 1992). Miskimmin *et al.* (1992) found that net methylation rate increased with a decrease in pH from 7.0 to 5.0 at low and high concentrations of DOC. However, this could also be due to the effect of pH on the structure of the microbial ecosystem, or the availability of Hg to methylating organisms.

Ramlal *et al.* (1985) found that acidifying surface sediment causes MeHg production rates to decrease in anoxic sediment, possibly because inorganic Hg is less available in pore waters as Hg adsorbed onto particulate matter. Acidification affects the Hg availability by decreasing the solubility of inorganic Hg. Under these conditions, inorganic Hg partitions more strongly with particulate matter (Mason *et al.* 1996; Schindler *et al.* 1980). Furthermore, a mercury cycling model shows that increases in pH cause the ratio of Hg^0 to Hg^{2+} to increase and Hg^0 fluxes out of the system (Hudson *et al.* 1994). It is possible that pH could affect the population distribution of methylating versus demethylating bacteria in sediments such that demethylating bacteria predominate under acidic conditions, but no evidence has been shown for this (reviewed by Ullrich *et al.* 2001). French *et al.* (1999) report another contradiction; MeHg concentrations in the lake sediment of 34 headwater lakes in Newfoundland were not related to acidity. The conflicting effects of low pH on Hg partitioning and its effect on methylation need clarification.

Effects of sulphur on mercury methylation

SRB require sulphate as an electron acceptor. However, Hg methylation and sulphate concentrations correlate inversely (Compeau and Bartha 1987; Benoit *et al.* 2001). This paradox may be explained by the formation of sulphur ligands complexes

with ionic Hg that limit the availability of Hg for methylation, or by precipitation of HgS in sulphate-rich environments. Methylation declines with increasing oxic and sulphidic conditions because sulphide precipitates or adsorbs dissolved inorganic Hg, decreasing the availability of ionic Hg to bacteria (Regnell *et al.* 1996; Benoit *et al.* 1999a). Methylation rates are greatest when sulphate is not overly abundant.

In a laboratory experiment, optimum methylation occurred when uncharged HgS species, such as HgS^0, were available because these molecules passively diffuse across the cell membrane of the bacteria (Benoit *et al.* 1999b). In the presence of excess cinnabar (solid HgS), adding sulphate dissolved Hg and increased its bioavailability to microorganisms, thus increasing microbial methylation of Hg. However, the fraction of neutral dissolved Hg complexes decreased with increasing sulphide concentrations (Benoit *et al.* 1999a). The optimal sulphate concentration range for bacterial methylation of Hg in sediments is 0.2 to 0.5 mM of SO_4^{2-} (Gilmour and Henry 1991). These experiments did not use ambient Hg concentrations because the analytical methods were not sensitive enough to detect natural Hg concentrations. As a result, the mechanisms of Hg uptake during microbial methylation in sediment pore water needs to be determined at ambient Hg concentrations to understand the biogeochemical cycle of MeHg and the relative importance of MeHg produced within the sediments (Benoit *et al.* 1999a).

Effects of iron on mercury methylation

Redox states of iron in lake sediment influence the partitioning of inorganic and MeHg between the aqueous and solid phases. Hg binds strongly to iron oxides (Campbell and Stokes 1985). One molecule of inorganic Hg binds to two surface

hydroxyl groups on hydrous ferric oxide (HFO), but MeHg binds only to one surface hydroxyl group. Binding is best explained by a combination of reactions.

Inorganic Hg

$$FeOH + Hg^{2+} \leftrightarrow FeOHg^{+} + H^{+}$$

$$2FeOH + Hg^{2+} \leftrightarrow (FeOH)_2Hg$$

$$2FeOH + Hg^{2+} \leftrightarrow (FeO)_2Hg + 2H^{+}$$

Methyl Hg

$$FeOH + MeHg^{+} \leftrightarrow FeOHMeHg$$

$$FeOH + MeHg^{+} \leftrightarrow FeOMeHg + H^{+}$$

Reduction of HFO results in release of MeHg from sediment to water. For example, in anoxic and sulphidic hypolimnetic waters in a polluted lake, aqueous MeHg increased while sediment MeHg decreased. In bottom waters, elevated MeHg concentrations correlated with higher Fe^{3+} concentrations.

Total iron correlates more strongly with MeHg than with inorganic Hg indicating that MeHg concentrations are more sensitive to changes in redox conditions (Regnell *et al.* 2001). Concentrations of Fe^{2+} and inorganic Hg increased simultaneously in the hypolimnion. However, the rise in inorganic Hg concentration lags behind that of iron, possibly due to Hg depletion by methylation processes. In anoxic conditions, reductive dissolution of HFO decreased the concentration of Fe^{3+} and freed associated inorganic Hg (Regnell *et al.* 2001). Binding of Hg and MeHg to HFO may be significant in environments with low organic content, but, when present, DOC in the water competes for binding sites on HFO and therefore Hg associated with DOC indirectly binds to HFO.

DOC influences Fe-Hg associations because Hg species bond strongly with sulphur that is associated with organic matter. The carboxylic acid group on DOC binds to the surface hydroxyl groups on HFO. Therefore Hg and HFO both associate with DOC, but through different functional groups. DOC competes with Hg for binding sites on HFO, decreasing the amount of Hg associated with HFO in high organic environments, but because of ternary complexation Fe-Hg associations are never eliminated. Below the sediment-water interface, or redox boundary, iron sulphide controls the partitioning of Hg.

In deeper sediments, iron and MeHg are positively correlated because MeHg is bound to the iron oxides and iron sulphide leaving inorganic Hg more available for methylation. Sulphide binds Hg^{2+} and increases its mobility. High porewater concentrations of iron interfere with Hg methylation by limiting the concentration of dissolved hydrogen sulphide, and because the solubility of inorganic Hg bound to sulphide also decreases (Gagnon *et al.* 1996). When iron reducers are present they out-compete SRB for hydrogen and acetate, and therefore suppress sulphate reduction (Lovley and Phillips 1987).

Formation of dimethyl mercury

Dimethyl Hg is volatile and hydrophobic. It forms in high sulphide and high MeHg conditions as an intermediate unstable organic mercuric sulphide compound $(MeHg)_2S$. It decomposes to dimethyl Hg and HgS (Baldi *et al.* 1995). In nature, this process mainly occurs in marine environments where it is potentially an important loss mechanism.

Demethylation

Demethylation of MeHg is the principle source of Hg^0 in low oxygen waters (Mason and Fitzgerald 1993). SRB are the primary group of microorganisms that demethylate Hg (Robinson and Tuovinen 1984). Some microorganisms have Hg resistant mechanisms, like volatilization of the element, to prevent toxicity. Demethylation rates increase linearly with MeHg concentrations (Xun *et al.* 1987). Demethylation is favoured at low temperatures (Bodaly *et al.* 1993; Ramlal *et al.* 1993). MeHg degradation is greatest under aerobic and low pH conditions. For example, Matilainen *et al.* (1991) observed a decrease in net methylation rates with increasing acidity at the aerobic sediment surface. Ramlal *et al.* (1985) observed that net sediment methylation rates decrease slightly as acidity increases, then sharply at pH levels less than 4.5, at which point demethylation becomes more important.

Sinks for mercury in aquatic ecosystems

Hg may be leave lakes and reservoirs through three mechanisms. First, some of the Hg present in the ecosystem will flow out of the water body through streams. Second, evasion of Hg from the surface of water bodies occurs after reduction processes convert ionic Hg to Hg^0. Third, sedimentation and burial of Hg may remove a substantial amount of Hg from the water column and sequester it in sediments.

Photoreduction of methyl mercury and evasion of gaseous mercury to the atmosphere

THg can flux from water to the atmosphere following the reduction of ionic Hg to Hg^0. Amyot *et al.* (1997b) found that rates of production of dissolved gaseous mercury (DGM) depend on concentrations of photoreducible Hg. In two freshwater lakes in Ontario, transparent bottles filled with lake water and incubated in the lakes had up to nine times more DGM than opaque bottles; this phenomenon was greatest in epilimnetic waters (Amyot *et al.* 1994). DGM was produced in transparent bottles because the intensity of ultraviolet solar radiation controls the degradation of MeHg in aquatic ecosystems (Amyot *et al.* 1997a; Amyot *et al.* 1997b; Sellers *et al.* 1996), which is most significant in shallow, relatively clear water. (Sellers *et al.* 1996) found that in the epilimnetic water of an oligotrophic lake during the ice-free season, the average MeHg concentration was 0.07 $ng \cdot L^{-1}$, the rates of MeHg production and photoreduction were probably 1.0 and 1.5 $\mu g \cdot m^{-2} yr^{-1}$, respectively, and that photoreduction was the most important mechanisms of MeHg loss in unfiltered water. At high concentrations of DOC the penetration of ultraviolet radiation would be limited and therefore the rate of photoreduction would also be limited, as evidenced by the concentration of DGM relative to DOC concentrations in the FLUDEX reservoirs (Hall *et al.* in press). In the water column of five lakes in Wisconsin there was significant correlation between the percentage of Hg^0 saturation and pH values (r^2=0.99 and P<0.001), which suggested that production of Hg^0 by photoreduction was enhanced in areas of high pH values (Vandal *et al.* 1991).

Sedimentation of mercury and burial during diagenesis

Particulate Hg may deposit in slow moving water. When reactive iron is in excess of sulphide in sediment, iron traps almost all the reduced sulphur as pyrite (Hartgers *et al.* 1997). Pyrite formation may be limited either by iron or organic matter. Sedimentary pyrite is an important sink for Hg and sulphur in anoxic environments even at low degrees of pyritization and the importance of this sink for Hg increases with increasing degrees of pyritization (Huerta-Diaz and Morse 1992). Hg is rapidly and completely incorporated into the lattice structure of pyrite. Rates of Hg pyritization depend on Hg concentrations, and concentrations of iron sulphide, irrespective of the environment (i.e. sulphidic or nonsulphidic, iron poor or rich, nutrient poor or rich). Dredging and bioturbation oxidize pyrite and solubilize Hg (Huerta-Diaz and Morse 1992).

Accumulation of mercury in aquatic organisms

MeHg concentrations in organisms are influenced by the chemical speciation and concentration of MeHg (bioavailability), bioconcentration (direct uptake of MeHg from the water), uptake mechanisms, life stage and developmental history, trophic position, biomagnification (trophic transfer), respiration, biodilution (growth rate), taxa, DOC, pH, and selenium concentrations. Aquatic organisms at the base of the food web accumulate MeHg from water. In higher trophic levels, dietary exposure is the main source of MeHg. MeHg biomagnifies, and as a result, predaceous organism contain the highest concentrations of MeHg. The principal route of accumulation of both inorganic and MeHg in phytoplankton is by passive diffusion of uncharged lipophilic chloride

complexes (Mason *et al.* 1996). MeHg and inorganic Hg concentrate in the cytoplasm and cell membrane, respectively (Mason *et al.* 1995). Zooplankton may acquire Hg directly from the water (Heyes *et al.* 1998; Matilainen *et al.* 2001) and from their diet (French *et al.* 1998; Meili 1991; Watras *et al.* 1998). In the latter case, algal cytoplasm is digested and the contained MeHg is assimilated. Inorganic Hg is excreted with the cellular membrane. In water containing natural concentrations of MeHg, Hall *et al.* (1997) found dietary MeHg exposure accounts for at least 85% of fish Hg concentrations. This supports estimates made using a bio-energetic model (Harris and Snodgrass 1993). About 99% of Hg within fish is bound to sulphur proteins in muscle tissue as MeHg (Bloom 1992).

Mercury assimilation by phytoplankton

Phytoplankton can assimilate THg and MeHg directly from water. The principal route of accumulation of both inorganic and MeHg in phytoplankton is by passive diffusion of uncharged lipophilic chloride complexes (Mason *et al.*1996). MeHg concentrates in the cytoplasm of the phytoplankton and inorganic Hg associates with the cell membrane (Mason *et al.* 1995). The bioaccumulation factor (BAF) of Hg in phytoplankton is directly related to the aqueous concentration of Hg, which is controlled by pH and DOC concentrations. The availability of MeHg to phytoplankton is greatest in environments that have low DOC concentrations because DOC binds Hg (Mason and Lawrence 1999).

Methyl mercury accumulation by zooplankton

Zooplankton can acquire MeHg from seston (Mason *et al.* 1995; Meili 1991) (Watras *et al.* 1998) and directly from water (Peech Cherewyk 2002; Watras *et al.* 1998). The relative importance of dietary and waterborne exposure to MeHg is not known. MeHg may be transferred to higher trophic levels from periphyton by assimilation of algal cytoplasm. Through dietary exposure, zooplankton can assimilate MeHg from phytoplankton four times more efficiently than inorganic Hg because they digest the algal cytoplasm that is rich in MeHg and excrete the cellular membrane, with which the inorganic Hg is associated (Mason *et al.* 1995). Further studies are required to determine the importance of waterborne versus dietary exposure of MeHg to zooplankton.

Concentrations of suspended particulate matter influence the concentrations of MeHg in zooplankton. Two reservoirs and four natural lakes in northern Québec did not differ significantly in inorganic Hg concentrations, but the MeHg concentrations associated with suspended particulate matter and zooplankton were seven and five times higher, respectively, in reservoirs (Plourde *et al.* 1997). In new reservoirs, rapid decomposition of labile organic matter releases carbon bound MeHg. Consequently, seston in new reservoirs also has elevated MeHg concentrations. Zooplankton feed on seston, which directly bioamplifies the zooplankton MeHg concentrations (Plourde *et al.* 1997). Slight increases in DOC may increase the availability of MeHg to zooplankton, but DOC competes with zooplankton for MeHg. Therefore higher DOC concentrations decrease the availability of Hg when the amount of MeHg in the water is constant (M. J. Paterson pers. comm.).

Methyl mercury accumulation by fish

Fish are exposed to Hg through their diet and, as a result, top predators contain the greatest concentrations of MeHg. A bioenergetic model for Hg uptake in walleye (*Stizostedion vitreum*) and yellow perch (*Perca flavenscens*) predicted that diet is responsible for about 90% of MeHg tissue concentrations in oxygenated unpolluted freshwaters (Harris and Bodaly 1998). Hall *et al.* (1997) found that in water containing natural concentrations of MeHg, food is the primary source of MeHg to fish. Dietary exposure accounted for at least 85% of the Hg burden in fish muscle tissue (Hall *et al.* 1997). About 99% of the Hg within fish is stored in muscle tissue bound to sulphur proteins as MeHg (Bloom 1992). Fish assimilate MeHg more readily than inorganic Hg because inorganic Hg is not efficiently absorbed by the gills or the gut, and its elimination is rapid (Niimi and Kissoon 1994). Ingested inorganic Hg is not methylated within tissues (Huckabee *et al.* 1978) although it can be methylated in the gut (Rudd *et al.* 1980). The gut membrane assimilates 65 to 85% of the ingested MeHg (Rodgers 1994). In addition, the trophic position is extremely important in the biomagnification of MeHg. Piscivorous fish contain elevated Hg concentrations because they feed at higher trophic levels (Harris and Snodgrass 1993). Hg concentrations in fish increase with fish age and size (Driscoll *et al.* 1995). Biomagnification of MeHg in predatory species occurs because organisms are ingesting more MeHg than they excrete.

Hg concentrations of fish in reservoirs correlate with the terrestrial area flooded (Bodaly et al. 1984), as well as the ratio of watershed to basin area (Lee and Iverfeldt 1991). Hg concentrations in fish from different lakes tend to be related to the variation in the methylation rate of Hg in the epilimnetic sediments, which is temperature dependent

(Bodaly *et al.* 1993). Reservoirs often contain extensive littoral areas. The bathymetry of reservoirs may be an important factor controlling MeHg contamination.

Fish in clear lakes often contain much higher concentrations of Hg than fish from eutrophic lakes. When large species of phytoplankton dominate, the result is lower MeHg accumulation in fish (Mason *et al.* 1996). Therefore smaller species of phytoplankton, which predominate in oligotrophic lakes, may cause higher fish Hg concentrations. Alternatively, this relationship could be due to bloom dilution. Algal blooms may substantially decrease the uptake of MeHg in cladocerans because the amount of Hg per algal cell decreases as the algal biomass increases (Pickhardt 2002).

DOC affects the availability of MeHg at lower trophic concentrations, and this indirectly affects the MeHg concentrations in fish (Driscoll *et al.* 1995; Watras *et al.* 1998). In Adirondack lakes, total Hg and MeHg concentrations in the water increased with increasing DOC and with an increasing percentage of near shore wetlands. The concentration of Hg in perch also increased in proportion to DOC, but decreased at extremely high concentrations (Driscoll *et al.* 1995). Further, Swedish lakes that received high DOC from wetlands had high fish Hg concentrations (Meili 1991). There was a strong positive correlation between the Hg content in fish and the ratio of catchment area to lake area in eight Swedish drainage lakes (Lee and Iverfeldt 1991).

Fish MeHg concentrations increase with increasing degrees of acidification, possibly due to an increase in the concentration of bioavailable MeHg in the water column by decreasing the available binding sites on DOC (Driscoll *et al.* 1998). MeHg concentrations may become elevated due to an increase in inputs of MeHg from runoff of acidic precipitation, or increased production and diffusion of MeHg across the sediment-

water interface (Winfrey and Rudd 1990). Further, low pH increases the permeability of fish gills (Rodgers and Beamish 1983).

CONCLUSION

Flooding terrestrial areas causes high MeHg concentrations in fish (Bodaly *et al.* 1984). Terrestrial soils are sinks for THg and MeHg (St. Louis *et al.* 1996). The distribution of Hg in the soil is controlled by the quality of organic matter and redox conditions (Roulet and Lucotte 1995). Methylation can occur in non-flooded surface organic soils (Matilainen *et al.* 2001), and be transported on DOC by surface runoff from the upland catchment to lakes (French *et al.* 1999; Caldwell *et al.* 2000). Reservoir creation may liberate some Hg stored in soils. Shoreline erosion may re-suspend particulate bound Hg. Re-suspension of humic substances may increase the bioavailability of Hg to microorganisms (Driscoll *et al.* 1995), but it decreases dissolved concentrations of Hg by scavenging soluble Hg compounds (Mucci *et al.* 1995). Inundation of soils promotes anoxic conditions under which Hg can be released, but it is most likely to be trapped by authigenic iron oxides and other binding substrates if an oxic zone exists at the sediment water interface (Dmytriw *et al.* 1995). Hg that is released from the soil is usually associated with DOC (Krabbenhoft and Babiarz 1992) and has the potential to be methylated by microorganisms. Hg methylation by microorganisms is crucial to Hg bioaccumulation.

MeHg concentrations in fish reflect uptake of MeHg at the base of the food web. The MeHg burden in seston depends on the aqueous concentration of MeHg because they

primarily acquire MeHg by passive diffusion (Mason *et al.* 1996). DOC decreases the availability of MeHg to phytoplankton, but DOC-Hg complexation decreases with decreasing pH (Mason and Lawrence 1999). In addition, the amount of MeHg in the system increases with decreasing pH because evasion of Hg from the water to the atmosphere decreases (Lodenius *et al.* 2003; Watras *et al.* 1998). In summary, the bioavailability of MeHg and the ease at which it diffuses into phytoplankton is positively related to acidity. The distribution of Hg within phytoplankton is important. MeHg concentrates in the algal cytoplasm and inorganic Hg is associated with the cell membrane (Mason *et al.* 1995). The accumulation of MeHg in zooplankton occurs through accumulation from water and through dietary exposure. Further research is necessary to elucidate the contribution of each route of exposure. Higher trophic levels acquire MeHg predominantly from their food. Fish accumulate almost their entire MeHg burden from their diet (Hall *et al.* 1997). Fish MeHg levels are governed by the ratio of watershed to basin area (Lee and Iverfeldt 1991), temperature (Bodaly *et al.* 1993), trophic position (Harris and Snodgrass 1993), pH (Rodgers and Beamish 1983; Winfrey and Rudd 1990; Watras *et al.* 1998), DOC (Driscoll *et al.* 1995; Watras *et al.* 1998), and lake productivity (Mason *et al.* 1996). The concentration of MeHg in reservoir fish depends on the terrestrial area flooded (Bodaly *et al.* 1984). Since MeHg is toxic and because it readily bioaccumulates to levels of concern for the health of fish consumers (Clarkson 1992), especially in flooded terrestrial environments, it is imperative to develop a method to decrease the extent of MeHg contamination in reservoirs.

LITERATURE CITED

Allard, B. and Arsenie, I. 1991. Abiotic reduction of mercury by humic substances in aquatic system -- an important process for the mercury cycle. Water, Air, and Soil Pollution **56**: 457-464.

Amyot, M., Mierle, G., Lean, D.R.S., and McQueen, D.J. 1994. Sunlight-induced formation of dissolved gaseous mercury in lake waters. Environmental Science and Technology **28**: 2366-2371.

Baldi, F., Parati, F., and Filippelli, M. 1995. Dimethylmercury and dimethylmercury-sulfide of microbial origin in the biogeochemical cycle of Hg. Water, Air, and Soil Pollution **80**: 805-815.

Barkay, T., Gillman, M., and Turner, R.R. 1997. Effects of dissolved organic carbon and salinity on bioavailability of mercury. Applied and Environmental Microbiology **63**: 4267-4271.

Benoit, J.M., Gilmour, C.C., and Mason, R.P. 2001. Aspects of bioavailability of mercury for methylation in pure cultures of *Desulfobulbus propionicus* (1pr3). Applied and Environmental Microbiology **67**: 51-58.

Benoit, J.M., Gilmour, C.C., Mason, R.P., and Heyes, A. 1999a. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Environmental Science and Technology **33**: 951-957.

Benoit, J.M., Mason, R.P., and Gilmour, C.C. 1999b. Estimation of mercury-sulfide speciation in sediment pore waters using octanol-water partitioning and implications for availability to methylating bacteria. Environmental Toxicology and Chemistry **18**: 2138-2141.

Bishop, K., Lee Y.-H., Pettersson, C., and Allard, B. 1995. Terrestrial sources of methylmercury in surface waters: The importance of the riparian zone on the Svartberget Catchment. Water, Air, and Soil Pollution **80**: 435-444.

Bishop, K.H., Lee Ying-Hua, Munthe, J., and Dambrine, E. 1998. Xylem sap as a pathway for total mercury and methylmercury transport from soils to tree canopy in the boreal forest. Biogeochemistry **40**: 101-113.

Bloom, N.S. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. Canadian Journal of Fisheries and Aquatic Sciences **49**: 1010-1017.

Bloom, N.S., Watras, C.J., and Hurley, J.P. 1991. Impact of acidification on the methylmercury cycle of remote seepage lakes. Water, Air, and Soil Pollution **56**: 477-491.

Bodaly, R.A., Hecky, R.E., and Fudge, R.J.P. 1984. Increases in fish mercury levels in lakes flooded by the Churchill River diversion, northern Manitoba. Canadian Journal of Fisheries and Aquatic Sciences **41**: 682-691.

Bodaly, R.A., Rudd, J.W.M., Fudge, R.J.P., and Kelly, C.A. 1993. Mercury concentrations in fish related to size of remote Canadian Shield lakes. Canadian Journal of Fisheries and Aquatic Sciences **50**: 980-987.

Branfireun, B.A., Hilbert, D., and Roulet, N.T. 1998. Sinks and sources of methylmercury in a boreal catchment. Biogeochemistry **41**: 277-291.

Bubb, J.M., Williams, T.P., and Lester, J.N. 1993. Behaviour of mercury within a contaminated tidal river system. Water Science and Technology **28**: 329-338.

Caldwell, C.A., Canavan, C.M., and Bloom, N.S. 2000. Potential effects of forest fire and storm flow on total mercury and methylmercury in sediments of an arid-lands reservoir. Science of the Total Environment **260**: 125-133.

Campbell, P.G.C. and Stokes, P.M. 1985. Acidification and toxicity of metals to aquatic biota. Canadian Journal of Fisheries and Aquatic Sciences **42**: 2034-2049.

Choi, S.C. and Bartha, R. 1994. Environmental factors affecting mercury methylation in estuarine sediments. Bulletin of Environmental Contamination and Toxicology **53**: 805-812.

Choi, S.-C., Chase, T. Jr, and Bartha, R. 1994. Enzymatic catalysis of mercury methylation by *Desulfovibrio desulfuricans* LS. Applied and Environmental Microbiology **60**: 1342-1346.

Clarkson, T.W. 1990. Human health risks from methylmercury in fish. Environmental Toxicology and Chemistry **9**: 957-961.

Clarkson, T.W. 1992. Mercury: Major Issues in Enviromental Health. Enviromental Health Prespectives **100**: 31-38.

Compeau, G. and Bartha, R. 1985. Sulfate-reducing bacteria: Principal methylators of mercury in anoxic estuarine sediment. Applied and Environmental Microbiology **50**: 498-502.

Compeau, G.C. and Bartha, R. 1987. Effect of salinity on mercury-methylating activity of sulfate-reducing bacteria in estuarine sediments. Applied and Environmental Microbiology **53**: 261-265.

Davis, R.B., Anderson, D.S., and Berge, F. 1985. Paleolimnological evidence that lake acidification is accompanied by loss of organic matter. Nature **316**: 436-438.

Dmytriw, R., Mucci, A., Lucotte, M., and Pichet, P. 1995. The partitioning of mercury in the solid components of dry and flooded forest soils and sediments from a hydroelectric

reservoir, Québec (Canada). Water, Air, and Soil Pollution **80**: 1099-1103.

Driscoll, C.T., Blette, V., Yan, C., Schofield, C.L., Munson, R.J., and Holsapple, J. 1995. The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack Lakes . Water, Air, and Soil Pollution **80**: 499-508.

Ebinghaus, R., Hintelmann, H., and Wilken, R.D. 1994. Mercury-cycling in surface waters and in the atmosphere - species analysis for the investigation of transformation and transport properties of mercury. Fresenius' Journal of Analytical Chemistry **350**: 21-29.

French, K.J., Anderson, M.R., Scruton, D.A., and Ledrew, L.J. 1998. Fish mercury levels in relation to characteristics of hydroelectric reservoirs in Newfoundland, Canada. Biogeochemistry **40**: 217-233.

French, K.J., Scruton, D.A., Anderson, M.R., and Schneider, D.C. 1999. Influence of physical and chemical characteristics on mercury in aquatic sediments. Water, Air, and Soil Pollution **110**: 347-362.

Gagnon, C., Pelletier, E., Mucci, A., and Fitzgerald, W.F. 1996. Diagenetic behavior of methylmercury in organic-rich coastal sediments. Limnology and Oceanography **41**: 428-434.

Gilmour, C.C. and Henry, E.A. 1991. Mercury methylation in aquatic systems affected by acid deposition. Environmental Pollution **71** : 131-169.

Grondin, A., Lucotte, M., Mucci, A., and Fortin, B. 1995. Mercury and lead profiles and burdens in soils of Quebec (Canada) before and after flooding. Canadian Journal of Fisheries and Aquatic Sciences **52**: 2493-2506.

Gutknecht J.J. 1981. Inorganic mercury (Hg2+) transport through lipid bilayer membranes. Membrane Biology **61**: 61-66.

Hall, B.D., St. Louis, V.L., Rolfhus, K.R., Bodaly, R.A., Beaty, K.G., and Paterson, M. The impact of reservoir creation on the biogeochemical cycling of methyl and total mercury in boreal upland forests. In press.

Hall, B.D., Bodaly, R.A., Fudge, R.J.P., Rudd, J.W.M., and Rosenberg, D.M. 1997. Food as the dominant pathway of methylmercury uptake by fish. Water, Air, and Soil Pollution **100**: 13-24.

Harris, R.C. and Bodaly, R.A. 1998. Temperature, growth and dietary effects on fish mercury dynamics in two Ontario lakes. Biogeochemistry **40**: 175-187.

Harris, R.C. and Snodgrass, W.J. 1993. Bioenergetic simulations of mercury uptake and retention in walleye (*Stizostedion vitreum*) and yellow perch (*Perca flavescens*). Water Pollution Research Journal of Canada **28**: 217-236.

Hartgers, W.A., Lopez, J.F., Sinninghe Damste, J.S., Reiss C, Maxwell JR, and Grimalt JO 1997. Sulfur-binding in recent environments: II. Speciation of sulfur and iron and implications for the occurrence of organo-sulfur compounds. Geochimica et Cosmochimica Acta **61**: 4769-4788.

Heyes, A., Moore, T.R., and Rudd, J.W.M. 1998. Mercury and methylmercury in decomposing vegetation of a pristine and impounded wetland. Journal of Environmental Quality **27**: 591-599.

Hintelmann, H., Welbourn, P.M., and Evans, R.D. 1995. Binding of methylmercury compounds by humic and fulvic acids. Water, Air, & Soil Pollution **80**: 1031-1034.

Huckabee, J.W., Janzen, S.A., Blaylock, B.G., Talmi, Y., and Beauchamp, J.J. 1978. Methylated mercury in brook trout (*Salvelinus fontinalis*): Absence of an *in vivo* methylating process. Transactions of the American Fisheries Society **107**: 848-852.

Hudson, R.J.M., Gherini, S.A., Watras, C.J., and Porcella, D.B. 1994. Modeling the biogeochemical cycle of mercury in lakes: The Mercury Cycling Model (MCM) and its application to the MTL study lakes. *In Mercury Pollution---Integration and Synthesis. Edited by* C.J. Watras and J.W. Huckabee. Lewis Publishers, Boca Raton, Florida. pp. 473-523.

Huebert, D. 2002. Experimental Lakes Area Upland Flooding Experiment Vegetation Analysis. Dave Huebert. Winnipeg, Manitoba

Huerta-Diaz, M.A. and Morse, J.W. 1992. Pyritization of Trace Metals in Anoxic Marine Sediments. Geochimica et Cosmochimica Acta **56**: 2681-2702.

Hurley, J.P., Benoit, J.M., Babiarz, C.L., Andren, A.W., and Sullivan, J.R. 1995. Influences of watershed characteristics on mercury levels in Wisconsin Rivers. Environmental Science and Technology **29**: 1867-1875.

Iverfeldt, A. 1991. Occurrence and turnover of atmospheric mercury over the nordic countries. Water, Air, and Soil Pollution **56**: 251-265.

Jensen, S. and Jernelov, A. 1969. Biological methylation of mercury in aquatic organisms. Nature 753-754.

Johnson, D.W. and Lindberg, S.E. 1995. The biogeochemical cycling of Hg in forests: Alternative methods for quantifying total deposition and soil emission. Water, Air, and Soil Pollution **80**: 1069-1077.

Kim, K.-H. and Lindberg, S.E. 1995. Design and initial tests of a dynamic enclosure chamber for measurements of vapor-phase mercury fluxes over soils. Water, Air, and Soil Pollution **80**: 1059-1068.

Korthals, E.T. and Winfrey, M.R. 1987. Seasonal and spatial variations in mercury methylation and demethylayion in an oligotrophic lake. Applied and Environmental

Microbiology **53**: 2397-2404.

Krabbenhoft, D.P., Hurley, J.P., Olson, M.L., and Cleckner, L.B. 1998. Diel variability of mercury phase and species distributions in the Florida Everglades. Biogeochemistry **40**: 311-325.

Krabbenhoft, D.P. and Babiarz, C.L. 1992. The role of groundwater transport in aquatic mercury cycling. Water Resources Research **28**: 3119-3128.

Lee, Y.-H. and Iverfeldt, A. 1991. Measurement of Methylmercury and Mercury in Run-Off, Lake and Rain Waters. Water, Air and Soil Pollution **56**: 309-321.

Lindberg, S.E., Turner, R.R., Meyers, T.P., Taylor, G.E., and Schroeder, W.H. 1991. Atmospheric concentrations and deposition of Hg to a deciduous forest at Walker Branch Watershed, Tennessee, USA. Water, Air, and Soil Pollution **56**: 577-594.

Lindberg, S.E., Zhang, H., Gustin, M., Vette, A., Marsik, F., Owens, J., Casimir, A., Ebinghaus, R., Edwards, G., Fitzgerald, C., Kemp, J., Kock, H.H., London, J., Majewski, M., and et al. 1999. Increases in mercury emissions from desert soils in response to rainfall and irrigation. Journal of Geophysical Research **104**: 21879-21888.

Lindberg, S.E., Meyers, T.P., Taylor, G.E.Jr., Turner, R.R., and Schroeder, W.H. 1992. Atmosphere-surface exchange of mercury in a forest: Results of modeling and gradient approaches. Journal of Geophysical Research **97**: 2519-2528.

Lindqvist, O., Johansson, K., Aastrup, M., Andersson, A., Bringmark, L., Hovsenius, G., Haakanson, L., Iverfeldt, A., Meili, M., and Timm, B. 1991. Mercury in the Swedish environment - recent research on causes, consequences and corrective methods. Water, Air, and Soil Pollution **55**: 1-261.

Lodenius, M., Tulisalo, E., and Soltanpour-Gargari, A. 2003. Exchange of mercury between atmosphere and vegetation under contaminated conditions. Science of the Total Environment **304**: 169-174.

Lovley, D.R. and Phillips, E.J.P. 1987. Competitive mechanisms for inhibition of sulphate reduction and methane production in the zone of ferric iron reduction in sediments. Applied and Environmental Microbiology **53**: 2636-2641.

Macalady, J.L., Mack, E.E., Nelson, D.C., and Scow, K.M. 2000. Sediment microbial community structure and mercury methylation in mercury-polluted Clear Lake, California. Applied and Environmental Microbiology **66**: 1479-1488.

Mason, R.P. and Fitzgerald, W.F. 1993. The distribution and biogeochemical cycling of mercury in the Equatorial Pacific Ocean. Deep-Sea Research **40**: 1897-1924.

Mason, R.P., Fitzgerald, W.F., and Morel, F.M.M. 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. Geochimica et Cosmochimica Acta **58**: 3191-3198.

Mason, R.P. and Lawrence, A.L. 1999. Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore Harbor and Chesapeake Bay, Maryland, USA. Environmental Toxicology and Chemistry **18**: 2438-2447.

Mason, R.P., Reinfelder, J.R., and Morel, F.M.M. 1995. Bioaccumulation of mercury and methylmercury. Water, Air, & Soil Pollution **80**: 915-921.

Mason, R.P., Reinfelder, J.R., and Morel, F.M.M. 1996. Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. Environmental Science and Technology **30**: 1835-1845.

Mason, R.P., Morel, F.M.M., and Hemond, H.F. 1995. The role of microorganisms in elemental mercury formation in natural waters. Water, Air, and Soil Pollution **80**: 775-787.

Matilainen, T., Verta, M., Korhonen, H., Uusi-Rauva, A., and Niemi, M. 2001. Behavior of mercury in soil profiles: Impact of increased precipitation, acidity, and fertilization on mercury methylation. Water, Air, and Soil Pollution **125**: 105-119.

Matilainen, T., Verta, M., Niemi, M., and Uusi-Rauva, A. 1991. Specific rates of net methylmercury production in lake sediments. Water, Air, and Soil Pollution **56**: 595-605.

Meili, M. 1991. The coupling of mercury and organic matter in the biogeochemical cycle--towards a mechanistic model for the boreal forest zone. Water, Air, and Soil Pollution **56**: 333-347.

Meili M 1991. Fluxes, pools and turnover of mercury in Swedish forest lakes. Water, Air, and Soil Pollution **56**: 719-727.

Mierle, G. and Ingram, G. 1991. The role of humic substances in the mobilization of mercury from watersheds. Water, Air, and Soil Pollution **56**: 349-357.

Miskimmin, B.M., Rudd, J.W.M., and Kelly, C.A. 1992. Influence of dissolved organic carbon, pH, and microbial respiration rates on mercury methylation and demethylation in lake water. Canadian Journal of Fisheries and Aquatic Sciences **49**: 17-22.

Morel, F.M.M., Kraepiel, A.M.L., and Amyot, M. 1998. The chemical cycle and bioaccumulation of mercury. Annual Review of Ecology and Systematics **29**: 543-566.

Morrison, K.A. and Thérien, N. 1991. Experimental evaluation of mercury release from flooded vegetation and soils. Water, Air, and Soil Pollution **56**: 607-619.

Mucci, A., Lucotte, M., Montgomery, S., Plourde, Y., Pichet, P., and Van Tra, H. 1995. Mercury remobilization from flooded soils in a hydroelectric reservoir of northern Quebec, La Grande. 2. Results of a soil resuspension experiment. Canadian Journal of Fisheries and Aquatic Sciences **52**: 2507-2517.

Munthe, J., Hultberg, H., and Iverfeldt, A. 1995. Mechanisms of deposition of

methylmercury and mercury to coniferous forests. Water, Air, and Soil Pollution **80**: 363-371.

Niimi, A.J. and Kissoon, G.P. 1994. Evaluation of the critical body burden concept based on inorganic and organic mercury toxicity to rainbow trout (*Oncorhynchus mykiss*). Archives of Environmental Contamination and Toxicology **26**: 169-178.

Nriagu, J.O. 1989. A global assessment of natural sources of atmospheric trace metals. Nature **338**: 47-49.

Pak, K.-R. and Bartha, R. 1998. Mercury methylation and demethylation in anoxic lake sediments and by strictly anaerobic bacteria. Applied and Environmental Microbiology **64**: 1013-1017.

Peech Cherewyk, K.A. *Methylmercury bioaccumulation in zooplankton: an assessment of exposure routes and accumulation in newly flooded reservoirs*. M. Sc. Thesis, University of Manitoba, Department of Entomology, Winnipeg, Manitoba. 86pp.

Pickhardt, P.C., Folt, C.L., Chen, C.Y., Klaue, B., and Blum, J.D. 2002. Algal blooms reduce the uptake of toxic methylmercury in freshwater food webs. Proceedings of the National Academy of Sciences **99**: 4419-4423.

Plourde, Y., Lucotte, M., and Pichet, P. 1997. Contribution of suspended particulate matter and zooplankton to MeHg contamination of the food chain in midnorthern Québec (Canada) reservoirs. Canadian Journal of Fisheries and Aquatic Sciences **54**: 821-831.

Ramamoorthy, S., Cheng, T.C., and Kushner, D.J. 1982. Effect of microbial life stages on the fate of methylmercury in natural waters. Bulletin of Environmental Contamination and Toxicology **29**: 167-173.

Ramlal, P.S., Kelly, C.A., Rudd, J.W.M., and Furutani, A. 1993. Sites of methyl mercury production in remote Canadian Shield lakes. Canadian Journal of Fisheries and Aquatic Sciences **50**: 972-979.

Ramlal, P.S., Rudd, J.W.M., Furutani, A., and Xun, L. 1985. The effect of pH on methyl mercury production and decomposition in lake sediments. Canadian Journal of Fisheries and Aquatic Sciences **42**: 685-692.

Ramlal, P.S., Rudd, J.W.M., and Hecky, R.E. 1986. Methods for measuring specific rates of mercury methylation and degradation and their use in determining factors controlling net rates of mercury methylation. Applied and Environmental Microbiology **51**: 110-114.

Ravichandran, M., Aiken, G.R., Reddy, M.M., and Ryan, J.N. 1998. Enhanced dissolution of cinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades. Environmental Science & Technology **32**: 3305-3311.

Ravichandran, M., Aiken, G.R., Ryan, J.N., and Reddy, M.M. 1999. Inhibition of precipitation and aggregation of metacinnabar (mercuric sulfide) by dissolved organic

matter isolated from the Florida Everglades. Environmental Science & Technology **33**: 1418-1423.

Rea, A.W., Lindberg, S.E., and Keeler, G.J. 2001. Dry deposition and foliar leaching of mercury and selected trace elements in deciduous forest throughfall. Atmospheric Environment **35**: 3453-3462.

Regnell, O., Hammar, T., Helgee, A., and Troedsson, B. 2001. Effects of anoxia and sulfide on concentrations of total and methyl mercury in sediment and water in two Hg-polluted lakes. Canadian Journal of Fisheries and Aquatic Sciences **58**: 506-517.

Regnell, O., Tunlid, A., Ewald, G., and Sangfors, O. 1996. Methyl mercury production in freshwater microcosms affected by dissolved oxygen levels: Role of cobalamin and microbial community composition. Canadian Journal of Fisheries and Aquatic Sciences **53**: 1535-1545.

Richardson, M., Mithchell, M., Coad, S., and Raphael, R. 1995. Exposure to mercury in Canada: A multimedia analysis. Water, Air, and Soil Pollution **80**: 31-39.

Robinson, J.B. and Tuovinen, O.H. 1984. Mechanisms of microbial tesistance and detoxification of mercury and organomercury compounds: physiological, biochemical, and genetic analyses. Microbiological Reviews **48**: 95-124.

Rodgers, D.W. and Beamish, F.W.H. 1983. Water quality modifies uptake of waterborne methylmercury by rainbow trout, *Salmo gairdneri* . Canadian Journal of Fisheries and Aquatic Sciences **40**: 824-828.

Rodgers DW. 1994. You are what you eat and a little bit more: Bioenergetics-based models of methylmercury accumulation in fish revisited. *In* Mercury Pollution: Integration and Synthesis. *Edited by* C.J Watras and J. W. Huckabee. Lewis Publishers, Boca Raton, Florida. pp. 427-439.

Roulet, M. and Lucotte, M. 1995. Geochemistry of mercury in pristine and flooded ferralitic soils of a tropical rain forest in French Guiana, South America. Water, Air, and Soil Pollution **80**: 1079-1088.

Rudd, J.W.M. 1995. Sources of methyl mercury to freshwater ecosystems: A review. Water, Air, and Soil Pollution **80**: 697-713.

Rudd, J.W.M., Furutani, A., and Turner, M.A. 1980. Mercury methylation by fish intestinal contents. Applied and Environmental Microbiology **40**: 777-782.

Schindler, D.W., Hesslein, R.H., Wagemann, R., and Broecker, W.S. 1980. Effects of acidification on mobilization of heavy metals and radionuclides from the sediments of a freshwater lake. Canadian Journal of Fisheries and Aquatic Sciences **37**: 373-377.

Schuster, E. 1991. The behaviour of mercury in the soil with special emphasis on complexation and adsorption processes-A review of the literature. Water, Air, and Soil

Pollution **56**: 667-680.

Schwesig, D. and Matzner, E. 2001. Dynamics of mercury and methylmercury in forest floor and runoff of a forested watershed in Central Europe. Biogeochemistry **53**: 181-200.

Sellers, P., Kelly, C.A., and Rudd, J.W.M. 2001. Fluxes of methylmercury to the water column of a drainage lake: The relative importance of internal and external sources. Limnology and Oceanography **46**: 623-631.

Sellers, P., Kelly, C.A., Rudd, J.W.M., and MacHutchon, A.R. 1996. Photodegradation of methylmercury in lakes. Nature **380**: 694-697.

St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., Beaty, K.G., Bloom, N.S., and Flett, R.J. 1994. Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. Canadian Journal of Fisheries and Aquatic Sciences **51**: 1065-1076.

St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., Beaty, K.G., Flett, R.J., and Roulet, N.T. 1996. Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. Environmental Science & Technology **30**: 2719-2729.

Ullrich, S.M., Tanton, T.W., and Abdrashitova, S.A. 2001. Mercury in the aquatic environment: A review of factors affecting methylation. Critical Reviews in Environmental Science and Technology **31**: 241-293.

Vandal, G.M., Mason, R.P., and Fitzgerald, W.F. 1991. Cycling of volatile mercury in temperate lakes. Water, Air, and Soil Pollution **56**: 791-803.

Vandal, G.M., Mason, R.P., McKnight, D., and Fitzgerald, W. 1998. Mercury speciation and distribution in a polar desert lake (Lake Hoare, Antarctica) and two glacial meltwater streams. Science of the Total Environment **213**: 229-237.

Verta, M., Rekolainen, S., and Kinnunen, K. 1986. Causes of increased fish mercury levels in Finnish reservoirs. Publication of the Water Research Institute **65**: 44-58.

Watras, C.J., Back, R.C., Halvorsen, S., Hudson, R.J.M., Morrison, K.A., and Wente, S.P. 1998. Bioaccumulation of mercury in pelagic freshwater food webs. Science of the Total Environment **219**: 183-208.

Watras, C.J., Morrison, K.A., and Back, R.C. 1996. Mass balance studies of mercury and methylmercury in small, temperate/boreal lakes of the northern hemisphere. *In* Regional and global mercury cycles: sources, fluxes and mass balances. *Edited by* W. Baeyens, R. Ebinghaus, and O. Vasiliev. Kluwer Academic Publishers, Netherlands. pp. 329-358.

Wiener, J.G. and Spry, D.J. 1996. Toxicological Significance of Mercury in Freshwater Fish. *In* Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations. *Edited by* Beyer WN, Heinz GH, and Redmon-Norwood AW. Lewis Publishers, Boca Raton, Florida p. 494.

Winfrey, M.R. and Rudd, J.W.M. 1990. Environmental factors affecting the formation of methylmercury in low pH lakes. Environmental Toxicology and Chemistry **9**: 853-869.

Xiao, Z.F., Munthe, J., and Lindqvist, O. 1991a. Sampling and determination of gaseous and particulate mercury in the atmosphere using gold-coated denuders. Water, Air, and Soil Pollution **56**: 141-151.

Xiao, Z.F., Munthe, J., Schroeder, W.H., and Lindqvist, O. 1991b. Vertical fluxes of volatile mercury over forest soil and lake surfaces in Sweden. Tellus. Series B: Chemical and Physical Meteorology **43B**: 267-279.

Xu, H. and Allard, B. 1991. Effects of a fulvic acid on the speciation and mobility of mercury in aqueous solutions. Water, Air, and Soil Pollution **56**: 709-717.

Xun, L., Campbell, N.E.R., and Rudd, J.W.M. 1987. Measurements of specific rates of net methyl mercury production in the water column and surface sediments of acidified and circumneutral lakes. Canadian Journal of Fisheries and Aquatic Sciences **44**: 750-757.

Zhang, H. and Lindberg, S.E. 1999. Processes influencing the emission of mercury from soils: A conceptual model. Journal of Geophysical Research **104**: 21889-21896.

Zhang, H., Lindberg, S.E., Marsik, F.J., and Keeler, G.J. 2001. Mercury Air/Surface Exchange Kinetics of Background Soils of the Tahquamenon River Watershed in the Michigan Upper Peninsula. Water, Air, and Soil Pollution **126**: 151-169.

CHAPTER 2: STRATEGIES OF METHYL MERCURY MITIGATION IN LAKES AND RESERVOIRS

ABSTRACT

In newly flooded reservoirs, fish accumulate elevated concentrations of methyl mercury (MeHg), which may be sustained for 10 to 30 years after impoundment. After flooding, mercury (Hg) can be released from flooded organic matter, and particulate bound Hg can be suspended by waves. Microorganisms can convert inorganic Hg into MeHg. MeHg is the most toxic form of Hg and accumulates in aquatic organisms and biomagnifies. Consumption of fish is the primary route of exposure of MeHg to higher trophic levels such as raptors and humans. Populations of people or birds that live near to and feed on reservoir fishes have an elevated risk of MeHg poisoning. Since demand for hydroelectricity will lead to creation of new reservoirs, hydroelectric companies and governing agencies are investigating strategies to mitigate MeHg contamination. Mitigation methods may involve either eliminating the source of Hg before flooding, or disrupting the production or trophic transfer of MeHg. Possible mitigation methods include site selection, clearing and burning before flooding, additions of selenium, clay, or lime, intensive fishing, and introducing genetically modified bacteria. Less MeHg may be produced in upland sites that contain less carbon than in wetland sites, as well as in run-of-the-river style reservoirs. Burning before flooding lowers the production of MeHg in the water, but not through the food web. Burning before flooding would also release a substantial amount of Hg to the atmosphere. Additions of selenium are extremely effective in lowering MeHg bioaccumulation, but there are concerns over the

toxicity of selenium. Intensive fishing has been demonstrated to lower MeHg in food webs, but may not be practical in large reservoirs.

INTRODUCTION

It is desirable to develop a method of lowering MeHg concentrations in aquatic organisms because MeHg is toxic to fish, and to birds and mammals that prey on fish. The previous chapter reviewed the biogeochemical cycle of Hg and evidence of high MeHg concentrations in food webs of flooded ecosystems. Reservoir formation causes MeHg concentrations to increase because of several conditions. After flooding, inorganic Hg in flooded organic matter becomes available to methylating microorganisms. Organic carbon released from the flooded organic matter stimulates the methylation rate of Hg. MeHg is assimilated from water by algae. Zooplankton and benthic invertebrates may acquire MeHg from water or diet, although the relative importance of each route of entry is unclear. In higher trophic levels, MeHg is transferred primarily via diet. MeHg also biomagnifies and top predators, such as fish-eating fish and raptors accumulate very high levels of MeHg. Fish is the main source of MeHg to humans. People who live near reservoirs and depend heavily on fish for sustenance, often indigenous people, have a high risk of MeHg poisoning.

Government regulators, aboriginal peoples, and hydroelectric companies are interested in lowering the impact of MeHg contamination in reservoirs. Possible mitigation options to lower fish MeHg concentrations include intensive fishing (Göthberg 1983; Verta 1990), additions of clay and sediment (Hecky *et al.* 1987; Rudd and Turner 1983), addition of zeolite-rich sediment (Misaelides *et al.* 1994; Soupioni *et al.* 1999), addition of lime to the catchment area or aquatic ecosystem (Andersson *et al.* 1995; Rask and Verta 1995), selenium additions (Paulsson and Lundbergh 1991; Southworth *et al.*

2000; Turner and Rudd 1983; H. Hultberg pers. comm.), addition of genetically engineered bacteria to demethylate MeHg, site selection and project configuration (Bodaly et al. accepted), and controlled burning before flooding (Table 2.1).

The purpose of this chapter is to review a number of possible mitigation options for lowering elevated MeHg in the food web of new reservoirs. This review will include mechanisms by which each mitigation method decreases MeHg contamination, supporting experimental evidence of its usefulness, and the practicality and limitations of its application. Some mitigation methods may be useful for new reservoirs and existing reservoirs and lakes. The context of this research was an evaluation, using an experimental approach, of controlled burning before flooding as a mitigation method. In the following section, the mechanisms of lowering MeHg bioaccumulation are reviewed and examples of past or ongoing research projects are mentioned. Advantages and disadvantages of each mitigation strategy are discussed.

DISCUSSION OF STRATEGIES TO MITIGATE METHYL MERCURY CONTAMINATION

Intensive fishing

Intensively fishing a lake or reservoir of any age may potentially lower MeHg concentrations in fish. Almost all of the Hg present in fish muscle is MeHg. Intensive fishing may lower MeHg concentrations in fish by several different mechanisms including (1) removal of MeHg from the system, (2) changes in fish growth rates, and (3) alteration of the food web structure. Each mechanism is discussed below. It was thought that fish populations might contain a significant portion of the total MeHg in freshwater

ecosystems. Therefore removing fish biomass from the system was hypothesized as a method to decrease the pool of MeHg in the system (Verta 1990). Verta (1990) further hypothesized that decreasing the population density of fish may lower MeHg concentrations by increasing fish growth rates. This is sometimes referred to as growth dilution. When an organism grows more quickly, the amount of MeHg they ingest is incorporated into a larger mass of tissue. The burden of MeHg per unit mass of tissue is lower. In addition, decreasing the population of certain fish may also restructure the food web; for example, piscivores may depredate on less contaminated species (Verta 1990).

This method has been tested in Finland and Sweden, and is presently under examination at the University of Québec at Montréal. Preliminary results of this study suggest that biodilution is the main cause of changes in fish MeHg concentrations. This is because stable nitrogen isotopic analysis in the fish tissue indicated that the structure of the food web had not changed (J. Doire *et al.* unpublished data). Similarly, one to three years after removing 50% of the fish biomass from a lake in Finland, Hg concentrations decreased significantly (Verta 1990). For example, the Hg concentrations in small roach decreased from 0.29-0.51 to 0.21-0.35 $\mu g \cdot g^{-1}$ (Verta 1990). Although the amount of Hg accumulated by fishes did not change, the growth rate in some species increased, suggesting that growth dilution lowered the Hg concentrations in fish tissue (Verta 1990). In cases where the growth rate did not change significantly, a change in diet was suggested to be the cause of lower Hg concentrations in fish tissue (Verta 1990). In Sweden, intensive fishing was performed in one lake where the amount of fish removed was not more than yearly recruitment and Hg concentrations were significantly lowered ($P<0.001$) by about 50% for up to four years after intensive fishing (Göthberg 1983).

Intensive fishing removed 1% of the THg in the lake in Sweden (Göthberg 1983) and <20% of the MeHg in the lake in Finland (Verta 1990). Since methylation in the sediment would still continue in new reservoirs, intensive fishing would have to be repeated periodically until the rate of methylation subsides. The biomass of fish that may have to be removed from large reservoirs would be substantial. In many cases, fishing with nets would require removal of trees at selected fishing sites before flooding. Another concern is if intensive fishing activities would re-suspend sediments and thereby increase the supply of MeHg to biota. There is also concern about where the harvested fish should be disposed. Overall, employment of this method in conjunction with other methods may be sufficient to maintain lower MeHg concentrations in fishes for the duration of elevated MeHg production in reservoirs.

Additions of clay, bottom sediment, and zeolite-rich sediment

Since Hg adsorbs to particulate matter, addition of fine-grained sediment to aquatic ecosystems may complex enough Hg to lower the availability of MeHg to aquatic organisms. Organic material stimulates Hg methylation (Furutani and Rudd 1980). Therefore diluting sediment Hg and organic carbon concentrations in surface sediment by increasing sedimentation rates of inorganic material may lower MeHg production and bioaccumulation rates. In quiescent water, deposition of clay over organic-rich substrates may create a barrier at the sediment-water interface that would minimize MeHg diffusion from pore water into the water column. On the other hand, increasing the amount of suspended sediment would decrease light penetration and thereby decrease photodegradation of MeHg (Sellers *et al.* 1996). In addition, covering the organic-rich

substrate of a new reservoir may lower the available nutrients and decrease algal productivity, which would decrease the growth rates of other organisms.

In experimental limnocorrals in Southern Indian Lake, Manitoba, the effect of two methods of clay suspension on Hg dynamics were tested (Hecky *et al.* 1987). One was addition of clay-rich glaciolacustrine sediments collected from the bank of the reservoir (bank clay). The second method was dredging to re-suspend bottom sediment. Additions of bank clay caused MeHg bioaccumulation in muscle tissue of yellow perch to either increase or stay the same, but re-suspension of bottom sediments decreased MeHg contamination (Hecky *et al.* 1987). The reason that bank clay additions did not decrease MeHg bioaccumulation was not clear, but suspended bank clay could have supplied the system with mercuric ion or it could have increased the surface area for colonization of bacteria (Hecky *et al.* 1987). Additional causes for this inconsistency could be due to variations in the content of organic carbon or zeolite in sediment, or saturation of Hg-binding sites on clay particles. Re-suspension of bottom sediments by dredging in Clay Lake, Ontario, also decreased rates of MeHg production (Rudd and Turner 1983).

Zeolite minerals are a group of hydrated aluminosilicate minerals that bind aqueous Hg and other heavy metals through adsorption, ion exchange, and precipitation (Misaelides *et al.* 1994; Soupioni *et al.* 1999). They are natural constituents of many types of sediment and are globally abundant at the surface of Earth. They are mined mainly from volcaniclastic deposits. The efficiency of Hg adsorption by zeolite-rich sediment doubles after it is pretreated with a solution of sodium chloride (Misaelides *et al.* 1994).

Lime addition to acidified ecosystems

MeHg concentrations in fish were negatively correlated with acidity in Little Rock Lake, a whole lake experiment in Wisconsin (Wiener *et al.* 1990). In a set of Swedish lakes, the highest fish Hg concentrations were in lakes with pH values of 5.0; Hg concentrations in fish were lower in lakes that had pH levels lower than or higher than 5.0 (Andersson *et al.* 1995). This could have been due to restructuring of the food web when acid sensitive species died (Cabana et al. 1994). Changes in pH also affect methylation of Hg (Ramlal *et al.* 1985).

In the literature, effects of changes in pH on Hg methylation are contradictory. In some studies, methylation is reported to increase at lower pH. For example, Hg bound to DOC decreases with acidity and results in the release of MeHg from sediments (Hintelmann et al. 1995). This stimulates Hg methylation because Hg binds directly to microbial cells (Winfrey and Rudd 1990). Therefore the rate of methylation is inversely related to pH (Bloom et al. 1991; Miskimmin et al. 1992). Miskimmin et al. (1992) found that net methylation rate increased with a decrease in pH from 7.0 to 5.0 at low and high concentrations of DOC. However, this could also be due to the effect of pH on the structure of the microbial ecosystem, or the availability of Hg to methylating organisms. Some studies demonstrate that increases in acidity decrease Hg methylation. Ramlal et al. (1985) found that acidifying surface sediment causes MeHg production rates to decrease in anoxic sediment, possibly because inorganic Hg is less available in pore waters as Hg adsorbed onto particulate matter. Further, a study by French et al. (1999) indicates that MeHg concentrations in the lake sediment of 34 headwater lakes in Newfoundland were not related to acidity.

In Sweden, acidified lakes (pH values of 4.9 to 5.5) were treated with lime to elevate pH values to 6.5 to 7.0, and during this process, fish Hg concentrations decreased by up to two times (Andersson et al. 1995). In the Swedish study, Hg concentrations in fish decreased rapidly and significantly ($p<0.05$) in the first two years after lime was added in less acidified lakes (initial pH values of 5.4 to 5.8). Moderately acidified lakes (initial pH values 0.5 units lower) responded slowly and significantly over six years ($p<0.001$). The most acidified lake (initial pH value of 4.9) increased before decreasing significantly over nine years ($p<0.01$). Similar results were observed in Lake Iso Valkjarvi, Finland, where mean Hg concentrations in perch decreased in the lake basin with lime added by about 50% relative to the control basin (Rask and Verta 1995). In all studies it was demonstrated that addition of lime lowered Hg in fish.

Addition of lime could be a useful mitigation method to lower MeHg concentrations in flooded ecosystems that are low in pH. It creates beneficial effects in lakes situated downstream (reviewed by Andersson *et al.* 1995). Where local sources of limestone are not present, transportation of tons of rock to remote boreal reservoirs may be challenging.

Addition of selenium

Adding selenium to aquatic ecosystems may lower Hg concentrations in fish by several mechanisms. First, selenite in fish diets decreases the trophic transfer of MeHg (Turner and Swick 1983). Second, selenium redistributes MeHg within organisms by cleaving MeHg molecules from proteins that are then translocated in the liver and kidneys (Sumino *et al.* 1977). Third, selenite can enhance demethylation of MeHg in fish

guts (Klaverkamp *et al.* 1983). Selenium may lower MeHg bioaccumulation by decreasing methylation rates of Hg (Jin *et al.* 1997). Southworth *et al.* (2000) found an increase in MeHg concentrations in fish in a pond receiving fly ash slurry after removal of selenium from the effluent, even though selenium concentrations in fish remained high, suggesting a mechanism external to fish.

Selenium additions can be applied to lakes and established reservoirs. This option may require repeated applications to maintain target concentrations. Effects of selenium loading to downstream habitats is not well understood and may pose a substantial threat to wildlife and humans (reviewed by Lemly 1999). Moreover, these mechanisms of MeHg mitigation may not be effective at non-toxic concentrations. For example, in Swedish lakes, sodium selenite additions increased aqueous concentration to 0.4 $\mu g \cdot L^{-1}$. This effectively lowered fish MeHg concentrations by up to five times (H. Hultberg pers. comm.). The upper limit of natural selenium concentrations in freshwater is 0.04 $\mu g \cdot L^{-1}$. This falls below the water quality standard in Canada of 1 $\mu g \cdot L^{-1}$. There is no established safe level of selenium in fish tissue.

At selenium concentrations of 0.4 $\mu g \cdot L^{-1}$ in water, toxic effects in fish may occur. Selenium is unique in that it has the narrowest window between being an essential dietary element and a toxin. Fish require 0.1 to 0.5 $\mu g \cdot g^{-1}$ dry weight (d. w.) of selenium in their tissues (Hodson and Hilton 1983). Generally, selenium becomes a poison at concentrations greater than 3 $\mu g \cdot g^{-1}$ d. w. (Lemly 1997). Aqueous concentrations of 0.4 $\mu g \cdot L^{-1}$ in Swedish lakes that were treated with selenium corresponded to fish selenium concentrations of 2 to 6 $\mu g \cdot g^{-1}$ wet weight (w. w.) (10 to 30 $\mu g \cdot g^{-1}$ d. w.). Selenium accumulates in aquatic organisms and biomagnifies through the food web. For example,

in Belews Lake the aqueous selenium concentrations of 2 $\mu g \cdot L^{-1}$ resulted in fish concentrations up to 50 $\mu g \cdot g^{-1}$ w. w. (250 $\mu g \cdot g^{-1}$ d. w.) (Lemly 2002). The toxic effects of selenium are caused by its similarity to sulphur. Selenium substitutes for sulfur during protein synthesis. This substitution of a different sized molecule destroys the helix structure of the protein. The helix structure is necessary for proper functioning of the protein. As a result, tissue damage, reproductive failure, and teratogenic deformities may occur. Trout eggs that contained 7 to 8 $\mu g \cdot g^{-1}$ w. w. (30 to 40 $\mu g \cdot g^{-1}$ d. w.) of selenium were collected from Luscar Creek, Alberta. About 25% of these trout fry had edema, or fluid retention, in the yolk sack (J. Holm pers. comm.). Edema caused spinal curvature in the developing fry. Other teratogenic effects included cranial deformities, such as shortened snout, severely shortened jaws, and malformed eyes and fins. Overall, the biogeochemical cycle of selenium is not well understood. It is not currently known if selenium additions at non-hazardous concentrations can effectively lower MeHg concentrations in fish.

Genetically modified microorganisms

It is possible that microorganisms could be genetically engineered to demethylate MeHg (Rudd *et al.* 1983), however, even with substantial laboratory experimentation, there may be unforeseen effects from releasing genetically modified organisms to the environment. Further public resistance to introducing genetically modified organisms into lakes and reservoirs may be an obstacle.

Site selection and project configuration

Site selection could be an effective mitigation method to lower Hg in the food webs of reservoirs. High concentrations of nutrients enhance methylation rates. For these reasons, choosing an area with minimal carbon storage would be optimal. The flooded site can be selected based on known methylation capacities of the catchment type. Because methylation rates are high in warm shallow water (Bodaly *et al.* 1993), steep sided catchment areas, like river valleys, would be most favourable to create reservoirs. Selecting areas with minimal soil coverage and high percentages of bedrock exposure may decrease the pool of Hg available for remobilization, if the bedrock does not contain a high percentage of Hg. Microorganism populations proliferate on organic-rich substrate.

Ecosystem scale experiments, namely the Experimental Lakes Area Reservoir Project (ELARP) (Kelly *et al.* 1997) and the FLooded Upland Dynamics EXperiment (FLUDEX) (Bodaly *et al.* in press) have examined the differences in MeHg cycling in a wetland and an upland catchment that vary in carbon content. Flooded upland boreal catchments produce less MeHg than flooded wetlands (Hall *et al.* in press). MeHg production diminished after five years of flooding the upland sites, but the wetland site still produced substantial amounts of MeHg after 13 years of flooding (D. Bodaly pers. comm.). Despite lower MeHg production rates in upland reservoirs, MeHg in the food web did not decrease.

A limitation of this method is that flooding of wetlands and areas with gentle topography cannot always be avoided. In addition, extensive flooding would tend to flood a mixture of upland and wetland terrain.

Controlled burning before flooding

Burning terrestrial plants and soil before flooding may mitigate MeHg contamination in reservoirs. At high temperatures, greater than 100°C, ionic Hg is reduced to gaseous elemental Hg (Hg^0). Forest fires cause Hg^0 to flux into the atmosphere. Lower organic carbon concentrations may inhibit colonization of methylating microorganisms, or decrease their metabolism. As a result, rates of MeHg production may be lowered. Sulphate-reducing bacteria convert Hg to MeHg in anoxic conditions. Mineralization of the organic matter minimizes decomposition and anoxia. Therefore burning may change the conditions that are necessary for Hg methylation to occur. Further, burning may lower MeHg contamination by sorption of Hg to charcoal. Presently it is unclear whether wildfires have consistent effects on aqueous MeHg levels. After a natural fire adjacent to the Caballo Reservoir in south-central New Mexico, Hg concentrations in sediments increased (Caldwell *et al.* 2000). This was explained by the transport of organic Hg complexes and nutrients by runoff into the reservoir after the fire. Although some forest fires may burn 15 to 20 cm into the forest soil (reviewed in Friedli *et al.* 2003), some forest fires leave organic-rich soils exposed. Nutrient loading increases microbial activity, which may increase the rate of MeHg production. In addition, elevated MeHg concentrations in water, sediment, periphyton and invertebrates were observed in the Florida Everglades after a period of intense desiccation followed by

a natural fire, then re-flooding (Krabbenhoft and Fink 2001). This may have occurred as a result of peat oxidation during desiccation or burning causing an increase in the availability of sulfate, labile carbon, or ionic Hg species to microorganisms. In recently burned watersheds in northern Québec, MeHg concentrations in zooplankton and fish did not differ from zooplankton in reference watersheds (Garcia and Carignan 1999; 2000).

Burning before flooding may be beneficial locally, but it would redistribute Hg into other ecosystems. Burning would also emit carbon dioxide, a greenhouse gas, to the atmosphere. If successful, this mitigation method would not require maintenance. On the other hand, if fires are incomplete and leave organic-rich soil exposed, runoff and flooding may leach Hg-DOC complexes, which may increase the availability of MeHg to aquatic organisms and the amount of inorganic Hg available to microorganisms for methylation. Burning before flooding has the potential to prevent Hg contamination in reservoirs, but cannot be applied to existing reservoirs or contaminated lakes. A pre-impoundment prescribed burn can be applied to uplands, but probably not to wetlands. Over long periods of time, reservoirs may emit substantial amounts of carbon dioxide. Reservoirs would also emit methane from anoxic decomposition of carbon, which is more powerful than carbon dioxide at trapping heat in the atmosphere. Burning emits relatively little methane. Therefore an additional benefit of burning before flooding would be lower production of methane. Natural forests fires occur cyclically in the boreal region. Forest fires occurred about every 136 +/- 29 years from 1923 to 1998 in Québec (Lesieur *et al.* 2002). Therefore burning should not alter the long-term carbon budget in the boreal forest.

Biogeochemical effects of fires on aqueous MeHg concentrations must be understood before pre-impoundment prescribed burns can be applied to prevent Hg contamination in new hydroelectric reservoirs. In 2001, I conducted a burning experiment at the Experimental Lakes Area in northwestern Ontario. The purpose of this experiment was to test the effects of burning before flooding on MeHg concentrations in the water, sediment, periphyton, zooplankton and benthic invertebrates. The results from this limnocorral experiment showed that burning terrestrial plants and soils before flooding lowered the pool of Hg by more than 95%. Aqueous THg and MeHg concentrations of surface water in mesocosms were lower after controlled burning. However, the concentrations of MeHg in biota from the lower trophic levels did not reflect aqueous concentrations, but were modified by dissolved organic carbon (DOC). Treatments that received burned vegetation and soil contained less DOC than treatments that received unburned vegetation and soil. As a result, the biota in mesocosms with burned vegetation and soil had higher concentrations of MeHg than those with fresh vegetation and soil.

CONCLUSIONS

The most promising strategies to mitigate MeHg contamination in fish from boreal reservoirs may be site selection, lime addition, selenium additions, and intensive fishing. Selenium additions would be a relatively easy solution because it would require little effort to apply, it is inexpensive, and it is applicable to existing reservoirs and lakes. However, the possibility of selenium toxicity to fish and fish consumers is high, since the

safe range of selenium concentrations is extremely narrow. Enhancing the growth rate in fish by selectively removing a portion of the fish population effectively lowers the MeHg levels in fish. The drawbacks of this method are that intensive fishing may need to be repeated, as Hg methylation in the sediment will continue, and a portion of the land must be cleared before flooding to facilitate fishing with nets. In an experimental study, burning before flooding lowered MeHg concentrations in the substrate and the surface water. However, due to modification by DOC, this strategy did not lower MeHg bioaccumulation. The risk and cost of losing control of the burn would be a major concern, as well as the possibility of toxicity by incomplete combustion products. Presently, the most promising method to prevent elevated MeHg levels in fish is site selection and liming.

LITERATURE CITED

Andersson, P., Borg, H., and Kaerrhage, P. 1995. Mercury in fish muscle in acidified and limed lakes. Water, Air, and Soil Pollution **80**.

Bodaly, R.A., Rudd, J.W.M., Fudge, R.J.P., and Kelly, C.A. 1993. Mercury concentrations in fish related to size of remote Canadian Shield lakes. Canadian Journal of Fisheries and Aquatic Sciences **50**: 980-987.

Bodaly, R.A., Rolfhus, K.R., Penn, A.F., Beaty, K.G., Hall, B.D., Hendzel, L.H., Mailman, M., Majewski, A.R., Matthews, K.J.D., Paterson, M.J., Peech Cherewyk, K.A., St. Louis, V.L., Schiff, S.L., and Venkiteswaran, J.J. The use of experimental reservoirs to explore the impacts of hydro-electric developments on methylmercury and greenhouse gas production: The FLUDEX experiment. Environmental Science and Technology. Accepted.

Cabana, G., Tremblay, A., Kalff, J., and Rasmussen, J.B. 1994. Pelagic food chain structure in Ontario lakes: A determinant of mercury levels in lake trout (*Salvelinus namaycush*). Canadian Journal of Fisheries and Aquatic Sciences **51**: 381-389.

Caldwell, C.A., Canavan, C.M., and Bloom, N.S. 2000. Potential effects of forest fire and storm flow on total mercury and methylmercury in sediments of an arid-lands reservoir. Science of the Total Environment **260**: 125-133.

Campbell, P.G.C. and Stokes, P.M. 1985. Acidification and toxicity of metals to aquatic biota. Canadian Journal of Fisheries and Aquatic Sciences **42**: 2034-2049.

Friedli, H.R., Radke, L.F., Lu, J.Y., Banic, C.M., Leaitch, W.R., and MacPherson, J.I. 2003. Mercury emissions from burning of biomass from temperate North American forests: laboratory and airborne measurements. Atmospheric Environment **37**: 253-267.

Furutani, A. and Rudd, J.W.M. 1980. Measurement of mercury methylation in lake water and sediment samples. Applied and Environmental Microbiology **40**: 770-776.

Garcia, E. and Carignan, R. 1999. Impact of wildfire and clear-cutting in the boreal forest on methyl mercury in zooplankton. Canadian Journal of Fisheries and Aquatic Sciences **56**: 339-345.

Garcia, E. and Carignan, R. 2000. Mercury concentrations in northern pike (Esox lucius) from boreal lakes with logged, burned, or undisturbed catchments. Canadian Journal of Fisheries and Aquatic Sciences. Suppl. 2. Impacts of major watershed perturbations on aquatic ecosystems. **57**: 129-135.

Gothberg, A. 1983. Intensive Fishing---A way to reduce the mercury level in fish. Ambio **12**: 259-261.

Hall, B.D., Bodaly, R.A., Fudge, R.J.P., Rudd, J.W.M., and Rosenberg, D.M. 1997. Food as the dominant pathway of methylmercury uptake by fish. Water, Air, and Soil Pollution **100**: 13-24.

Hall, B.D., St. Louis, V.L., Rolfhus, K.R., Bodaly, R.A., Beaty, K.G., and Paterson, M. The impact of reservoir creation on the biogeochemical cycling of methyl and total mercury in boreal upland forests. In press.

Hecky, R. E., Bodaly, R. A., Ramsey, D. J., and Strange, N. E. 1987. Enhancement of mercury bioaccumulation in fish by flooded terrestrial materials in experimental ecosystems. A summery report for the Canada-Manitoba Agreement on the study and monitoring of mercury in the Churchill River diversion: Project 2.1 Experimental ecosystems. Department of Fisheries and Oceans. Winnipeg, Manitoba.

Hodson, P.V. and Hilton, J.W. 1983. The nutritional requirements and toxicity to fish of dietary and waterborne selenium. Environmental Biogeochemistry **35**: 335-340.

Jin, L.-J., Guo, P., Xu, X.-Q. 1997. Effect of selenium on mercury methylation in anaerobic lake sediments. Bulletin of Environmental Contamination and Toxicology 59: 994-999.

Kelly, C.A., Rudd, J.W.M., Bodaly, R.A., Roulet, N.P., St. Louis, V.L., Heyes, A., Moore, T.R., Schiff, S., Aravena, R., Scott, K.J., Dyck, B., Harris, R., Warner, B., and Edwards, G. 1997. Increases in fluxes of greenhouse gases and methyl mercury following flooding of an experimental reservoir. Environmental Science and Technology **31**: 1334-1344.

Klaverkamp, J.F., Hodgins, D.A., and Lutz, A. 1983. Selenite toxicity and mercury-selenium interactions in juvenile fish. Archives of Environmental Contamination and Toxicology **12**: 405-413.

Krabbenhoft, D. and Fink, L.E. 2001. The effect of dry down and natural fires on mercury methylation in the Florida Everglades. 25th International Conference on Heavy Metals in the Environment 6-10 August 2000, Ann Arbor, Michigan, USA 1-5. http://www.sph.umich.edu/eih/heavymetals/Manuscripts/KrabbenhoftD.htm. Accessed 26 January 2001.

Lemly, A.D. 1997. Ecosystem recovery following selenium contamination in a freshwater reservoir. Ecotoxicology and Environmental Safety **36**: 275-281.

Lemly, A.D. 1999. Selenium transport and bioaccumulation in aquatic ecosystems: A proposal for water quality criteria based on hydrological units. Ecotoxicology and Environmental Safety **42**: 150-156.

Lemly, A.D. 2002. Symptoms and implications of selenium toxicity in fish: The Belews Lake case example. Aquatic Toxicology **57**: 39-49.

Lesieur, D., Gauthier, S., and Bergeron, Y. 2002. Fire frequency and vegetation dynamics

for the south-central boreal forest of Quebec, Canada. Canadian Journal of Forest Research **32**: 1996-2009.

Misaelides P, Godelitsas A, Charistos V, Ioannou D, and Charistos D 1994. Heavy metal uptake by zeoliferous rocks from Metaxades, Thrace, Greece: an exploratory study. Journal of radioanalytical and Nuclear Chemistry **183**: 159-166.

Paulsson, K. and Lundbergh, K. 1991. Treatment of mercury contaminated fish by selenium addition. Water, Air, & Soil Pollution **56**: 833-841.

Ramlal, P.S., Rudd, J.W.M., Furutani, A., and Xun, L. 1985. The effect of pH on methyl mercury production and decomposition in lake sediments. Canadian Journal of Fisheries and Aquatic Sciences **42**: 685-692.

Rask, M. and Verta, M. 1995. Concentrations and amounts of methylmercury in water and fish in the limed and acid basins of a small lake. Water, Air, and Soil Pollution **80**: 577-580.

Rudd, J.W.M. and Turner, M.A. 1983. The English-Wabigoon River system: 2. Suppression of mercury and selenium bioaccumulation. Canadian Journal of Fisheries and Aquatic Sciences **40**: 2218-2227.

Rudd, J.W.M., Turner, M.A., Furutani, A., Swick, A.L., and Townsend, B.E. 1983. The English-Wabigoon River system: 1. A synthesis of recent research with a view towards mercury amelioration. Canadian Journal of Fisheries and Aquatic Sciences **40**: 2206-2217.

Sellers, P., Kelly, C.A., Rudd, J.W.M., and MacHutchon, A.R. 1996. Photodegradation of methylmercury in lakes. Nature **380**: 694-697.

Soupioni M, Symeopoulos B, Athanasiou J, Gioulis A, Koutsoukos P, and Tsolis-Katagas P. 1999. A preliminary study of mercury uptake by a Greek zeoliferous rock. *In* Natural microporous materials in environmental technology. *Edited by* P. Misaelides, P.T.J. Macášek, C. Colella. Kluwer Academic Publishers, Netherlands. pp. 365-369.

Southworth, G.R., Peterson, M.J., and Ryon, M.G. 2000. Long-term increased bioaccumulation of mercury in largemouth bass follows reduction of waterborne selenium. Chemosphere **41**: 1101-1105.

Sumino, K., Yamamoto, R., and Kitamura, S. 1977. A role of selenium against methylmercury toxicity. Nature **268**: 73-74.

Turner, M.A. and Rudd, J.W.M. 1983. The English-Wabigoon River system: 3. Selenium in lake enclosures: Its geochemistry, bioaccumulation, and ability to reduce mercury bioaccumulation. Canadian Journal of Fisheries and Aquatic Sciences **40**: 2228-2240.

Turner, M.A. and Swick, A.L. 1983. The English-Wabigoon River system: 4. Interaction between mercury and selenium accumulated from waterborne and dietary sources by

northern pike (*Esox lucius*). Canadian Journal of Fisheries and Aquatic Science **40**: 2241-2250.

Verta, M. 1990. Changes in fish mercury concentrations in an extensively fished lake. Canadian Journal of Fisheries and Aquatic Sciences **47**: 1888-1897.

Wiener, J.G., Fitzgerald, W.F., Watras, C.J., and Rada, R.G. 1990. Partitioning and bioavailability of mercury in an experimentally acidified Wisconsin lake. Environmental Toxicology and Chemistry **9**: 909-918.

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TABLES

Table 2.1. Strategies of MeHg mitigation for reservoirs and lakes.

Strategy	Mechanisms	Advantages	Disadvantages
Liming	Neutralizes pH	No repeated application necessary	Boreal reservoirs may not be acidic
Sodium selenite additions	May lower rate of methylation Decreases trophic transfer of MeHg	Very effective	Requires repeated applications Teratogenic effects May accumulate downstream Public resistance
Zeolite additions	Adsorbs heavy metals	Natural constituent of clay	No experimental evidence in aquatic ecosystems May remobilize other elements
Intensive fishing	Growth dilution Restructure food web	No chemicals Creates employment for local people	Repeated intensive fishing required Clearing sites for fishing before flooding
Site selection: uplands or steep sided river valleys	Decrease littoral area where Hg methylation is high	No chemicals	Location may not be feasible
Genetically modified microorganisms	Microorganisms demethylate MeHg	Lowers amount of MeHg in ecosystems	Introducing genetically modified organisms may have unforeseen consequences Public resistance
Controlled burning before flooding	Less inorganic Hg present May lessen amount and/or metabolism of microorganisms Charcoal may sequester THg and MeHg	No repeated application Decreases production of methane in reservoirs	Adds Hg to atmosphere Not applicable to existing reservoirs or lakes Risk of losing control of burn High cost to control burn

CHAPTER 3: TOTAL AND METHYL MERCURY IN FRESH AND BURNED PLANTS AND SOIL

ABSTRACT

Flooding terrestrial organic carbon stimulates methyl mercury (MeHg) production. MeHg bioaccumulates and biomagnifies through food webs, and elevates the risk of MeHg poisoning in organisms that consume fish. Methods to decrease MeHg contamination in new reservoirs are being investigated, such as burning catchment soils and vegetation before flooding. Burning will volatilize Hg in vegetation and soil, thus decreasing the amount of mercury (Hg) available for methylation. In addition, it will decrease the amount of organic carbon present, which may decrease bacterial activity and MeHg production. The purpose of this study was to determine how much Hg, MeHg, and carbon was lost after burning boreal vegetation and soil. I collected upland soils and 14 species of plants at the Experimental Lakes Area, northwestern Ontario and burned them with propane torches. Mean total Hg (THg) concentrations in fresh plant samples ranged from 4 to 52 $ng \cdot g^{-1}$ dry weight (d. w.). Bryophytes contained the highest THg concentrations, and trees and shrubs contained the lowest concentrations. The mean concentrations of MeHg in fresh plants ranged from 0.1 for green alder to 1.3 $ng \cdot g^{-1}$ (d. w.) for willow. Upland soils had higher THg and MeHg concentrations (162 +/- 76 $ng \cdot g^{-1}$ d. w.) than any plants, and mean MeHg concentrations of 0.6 +/- 0.6 $ng \cdot g^{-1}$. My results of Hg in fresh vegetation were generally higher than other studies. After burning, the amount of carbon, THg, and MeHg decreased substantially in all samples. Plants lost a mean of 96.3% (92.6 to 98.7) of mass, 97.8% (94.7 to 99.5) of carbon, 96.6% (84.5 to

99.5) of THg, and 94.2% (63.1 to 100.0) of MeHg. Loss of THg and MeHg in vegetation correlated significantly with the loss of vegetation mass using Spearman's rank correlation procedure ($r=0.73$, $p<0.01$), but not with the loss of carbon. Of the original mass, carbon, THg, and MeHg in upland soil at ELA, 27.3, 94.8, 78.8, and 81.8% was lost, respectively. My results are similar to other studies and demonstrate that burning causes a substantial loss of Hg from the terrestrial plants and soil in this study.

INTRODUCTION

Exposure to methyl mercury (MeHg) through the consumption of fish is a significant concern. Anthropogenic emissions of mercury (Hg) have approximately tripled the amount of Hg cycling in the biosphere (Mason *et al.* 1994; Morrison and Thérien 1991). Flooding causes Hg concentrations in fish to increase (Abernathy and Cumbie 1977; Cox *et al.* 1979; Lodenius *et al.* 1983; Bodaly *et al.* 1984; Verdon *et al.* 1991; Yingcharoen and Bodaly 1993). Soil and vegetation contribute to the MeHg problem in new reservoirs because Hg deposited from the atmosphere as elemental Hg (Hg^0) or ionic Hg (Hg^{2+}) accumulates with organic matter (Zhang *et al.* 2001; St. Louis *et al.* 2001). When terrestrial ecosystems become flooded, particulate Hg may be suspended by wave activity or fluctuations in water levels (Mucci *et al.* 1995). Microorganisms that methylate inorganic Hg proliferate on organic-rich substrates (Macalady *et al.* 2000), which are common in flooded ecosystems, and microbial methylation of Hg is stimulated by decomposition of flooded organic carbon (Hecky *et al.* 1991; Morrison and Thérien 1995; Kelly *et al.* 1997; Heyes *et al.* 1998), the presence of sulphide (Benoit *et al.* 2001), and anoxic conditions that persist during decomposition after impoundment (Gilmour *et al.* 1992).

The high risk of MeHg poisoning to communities that depend on reservoir fisheries is of primary concern in Canada. Consequently, hydroelectric companies and governmental agencies are researching MeHg mitigation methods, such as intensive fishing, selenite additions, clay additions, project configuration and site selection, and controlled burning before flooding.

Burning terrestrial catchments prior to flooding for hydroelectric development may decrease MeHg contamination in new reservoirs. This may occur by 1) decreasing the amount of Hg available for methylation by loss during combustion, 2) decreasing the amount of organic-rich substrate on which methylating microorganisms proliferate, and 3) binding of THg and MeHg by the remaining charcoal, rendering it less available to methylating microorganisms or to biota.

After burning of vegetation, 87 to 95% of the Hg present is emitted as elemental Hg (Hg^0) and particulate Hg^{2+} (Friedli *et al.* 2003). During fossil fuel combustion, most of the emission of Hg occurs as Hg^0 (Pacyna and Munch 1991). Hg^0 fluxes into the atmosphere and can be oxidized to Hg^{2+}, which has a high affinity for particulate matter (reviewed in Mason *et al.* 1994). Particulate Hg^{2+} falls quickly out of the atmosphere to the surface of Earth, but Hg^0 is light in mass and can travel long distances through the atmosphere (reviewed in Mason *et al.* 1994). Since most of the Hg is emitted as Hg^0 to the atmosphere during combustion, Hg^0 probably travels long distances from the site of combustion.

The purpose of this study is to quantify the amount of carbon, THg and MeHg in vegetation and soil before and after burning. I report changes in concentrations of carbon, THg, and MeHg in several different wetland and upland plants and in upland soil with burning. I also estimate the amount of Hg that may flux to the atmosphere during wildfires in boreal regions of Canada.

METHODS AND MATERIALS

Location

This research was conducted at the Experimental Lakes Area (ELA) in northwestern Ontario (49° 34' N to 49° 47' N and 93° 36' W to 93° 58' W). The forests at the ELA were burned extensively in a forest fire in 1980 and consist mainly of jack pine (*Pinus banksiana*), black spruce (*Picea mariana*), and paper birch (*Betula papyrifera*). Numerous small lakes characterize the area. Peat bogs are developed in low areas and around wetland ponds. Point sources of Hg and geological anomalies with high Hg levels are not known to exist there.

Sample collection

Soil and vegetation samples were collected in early July 2001 over a two week period. Triplicate samples of organic soil, including litter, were collected from an upland catchment under jack pine canopy. The area was relatively free of vegetation that covered the ground. There was a layer of jack pine needles about 5 cm thick, about 2 cm of humus, and more than 10 cm of organic soil. I collected soil with a steel shovel to a depth of 10 cm, without encountering the mineral soil, and placed the soil into polyethylene bags.

I collected duplicate samples of 14 species of vegetation (above ground material only) from either wetland or forested upland ecosystems that had been previously surveyed for vegetation (Dyck and Shay 1999; Huebert 2002). For shrubs, I collected composite samples of leaves, twigs, and branches less than 2 cm in diameter, and

Sphagnum spp. from peat hummocks that surrounded a bog pond. I used stainless steel shears and powder-free vinyl gloves during sample collection, and placed all samples into polyethylene bags. I froze one of the duplicate samples for later analysis of carbon, THg, and MeHg in fresh vegetation, and I weighed the other sample and then burned it with propane torches until no glowing embers remained. I measured the temperatures of combustion with a digital thermocouple that registered temperatures up to 800°C. Vegetation samples were burned in new steel cans at a minimum of 800°C. Soil samples were air dried for 24 hours. The maximum daytime temperature on the day the soil dried was 24°C. Burning of soil took place on steel trays at temperatures between 650 and 700°C. After burning I re-weighed the samples and froze them in polyethylene bags. There were no unburned controls to assess contamination due to handling.

Sample preparation and chemical analysis

I prepared samples at the Freshwater Institute in Winnipeg. In other studies of Hg in plants, samples were rinsed with deionized water before analyzing (Moore *et al.* 1995; Rasmussen *et al.* 1991). I did not wash fresh plants with deionized water before digestion because I wanted to know how much Hg would be available for methylation if the plants were flooded. I freeze dried the fresh and burned samples, and then homogenized them with electric steel grinders. Before grinding each sample, I washed the grinders with distilled water and Kim wipes. After homogenizing the samples, I weighed a sub-sample of each species of vegetation on a Perkin Elmer microbalance (50 to 60 mg and 10 to 20 mg for THg and MeHg, respectively) using an acid rinsed stainless steel scoop to transfer the material into trace-metal-clean weigh boats. I placed the sub-

samples in hot-acid (HNO_3) washed conical Teflon vials. I sent the homogenized soil in polyethylene bags for analysis.

Flett Research Limited analyzed the samples for THg and MeHg by cold vapor atomic fluorescence spectrophotometery (CVAFS) (Bloom 1989; Horvat *et al.* 1993). Determinations of THg and MeHg were made in duplicate for two of the single samples of 14 plant species. The standard error of the duplicate samples ranged from 3 to 10% for THg in fresh plants, 1% for THg in burned plants, 0 to 14% for MeHg in fresh plants, and 0 to 100 for MeHg in burned plants.

I weighed sub-samples for carbon content for the Freshwater Institute chemistry laboratory to analyze according to the methodology of Hauser (1973). Samples were combusted at temperatures of 950 to 975°C in an oxygen and helium atmosphere. After removal of interfering compounds and reduction of nitrous oxide to nitrite, carbon was measured using a high precision thermal conductivity detector on a Control Equipment Corporation Model 240-XA Elemental Analyzer. The detection limit of carbon was 1000 $\mu g \cdot g^{-1}$ and the standard deviation was 30 $\mu g \cdot g^{-1}$.

Percentage loss of plant mass, carbon, THg, and MeHg was compared using Spearman rank correlation using Statistical Analysis Software (SAS). I used a non-parametric statistical method, Spearman's rank correlation coefficient, to compare my data. The Pearson coefficient of correlation, a parametric method, was also used for comparison, and it gave similar results.

RESULTS

Mass and carbon loss in soil and vegetation after burning

After burning, soil lost an average of 27.3% of the original mass and 94.8% of the carbon. The amount of carbon that was lost in plants after burning ranged from 94.7 to 99.5%, but most species lost 97 to 99%. Three species were outside of this range. *Polytrichum spp.* lost the least carbon at 94.7%. *Larix larcinia* and *Pinus banksiania* lost 99.5% of the carbon.

THg and MeHg in soil and vegetation before and after burning

Fresh soil contained a mean concentration of 162 +/- 6 ng THg·g^{-1} d. w. and 0.6 +/- 0.6 ng MeHg·g^{-1} d. w.. Burned soil lost 78.8% of the original THg and 81.8% of the original MeHg.

Concentrations of THg in fresh vegetation ranged from 4 to 52 ng·g^{-1} d. w. (Figure 3.1). Shrubs and trees contained the lowest concentrations of THg and were generally about 10 ng·g^{-1}, with the exception of Tamarak (*Larix larcinia*), green alder (*Alnus crispa*), and pin cherry (*Prunus pensylvanica*) that contained 29, 4, and 5 ng·g^{-1}, respectively. Upland bryophytes, feathermoss (*Plurozium schreberi*) and haircap moss (*Polytrichum spp.*), contained the greatest THg concentrations at 52 and 36 ng·g^{-1}, respectively. Concentrations of THg in burned vegetation ranged from 4 to 16 ng·g^{-1} (Table 3.1). After burning vegetation, the change in THg concentrations was variable among species.

Concentrations of MeHg in fresh vegetation ranged from 0.1 to 1.3 ng·g^{-1} (Table 3.1). *A. crispa* contained the least MeHg and fresh upland willow (*Salix humilis*)

contained the greatest MeHg concentration (2.6 $ng \cdot g^{-1}$). Concentrations of MeHg in burned vegetation ranged from undetectable to 0.8 $ng \cdot g^{-1}$ (Table 3.1). *P. pensylvanica* and *S. humilis* contained undetectable concentrations of MeHg. *Polytrichum spp.* had the highest concentration of MeHg after burning. After burning, the changes in MeHg concentrations were also variable among vegetation species.

Mass of THg, MeHg, and carbon in vegetation after burning

The mass of Hg, MeHg, and carbon in vegetation decreased substantially after burning. An average of 97.8% of carbon was lost from the vegetation samples after combustion. The mass of Hg was also substantially lower among all species after burning. On average, vegetation lost 96.6% (84.5 to 99.5%) of the original THg (Table 3.1). *A. crispa* lost the least THg and *L. larcinia* lost the most THg. Similarly, plants lost a mean of 94.2% (63.1 to 100.0%) of the original MeHg after burning (Table 3.1). *A. crispa* and *Polytrichum spp.* lost the least MeHg. The remaining plant species lost more than 90% of the original MeHg.

DISCUSSION

Mercury in fresh vegetation and soil

In this section I discuss variations in THg and MeHg among plant species and compare my results with other studies. I also discuss trends in THg concentrations with plant physiology and geographically. Finally, I compare my results of THg and MeHg in soil with other studies and review possible reasons for the differences.

Possible reasons for differences in Hg concentrations among plant species may be temporal and regional variation, sampling techniques, age and type of tissue, and environmental conditions. Temporal variation in sample collection is a source of variation in THg concentrations in plant tissues of the same species, and therefore samples should be collected within a three week time span (Rasmussen 1995). THg concentrations in plant tissues vary with type of tissue (foliage or needles). For example, Rasmussen *et al.* (1991) found Hg concentrations in foliage to be two to three times more than in twigs in southern Ontario and Bodaly *et al.* (1987) found THg concentration in foliage to be the same or two times less than in twigs in northern Manitoba. The most probable reason for these contradictory results is regional differences in geology or in atmospheric deposition. Also, the moisture content of the soil influences the Hg concentrations in bryophytes (Moore *et al.* 1995).

I found a range of concentrations in fresh plants from 3.6 to 51.6 $ng \cdot g^{-1}$ of THg and 0.05 to 1.3 $ng \cdot g^{-1}$ of MeHg, which I used to compare to other results (Table 3.2). The research papers with which I drew comparisons were from remote settings with no known point sources of Hg pollution. Plant samples collected by Moore *et al.* (1995) from uplands and wetlands at ELA had 4 to 160 $ng \cdot g^{-1}$ of THg and 0.1 to 139 $ng \cdot g^{-1}$ of MeHg. The range in concentrations in my research was within the range of concentrations measured by Moore *et al.* (1995), but their range contained up to three times more THg and 70 times more MeHg. The higher THg concentrations were found in environments that differed from those in my study. Moore *et al.* (1995) collected *Sphagnum spp.* from hummocks and in wetland hollows and pools whereas I collected mine only in wetland hummocks. Also, their samples of *P. schreberi* were collected

under wetland canopy and forested sites whereas mine were collected under upland forest canopy (see Table 3.2 for further details). THg concentrations in *Sphagnum spp.* that I collected in hummocks from a bog lake (20.4 ng of THg·g^{-1}) were lower than *Sphagnum spp.* collected from other hummocks (36.6 ng of THg·g^{-1}) and *Sphagnum spp.* from hollows or pools of water contained 2 to 4 times more THg than samples I collected in hummocks (46.7 to 92.5 ng of THg·g^{-1}) (Moore *et al.* 1995). Variability in canopy cover may also affect THg concentrations in low shrubs and mosses. THg in *P. schreberi* (51.6 ng of THg·g^{-1}) in my study, collected beneath *P. banksiana* and *P. mariana*, was higher than samples of *P. schreberi* collected from a similar environment (41.5 ng of THg·g^{-1}), but lower than samples collected beneath leatherleaf (*Chamaedaphne calyculata*) (79.8 ng of THg·g^{-1}) (Moore *et al.* 1995).

In another study, plants collected throughout the United States contained 14 to 70 ng of THg·g^{-1} (Friedli *et al.* 2003). Although none of the species were the same as in my study, this range in THg concentration is very similar to the range that I found. Overall my results compared well with other studies, although the upper range of THg concentrations in my study was often not as high as others reported in the literature. My results were probably lower because ELA is a very remote site with no known point sources of Hg pollution and mean annual wet deposition concentrations of only 4.0 ng of THg·L^{-1} from 1992 to 1995 (St. Louis *et al.* 1995) to 9.8 ng of THg·L^{-1} from 1998 to 1999 (St. Louis *et al.* 2001).

My results show that trees or shrubs tend to have lower THg concentrations than bryophytes, with the exception of *L. larcinia*. *L. larcinia* was collected from a flooded

wetland pond and had a high THg concentration. Concentrations of THg also appear to be higher in bryophytes as compared to vascular plants (Moore *et al.* 1995).

There appears to be a trend in THg concentrations in *Sphagnum spp.* from low latitudes to high latitudes. Results from my study were similar to Moore *et al.* (1995), which both took place in northwestern Ontario. *Sphagnum spp.* collected in northern Manitoba had almost three times as much THg as in northwestern Ontario. Results from the James Bay lowlands and the Northwest Territories (Glooschenko and Capobianco 1978) are two orders of magnitude higher than other studies in uncontaminated regions, and therefore may have been exposed to Hg pollution, contaminated during collection or analysis, or may be situated near geological anomalies. However, the trend of increasing THg concentrations with latitude is also seen in feather mosses from northwestern Ontario to northern Manitoba to the North Sea (see Table 3.2 for summary of these results). Regional differences in the geochemistry of the environment apparently do affect THg concentrations in vegetation (Rasmussen *et al.* 1991), and deducing any spatial trends is beyond the scope of this research project.

Results from composite samples of soil and litter in this research were generally higher than other studies. Soil samples including litter, humus, and organic soil that were collected from a well-drained upland forest site on a bedrock ridge in northwestern Ontario contained 162 ng of $THg \cdot g^{-1}$ and 0.6 ng of $MeHg \cdot g^{-1}$. In other studies, the concentration of THg in organic soil has ranged from 22 to 99 ng of $THg \cdot g^{-1}$ (Bodaly *et al.* 1987; Munthe *et al.* 1998; Severson *et al.* 1992; Siegel *et al.* 1987). In the same geographic area, St. Louis *et al.* (2001) found mean concentrations in the surface litter layer of 104 ng of $THg \cdot g^{-1}$ and 0.4 ng of $MeHg \cdot g^{-1}$. Soils at ELA contained more THg

compared to any other uncontaminated upland soil reported in the literature (see Table 3.2). In the Gårdjön catchment area in Sweden, mean concentrations of MeHg in litter, humus, and organic soil were 0.97, 0.53, and 0.035 $ng \cdot g^{-1}$ d. w. (Munthe *et al.* 1998), and the ELA soil MeHg concentrations were within this range.

High THg concentrations in soil at ELA may be due to differences in soil composition, inclusion of the complete organic soil horizon, or exposure to sunlight. I collected soil under jack pine canopy. It was mostly shaded, and had an organic soil horizon of more than 10 cm. The area was burned 21 years prior to collection and the organic soil profiles in the area were generally thin. The thicker lens of soil that I sampled may indicate a greater accumulation of organic matter. In northern Manitoba, soil samples were divided into 1) living moss, lichen, and broad leaf litter, and 2) brown to black humic-rich soil (Bodaly *et al.* 1987). No moss was present in soil analyzed in my research. It is possible that litter from coniferous forests in these northern regions contains more THg than deciduous litter, although results from Rasmussen *et al.* (1991) do not support this idea. In the study performed by Severson et al. (1992) on the Frisan Islands, the organic-rich soil horizon was only 1 to 2 cm thick, had no litter component, and was probably exposed to full sunlight. These factors may account for the lower concentrations of THg that were observed. In the study by Siegel *et al.* (1987), only soil from 3 to 5 cm below the soil surface was analyzed for Hg, and the composition was clay loam to sandy loam. I assume that these soils were not rich in organic carbon, with which Hg forms complexes.

Loss of mass, carbon, Hg, and MeHg during combustion

My results show that Hg, MeHg, mass, and carbon in vegetation decreased considerably after burning. Vegetation samples lost 92.6 to 98.7% of their original mass, and loss of carbon was between 94.7 and 99.5%. In my experiments the loss of mass was greater than in a similar study where live vegetation lost 42.5 to 88.8% of mass during laboratory burning experiments at the US Forest Service in Missoula, Montana (Friedli *et al.* 2003).

In my research, a mean of 96.6% of the original mass of THg was lost from vegetation during combustion. Loss of THg was 97.5 to 99.8% in laboratory experiments conducted by Friedli *et al.* (2001; 2003), which are similar to my results. In their subsequent study, laboratory experiments and measurements of Hg in smoke plumes from a natural wildfire near Hearst, Ontario, both gave similar results indicating that between 97 and 99% of THg was lost (Friedli *et al.* 2003).

The temperatures of my experimental burns were >650°C, which is within the range of natural vegetation fires (Raison *et al.* 1985). Hg volatilizes at temperatures greater than 25 to 450°C (reviewed in Veiga *et al.* 1994) and Hg^0 is reported to be highly volatile at temperatures greater than 100 to 200°C (Pacyna and Munch 1991). In my experiments, burning temperatures exceeded those at which Hg is known to volatilize. Therefore my results provide a good estimate of the mass of Hg that would remain after a prescribed burn.

I have estimated the amount of THg emitted from a fire in the boreal ecoregion of Canada using biomass surveys from an upland forest catchment area (Huebert 2002) and from wetlands (Dyck and Shay 1999) at the ELA and my data of the percentage of THg

lost during combustion. Assuming that (1) the area burned consists of approximately 12% wetlands and 88% upland boreal forests, and (2) that above ground vegetation, only foliage and branches up to 2 cm in diameter, and litter and organic–rich soil burn completely, then about 20 g of THg·ha^{-1} could flux into the atmosphere. This estimate is similar to the estimate of Veiga *et al.* (1994) for burned Amazonian forests, of 17.6 g of Hg of Hg·ha^{-1} and about two times higher than that estimated from forest fires in the Brazilian Amazon (de Lacerda 1995).

Implications of burning before flooding

Below I consider the effects of burning on Hg emissions to the atmosphere, greenhouse gas emissions, toxic by-products of burning, costs of controlling prescribed burns, and risks of uncontrolled fire. The natural cycling of Hg has been altered by humans. About $6*10^6$ g of Hg·y^{-1} are naturally emitted from Earth into the atmosphere, and human activities emit about $9*10^8$ to $10*10^{10}$ g of Hg·y^{-1} (Lindqvist and Rodhe 1985; Nriagu and Pacyna 1988). Of these emissions, $6*10^7$ to $3*10^8$ g of Hg·y^{-1} are from combustion of wood products (Nriagu and Pacyna 1988). Forest fires in the Amazon emit 7.8 to 17.6 g of Hg·ha^{-1} to the atmosphere (de Lacerda 1995; Veiga *et al.* 1994), and globally, wild forest fires may contribute up to $5*10^7$ g of Hg·y^{-1} (mean of $2*10^7$ g of Hg·y^{-1}) (Nriagu and Pacyna 1988). This estimate was derived using concentrations of Hg in vegetation from the literature and 70% loss of Hg during forest fires. Results from Friedli et al. (2001, 2003) and this study indicate that the release of Hg during fires can be greater than 70%. Assessing annual emissions of Hg from forest fires is challenging because fires are episodic and highly variable. For example, in Canada 0.74 and 7.28

million ha burned in 1984 and 1989, respectively, and through the 1990's an average of 2.8 million $ha \cdot y^{-1}$ burned (Stokes 2002). Using that average and my estimate of about 20 g of $THg \cdot ha^{-1}$ released from combustion of boreal plants and soil, forest fires in Canada could emit $56*10^6$ g of $Hg \cdot y^{-1}$ to the atmosphere. My estimate for annual Hg emissions from fires in Canada, on an aerial basis, is within the range of Hg emitted annually by biomass burning on a global scale (Nriagu and Pacyna 1988).

Controlled burning of a reservoir site before flooding will increase atmospheric concentrations of Hg and other chemicals. Hg in plants and soil will flux into the atmosphere during combustion, and will subsequently deposit elsewhere, contributing to atmospheric Hg pollution, which may be deposited downwind in terrestrial or aquatic ecosystems. The long residence time of Hg^0 in the atmosphere may allow Hg emissions to travel great distances.

Forest fires are also a source of carbon dioxide, carbon monoxide, methane, nitric oxide, hydrogen cyanide, methyl cyanide, methyl chloride, and particulate matter to the atmosphere (Crutzen and Andreae 1990). The amount of greenhouse gases released during combustion depends on (1) the amount of carbon oxidized and (2) the relative proportion of carbon dioxide to methane. Flooding of soils and vegetation results in anoxic decomposition of organic carbon and the production of methane (Kelly *et al.* 1997), which is 21 times more effective at trapping heat in the atmosphere than carbon dioxide. Forest soils appear to be sinks for methane, but after flooding, submerged soils become a methane source (Bodaly *et al.* accepted). Wetlands are carbon sinks before flooding, and controlled burning would probably not burn wet peat. However, we would need to consider the significance of the rate of greenhouse gas emissions to the

atmosphere and its ability to buffer or adapt to environmental changes. Burning will emit substantial amounts of carbon dioxide to the atmosphere. Flooding unburned organic carbon may not ever mineralize as much carbon as burning. In this case, burning before flooding could load more carbon dioxide into the atmosphere than flooding alone.

If controlled burning is used as a mitigation method to decrease MeHg contamination in flooded ecosystems, there could be at least 5 mg of $MeHg \cdot ha^{-1}$ remaining in the substrate that could be leached into the water column and taken up by aquatic biota and at least 182 mg of $THg \cdot ha^{-1}$ could be available for methylation. Additionally, some by-products of combustion can remain at the surface of Earth and be transported in runoff. Cyanide concentrations in ash after forest fires can reach toxic concentrations, and runoff from these areas can cause fish kills (Barber *et al.* 2003).

A practical implication of controlled burning before flooding is the cost of controlling the fire. Fine fuel would have to be removed from the perimeter of the area to be burned. The perimeter of the burn would also have to be prepared by digging a trench so that the fire would not spread underground. The cost of these procedures has been estimated at 1 million Canadian dollars per ha (R. Schetagne pers. comm.). Clearing and burning the boreal landscape can be extremely expensive, and the risk of losing control of the fire may impede the application of burning before flooding as a MeHg mitigation option.

CONCLUSION

I determined the loss of mass, carbon, THg, and MeHg during controlled burning in 14 species of plants and soil collected from the boreal forest region in northwestern Ontario. After burning, plants lost a mean of 96.3% (92.6 to 98.7) of the mass, 97.8% (94.7 to 99.5) of the carbon, 96.6% (84.5 to 99.5) of the THg, and 94.2% (63.1 to 100.0) of the MeHg. Carbon decreased drastically, which would limit the amount of organic-rich substrate to methylating microorganisms. The mass of THg and MeHg also decreased substantially, which may provide less Hg to microorganisms for methylation and less leaching of MeHg, but at least 182 mg of inorganic $Hg \cdot ha^{-1}$ could still be present, which could become available for methylation. If burning before flooding were used as a mitigation method in the boreal region of Canada, I estimate it could emit about 20 g of $THg \cdot ha^{-1}$ to the atmosphere. One of the environmental consequences of controlled burning before flooding on the cycling of Hg is increased amounts of Hg in the atmosphere, which could travel some distance from the site of the fire and be deposited into other ecosystems. In addition, greenhouse gas emissions would occur with burning. The possibility of losing control of the prescribed burn is a significant concern among environmental managers and the public, especially for communities living in the vicinity of the hydroelectric development. Before controlled burning before flooding could be applied, a considerable amount of research would have to demonstrate that burning before flooding could lower the bioaccumulation of MeHg in aquatic food webs, which is the focus of the next chapter of my thesis.

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LITERATURE CITED

Abernathy, A.R. and Cumbie, D.M. 1977. Mercury accumulation by largemouth bass (*Micropterus salmoides*) in recently impounded reservoirs. Bulletin Environmental Contamination and Toxicology **17**: 595-602.

Allan, C., Heyes, A., Roulet, N., St. Louis, V., and Rudd, J. 2001. Spatial and temporal dynamics of mercury in Precambrian Shield upland runoff. Biogeochemistry **52**: 13-40.

Barber, T., Fuchsman, P., Lutes, C., and Doorn, M. 2003. Aquatic ecological risks due to cyanide releases from biomass burning. Chemosphere **50**: 343-348.

Benoit, J.M., Gilmour, C.C., and Mason, R.P. 2001. The influence of sulfide on solid-phase mercury bioavailability for methylation by pure cultures of *Desulfobulbus propionicus* (1pr3). Environmental Science and Technology **35**: 127-132.

Bishop, K., Lee Ying-Hua, Pettersson, C., and Allard, B. 1995. Terrestrial sources of methylmercury in surface waters: The importance of the riparian zone on the Svartberget Catchment. Water, Air, and Soil Pollution **80**: 435-444.

Bishop, K.H., Lee Ying-Hua, Munthe, J., and Dambrine, E. 1998. Xylem sap as a pathway for total mercury and methylmercury transport from soils to tree canopy in the boreal forest. Biogeochemistry **40**: 101-113.

Bloom, N.S. 1989. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. Canadian Journal of Fisheries and Aquatic Sciences **46**: 1131-1140.

Bodaly, R.A., Hecky, R.E., and Fudge, R.J.P. 1984. Increases in fish mercury levels in lakes flooded by the Churchill River diversion, northern Manitoba. Canadian Journal of Fisheries and Aquatic Sciences **41**: 682-691.

Bodaly, R. A., Strange, N. E., Hecky, R. E., Fudge, R. J. P., and Anema, C. 1987. Mercury content of soil, vegetation, lake sediment, net plankton and forage fish in the area of the Churchill River diversion, Manitoba, 1981-82. Central and Arctic Region Department of Fisheries and Oceans, Winnipeg, Manitoba No. no. 610.

Bodaly, R.A., Rolfhus, K.R., Penn, A.F., Beaty, K.G., Hall, B.D., Hendzel, L.H., Mailman, M., Majewski, A.R., Matthews, K.J.D., Paterson, M.J., Peech Cherewyk, K.A., St. Louis, V.L., Schiff, S.L., and Venkiteswaran, J.J. The use of experimental reservoirs to explore the impacts of hydro-electric developments on methylmercury and greenhouse gas production: The FLUDEX experiment. Environmental Science and Technology. Accepted.

Cox, J.A., Carnahan, J., DiNunzio, J., McCoy, J., and Meister, J. 1979. Source of

Mercury in Fish in New Impoundments. Bulletin of Environmental Contamination and Toxicology **23**: 779-783.

Crutzen, P.J. and Andreae, M.O. 1990. Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles. Science **250**: 1669-1678.

de Lacerda, L.D. 1995. Amazon mercury emissions. Nature **374**: 20-21.

Dyck, B.S. and Shay, J.M. 1999. Biomass and carbon pool of two bogs in the Experimental Lakes Area, northwestern Ontario. Canadian Journal of Botany **77**: 291-304.

Friedli, H.R., Radke, L.F., and Lu, J.Y. 2001. Mercury in Smoke from Biomass Fires. Geophysical Research Letters **28**: 3223-3226.

Friedli, H.R., Radke, L.F., Lu, J.Y., Banic, C.M., Leaitch, W.R., and MacPherson, J.I. 2003. Mercury emissions from burning of biomass from temperate North American forests: laboratory and airborne measurements. Atmospheric Environment **37**: 253-267.

Gill, G.A., Bloom, N.S., Cappellino, S., Driscoll, C.T., Dobbs, C., McShea, L., Mason, R., and Rudd, J.W.M. 1999. Sediment---water fluxes of mercury in Lavaca Bay, Texas. Environmental Science and Technology **33**: 663-669.

Gilmour, C.C., Henry, E.A., and Mitchell, R. 1992. Sulfate stimulation of mercury methylation in freshwater sediments. Environmental Science and Technology **26**: 2281-2287.

Glooschenko, W.A. and Capobianco, J.A. 1978. Metal Content of Sphagnum Mosses from Two Northern Canadian Bog Ecosystems. Water, Air, and Soil Pollution **10**: 215-220.

Hall, B.D., Bodaly, R.A., Fudge, R.J.P., Rudd, J.W.M., and Rosenberg, D.M. 1997. Food as the dominant pathway of methylmercury uptake by fish. Water, Air, & Soil Pollution **100**: 13-24.

Hanson, P.J., Lindberg, S.E., Tabberer, T.A., Owens, J.G., and Kim, K.H. 1995. Foliar exchange of mercury vapor: Evidence for a compensation point. Water, Air, & Soil Pollution **80**: 373-382.

Hauser, B.W. 1973. Modifications to Carlo Erba elemental analyzer for rapid determination of carbon and nitrogen in suspended matter of natural water. Fisheries Research Board of Canadian Technical Reports. No. 412. Winnipeg, Manitoba.

Hecky, R.C., Ramsey, D.J., Bodaly, R.A., and Strange, N.E. 1991. Increased methylmercury contamination in fish in newly formed freshwater reservoir. *Edited by* T. Clarkson and T. Suzuki. Plenum Press, New York.

Heyes, A., Moore, T.R., and Rudd, J.W.M. 1998. Mercury and methylmercury in

decomposing vegetation of a pristine and impounded wetland. Journal of Environmental Quality **27**: 591-599.

Heyes, A., Moore, T.R., Rudd, J.W.M., and Dugoua, J.J. 2000. Methyl mercury in pristine and impounded boreal peatlands, Experimental Lakes Area, Ontario. Canadian Journal of Fisheries and Aquatic Sciences **57**: 2211-2222.

Horvat, M., Liang, L., and Bloom, N.S. 1993. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part 2. Water. Analytica Chimica Acta **282**: 153-168.

Huebert, D. 2002. Experimental Lakes Area Upland Flooding Experiment Vegetation Analysis. Dave Huebert.

Iverfeldt, A. 1991a. Mercury in forest canopy throughfall water and its relation to atmospheric deposition. Water, Air, and Soil Pollution **56**: 553-564.

Iverfeldt, A. 1991b. Occurrence and turnover of atmospheric mercury over the nordic countries. Water, Air, & Soil Pollution **56**: 251-265.

Kelly, C.A., Rudd, J.W.M., Bodaly, R.A., Roulet, N.P., St. Louis, V.L., Heyes, A., Moore, T.R., Schiff, S., Aravena, R., Scott, K.J., Dyck, B., Harris, R., Warner, B., and Edwards, G. 1997. Increases in fluxes of greenhouse gases and methyl mercury following flooding of an experimental reservoir. Environmental Science & Technology **31**: 1334-1344.

Lindberg, S.E., Turner, R.R., Meyers, T.P., Taylor, G.E., and Schroeder, W.H. 1991. Atmospheric concentrations and deposition of Hg to a deciduous forest at Walker Branch Watershed, Tennessee, USA. Water, Air, and Soil Pollution **56**: 577-594.

Lindqvist, O. and Rodhe, H. 1985. Atmospheric mercury - a review. Tellus **37B**: 136-159.

Lodenius, M., Seppänen, A., and Herranen, M. 1983. Accumulation of Mercury in Fish and Man from Reservoirs in Northern Finland. Water, Air, and Soil Pollution **19**: 237-246.

Macalady, J.L., Mack, E.E., Nelson, D.C., and Scow, K.M. 2000. Sediment microbial community structure and mercury methylation in mercury-polluted Clear Lake, California. Applied and Environmental Microbiology **66**: 1479-1488.

Mason, R.P., Fitzgerald, W.F., and Morel, F.M.M. 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. Geochimica et Cosmochimica Acta **58**: 3191-3198.

Mason, R.P. and Lawrence, A.L. 1999. Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore Harbor and Chesapeake Bay, Maryland, USA. Environmental Toxicology and Chemistry **18**: 2438-2447.

Moore, T.R., Bubier, J.L., Heyes, A., and Flett, R.J. 1995. Methyl and total mercury in boreal wetland plants, Experimental Lakes Area, northwestern Ontario. Journal of Environmental Quality **24**: 845-850.

Morrison, K.A. and Thérien, N. 1991. Experimental evaluation of mercury release from flooded vegetation and soils. Water, Air, & Soil Pollution **56**: 607-619.

Morrison, K.A. and Thérien, N. 1995. Fluxes of mercury through biota in the LG-2 reservoir after flooding. Water, Air, and Soil Pollution **80**: 573-576.

Mucci, A., Lucotte, M., Montgomery, S., Plourde, Y., Pichet, P., and Van Tra, H. 1995. Mercury remobilization from flooded soils in a hydroelectric reservoir of northern Quebec, La Grande. 2. Results of a soil resuspension experiment. Canadian Journal of Fisheries and Aquatic Sciences **52**: 2507-2517.

Munthe, J., Hultberg, H., and Iverfeldt, A. 1995. Mechanisms of deposition of methylmercury and mercury to coniferous forests. Water, Air, and Soil Pollution **80**: 363-371.

Munthe, J., Lee, Y.-H., Hultberg, H., Iverfeldt, A., Borg, G.C., and Andersson B. I. 1998. Cycling of mercury and methyl mercury in the Gardsjon catchments. *In* Experimental Reversal of Acid Rain Effects: The Gardsjon Roof Project. *Edited by* H. Hultberg and R. Skeffington. John Wiley & Sons Ltd., pp. 261-276.

Nriagu, J.O. and Pacyna, J.M. 1988. Quantitative Assessment of Worldwide Contamination of Air, Water and Soils by Trace Metals. Nature **333**: 134-139.

Pacyna, J.M. and Munch, J. 1991. Anthropogenic mercury emission in Europe. Water, Air, and Soil Pollution **56**: 51-61.

Raison, R.J., Khanna, P.K., and Woods, P.V. 1985. Canadian Journal of Forest Research **15**: 132-140.

Rasmussen, P.E. 1995. Temporal variation of mercury in vegetation. Water, Air, and Soil Pollution **80**: 1039-1042.

Rasmussen, P.E., Mierle, G., and Nriagu, J.O. 1991. The analysis of vegetation for total mercury. Water, Air, and Soil Pollution **56**: 379-390.

Rea, A.W., Lindberg, S.E., and Keeler, G.J. 2000. Assessment of Dry Deposition and Foliar Leaching of Mercury and Selected Trace Elements Based on Washed Foliar and Surrogate Surfaces. Environmental Science & Technology **34**: 2418-2425.

Regnell, O., Tunlid, A., Ewald, G., and Sangfors, O. 1996. Methyl mercury production in freshwater microcosms affected by dissolved oxygen levels: Role of cobalamin and microbial community composition. Canadian Journal of Fisheries and Aquatic Sciences **53**: 1535-1545.

Richardson, M., Mithchell, M., Coad, S., and Raphael, R. 1995. Exposure to mercury in Canada: a Multimedia analysis. Water, Air, and Soil Pollution **80**: 31-39.

Severson, R.C., Gough, L.P., and Van Den Boom, G. 1992. Baseline element concentrations in soils and plants. Wattenmeer National Park, North and East Frisian Islands, Federal Republic of Germany. Water, Air, and Soil Pollution **61**: 169-184.

Siegel, S.M., Siegel, B.Z., Barghigiani, C., Aratani, K., Penny, P., and Penny, D. 1987. A contribution to the environmental biology of mercury accumulation in plants. Water, Air, and Soil Pollution **33**: 65-72.

St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., and Barrie, L.A. 1995. Wet deposition of methyl mercury in northwestern Ontario compared to other geographic locations. Water, Air, and Soil Pollution **80**: 405-414.

St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., Hall, B.D., Rolfhus, K.R., Scott, K.J., Lindberg, S.E., and Dong, W. 2001. Importance of the Forest Canopy to Fluxes of Methyl Mercury and Total Mercury to Boreal Ecosystems. Environmental Science and Technology **35**: 3089-3098.

Stokes, B.J. 2002. Forest fire management in Canada. <http://www.fire.uni-freiburg.de/iffn/country/ca/ca_7.htm>. Accessed 26 November 2003.

Veiga, M.M., Meech, J.A., and Onate, N. 1994. Mercury pollution from deforestation. Nature **368**: 816-817.

Verdon, R., Brouard, D., Demers, C., Lalumiere, R., Laperle, M., and Schetagne, R. 1991. Mercury evolution (1978-1988) in fishes of the La Grande hydroelectric complex, Quebec, Canada. Water, Air, & Soil Pollution **56**: 405-417.

Yingcharoen, D. and Bodaly, R.A. 1993. Elevated mercury levels in fish resulting from reservoir flooding in Thailand. Asian fisheries science **6**: 73-80.

Zhang, H., Lindberg, S.E., Marsik, F.J., and Keeler, G.J. 2001. Mercury Air/Surface Exchange Kinetics of Background Soils of the Tahquamenon River Watershed in the Michigan Upper Peninsula. Water, Air, and Soil Pollution **126**: 151-169.

Zhang, L.I., Qian, J.-L., and Planas, D. 1995. Mercury concentration in tree rings of black spruce (*Picea mariana* Mill. B.S.P.) in Boreal Quebec, Canada. Water, Air, and Soil Pollution **81**: 163-173.

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TABLES

Table 3.1. Mass and concentrations of total mercury (THg) and methyl mercury (MeHg) in fresh and burned samples of 14 species of plants and composite samples of organic soil ($ng \cdot g^{-1}$ of sample d. w.) and THg and MeHg concentrations standardized to carbon. The percentage of plant mass, carbon, THg, and MeHg that remained after controlled burning are given. Samples were from the Experimental Lakes Area in northwestern Ontario.

Species	Mass			THg			MeHg		
	Fresh	Burned	Left	Fresh	Burned	Left	Fresh	Burned	Left
	(g)		(%)	($ng \cdot g^{-1}$)		(%)	($ng \cdot g^{-1}$)		(%)
Trees									
Betula papyrifera	150	6	4	6.2	11.1	7	0.3	0.5	6
Larix larcinia	121	2	2	29.0	9.4	1	0.6	0.1	0
Picea mariana	593	19	3	12.9	5.4	1	0.2	0.5	9
Pinus banksiana	470	12	2	10.6	3.5	1	0.2	0.2	2
Shrubs									
Alnus crispa	249	18	7	3.5	7.4	15	0.1	0.3	37
Chamaedaphne calyculata	222	10	4	10.7	5.9	2	0.4	0.1	1
Kalmia polifolia	54	2	4	10.5	7.8	3	0.8	0.5	2
Ledum groenlandicum	207	7	3	10.3	5.0	2	0.2	0.2	3
Prunus pensylvanica	256	12	5	4.9	4.0	4	0.5	0.0	0
Salix humilis	290	14	5	9.5	15.6	8	1.3	0.0	0
Vaccinium spp.	146	2	1	11.1	8.8	1	0.4	0.6	2
Bryophytes									
Pleurozium schreberi	270	12	4	51.6	9.4	1	0.8	0.3	2
Polytrichum spp.	205	12	6	36.1	9.1	1	0.3	0.8	15
Sphagnum spp.	151	3	2	20.4	8.3	1	0.5	0.1	0

Table 3.2. THg concentrations from this research and from comparable research papers.

Trees	Tissue	THg ($ng \cdot g^{-1}$ d. w.)	Environment	Location	Citation
Betula papyrifera	Twigs and foliage	6.2	Well-drained boreal forest	ELA, northwestern Ontario	My study
B. papyrifera	Twigs	29		Churchill River, Manitoba	Bodaly et al. 1987
B. papyrifera	Foliage	14		Churchill River, Manitoba	Bodaly et al. 1987
Larix larcinia	Twigs and needles	29.0	Flooded bog	ELA, northwestern Ontario	My study
L. larcinia	Twigs and needles First year growth	10.4	Well-drained, upland	Huntsville, southern Ontario	Rasmussen et al. 1991
Picea mariana	Twigs and needles	12.9	Well-drained boreal forest	ELA, northwestern Ontario	My study
P. mariana	twigs	49.3		Churchill River, Manitoba	Bodaly et al. 1987
P. mariana	needles	20.3		Churchill River, Manitoba	Bodaly et al. 1987
P. glauca	Twigs and needles 1^{st} and 2^{nd} year	13.9	Well-drained upland	Huntsville, southern Ontario	Rasmussen et al. 1991
P. abies	Needles	45.2 s.d. 15.0, n=14 (20 to 80)	Boreal forest, upland podzols	Lake Gårdsjön catchment, Sweden	Iverfeldt 1991 WASP 56:553-564
Pinus banksiana	Twigs and needles	10.6	Boreal forest, well-drained upland	ELA, northwestern Ontario	My study
P. banksiana	Twigs	9.5		Churchill River, Manitoba	Bodaly et al. 1987
P. banksiana	Needles	<5.0		Churchill River, Manitoba	Bodaly et al. 1987

Table 3.2 continued.

Shrubs	**Tissue**	**THg ($ng \cdot g^{-1}$ d. w.)**	**Environment**	**Location**	**Citation**
Alnus crispa	Twigs and foliage	3.6		ELA, northwestern Ontario	This research
Alnus spp.		12.8		Churchill River, Manitoba	Bodaly et al. 1987
Ledum groenlandicum	Twigs and foliage	10.3	Forest among jack pine and black spruce	ELA, northwestern Ontario	This research
L. groenlandicum	Twigs	17.0		Churchill River, Manitoba	Bodaly et al. 1987
L. groenlandicum	Foliage	18.0		Churchill River, Manitoba	Bodaly et al. 1987
Salix humilis	Twigs and foliage	9.6		ELA, northwestern Ontario	This research
Salix spp.	twigs	10.0		Churchill River, Manitoba	Bodaly et al. 1987
Salix spp.	foliage	12.8		Churchill River, Manitoba	Bodaly et al. 1987
Salix repens	Leaves from current year's growth	36 to 76	Vegetated sand dunes (grasses and shrubs)	Frisan Islands, Germany	Severson et al. 1992

Table 3.2 continued.

Bryophytes	**Tissue**	**THg ($ng \cdot g^{-1}$ d. w.)**	**Environment**	**Location**	**Citation**
Pleurozium schreberi		51.6	Growing beneath *P. mariana*	ELA, northwestern Ontario	This research
Pleurozium spp.		41.5	Growing beneath *P. mariana*	ELA, northwestern Ontario	Moore et al. 1995
P. schreberi		79.8	Growing beneath *Chamaedaphne calyculata*	ELA, northwestern Ontario	Moore et al. 1995
Hylocomium splendens		86 to 170	Vegetated sand dunes collected from dune crest	Frisan Islands, Germany	Severson et al. 1992
Sphagnum spp.		20.4	peat hummocks	ELA, northwestern Ontario	This research
Sphagnum spp		36.6	peat hummocks	ELA, northwestern Ontario	Moore et al. 1995
Sphagnum spp		46.7 to 92.5	Hollows or pools of water	ELA, northwestern Ontario	Moore et al. 1995
Sphagnum spp		57.4		Churchill River, Manitoba	Bodaly et al. 1987
Sphagnum spp	Top 10 cm, mostly living, some brown	6100	Low shrub treed bog	Poter Lake, Caribou Range, NWT	Glooschenko & Capobianco 1978
Sphagnum spp	Top 10 cm, mostly living, some brown	8300	Open bog to low shrub bog and treed bog	Kinoje Lake, northern Ontario	Glooschenko & Capobianco 1978

Table 3.2 continued.

Soil	Composition	THg ($ng \cdot g^{-1}$ d. w.)	Environment	Location	Reference
	Composite of litter, humus, and 10 cm of organic soil	162	20 year, old well drained, upland, jack pine forest	ELA, northwestern Ontario	This study
	Living moss, lichen, and broad leaf litter Organic soil	96 99	Forest catchment	Churchill River, Manitoba	Bodaly et al. 1987
	Litter Humus Organic soil	146 109 28	Forest catchment area	Lake Gårdsjön, Sweden	Munthe et al. 1998
	Surface litter layer	104		ELA, northwestern Ontario	St. Louis et al. 2001
	1-2 cm thick organic soil with no litter component	68	Vegetated sand dunes collected from dune crest	Frisan Islands, Germany	Severson et al. 1992
	Clay to sandy loams 3-5 cm below the soil surface	24 25 22	 Geological anomaly Volcanic	Columbia Icefield, Alberta Prince George, British Columbia Manoa, Honolulu, Hawaii	Siegel et al. 1987
	Coniferous litter Deciduous litter	30 59		Various locations throughout the USA	Friedli et al. 2001

CHAPTER 4: EFFECTS OF BURNING BEFORE FLOODING ON METHYL MERCURY (MeHg) AND GREENHOUSE GAS (GHG) CONCENTRATIONS

ABSTRACT

In hydroelectric reservoirs, fish accumulate high levels of methyl mercury (MeHg), which is highly toxic to fish and fish consumers. After flooding, decomposition of terrestrial vegetation and soil releases carbon and depletes dissolved oxygen, two conditions which promote microbial conversion of inorganic mercury (Hg) to MeHg. MeHg transfers through the food web, mainly via dietary exposure, and biomagnifies in predaceous organisms. Fish are the main source of MeHg to humans and the main cause of fish consumption advisories, yet after 30 years of research, mitigation approaches remain elusive. A replicated field experiment was used to investigate the effects of burning vegetation and soil before flooding. Vegetation and soil were added to limnocorrals in the following combinations: unburned vegetation and soil (Fresh treatments), burned vegetation and unburned soil (Partial Burn treatments), and burned vegetation and burned soil (Complete Burn treatments). Controls had no added vegetation or soil. During combustion, about 96.6 and 94.2% of the Hg and MeHg, respectively, was lost from vegetation and 78.8 and 81.8% of THg and MeHg, respectively, was lost from soil. Aqueous concentrations of THg and MeHg were highest in Fresh treatments and considerably lower in Partial Burn treatments. THg and MeHg in Complete Burn treatments were lower than in Partial Burn treatments and similar to Controls. Differences in concentrations of MeHg in zooplankton, Chironomid larvae, and emerging insects were consistent among treatments, but did not follow aqueous

concentrations. On the final sample date, MeHg concentrations in biota of Controls and Partial Burn treatments were greater than in Complete Burn and Fresh treatments. The lack of relationship between MeHg in biota and MeHg in water may have been due to modification of the bioavailability of MeHg by dissolved organic carbon (DOC). The bioaccumulation factors ($[MeHg]_{biota}/[MeHg]_{water}$) of MeHg in zooplankton, Chironomid larvae, and emerging insects were inversely correlated with DOC ($r^2 = 0.52$, 0.72, and 0.89, respectively). Although burning before flooding decreased MeHg concentrations in the water, it did not ameliorate MeHg accumulation in the lower food web.

Another component of my study was to examine the effects of burning before flooding on greenhouse gas production. Hydroelectric reservoirs are sources of carbon dioxide (CO_2) and methane (CH_4) to the atmosphere. These gases trap heat in the troposphere and contribute to accelerated rates of global warming. Weekly to biweekly measurements showed that partial pressures of CO_2 and CH_4 in the surface water of Burned treatments were up to 40 and 97% lower, respectively, than in Fresh treatments.

INTRODUCTION

Flooding terrestrial landscapes results in elevated Hg contamination of fish (Abernathy and Cumbie 1977; Bodaly and Fudge 1999; Bodaly *et al.* 1984; Lodenius *et al.* 1983; Rehulka 2002; Verdon *et al.* 1991; Yingcharoen and Bodaly 1993). Reservoirs are often depended upon for marketing fish and fish sustenance by indigenous peoples. Hence, the risk of Hg exposure through consumption of fish from new reservoirs is of concern.

Consumption of fish is the most important route of Hg exposure to humans (Richardson *et al.* 1995). The predominant form of Hg in fish is monomethyl Hg, hereafter called methyl Hg (MeHg) (Bloom 1992). MeHg poisoning affects the central nervous system in vertebrates, inducing symptoms ranging from subtle learning difficulties to death (Clarkson 1990; Weihe *et al.* 1996; Wheatley and Wheatley 2000), however, exposure of MeHg from fish consumption may have less severe risks than previously thought (Axtell *et al.* 2000; Davidson *et al.* 2000; Myers *et al.* 2000). Fish in reservoirs often contain MeHg concentrations in their muscle tissue that exceed the acceptable limit for marketing fish in Canada (0.5 $\mu g \cdot g^{-1}$).

Flooding terrestrial landscapes causes increased rates of Hg methylation (Bodaly *et al.* accepted; Hecky *et al.* 1991; Heyes *et al.* 2000; Kelly *et al.* 1997). After flooding, inundated organic carbon decomposes and may deplete the water of oxygen, release carbon, and remobilize Hg. Under these conditions, sulphate reducing bacteria (SRB) convert inorganic Hg to MeHg (Choi and Bartha 1994; Gilmour *et al.* 1992). Further, methylation of Hg may be greatest in organic-rich sediment (Compeau and Bartha 1985; Choi *et al.* 1994; Macalady *et al.* 2000; Pak and Bartha 1998), such as flooded soils. For

example, dissolved and particulate MeHg concentrations increased within two one month of impoundment of the Laforge-40 reservoir in northern Québec and within one year zooplankton MeHg concentrations increased (Plourde *et al.* 1997). In an experimentally flooded wetland pond, concentrations of MeHg in zooplankton increased within weeks of flooding (Paterson et al. 1998).

In addition to MeHg, substantial production of greenhouse gases (GHGs) may follow flooding of terrestrial landscapes (Duchemin *et al.* 2002; Kelly *et al.* 1997; St. Louis *et al.* 2000; Bodaly *et al.* accepted). This is because flooding lessens the photosynthetic sequestration of carbon dioxide by terrestrial vegetation and increases decomposition. Aquatic primary production in new reservoirs may be substantial. Sub-aqueous decay of organic carbon produces carbon dioxide (CO_2) and methane (CH_4). Although reservoirs were once thought to be neutral with respect to carbon cycling, they contribute an important proportion of human generated GHGs to the atmosphere (St. Louis *et al.* 2000).

The purpose of my experiment was to examine the effects of controlled burning of vegetation and soil before flooding on MeHg concentrations in water and aquatic biota. I also examined the effect of burning on concentrations of GHGs. I conducted my experiment using limnocorrals. Combustion of terrestrial soils and vegetation may minimize production of MeHg in new reservoirs by 1) decreasing the amount of decomposable organic carbon that supports methylating bacteria, (2) causing less oxygen depletion, and therefore decreasing the production of MeHg by anaerobic microorganisms, and (3) any remaining charcoal may sequester THg and MeHg. GHG emissions may be lowered because a greater proportion of decomposition may occur

under oxic conditions, which may decrease the proportion of CH_4 in greenhouse gas emissions from flooded environments. This is desirable because CH_4 is a more potent GHG than CO_2.

MATERIALS AND METHODS

Location

The Experimental Lakes Area (ELA) is located on the Precambrian Shield 70 km south-east of Kenora in northwestern Ontario (49°40' N, 93°43' W). This area has many small glacially formed lakes surrounded predominantly by jack pine (*Pinus banksiana*) forest. In this study, limnocorrals were set up on the two-metre contour of the eastern-most bay in Lake 240, a natural oligotrophic lake with a surface area of 44 ha.

Design

I designed my experiment to test the following hypotheses: (1) H_o: burning before flooding will not affect the level of MeHg contamination in flooded systems (2) H_o: after burning, the remaining charcoal will not sequester MeHg and (3) H_o: burning before flooding will not affect the partial pressures of CO_2 and CH_4. To test the effects of controlled burning before flooding, I randomly assigned combinations of unburned (hereafter referred to as fresh) and burned terrestrial vegetation and soil to limnocorrals. Some limnocorrals were not treated and served as Controls to which I compared treatment effects. The four treatments applied in triplicate were:

- Controls: nothing added

- Fresh treatments: fresh vegetation and fresh soil added to simulate flooding of natural terrestrial ecosystems.
- Partial Burn treatments: burned vegetation and fresh soil added to simulate flooding of terrestrial ecosystems that had undergone a forest fire that burned only above-ground vegetation, and not organic soil.
- Complete Burn treatments: burned vegetation and burned soil added to simulate flooding of terrestrial ecosystems that had undergone a forest fire that burned both above-ground vegetation and organic soil.

Materials

During the summer of 2001, 12 limnocorrals were used. The limnocorrals were two metres in diameter and two metres deep. Styrofoam collars covered with vinyl floated on the surface of the water and were anchored in place. The collars supported cylindrical walls made of impermeable woven plastic. The walls were sealed to the sediment surface preventing circulation of enclosed water with the lake. The water inside the limnocorrals was open to the bottom sediment. During limnocorral installation, the walls were tied to the collars for transport to the site. The collars were anchored in a row along the two metre deep contour in the east bay of L240. The walls were lowered and pinned after dusk in an attempt to enclose more zooplankton than might have been the case during the day. The next day, SCUBA divers placed bags of sand around the base of the walls in a manner to minimize the disturbance of the enclosed lake sediment. Once in place, the limnocorrals were fished intensively with gill nets and minnow traps to remove any fish that may have been enclosed in the installation process. Small pike and crayfish

were removed. No fish were introduced to the limnocorrals. 5 μCu of tritiated water (^3H) was added to each limnocorral to monitor the seal of the limnocorrals and ensure that there was no water exchange with the host water body.

Selection of vegetation

I added vegetation and soil to the limnocorrals that represented the average mass of vegetation and soil in a 2 m diameter area at ELA. The type and biomass of vegetation added to the limnocorrals was based on two previous vegetation surveys conducted at ELA. One survey was of wetland environments including open bogs and communities with low to high density of shrubs (Dyck and Shay 1999). The second survey was of upland mixed forest consisting predominantly of *P. banksiana* and *Betula paperifera* (Huebert 2002). Only the main species were used to represent these communities. The mass of the vegetation in dry weight, reported in Dyck and Shay (1999) and Huebert (2002), was converted to wet weight. I estimated a conversion factor by drying 100 g of every species of vegetation at 80°C until the weight was constant. The wet weight of vegetation was then scaled to the area of the limnocorrals (3.14 m^2). I multiplied the biomass of each species from the upland vegetation survey by 88% and from the wetland vegetation survey by 12%. These percentages were roughly estimated to represent the proportion of upland to wetland area that could be flooded by a hydroelectric development in the Canadian boreal region.

Collection of vegetation and soil

Vegetation was collected using steel pruning shears for woody vegetation and bagged in new polyethylene bags. Vegetation was weighed to the nearest gram. The vegetation added to Partial and Complete Burn treatments was burned in metal cans with propane torches at more than 800°C. The ash and charcoal were left in the metal cans to cool before they were transferred into plastic garbage cans.

Organic soil and litter were collected from one site in a well-drained forest in the same location as the upland vegetation survey (Huebert 2002). Soil was collected with metal shovels and transported in new plastic garbage cans. The volume of soil removed was representative of a 2.8 cm thick soil layer covering 88% (an estimate of the proportion of upland area in the boreal region of Canada) of the limnocorral area. The soil for Complete Burn treatments was dried in the sun on a plastic tarpaulin and burned at 600 to 650°C with propane torches on sheet metal, where it was allowed to cool before it was transferred back into the plastic garbage cans. Separate samples of vegetation and soil were collected for analysis. Fresh and burned samples were frozen in polyethylene bags.

Addition of vegetation and soil to limnocorrals

Treatments were randomly assigned to the limnocorrals. Fresh vegetation and soil were evenly distributed to the surface of the limnocorrals. Most of the material sunk rapidly, and woody species were pushed down with oars and left to saturate and sink, which occurred within the first week. All of the burned vegetation was mixed with lake water and poured into the surface of the limnocorrals, and the burned soil was poured

slowly and evenly across the surface. Most of the burned material sank right away and some particles remained in suspension.

Collection of water, sediment, and biota from limnocorrals

Before treatment addition, limnocorrals were sampled for aqueous THg, MeHg, and water chemistry. Treatments were added on June 27th 2001. The response of MeHg was monitored biweekly in surface water, sediment, periphyton, and zooplankton; benthic invertebrates were collected on the final sampling date; emergent insects were collected every few days. The sampling dates for Hg in water after treatment addition were: June 26th (time zero), July 4th (1 week), July 18th (3 weeks), August 1st (5 weeks), August 16th (7 weeks), August 30th (9 weeks), and September 11th (11 weeks). Unfiltered water samples for Hg were collected at 10 cm depth. The "clean-hands dirty-hands" protocol was used (St. Louis *et al.* 1994). Water was transported in Teflon bottles sealed in two Ziploc bags within two polyethylene bags, each sealed with twist ties. These were placed within a plastic cooler which was in turn sealed within two large polyethylene bags each sealed with twist ties. Sampling was done from an aluminum boat. At the sample site, Teflon sample bottles sealed within two Ziploc bags were arranged on the inside of the cooler lid. If zooplankton or particles of charcoal or vegetation were observed, the water was released and re-sampled. Water samples for MeHg were frozen in a freezer designated for low-level Hg samples. THg water samples were acidified with ultra-clean hydrochloric acid.

Water samples for chemical analysis were taken at the same time as water samples for Hg. Acid-washed high-density polyethylene bottles were rinsed three times

with lake water before filling at 10 cm depth. These samples were submitted to the ELA chemistry laboratory and analyzed for suspended particulate matter, major nutrients, acidity, and major anions according to Stainton *et al.* (1977).

Sediment cores were collected biweekly, on the same week that water samples were collected. A three metre long piece of polycarbonate pipe with a suction device was fitted with 24 cm sections of polycarbonate pipe. The suction was open while the pipe was lowered from the boat into the sediment, then closed and gently lifted to the surface where the coring tube was plugged with a rubber stopper, suction released, and the coring tube was removed from the three metre pipe and capped. Sediment cores were generally 15 to 20 cm deep with water filling the headspace. One core from each limnocorral was placed in a rack within a Coleman cooler. Sediment cores were transported to the ELA laboratory where they were described according to grain size and colour by visual inspection. Sediment cores were slowly extruded from coring tubes by fitting the coring tube over an erect graduated dowel topped with a silicone stopper. In ambient conditions, black surface sediment was spooned with an acid washed plastic spoon off the top and bagged, and then each successive 2-cm layer was placed into separate labeled bags. Sediment samples were frozen, transported to Winnipeg and sent to Flett Research Limited for MeHg analysis only.

To allow for the development and collection of periphyton, four strips of the same material as the limnocorral walls were suspended in each limnocorral from a natural cedar plank and weighted on the end with rocks. On the week of water sampling, one periphyton strip was collected from each limnocorral. Clean gloves were used. The strips were gently cut from the plank with scissors and slowly lifted out of the water

while carefully fitting it into a large Ziploc bag that was held open by a second person. The samples were transported to the ELA laboratory in a cooler. Periphyton (biofilm) was first rubbed off manually wearing clean gloves for each strip, scraped and scrubbed with an acid-washed ruler and a toothbrush, and rinsed with deionized water into an acid-washed 1000 mL glass beaker. The area of the collection strips was measured before discarding. Each sample was measured for volume, shaken thoroughly, and then sub-sampled for bacteria and algal composition, and preserved with 2% formalin and 2% Lugol's, respectively. Samples were transferred from the beaker into Ziploc freezer bags and frozen for later analysis of MeHg only.

Fish accumulate most of their MeHg burden from their diet (Hall *et al.* 1997). Accumulation of MeHg in the lower food web reflects the bioavailability of MeHg to fish. Concentrations of MeHg in zooplankton are variable and may contain 29 to 91% MeHg as THg (Watras and Bloom 1992). Analyzing MeHg in the lower food web provides important information regarding its availability to fish. I used zooplankton, Chironomid larvae, and emerging insects as indicators of MeHg bioavailability to higher trophic levels because my 2-metre diameter limnocorrals were insufficient to support enough fish for sampling.

Zooplankton in the limnocorrals were sampled every 2 weeks using a 150 μm mesh conical sweep net and drained into Whirlpac bags. No more than 10% of the zooplankton biomass in each limnocorral was removed during each sampling event. Samples from Controls rarely contained sufficient material for MeHg analysis. Zooplankton samples often contained a high proportion of suspended vegetation fragments and charcoal, which had to be removed before Hg analyses. Samples were

transferred from Whirlpac bags into acid-washed Teflon Petri dishes, and organisms were picked from the sample using acid-washed Teflon coated tweezers and 7 mL polyethylene transfer pipettes to separate zooplankton from particulate matter.

On the final sample date, samples of benthic invertebrates were collected using a Ponar dredge. Three dredge samples were collected from each limnocorral which were passed through various sieve sizes from 12.7 mm to 250 μm and picked from water and sediment in the laboratory. Only Chironomid larvae were sufficiently abundant for Hg analysis in every limnocorral.

Floating traps that covered 0.46 m^2 were deployed on the surface of each limnocorral to trap emerging insects within no-see-um mesh. Insects captured in these traps were collected live using a portable vacuum, frozen, transferred into Whirlpac bags, and stored frozen. Samples collected over two week periods were amalgamated to attain enough biomass for MeHg analysis.

Temperature and oxygen profiles were taken three times each week at 25 cm intervals beginning from the surface using an YSI Model 58 oxygen and temperature probe and meter.

Preparation of samples for analysis of Hg

All frozen samples were transported in coolers to the Freshwater Institute in Winnipeg, Manitoba. Vegetation and soil samples and periphyton samples were weighed before being freeze dried, and then reweighed and ground using a stainless steel electric grinder. Zooplankton, Chironomid larvae, and emerging insects were freeze dried, transferred into trace metal clean aluminum weigh boats with an acid rinsed metal scoop,

weighed to the nearest milligram, and transferred into acid washed conical Teflon vials. Prepared samples were sent to Flett Research for MeHg analysis.

Analysis of THg and MeHg

At Flett Research Limited, samples were analysed for THg and MeHg by cold vapour atomic fluorescence spectroscopy (CVAFS). Preparation procedures differed for aquatic organisms, lake sediment, soil, and water. Five to ten milligram samples of zooplankton, Chironomid larvae, and emergent insects were digested overnight in 300 to 500 μL of KOH/MeOH at 70°C. Periphyton samples were digested in potassium hydroxide and methyl hydroxide at 75°C overnight, distilled in 45 mL deionized water. Approximately 300 mg of homogenized lake sediment sample was acidified with KCl/H_2SO_4 and distilled in approximately 45 mL of deionized water. CH_2Cl_2 was used to extract MeHg from approximately 50 mg of Fresh or Burned soil using KBr and $CuSO_4$ and a sub-sample of CH_2Cl_2 was evaporated in deionized water. Approximately 45 mL of water sample was acidified with KCl/H_2SO_4 and distilled. Aliquots of each sample were ethylated in solution using sodium tetraethyl borate. Ethylmethyl Hg was purged from the solution with Hg-free nitrogen and collected on Tenax traps. To separate ethylmethyl Hg from Hg^0 and diethyl Hg, traps were heated and purged with UHP argon onto a GC column. MeHg was reduced to Hg^0 and analysed in a Brooks-Rand CVAFS model-2 collector (Horvat *et al.* 1993; Liang *et al.* 1994).

Analysis of carbon

The chemistry laboratory in the Freshwater Institute analyzed the carbon content of periphyton and sediment samples. Methods of analysis were modified from Hauser (2001) and Stockner and Armstrong (1971). Samples were combusted at 950 to 975°C in an oxygen and helium atmosphere. Combustion products were transported in a helium gas stream. Nitrous oxide was reduced to nitrite. Excess oxygen was removed, and then water and carbon dioxide were removed sequentially. Carbon was measured on a high precision thermal conductivity detector on a Control Equipment Corporation Model 240-XA Elemental Analyzer. The detection limit of carbon was 1000 $\mu g \cdot L^{-1}$ and the standard deviation was 30 $\mu g \cdot L^{-1}$.

Analysis of greenhouse gases

One sample of water for analysis of the partial pressure of CO_2 (pCO_2) and CH_4 (pCH_4) was collected from 10 to 20 cm below the surface of each limnocorral in 160 mL glass serum bottles by pushing an 18 gauge stainless steel needle into the submerged rubber cap (reviewed by Matthews 2002). Before collection, the bottles were heated to 56°C for 12 hours, had 8.9 g of potassium chloride preservative added, and were capped with butyl stoppers. Air was evacuated from the bottles and 10 mL of ultra-high purity N_2 gas was injected. At the time of collection, I recorded the atmospheric pressure and water temperature. pCO_2 and pCH_4 were analyzed on a Varian 3800 gas chromatograph (GC) by flame ionization detection. Sample bottles were agitated to equilibrate the liquid and gas phases and a sub-sample of the gas was injected into the GC. The GC was calibrated with standards and duplicate analyses were performed on every tenth sample.

pCO_2 and pCH_4 were corrected for atmospheric pressure and surface water temperature (C. Matthews pers. comm.).

Analysis of tritium activity

5 μCi of tritium was added to the limnocorrals on June 11th from 20 mL glass vials, which were rinsed in enclosed water three times. Tritium was mixed into the enclosed water using oars. Samples were collected every week from the surface water of the lake at two sites outside the limnocorrals and from two sites within each limnocorral using a 50 mL disposable glass pipette. 20 ml of sample water was transported in borosilicate scintillation vials to the ELA chemistry laboratory. To each vial, scintillation cocktail was added, and with the cap secured, the vials were agitated. The vials were placed in scintillation counter racks and left in the dark for at least four hours. Samples were analyzed on a Packard Tri-Carb Liquid Scintillation Analyzer Model 2100TR/2300TR.

Statistical analysis of data

Data analysis involved several statistical procedures. After analysis of variance, means from a single sample date were compared using the Tukey studentized multiple comparison procedure at α=0.5. The Tukey multiple comparison procedure tests all pairwise comparisons of factor level means. In the cases where samples were not available from one or more limnocorrals, the Tukey multiple comparison procedure was used. This method is conservative to account for differences in treatment sample sizes.

Since there was a treatment by time interaction, the Statistical Analysis System (SAS) for mixed models was used to analyze the variance of the THg and MeHg repeated measures data. The mixed model specifies the structure of the covariance matrices. Data were transformed to a univariate mode and log transformed. Treatments and time were fixed and random variables, respectively. The general linear mixed model assumes equal variance and covariance of each observation, also called the Huynh-Feldt condition or compound symmetry. Compound symmetry occurs when "a set of orthonormal contrasts of repeated measures variables have spherical covariance matrix; they are independent and have equal variances" (Littell *et al.* 1996). This condition must be met for univariate analysis of variance. The test for sphericity was used to verify this condition using the general linear model command (proc glm) and the summary statement (printe). The correlation between treatments decreases with each successive time interval indicating an interaction, and the possibility of error by the univariate assessment. Therefore the covariance structure of the mixed model was specified as "unstructured" using the proc mixed command and the repeated statement to validate the inferences about within-subject fixed effects.

RESULTS

Biomass and Hg added in vegetation and soil with each treatment

Each treatment consisted of a combination of vegetation and soil, either fresh or burned. I weighed the biomass of each species of vegetation added as treatments that totaled 10 712 g fresh and 183 g burned. Soil had a mass of 61 600 g fresh and 36 313 g

burned. THg and MeHg were analyzed in one sample of each species of vegetation once in fresh and burned samples (Table 4.1). Fresh treatments received the most THg and MeHg, and Partial Burn treatments received only slightly less than Fresh treatments (Table 4.2). Complete Burn treatments received much less THg and MeHg than Fresh treatments, and Controls had no added THg or MeHg. Mean THg concentrations in fresh (162 $ng \cdot g^{-1}$) and burned (47 $ng \cdot g^{-1}$) soil were not significantly different ($p<0.52$). MeHg in soil was below the detection limit in two of the three samples and the third sample contained 1.85 and 0.57 $ng \cdot g^{-1}$ before and after burning, respectively.

Hg in response variables

THg in water

In unfiltered surface water, concentrations of THg were lowest in Controls and greatest in Fresh treatments (Figure 4.1). The THg concentrations in Fresh treatments peaked at 7.3 $ng \cdot L^{-1}$ three weeks after treatment addition. Fresh treatments and Partial Burn treatments were highly significantly different from all other treatments ($p<0.0001$and $p<0.001$, respectively) (Table 4.3). Only Complete Burn treatments and Controls did not differ significantly.

MeHg in water

MeHg concentrations in unfiltered water ranged from a maximum of 0.9 $ng \cdot L^{-1}$ in Fresh treatments to a low of 0.1 $ng \cdot L^{-1}$ in the Controls (Figure 4.2). Concentrations of MeHg in Fresh treatments were greatest three weeks after treatment. MeHg concentrations in Fresh treatments were much greater than in all other treatments for the

first three sample times, but then became similar to Partial Burn treatments. I did not sample all limnocorrals for aqueous MeHg before treatment addition. Limnocorrals were randomized after the initial sample collection. It turns out that no Fresh treatments were sampled for MeHg at time zero. Statistical results for the MeHg data indicate that similar trends are present as in the THg data. Fresh treatments were highly significantly different from all other treatments ($p<0.0001$) (Table 4.3), and Partial Burn treatments were significantly different from Complete Burn treatments and Controls ($p<0.001$). There was no significant difference in aqueous MeHg concentrations between Complete Burn treatments and Controls.

MeHg in zooplankton

Concentrations of MeHg in zooplankton from Partial Burn treatments were higher than those in Complete Burn treatments on all sample dates (Figure 4.3). The highest mean concentration measured in zooplankton was 178 +/- 30 ng MeHg·g^{-1} in Partial Burn treatments on August 15th, about three weeks after peak MeHg concentrations were measured in surface water. Quantities of zooplankton obtained from Fresh treatments on August 1st and 15th were insufficient for analysis. Mean MeHg concentrations in Complete Burn treatments and Controls were also greatest on August 15th. Zooplankton concentrations decreased to a mean of 50 ng MeHg·g^{-1} or less in all treatments by September 19th, at which time surface water contained less than 0.2 ng MeHg·L^{-1} in all treatments. Final concentrations of MeHg in zooplankton did not follow the trends observed on August 15th. Rather, Controls and Partial Burn treatments had significantly greater concentrations than Fresh and Complete Burn treatments ($p<0.01$).

MeHg in Chironomid larvae

At the end of the experiment, MeHg concentrations in Chironomid larvae were higher in the Partial Burn and Control treatments (about 30 $ng \cdot g^{-1}$ d. w.) than in the Fresh (13 $ng \cdot g^{-1}$) and Complete Burn treatments (10 $ng \cdot g^{-1}$). Mean MeHg concentrations in Chironomid larvae also did not follow the trend of MeHg concentrations in water. Levels of MeHg were significantly greater ($p=0.003$) in Controls and Partial Burn treatments than in Fresh and Complete Burn treatments (Figure 4.4).

Emerging insects

Composite samples of emerging insects that were all dipterans, and mostly Chironomids, had mean MeHg concentrations that were, from lowest to highest, Fresh treatments, Complete Burn treatments, Partial Burn treatments, and Controls on the week of July 25th (Figure 4.5). The Partial and Complete Burn treatments were similar in concentration (~80 ng MeHg$\cdot g^{-1}$ d. w.). In July, only the Fresh treatment was significantly lower than Controls ($p<0.05$) using the conservative Tukey studentized multiple comparisons procedure because the treatment sample sizes were different. On the final sample date, Fresh and Complete Burn treatments contained little MeHg (~20 ng MeHg$\cdot g^{-1}$ d. w.) and Partial Burn treatments and Controls were relatively high in MeHg (~60 ng MeHg$\cdot g^{-1}$ d. w.). These results are similar to that seen for Chironomid larvae in September; however, there were no significant differences in MeHg concentrations in emerging insects among treatments on the final date ($\alpha=0.05$).

Bioaccumulation factors of MeHg in biota

MeHg in aquatic biota is often reported as a ratio of the concentration in biota to that in the water column, called the bioaccumulation factor (BAF) (Figure 4.6). The BAF of MeHg in zooplankton was greatest in Controls and then in Partial Burn treatments and the lowest BAFs were in the Fresh and Complete Burn treatments. BAFs for Chironomid larvae were, from highest to lowest, Controls, Partial Burn treatments, Complete Burn treatments, and Fresh treatments. BAFs of Chironomid larvae followed the same trend as zooplankton.

Dissolved organic carbon

DOC increased in Fresh treatments to about 2 000 $\mu mol \cdot L^{-1}$ three weeks after treatment addition (Figure 4.7). Thereafter, it decreased but remained elevated relative to other treatments. Concentrations of DOC also increased in Partial Burn and Complete Burn treatments, but only to about 900 $\mu mol \cdot L^{-1}$, where they remained for the duration of the experiment. Controls had fairly consistent concentrations of DOC (600 $\mu mol \cdot L^{-1}$). I compared the mean concentrations of DOC from weeks in which biota were analyzed using Tukey's multiple comparison procedure. On July 25th mean DOC concentrations in Fresh treatments were significantly higher than all other treatments ($p<0.001$). Partial Burn treatments, Complete Burn treatments, and Controls did not differ significantly. On September 15th, mean concentrations of DOC in Fresh treatments were still significantly higher than in all other treatments ($p<0.001$), Partial and Complete Burn treatments were not different from each other, and Controls were significantly lower from all other treatments ($p<0.001$).

The influence of DOC on MeHg concentrations in biota

The absence of any large changes in MeHg concentrations in biota after the addition of fresh vegetation was surprising. Previous studies have shown large increases in MeHg in biota after flooding (Bodaly et al. 2003; Hecky et al. 1991; Kelly et al. 1997). Because DOC is well known to depress MeHg bioaccumulation, I investigated the possibility that MeHg uptake by biota in my limnocorrals was strongly modified by the large increases in DOC concentrations. Regression analyses of DOC concentrations against the BAFs for zooplankton, Chironomid larvae, and emerging insects had r^2 of 0.53, 0.72, and 0.89, respectively (Figure 4.8). MeHg bioaccumulation was lower in mesocosms with higher DOC.

MeHg in sediment

In sediment samples, only the organic-rich surface sediment was analyzed for MeHg. This material was dark brown to black and liquid in consistency. It ranged from 5 to 10 mm in thickness. The composition of the surface sediment varied between treatments. It contained relatively more clastic material in Controls and Complete Burn treatments. The surface sediment in Complete Burn treatments was charcoal grey in colour. Partial Burn and Fresh treatments had organic-rich surface sediment, but none of the added soil was collected. The surface sediment in Fresh treatments often contained recognizable foliage. The high variability within treatments is due to the heterogeneity of the sediment and the uneven distribution of the material added.

Concentrations of THg were greatest in Fresh treatments (12.7 +/- 1.8 ng $THg \cdot g^{-1}$ d. w.) and were greater in Complete Burn (4.7 +/- 1.5 ng $THg \cdot g^{-1}$ d. w.) than Partial Burn treatments (7.7 +/- 1.2 ng $THg \cdot g^{-1}$ d. w.). Controls contained 5.0 +/- 0.6 ng $THg \cdot g^{-1}$. Mean THg concentrations in Fresh treatments were significantly higher than in Partial Burned treatments and Controls ($p<0.01$).

Mean MeHg concentrations in the top layer of sediment on August 8th (day 220) were lowest in Controls (0.15 +/- 0.07 ng $MeHg \cdot g^{-1}$ d. w.) and greatest in Fresh treatments (0.92 +/- 0.25 ng $MeHg \cdot g^{-1}$ d. w.). Partial and Complete Burn treatments contained two-thirds (0.78 +/- 0.34 ng $MeHg \cdot g^{-1}$ d. w.) and one-third (0.33 +/- 0.07 ng $MeHg \cdot g^{-1}$ d. w.), respectively, of that in Fresh treatments. There was no significant difference among treatments ($p=0.12$).

MeHg in periphyton

On July 25th, mean MeHg concentrations in periphyton were not significantly different (Tukey's studentized multiple comparison) (Figure 4.9). On September 9th, mean concentrations of MeHg in periphyton were greatest in Partial Burn treatments, followed closely by Fresh treatments, and then Complete Burn treatments and Controls, which both had relatively little MeHg. Fresh and Partial Burn treatments were significantly higher than Complete Burn treatments and Controls ($p<0.001$). In addition, MeHg in periphyton was much higher in the Fresh and Partial Burn treatments as compared to July, but not in Complete Burn treatments and Controls. This pattern is much different from that in water and biota. In September, bioconcentration factors

(BCFs) of MeHg in periphyton were highest in Fresh and Partial Burn treatments, moderate in Controls, and lowest in Complete Burn treatments (Figure 4.10).

Biomass of periphyton and bacteria

On August 13th, Fresh treatments contained a large mass of periphyton (15 000 $\mu g \cdot cm^{-2}$) whereas Controls, Partial Burn treatments, and Complete Burn treatments all contained less than 2 500 $\mu g \cdot cm^{-2}$ (Figure 4.11). On September 9th, the biomass of periphyton in Fresh treatments was similar to other treatments, which were all less than 3 000 $\mu g \cdot cm^{-2}$. However, the biomass of periphyton in Complete Burn treatments increased by three times. Bacterial biomass was similar among treatments and between two sampling dates (Figure 4.12). The biomass of bacteria increased in each treatment by 1 to 4 $\mu g \cdot cm^{-2}$ between August 13th and September 9th. Standard errors, depicted on the graphs as one standard error, were quite large.

Water Chemistry

Temperature

Temperatures were highest during the later half of July, and decreased substantially in late August (Figures 4.13). Fresh and Partial Burn treatments often had slightly higher surface temperatures than Complete Burn treatments and Controls.

Oxygen

All limnocorrals were stratified with respect to dissolved oxygen (O_2) on most days (Figures 4.14). Two days after treatment addition, O_2 concentrations in Fresh

treatments decreased to about 4 $mg \cdot L^{-1}$. Concentrations of O_2 dropped to less than 2 $mg \cdot L^{-1}$ from July 11th to 30th, after which they gradually increased, but they did not recover fully. Partial Burn treatments had low concentrations of O_2 in bottom waters. There was great variability among limnocorrals containing Partial Burn treatments. In Partial and Complete Burn treatments and Controls, O_2 concentrations were slightly depressed from week three to six (July 18th to August 10th).

Greenhouse gases

Carbon dioxide

Mean pCO_2 levels in surface water were lowest in Controls (5 000 µatms), similar in Partial (~12 000 µatms) and Complete Burned treatments (~10 000 µatms), and highest in Fresh treatments (~17 000 µatms) (Figure 4.15). These levels were fairly constant in each treatment throughout the experiment with a slight decreasing trend towards the end of the warm season.

Methane

Mean pCH_4 levels in Controls (~100 µatms) and Complete Burn treatments (~400 µatms) were very low, Partial Burn treatments peaked after about four weeks at 3 600 µatms, and Fresh treatments peaked after six weeks at 11 000 µatms (Figure 4.16). pCH_4 levels diminished by eight weeks and decreased to background levels in all treatments 11 weeks after treatment addition.

Tritium

Tritium was added to the limnocorrals to monitor for water exchange. Tritium activity was similar among all limnocorrals on each sample date (Figure 4.17). The activity ranged from 1 000 to 16 000 DPM four days after tritium was added. At the end of the season, the activity had decreased to 400 to 500 DPM. The decrease in activity was not consistent throughout the season. The activity initially decreased (600 to 1 000 DPM) five days after addition, and then increased (1 000 to 14 000 DPM) for one to two weeks after tritium was added. Thereafter the decrease in the activity of tritium was fairly smooth.

DISCUSSION

Effects of burning before flooding on aqueous THg and MeHg concentrations

I hypothesized that burning of vegetation and soils before flooding would lower MeHg contamination in flooded ecosystems. In the study limnocorrals, concentrations of THg and MeHg in the water column were significantly lower after burning only vegetation, and were decreased even further by burning both vegetation and soil. In contrast to these results, MeHg was not elevated in biota of Fresh treatments relative to Controls, the lake, or literature expectations. Concentrations of MeHg in aquatic biota from Partial and Complete Burn treatments did not decrease relative to Fresh treatments. Hence, my results provide little evidence that pre-impoundment controlled burning will lower MeHg contamination in flooded ecosystems in the first season of flooding. I hypothesize that MeHg bioaccumulation was lowered in Fresh and Partial Burn

treatments by the large increases in DOC in these treatments. When DOC was present in greater concentrations, biota contained lower concentrations of MeHg.

Burning before flooding lowered concentrations of THg in surface water, relative to Fresh treatments. THg concentrations were greatest in Fresh treatments and were 2.9 times greater on average than Controls. Partial Burn treatments had THg concentrations that were 1.7 times less than Fresh treatments. Complete Burn treatments contained THg concentrations that were similar to Controls.

Concentrations of THg ($ng \cdot L^{-1}$) from July 4th to August 16th				
	Fresh	Partial Burn	Complete Burn	Controls
Mean	5.0	3.2	1.9	1.7
Maximum	7.3	5.8	3.2	2.3
Minimum	1.9	1.3	0.8	1.1

Burning before flooding also lowered MeHg concentrations in water. Concentrations of MeHg were greatest in Fresh treatments and were 5 times greater than Controls. Partial Burn treatments had MeHg concentrations about three times greater than Controls, and, as with THg, were also 1.7 times less than Fresh treatments. Complete Burn treatments contained MeHg concentrations that were quite similar to Controls.

Concentrations of MeHg ($ng \cdot L^{-1}$) from July 4th to August 16th				
	Fresh	Partial Burn	Complete Burn	Controls
Mean	0.5	0.3	0.1	0.1
Maximum	0.9	0.3	0.2	0.2
Minimum	0.3	0.2	0.1	0.1

Comparison of THg and MeHg in Fresh treatments to other studies

Unlike my results, aqueous concentrations of THg did not differ significantly before and after flooding in other studies (Kelly *et al.* 1997; Hall *et al.* In press). This

could be because the vegetation and soil that I added to the water passed through the water column rather than flooding organic matter in place. My results for aqueous MeHg concentrations in flooded systems are comparable to other studies (Hall *et al.* In press; Submitted; Kelly *et al.* 1997; Plourde *et al.* 1997).

Could MeHg added with soil and vegetation account for concentrations in water?

Differences in concentrations of THg and MeHg in surface waters of the limnocorrals were related to the burning of the soil and vegetation. Fresh and Partial Burn treatments received THg present in soil and vegetation plus organic matter that can fuel microbial metabolism and elevate rates of Hg methylation. THg and MeHg concentrations peaked in July, one to two weeks after adding the treatments. The peak in THg occurred prior to the peak in MeHg. It is important to know if MeHg was derived from methylation or leaching because this may affect the duration of elevated MeHg levels in reservoirs. In my limnocorrals, the percentage of THg that occurred as MeHg was about 5 to 6% in Complete Burn treatments and Controls, and was 9 to 10% in Partial Burn and Fresh treatments. Thus, flooding caused the percentage of MeHg to approximately double in my study. I added approximately 30 000 ng of MeHg with the Fresh treatments. The maximum concentration of MeHg in the water of the Fresh treatments was 0.9 $ng \cdot L^{-1}$, which equates to a mass of only 5 652 ng of MeHg. Therefore, it seems that it was not necessary to invoke methylation of Hg to account for the MeHg observed in my study, but mass balance calculations have not been undertaken. My results of THg/MeHg differ from other studies (Kelly *et al.* 1997; Hall *et al.* Submitted).

Limnocorrals with Fresh treatments were completely anoxic for three weeks of the study. Oxygen depletion occurred due to high rates of decomposition of organic carbon added in treatments as evidenced by high pCH_4 levels. This response may be similar to some areas of reservoirs that are depleted in oxygen after impoundment. For example, the bottom water in the FLooded Upland Dynamics EXperiment (FLUDEX) reservoirs was anoxic for part of the summer (Bodaly *et al.* submitted) and the surface water of the ELA Reservoir Project (ELARP) flooded wetland was anoxic (Heyes *et al.* 2000). However, my Fresh treatments may differ from other reservoirs in which dissolved oxygen concentrations in the 3 m deep water column were 5 to 13 $mg \cdot L^{-1}$ (reviewed in Plourde *et al.* 1997). However, the deeper areas of reservoirs are generally anoxic (Canavan *et al.* 2000).

Effects of burning before flooding on MeHg concentrations in aquatic biota

I hypothesized that controlled burning before flooding would lower concentrations in the food web of flooded ecosystems. However, Partial and Complete Burn treatments did not consistently have lower MeHg concentrations in biota. On the final sample date, MeHg in zooplankton, Chironomid larvae, and emerging insects showed consistent patterns among the various treatments. Concentrations of MeHg in all of the biota were greater in Controls and Partial Burn treatments than in Fresh and Complete Burn treatments. These results are contrary to my main hypothesis, that burning before flooding would lower the amount of MeHg in aquatic organisms. I am surprised that adding fresh vegetation did not increase MeHg in biota.

Comparison with other published results

MeHg concentrations in biota from my study were low relative to real and experimental reservoirs (Bodaly *et al.* 1997). On all sample dates, concentrations of MeHg in biota in Fresh treatments were lower than in Controls (and the lake) and concentrations of MeHg in biota did not follow those in the surface water. In my study, zooplankton in Fresh treatments contained 25 +/- 3 ng MeHg·g^{-1} d. w. on the final sample date, whereas throughout my experiment Partial Burn treatments contained 42 +/- 18 to 178 +/- 30 ng MeHg·g^{-1} d. w., Complete Burn treatments contained 20 +/- 5 to 126 +/- 17 ng MeHg·g^{-1} d. w., and Controls contained 53 +/- 7 to 74 +/- 24 ng MeHg·g^{-1} d. w.. My results are low relative to those from ELARP in which there was a 10 fold increase in MeHg concentrations in zooplankton from 32 to >300 ng MeHg·g^{-1} d. w. after impoundment (Paterson *et al.* 1997). Zooplankton of reservoirs in northern Québec contained 280 to 430 ng MeHg·g^{-1} as compared to natural lakes in the region, which contained 20 to 80 ng MeHg·g^{-1} (Tremblay *et al.* 1998), indicating that zooplankton in flooded ecosystems may contain 3.5 to 24 times more MeHg than those in natural lakes. In addition, mean concentrations of MeHg in zooplankton in La Grande-2 reservoir were five times higher than reference lakes (Plourde *et al.* 1997).

Emerging insects contained much less MeHg in Fresh treatments (23 +/- 4 to 34 +/- 8 ng MeHg·g^{-1} d. w.) as compared to Controls (61 +/- 10 to 122 +/- 10 ng MeHg·g^{-1} d. w.) and Partial and Complete Burn treatments had intermediate concentrations. In Québec, insects emerging from reservoirs contained two to three times more than those in natural lakes (Tremblay *et al.* 1998). Further, concentrations of MeHg in Chironomid larvae from Fresh treatments (14 +/- 3 ng MeHg·g^{-1} d. w.) were significantly lower than

in Controls (29 +/- 3 ng MeHg·g^{-1} d. w.). This also disagrees with other studies. In northern Québec reservoirs, benthic insects rapidly acquired 3 to 5 times greater concentrations of MeHg than those in reference lakes (Tremblay *et al.* 1996a; Tremblay and Lucotte 1997). Specifically, Chironomid larvae in reservoirs contained 64 to 76 ng MeHg·g^{-1} d. w. (Tremblay *et al.* 1996a). However, natural lakes in northern Québec contained Chironomid larvae with 39 to 88 ng MeHg·g^{-1} d. w. (mean 70 ng MeHg·g^{-1}) (Tremblay *et al.* 1996b). Since it has been demonstrated that concentrations of MeHg in benthic invertebrates increase after impoundment (Hall *et al.* 1998), the similarity in Chironomid larvae MeHg concentrations between reservoirs and lakes in northern Québec may be due to modification of MeHg uptake in one of these ecosystems.

Why didn't MeHg concentrations increase in biota from my limnocorrals, as has been widely observed in enclosure and whole-ecosystem studies on the effects of impoundment (Bodaly *et al.* submitted; Kelly *et al.* 1997; Hecky *et al.* 1991)? Some possible explanations include: 1) differences in the timing of biotic sampling relative to elevated concentrations of MeHg in water; 2) differences in physical-chemical conditions in real reservoirs as compared with my enclosures; 3) reductions of bioaccumulation because of elevated DOC. Each of these possibilities is discussed further below.

I acquired enough zooplankton biomass for MeHg analysis only at the end of the experiment. In part, this is because several limnocorrals became anoxic and could not support zooplankton or benthos populations. In August and September, differences in aqueous MeHg concentrations among limnocorrals were much less than earlier in the experiment. As a result, it is also possible that zooplankton could have had greater concentrations of MeHg earlier in the experiment. In general, MeHg concentrations in

zooplankton respond to changes in aqueous MeHg concentrations within hours to days. My results may have been affected by the fact that I only sampled surface water for MeHg, whereas biota were sampled from the water column. As a result, maybe water concentrations are not good estimates of Hg exposure to biota. Temperature and dissolved oxygen data show considerable evidence of stratification and indicate that differences in water chemistry were likely present through the water column.

Factors governing MeHg accumulation and depuration by zooplankton in reservoirs are not well understood. Differences in physical or chemical properties of the water between my limnocorrals and impounded ecosystems may affect the concentrations of MeHg observed. For example, wave energy and fluctuating water levels in reservoirs can elevate the concentration of suspended particulate matter, from which zooplankton may assimilate MeHg (Mucci *et al.* 1995; Plourde *et al.* 1997). However, considerable uncertainties exist as to whether zooplankton assimilate MeHg directly from water or food (Monson and Brezonik 1998; Peech Cherewyk 2002).

My results demonstrate an inverse relationship between DOC and the proportion of MeHg present that ended up in biota as expressed by BAFs (the regression lines are $y = 14.7 - 3.2x$, $r^2 = 0.52$ for zooplankton; $y = 14.1 - 3.0x$, $r^2 = 0.72$ for Chironomid larvae; and $y = 15.9 - 3.6x$, $r^2 = 0.89$ for emerging insects). BAFs of MeHg in zooplankton also correlated negatively with DOC in 15 lakes in northern Wisconsin ($y = 6.19 - 0.07x$, $r^2 = 0.70$) (Watras *et al.* 1998), which was a less negative slope than in my regressions. Watras *et al.* (1998) found a strong positive correlation between aqueous Hg and DOC and suggest that complexation can occur and may lower the bioavailable portion of Hg to zooplankton to assimilate from the water. In addition, increased concentrations of DOC

resulted in decreased rates of net methylation (Miskimmin *et al.* 1992). As the proportion of DOC to MeHg increases, aquatic organisms take up less MeHg.

Some studies have shown that MeHg in zooplankton correlate positively with water colour or not at all (Westcott and Kalff 1996; Paterson *et al.* 1998). This observation has been made in drainage lakes where DOC could deliver MeHg to the system from wetlands (St. Louis et al. 1994) and retain Hg (Miskimmin 1991; Watras *et al.* 1995) possibly by inhibiting photoreduction (Sellers *et al.* 1996). Miskimmin *et al.* (1992) propose that biotic concentrations of MeHg may increase with water colour despite inhibition of methylation by DOC when terrestrial inputs of MeHg are important or when the pH is low.

It was demonstrated using stable isotopes of Hg in experimental limnocorrals that algal blooms dilute the amount of MeHg per algal cell as the algal biomass increases and this substantially decreases concentrations of MeHg taken up by zooplankton (Pickhardt *et al.* 2002). The biomass of periphyton was high in Fresh treatments. This needs further investigation.

Differences between MeHg in water and periphyton

The periphyton in Fresh treatments contained 1.6 +/- 0.3 and 5.3 +/- 0.88 ng $MeHg \cdot g^{-1}$ d. w. on July 25th and September 19th, respectively. In the FLUDEX reservoirs the periphyton communities had average concentrations of 44.3 ng $MeHg \cdot g^{-1}$ d. w. (Hall *et al.* In press), which is much greater than in my study. The trends in MeHg concentrations in periphyton did not follow the concentrations of MeHg in the water. Although aqueous MeHg concentrations in Fresh treatments were greater than in Partial

Burn treatments, periphyton in Fresh treatments contained less MeHg on both dates. The inconsistency in MeHg trends between water and periphyton may be due to methylation of Hg in periphyton. Methylation of Hg is coupled with the photosynthetic oxidation of sulphide and microbial sulphate reduction by SRB, and is enhanced under eutrophic conditions (Cleckner *et al.* 1999). Periphyton accumulate MeHg in proportion to the concentration of MeHg in the water (Hill *et al.* 1996). In a laboratory experiment, algae accumulated 98 to 100% of added MeHgCl (Boudou and Ribeyre 1981). In my treatments, DOC concentrations were highest in Fresh treatments, moderate in Partial and Complete Burn treatments, and lowest in Controls. Back and Watras (1995) found that inorganic Hg and MeHg bioconcentration factors (BCFs) for seston were lower when DOC concentrations were higher. In contrast, I observed high concentrations and BCFs of MeHg in periphyton of Fresh treatments which contained the highest concentration of DOC. In addition, BCFs of MeHg in periphyton of Partial Burn treatments were significantly higher than in Complete Burn treatments. Since Partial and Complete burn treatments contained similar concentrations of DOC, but different concentration of aqueous MeHg, it seems that the concentration of MeHg was more important in determining BCFs in my study.

In addition, phosphorus may have affected the concentrations of MeHg in periphyton in my study by altering the biomass of the periphyton communities. Phosphorus was greatest in Fresh treatments, lower with each successive level of burning, and lowest in Controls. Biomass of periphyton was greatest in Fresh treatments that contained the highest concentrations of phosphorus. In Haute-Mauricie, Québec, lakes surrounded by burned catchment areas showed 25 to 50% increases in algal biomass due

to increases in the concentration of total phosphorus (Planas *et al.* 2000). When concentration of MeHg are constant, increases in algae biomass results in lower concentrations of MeHg per unit of algae biomass (Pickhardt *et al.* 2002), but because Fresh treatments contained the highest concentrations of phosphorus and MeHg, my study did not lend itself reveal effects of biodilution.

Other issues related to the limnocorral experiment and Hg

Fate of THg and MeHg

After the peak in THg and MeHg concentrations in Fresh treatments in July, concentrations decreased substantially. In previous studies on the effects of impoundment, MeHg concentrations have typically remained elevated for longer periods. The main routes of Hg loss are demethylation, photoreduction, and sedimentation. In an attempt to explain losses of THg and MeHg in my limnocorrals, I compared my data with rates of demethylation and photoreduction in the literature and in a model being developed (R. Harris pers. comm.).

Demethylation of MeHg mainly occurs through microbial processes. Demethylation is the principle source of Hg^0 in low oxygen waters (Mason and Fitzgerald 1993). MeHg may be bacterially demethylated in the anoxic zone allowing upward diffusion of Hg^0. Primarily SRB demethylate Hg (Robinson and Tuovinen 1984; Gilmour *et al.* 1992). Some bacteria have Hg resistant mechanisms, like volatilization of the element, to prevent toxicity. Demethylation rates increase linearly with MeHg concentrations (Xun *et al.* 1987). Demethylation is favoured at low temperatures (Bodaly *et al.* 1993; Ramlal *et al.* 1993). MeHg degradation is greatest under aerobic and low pH

conditions. For example, Matilainen *et al.* (1991) observed a decrease in net methylation rates with increasing acidity at the aerobic sediment surface. THg can flux from water to the atmosphere following the reduction of ionic Hg to elemental Hg.

The rate of loss of MeHg in Fresh and Partial Burn treatments decreased with decreasing concentrations of aqueous MeHg in my limnocorrals and concentrations of MeHg did not change substantially in Complete Burn treatments and Controls (Table 4.5). Amyot *et al.* (1997b) also found that the rate of production of dissolved gaseous mercury (DGM) depends on concentrations of photoreducible Hg. Similar to my study, approximately 75% of the aqueous MeHg in a microcosm study was lost from the water (Morrison and Thérien 1991). This may be explained by the production of DGM. In two freshwater lakes in Ontario, transparent bottles filled with lake water and incubated in the lakes had up to nine times more DGM than opaque bottles; this phenomenon was greatest in epilimnetic waters (Amyot *et al.* 1994). DGM was produced in transparent bottles because the intensity of ultraviolet solar radiation controls the degradation of MeHg in aquatic ecosystems (Amyot *et al.* 1997a; Amyot *et al.* 1997b; Sellers *et al.* 1996), which is most significant in shallow, relatively clear water. Sellers *et al.* (1996) found that in the epilimnetic water of an oligotrophic lake during the ice-free season, the average MeHg concentration was 0.07 $ng \cdot L^{-1}$, the rates of MeHg production and photoreduction were probably 1.0 and 1.5 $\mu g \cdot m^{-2} yr^{-1}$, respectively, and that photoreduction was the most important mechanisms of MeHg loss in unfiltered water. At high concentrations of DOC, the penetration of ultraviolet radiation would be limited and therefore the rate of photoreduction would also be limited, as evidenced by the concentration of DGM relative to DOC concentrations in the FLUDEX reservoirs (Hall *et al.* submitted). Since my

limnocorrals were not shielded from sunlight, photoreduction could account for much of the loss of THg and MeHg that I observed. In addition, a modeling project currently estimates photoreduction in Lake 240 at the ELA at 0.5 $\mu g \cdot m^{-2} yr^{-1}$ (R. Harris pers. comm.). Further, the pH was much lower in my Fresh treatments relative to any other treatments, which may have enhanced demethylation relative to the other treatments. In the water column of five lakes in Wisconsin there was significant correlation between the percentage of Hg^0 saturation and pH values (r^2=0.99 and $p<0.001$), which suggested that production of Hg^0 by photoreduction was enhanced in areas of high pH values (Vandal *et al.* 1991). In addition, Ramlal *et al.* (1985) observed that net sediment methylation rates decrease slightly as acidity increases, then sharply at pH <4.5, at which point demethylation became more important. The low pH in Fresh treatments may have contributed to the faster rate of THg and MeHg loss. Rates of THg and MeHg loss in the enclosures were consistent with literature estimates of rates of demethylation and photoreduction.

Does charcoal sequester THg and MeHg?

My secondary hypothesis was that charcoal remaining after controlled burning would sequester MeHg because it is an extremely adsorbent material. If charcoal were able to adsorb a significant amount of Hg in an ecosystem, I would expect to see lower THg concentrations in surface waters of Complete Burn treatments than Controls. However, concentrations of THg and MeHg in unfiltered surface water samples from Complete Burn treatments were similar to, but slightly higher, than Controls. Therefore I

conclude that charcoal did not have a strong binding effect on THg and MeHg in the water column.

MeHg concentrations in surface sediment

Sediment MeHg concentrations followed similar trends as surface water and may be related to the amount of Hg and fresh organic carbon added with treatments. Fresh organic carbon stimulates rates of Hg methylation. Although charcoal did not sequester a significant amount of Hg from the water column, it is possible that deposited particles of charcoal could bind Hg at the sediment-water interface. The sediment composition (iron and sulphur content) and redox potentials control the degree to which sediments bind Hg. Generally, oxygenated sediment adsorbs Hg and anoxic sediment releases Hg (Regnell *et al.* 2001). Variability in sediment Hg concentrations in my study could be due to heterogeneity of the sediment and uneven distribution of treatment material.

Loss of THg and MeHg due to burning vegetation and soil

Controlled burning of soil and vegetation resulted in less THg and MeHg added with Partial and Complete Burn treatments as compared to Fresh treatments. After controlled burning, vegetation lost 96.6 and 94.2% and soil lost 78.8 and 88.1% of the original THg and MeHg, respectively (see Chapter 3). My results agree with results of Friedli *et al.* (2001; 2003) in which the loss of gaseous THg was 97 to 99.8% in laboratory burning experiments. Therefore Partial Burn treatments received less Hg than Fresh treatments and Complete Burn treatments received less Hg than Partial Burn treatments. Partial and Complete Burn treatments received substantially less carbon than Fresh treatments.

Implications of forest burning on the Hg cycle

With regard to Hg, my results suggest that burning before flooding would result in smaller increases in aqueous MeHg in new reservoirs, but not necessarily in biota. Burning vegetation and soil emits Hg to the atmosphere contributing to long-range transport of Hg and anthropogenic sources of Hg pollution in far removed and otherwise pristine ecosystems. Disruption of the forest floor may cause erosion and transportation of the repository of mercury in soil that is bound to organic carbon and inorganic binding agents (Caldwell *et al.* 2000). Yet studies by Garcia and Carignan (1999; 2000) show no significant differences in MeHg concentrations of zooplankton and fish in lakes with burned catchment areas. This disagreement in results may be due to the nature of the soils, whether they were consolidated, and the amount and intensity of precipitation events following the disturbance.

Effects of burning before flooding on greenhouse gases

The results from my study support my third hypothesis that burning before flooding will lower the amount of CH_4 emitted due to reservoir creation, but the total loss of carbon by burning may be much greater than that after flooding. In burned treatments the partial pressures were 30 to 40% lower for CO_2 and 60 to 97% lower for CH_4. Boreal forest ecosystems are considered to be approximately neutral with regard to GHG cycling because carbon fixed in the organic matter by photosynthesis fluxes back to the atmosphere during periodic wildfires in the boreal forest. Forest soils are also a sink for CH_4 from the atmosphere. Although burning emits substantial quantities of CO_2 to the atmosphere, CH_4 is a relatively insignificant by-product of combustion. In contrast, new reservoirs are sources of CH_4 to the atmosphere due to the anoxic decomposition of organic carbon (Bodaly *et al.* accepted; Duchemin *et al.* 2002; Kelly *et al.* 1997; St. Louis *et al.* 2000). This is a concern because CH_4 is 21 times more effective at trapping infrared radiation in the form of heat in the troposphere (reviewed in Baird 1995).

Benefits and limitations of using limnocorrals

In this section I will make a comparison between my experimental controls and the host lake and I will discuss the statistical benefits of using limnocorrals and their limitations in mimicking real ecosystems. My limnocorral experiment took place in an oligotrophic lake. Controls contained zooplankton that had similar MeHg concentrations as the host lake on August 15th and September 19th (Figure 4.3). It does not appear that the processes that took place in my limnocorrals deviated from the lake system.

Limnocorrals are used in ecological experiments to lower the error of the results and biases. Replicating treatments increases the precision of the results. By lowering the uncertainty, the results contain statistical credibility. Replicating treatments may also lower pseudoreplication, ensuring that the assumption of sample independence is met (Hurlbert 1984). Randomization of the treatments increases the accuracy of the results by lowering biases that may be introduced by spatial variation and sampling procedures (Hurlbert 1984). When gradations in substrate are present, interspersion of treatments may give more accuracy than randomization (Hurlbert 1984). Replicated experiments have a known degree of certainty in their results.

On the other hand, several realistic parameters of aquatic ecosystems are not accounted for in limnocorral experiments. Limnocorrals are generally used in littoral zones. They may or may not stratify. Processes that occur in pelagic or deep zones are not accounted (Schindler 1998). To isolate a set of variables, limnocorrals are sealed, and therefore have little to no circulation with the host lake. There is no catchment area or shoreline associated with limnocorrals (Schindler 1998). Further, limnocorrals may represent an incomplete food web (Schindler 1998). Top predators cannot be supported in a small closed system. The population dynamics or behavioural patterns of contained smaller biota may be altered. Limnocorrals contain a large surface area of wall material on which periphyton grows. Disturbance of the walls from wave activity and sampling can suspend particulates in the water column. Another limitation of limnocorrals is their longevity. Limnocorrals are often sampled for one ice-free season. If limnocorrals are sampled in subsequent seasons, the walls often need to be replaced or resealed due to disturbance from ice. The cost of running limnocorral experiments is very high. The

amount of work required for each limnocorral is similar to that of a whole-ecosystem. The cost of chemical analysis increases with each additional treatment and replicate. Limitations of limnocorral experiments may be acceptable, depending on the research questions being asked.

Ecological researchers may decide if isolation of specific variables and replication is the most effective way to answer the questions posed, or if the results will be strengthened by monitoring realistic processes that occur in whole-ecosystem manipulations.

CONCLUSION

My results suggest that controlled burning of large areas of land is probably not a useful mitigation strategy for decreasing MeHg contamination in reservoirs. Many hydroelectric reservoirs exist, and will continue to be developed, in remote areas where access roads may not exist. The terrain is often covered with lakes and bogs and poorly drained soils. The transport of all equipment and human resources would likely require helicopters or planes. In addition, producing a controlled fire that is hot enough to ignite the wet soils and peat in these areas would be difficult. Many small controlled burns would be required. The cost of trenching and brushing the area to be burned has been estimated at one million dollars per ha (R. Schetagne pers. comm.).

The detrimental effects of controlled burning may be worse than those normally incurred by flooding. If flooding after burning was to take place, MeHg may accumulate through the aquatic food web more than in reservoirs that flood unburned vegetation and

soil. The production of aerosols by combustion would affect local, regional, and global climates and air quality. By-products of combustion may remain in the substrate, such as cyanide, and may have toxic effects to the aquatic organisms. Further, the ability of animals to escape may be limited. Exposure of organic soils and peat after burning may leach substantial amounts of Hg and MeHg. Overall, I do not recommend controlled burning before flooding as a method to decrease MeHg contamination in hydroelectric developments.

At the current time, hydroelectric developments are going to continue to be constructed due to pressing demands for exporting hydroelectricity to the United States. In 2007, the Eastmain-1 complex in northern Québec is scheduled to be flooded. This development is adjacent to an aboriginal community. These people may fish from the reservoirs for food and income, or as guides for sport fishers. It is currently unclear how the MeHg contamination in reservoir fishes may affect people, however, the hydroelectric companies, and their proponents, the Cree people themselves, are responsible for devising a way to diminish the risk of MeHg poisoning, mainly from a human perspective.

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LITERATURE CITED

Abernathy, A.R. and Cumbie, D.M. 1977. Mercury accumulation by largemouth bass (*Micropterus salmoides*) in recently impounded reservoirs. Bulletin Environmental Contamination and Toxicology **17**: 595-602.

Amyot, M., Gill, G.A., and Morel, F.M.M. 1997a. Production and loss of dissolved gaseous mercury in coastal seawater. Environmental Science and Technology **31**: 3606-3611.

Amyot, M., Lean, D., and Mierle, G. 1997b. Photochemical formation of volatile mercury in high Arctic lakes. Environmental Toxicology and Chemistry **16**: 2054-2063.

Amyot, M., Mierle, G., Lean, D.R.S., and McQueen, D.J. 1994. Sunlight-induced formation of dissolved gaseous mercury in lake waters. Environmental Science and Technology **28**: 2366-2371.

Axtell, C.D., Cox, C., Myers, G.J., Davidson, P.W., Choi, A.L., Cernichiari, E., Sloane-Reeves, J., Shamlaye, C.F., and Clarkson, T.W. 2000. Association between methylmercury exposure from fish consumption and child development at five and a half years of age in the Seychelles child development study: An evaluation of nonlinear relationships. Environmental Research **84**: 71-80.

Back, R.C. and Watras, C.J. 1995. Mercury in zooplankton of northern Wisconsin lakes: Taxonomic and site-specific trends. Water, Air, and Soil Pollution **80**: 931-938.

Baird, C. 1995. Environmental Chemistry. W. H. Freeman and Company, New York.

Bloom, N.S. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. Canadian Journal of Fisheries and Aquatic Sciences **49**: 1010-1017.

Bodaly, R.A. and Fudge, R.J.P. 1999. Uptake of mercury by a cyprinid fish (*Finescale dace*) in two wetland ponds, ELA, Ontario. Archives of Environmental Contamination and Toxicology **37**: 103-109.

Bodaly, R.A., Hecky, R.E., and Fudge, R.J.P. 1984. Increases in fish mercury levels in lakes flooded by the Churchill River diversion, northern Manitoba. Canadian Journal of Fisheries and Aquatic Sciences **41**: 682-691.

Bodaly, R.A., Rolfhus, K.R., Penn, A.F., Beaty, K.G., Hall, B.D., Hendzel, L.H., Mailman, M., Majewski, A.R., Matthews, K.J.D., Paterson, M.J., Peech Cherewyk, K.A., St.Louis, V.L., Schiff, S.L., and Venkiteswaran, J.J. accepted. The use of experimental reservoirs to explore the impacts of hydro-electric developments on methylmercury and greenhouse gas production: The FLUDEX experiment. Environmental Science and Technology.

Bodaly, R.A., Rudd, J.W.M., Fudge, R.J.P., and Kelly, C.A. 1993. Mercury concentrations in fish related to size of remote Canadian Shield lakes. Canadian Journal of Fisheries and Aquatic Sciences **50**: 980-987.

Bodaly, R.A.D., St. Louis, V.L., Paterson, M.J., Fudge, R.J.P., Hall, B.D., Rosenberg, D.M., and Rudd, J.W.M. 1997. Bioaccumulation of mercury in the aquatic food chain in newly flooded areas. *In* Metal ions in biological systems: Mercury and its effects on environment and biology. *Edited by* A. Sigel and H. Sigel. Marcel Dekker, Inc., New York, NY pp. 259-287.

Boudou, A. and Ribeyre, F. 1981. Comparative study of the trophic transfer of two mercury compounds---HgCl2 and CH3HgCl---between *Chlorella vulgaris* and *Daphnia magna*: Influence of temperature. Bulletin of Environmental Contamination and Toxicology **27**: 624-629.

Cabana, G., Tremblay, A., Kalff, J., and Rasmussen, J.B. 1994. Pelagic food chain structure in Ontario lakes: A determinant of mercury levels in lake trout (*Salvelinus namaycush*). Canadian Journal of Fisheries and Aquatic Sciences **51**: 381-389.

Caldwell, C.A., Canavan, C.M., and Bloom, N.S. 2000. Potential effects of forest fire and storm flow on total mercury and methylmercury in sediments of an arid-lands reservoir. Science of the Total Environment **260**: 125-133.

Canavan, C.M., Caldwell, C.A., and Bloom, N.S. 2000. Discharge of methylmercury-enriched hypolimnetic water from a stratified reservoir. Science of the Total Environment **260**: 159-170.

Chen, C.Y., Stemberger, R.S., Klaue, B., Blum, J.D., Pickhardt, P.C., and Folt, C.L. 2000. Accumulation of heavy metals in food web components across a gradient of lakes. Limnology and Oceanography **45**: 1525-1536.

Choi, S.C. and Bartha, R. 1994. Environmental factors affecting mercury methylation in estuarine sediments. Bulletin of Environmental Contamination and Toxicology **53**: 805-812.

Choi, S.-C., Chase, T. Jr, and Bartha, R. 1994. Enzymatic catalysis of mercury methylation by *Desulfovibrio desulfuricans* LS. Applied and Environmental Microbiology **60**: 1342-1346.

Clarkson, T.W. 1990. Human health risks from methylmercury in fish. Environmental Toxicology and Chemistry **9**: 957-961.

Cleckner, L.B., Garrison, P.J., Hurley, J.P., Olson, M.L., and Krabbenhoft, D.P. 1998. Trophic transfer of methyl mercury in the northern Florida Everglades. Biogeochemistry **40**: 347-361.

Cleckner, L.B., Gilmour, C.C., Hurley, J.P., and Krabbenhoft, D.P. 1999. Mercury methylation in periphyton of the Florida Everglades. Limnology and Oceanography **44**:

1815-1825.

Compeau, G. and Bartha, R. 1985. Sulfate-reducing bacteria: Principal methylators of mercury in anoxic estuarine sediment. Applied and Environmental Microbiology **50**: 498-502.

Davidson, P.W., Palumbo, D., Myers, G.J., Cox, C., Shamlaye, C.F., Sloane-Reeves, J., Cernichiari, E., Wilding, G.E., and Clarkson, T.W. 2000. Neurodevelopmental outcomes of Seychellois children from the pilot cohort at 108 months following prenatal exposure to methylmercury from a maternal fish diet. Environmental Research **84**: 1-11.

Downs, S.G., Macleod, C.L., and Lester, J.N. 1998. Mercury in precipitation and its relation to bioaccumulation in fish: a literature review. Water Air and Soil Pollution **108**: 149-187.

Duchemin, E., Lucotte, M., St. Louis, V., and Canuel, R. 2002. Hydroelectric reservoirs as an anthropogenic source of greenhouse gases. World Resource Review **14**: 334-352.

Dyck, B.S. and Shay, J.M. 1999. Biomass and carbon pool of two bogs in the Experimental Lakes Area, northwestern Ontario. Canadian Journal of Botany **77**: 291-304.

Friedli, H.R., Radke, L.F., and Lu, J.Y. 2001. Mercury in smoke from biomass fires. Geophysical Research Letters **28**: 3223-3226.

Friedli, H.R., Radke, L.F., Lu, J.Y., Banic, C.M., Leaitch, W.R., and MacPherson, J.I. 2003. Mercury emissions from burning of biomass from temperate North American forests: laboratory and airborne measurements. Atmospheric Environment **37**: 253-267.

Garcia, E. and Carignan, R. 1999. Impact of wildfire and clear-cutting in the boreal forest on methyl mercury in zooplankton. Canadian Journal of Fisheries and Aquatic Sciences **56**: 339-345.

Garcia, E. and Carignan, R. 2000. Mercury concentrations in northern pike (*Esox lucius*) from boreal lakes with logged, burned, or undisturbed catchments. Canadian Journal of Fisheries and Aquatic Sciences. Suppl. 2. Impacts of major watershed perturbations on aquatic ecosystems. **57:** 129-135.

Gilmour, C.C., Henry, E.A., and Mitchell, R. 1992. Sulfate stimulation of mercury methylation in freshwater sediments. Environmental Science and Technology **26**: 2281-2287.

Hall, B.D., Bodaly, R.A., Fudge, R.J.P., Rudd, J.W.M., and Rosenberg, D.M. 1997. Food as the dominant pathway of methylmercury uptake by fish. Water, Air, & Soil Pollution **100**: 13-24.

Hall, B.D., Rosenberg, D.M., and Wiens, A.P. 1998. Methyl mercury in aquatic insects from an experimental reservoir. Canadian Journal of Fisheries and Aquatic Science **55**:

2036-2047.

Hall, B.D. and St. Louis, V.L. 2001. Impacts of reservoir creation on the biogeochemical cycling of methylmercury in boreal forest uplands.

Hall, B.D., St. Louis, V.L., and Bodaly, R.A.D. The stimulation of methylmercury production by decomposition of flooded birch leaves and jack pine needles. Biogeochemistry. In press.

Hall, B.D., St. Louis, V.L., Rolfhus, K.R., Bodaly, R.A., Beaty, K.G., and Paterson, M. The impact of reservoir creation on the biogeochemical cycling of methyl and total mercury in boreal upland forests. Submitted.

Hauser, B. 2001. Particulate Carbon and Nitrogen. Version 2.2. Freshwater Institute No. FWI-C/N-2. Winnipeg, Manitoba.

Hecky, R.C., Ramsey, D.J., Bodaly, R.A., and Strange, N.E. 1991. Increased Methylmercury Contamination in Fish in Newly Formed Freshwater Reservoir. *Edited by* T. Clarkson and T. Suzuki. Plenum Press, New York.

Heyes, A., Moore, T.R., Rudd, J.W.M., and Dugoua, J.J. 2000. Methyl mercury in pristine and impounded boreal peatlands, Experimental Lakes Area, Ontario. Canadian Journal of Fisheries and Aquatic Sciences **57**: 2211-2222.

Hill, W.R., Stewart, A.J., and Napolitano, G.E. 1996. Mercury speciation and bioaccumulation in lotic primary producers and primary consumers. Canadian Journal of Fisheries and Aquatic Sciences **53**: 812-819.

Horvat, M., Liang, L., and Bloom, N.S. 1993. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part 2. Water. Analytica Chimica Acta **282**: 153-168.

Huebert, D. 2002. Experimental Lakes Area Upland Flooding Experiment Vegetation Analysis. Dave Huebert. Winnipeg, Manitoba.

Hurlbert, S.H. 1984. Pseudoreplication and the design of ecological field experiments. Ecological Monographs **54**: 187-211.

Kelly, C.A., Rudd, J.W.M., Bodaly, R.A., Roulet, N.P., St. Louis, V.L., Heyes, A., Moore, T.R., Schiff, S., Aravena, R., Scott, K.J., Dyck, B., Harris, R., Warner, B., and Edwards, G. 1997. Increases in fluxes of greenhouse gases and methyl mercury following flooding of an experimental reservoir. Environmental Science and Technology **31**: 1334-1344.

Liang, L., Horvat, M., and Bloom, N.S. 1994. An improved speciation method for mercury by GC/CVAFS after aqueous phase ethylation and room temperature precollection. Talanta **41**: 371-379.

Littell, R.C., Milliken, G.A., Stroup, W.W., and Wolfinger, R.D. 1996. SAS System for Mixed Models. SAS Institute Incorporated, Cary, North Carolina.

Lodenius, M., A. Seppänen, and M. Herranen 1983. Accumulation of Mercury in Fish and Man from Reservoirs in Northern Finland. Water, Air and Soil Pollution 237-246.

Macalady, J.L., Mack, E.E., Nelson, D.C., and Scow, K.M. 2000. Sediment microbial community structure and mercury methylation in mercury-polluted Clear Lake, California. Applied and Environmental Microbiology **66**: 1479-1488.

Mason, R.P. and Fitzgerald, W.F. 1993. The distribution and biogeochemical cycling of mercury in the Equatorial Pacific Ocean. Deep-Sea Research **40**: 1897-1924.

Mason, R.P., Fitzgerald, W.F., and Morel, F.M.M. 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. Geochimica et Cosmochimica Acta **58**: 3191-3198.

Mason, R.P., Reinfelder, J.R., and Morel, F.M.M. 1996. Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. Environmental Science and Technology **30**: 1835-1845.

Matilainen, T., Verta, M., Niemi, M., and Uusi-Rauva, A. 1991. Specific rates of net methylmercury production in lake sediments. Water, Air, & Soil Pollution **56**: 595-605.

Matthews, C.J.D. Greenhouse gas production in boreal reservoirs. M. Sc. thesis, Edmonton, Alberta.

Miskimmin, B.M. 1991. Effect of natural levels of dissolved organic carbon (DOC) on methyl mercury formation and sediment-water partitioning. Bulletin of Environmental Contamination and Toxicology **47**: 743-750.

Miskimmin, B.M., Rudd, J.W.M., and Kelly, C.A. 1992. Influence of dissolved organic carbon, pH, and microbial respiration rates on mercury methylation and demethylation in lake water. Canadian Journal of Fisheries and Aquatic Sciences **49**: 17-22.

Monson, B. 1998. Mercury cycling in low alkalinity lakes and factors influencing bioavailability. Dissertation Abstracts International Part B: Science and Engineering **58**: 3536.

Monson, B.A. and Brezonik, P.L. 1998. Seasonal patterns of mercury species in water and plankton from softwater lakes in northeastern Minnesota. Biogeochemistry **40**: 147-162.

Morrison, K.A. and Thérien, N. 1991. Experimental evaluation of mercury release from flooded vegetation and soils. Water, Air, and Soil Pollution **56**: 607-619.

Mucci, A., Lucotte, M., Montgomery, S., Plourde, Y., Pichet, P., and Van Tra, H. 1995. Mercury remobilization from flooded soils in a hydroelectric reservoir of northern

Quebec, La Grande. 2. Results of a soil resuspension experiment. Canadian Journal of Fisheries and Aquatic Sciences **52**: 2507-2517.

Myers, G.J., Davidson, P.W., Cox, C., Shamlaye, C., Cernichiari, E., and Clarkson, T.W. 2000. Twenty-seven years studying the human neurotoxicity of methylmercury exposure. Environmental Research **83**: 275-285.

Pak, K.-R. and Bartha, R. 1998. Mercury methylation and demethylation in anoxic lake sediments and by strictly anaerobic bacteria. Applied and Environmental Microbiology **64**: 1013-1017.

Paterson, M.J., Findlay, D., Beaty, K., Findlay, W., Schindler, E.U., Stainton, M., and Mccullough, G. 1997. Changes in the planktonic food web of a new experimental reservoir . Canadian Journal of Fisheries and Aquatic Sciences **54**: 1088-1102.

Paterson, M.J., Rudd, J.W.M., and St. Louis, V. 1998. Increases in total and methylmercury in zooplankton following flooding of a peatland reservoir. Environmental Science & Technology **32**: 3868-3874.

Peech Cherewyk, K.A. *Methylmercury bioaccumulation in zooplankton: an assessment of exposure routes and accumulation in newly flooded reservoirs*. M. Sc. thesis. University of Manitoba, Department of Entomology, Winnipeg, Manitoba.

Pickhardt, P.C., Folt, C.L., Chen, C.Y., Klaue, B., and Blum, J.D. 2002. Algal blooms reduce the uptake of toxic methylmercury in freshwater food webs. Proceedings of the National Academy of Sciences **99**: 4419-4423.

Planas, D., Desrosiers, M., Groulx, S.R., Paquet, S., and Carignan, R. 2000. Pelagic and benthic algal responses in eastern Canadian Boreal Shield lakes following harvesting and wildfires. Canadian Journal of Fisheries and Aquatic Sciences. Suppl. 2. Impacts of major watershed perturbations on aquatic ecosystems. **57**: 136-145.

Plourde, Y., Lucotte, M., and Pichet, P. 1997. Contribution of suspended particulate matter and zooplankton to MeHg contamination of the food chain in midnorthern Québec (Canada) reservoirs. Canadian Journal of Fisheries and Aquatic Sciences **54**: 821-831.

Ramlal, P.S., Kelly, C.A., Rudd, J.W.M., and Furutani, A. 1993. Sites of methyl mercury production in remote Canadian Shield lakes. Canadian Journal of Fisheries and Aquatic Sciences **50**: 972-979.

Ramlal, P.S., Rudd, J.W.M., Furutani, A., and Xun, L. 1985. The effect of pH on methyl mercury production and decomposition in lake sediments. Canadian Journal of Fisheries and Aquatic Sciences **42**: 685-692.

Regnell, O., Hammar, T., Helgee, A., and Troedsson, B. 2001. Effects of anoxia and sulfide on concentrations of total and methyl mercury in sediment and water in two Hg-polluted lakes. Canadian Journal of Fisheries and Aquatic Sciences **58**: 506-517.

Rehulka, J. 2002. Content of inorganic and organic pollutants in the fish from the Slezska Harta reservoir. Czech Journal of Animal Science **47**: 30-44.

Richardson, M., Mithchell, M., Coad, S., and Raphael, R. 1995. Exposure to mercury in Canada: a Multimedia analysis. Water, Air, and Soil Pollution **80**: 31-39.

Robinson, J.B. and Tuovinen, O.H. 1984. Mechanisms of microbial tesistance and detoxification of mercury and organomercury compounds: physiological, biochemical, and genetic analyses. Microbiological Reviews **48** : 95-124.

Schindler, D.W. 1998. Replication versus realism: The need for ecosystem-scale experiments. Ecosystems **1**: 323-334.

Sellers, P., Kelly, C.A., Rudd, J.W.M., and MacHutchon, A.R. 1996. Photodegradation of methylmercury in lakes. Nature **380**: 694-697.

St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., Beaty, K.G., Bloom, N.S., and Flett, R.J. 1994. Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. Canadian Journal of Fisheries and Aquatic Sciences **51**: 1065-1076.

St. Louis, V.L., Kelly, C.A., Duchemin, E., Rudd, J.W.M., and Rosenberg, D.M. 2000. Reservoir surfaces as sources of greenhouse gases to the atmosphere: a global estimate. Bioscience **50**: 766-775.

St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., Beaty, K.G., Bloom, N.S., and Flett, R.J. 1994. Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. Canadian Journal of Fisheries and Aquatic Sciences **51**: 1065-1076.

Stainton, M. P., Capel, M. J., and Armstrong, F. A. J. 1977. The chemical analysis of freshwater. Canadian Fisheries and Marine Services Miscellaneous Special Publications No. 25.

Stockner, J.G. and Armstrong, F.A.J. 1971. Periphyton of the Experimental Lakes Area, northwestern Ontario. Journal of Fisheries Research Board of Canada **28**: 215-229.

Tremblay, A., Cloutier, L., and Lucotte, M. 1998. Total mercury and methylmercury fluxes via emerging insects in recently flooded hydroelectric reservoirs and a natural lake. Science of the Total Environment **219**: 209-221.

Tremblay, A. and Lucotte, M. 1997. Accumulation of total mercury and methyl mercury in insect larvae of hydroelectric reservoirs. Canadian Journal of Fisheries and Aquatic Sciences **54**: 832-841.

Tremblay, A., Lucotte, M., Meili, M., Cloutier, L., and Pichet, P. 1996b. Total mercury and methylmercury contents of insects from boreal lakes: Ecological, spatial and temporal patterns. Water Quality Research Journal of Canada **31**: 851-873.

Tremblay, A., Lucotte, M., and Rheault, I. 1996a. Methylmercury in a benthic food web

of two hydroelectric reservoirs and a natural lake of northern Québec (Canada). Water, Air, and Soil Pollution **91**: 255-269.

Tremblay, A., Lucotte, M., and Schetagne, R. 1998. Total mercury and methylmercury accumulation in zooplankton of hydroelectric reservoirs in northern Québec (Canada). Science of the Total Environment **213**: 307-315.

Ullrich, S.M., Tanton, T.W., and Abdrashitova, S.A. 2001. Mercury in the aquatic environment: A review of factors affecting methylation. Critical Reviews in Environmental Science and Technology **31**: 241-293.

Vandal, G.M., Mason, R.P., and Fitzgerald, W.F. 1991. Cycling of volatile mercury in temperate lakes. Water, Air, and Soil Pollution **56**: 791-803.

Verdon, R., Brouard, D., Demers, C., Lalumiere, R., Laperle, M., and Schetagne, R. 1991. Mercury evolution (1978-1988) in fishes of the La Grande hydroelectric complex, Quebec, Canada. Water, Air, and Soil Pollution **56**: 405-417.

Watras, C.J., Back, R.C., Halvorsen, S., Hudson, R.J.M., Morrison, K.A., and Wente, S.P. 1998. Bioaccumulation of mercury in pelagic freshwater food webs. Science of the Total Environment **219**: 183-208.

Watras, C.J., Morrison, K.A., Host, J.S., and Bloom, N.S. 1995. Concentration of mercury species in relationship to other site-specific factors in the surface waters of northern Wisconsin lakes. Limnology and Oceanography **40**: 556-565.

Watras, C.J. and Bloom, N.S. 1992. Mercury and methylmercury in individual zooplankton: Implications for bioaccumulation. Limnology and Oceanography **37**: 1313-1318.

Weihe, P., Grandjean, P., Debes, F., and White, R. 1996. Health implications for Faroe Islanders of heavy metals and PCBs from pilot whales. The Science of the Total Environment **186**: 141-148.

Westcott, K. and Kalff, J. 1996. Environmental factors affecting methyl mercury accumulation in zooplankton. Canadian Journal of Fisheries and Aquatic Sciences **53**: 2221-2228.

Wheatley, B. and Wheatley, M.A. 2000. Methylmercury and the health of indigenous peoples: a risk management challenge for physical and social sciences and for public health policy. The Science of the Total Environment **259**: 23-29.

Wiener, J.G. and Stokes, P.M. 1990. Enhanced bioaccumulation of mercury, cadmium and lead in low-alkalinity waters: An emerging regional environmental problem. Environmental Toxicology and Chemistry **9**: 821-823.

Xun, L., Campbell, N.E.R., and Rudd, J.W.M. 1987. Measurements of specific rates of net methyl mercury production in the water column and surface sediments of acidified

and circumneutral lakes. Canadian Journal of Fisheries and Aquatic Sciences **44**: 750-757.

Yingcharoen, D. and Bodaly, R.A. 1993. Elevated mercury levels in fish resulting from reservoir flooding in Thailand. Asian Fisheries Science **6**: 73-80.

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Figure 4.15. Mean partial pressure of carbon dioxide (pCO_2) in surface water. Bars represent one standard error of three replicates.

Figure 4.16. Mean partial pressure of methane (pCH_4) in surface water. Bars represent one standard error of three replicates.

Figure 4.17. Tritium activity in surface water of each limnocorral.

TABLES

Table 4.1. Mass of THg and MeHg (ng) in soil and vegetation before and after burning.

Species	Biomass g/limnocorral		THg ng/limnocorral		MeHg ng/limnocorral	
	Fresh	Burned	Fresh	Burned	Fresh	Burned
Alnus crispa	219	19	777	142	11	5
Betula papyrifera	814	37	5067	406	244	18
Chamaedaphne calyculata	392	18	4193	105	137	2
Kalmia polifolia	21	1	222	7	17	0
Larix larcinia	31	1	891	5	18	0
Ledum groenlandicum	114	4	1175	21	23	1
Picea mariana	370	13	4789	67	74	7
Pinus banksiana	2744	74	29084	262	549	15
Pleurozium schreberi	5	0	272	3	4	0
Polytrichum spp.	5	0	196	3	2	0
Prunus pensylvanica	30	2	149	7	15	0
Salix humilis	33	2	312	27	42	0
Sphagnum	219	6	4466	49	110	1
Vaccinium spp.	62	1	688	8	22	1
TOTAL vegetation	5060	177	52280	1111	1268	49
Soil	46852	35175	7590017	1661336	28377	5335
TOTAL soil and vegetation	51912	35352	7642297	1662447	29645	5384

Table 4.2. Summary of the amount of THg and MeHg added with each treatment.

Summary of added Carbon (g)				
	Fresh	Partial Burn	Complete Burn	Controls
Soil	5303	5303	377	0
Vegetation	202	81	81	0
Total	5505	5384	458	0

Summary of added THg (ng)				
	Fresh	Partial Burn	Complete Burn	Controls
Soil	7590017	7590017	1661336	0
Vegetation	52280	1111	1111	0
Total	7642297	7591128	1662447	0

Summary of added MeHg (ng)				
	Fresh	Partial Burn	Complete Burn	Controls
Soil	1268	1268	49	0
Vegetation	28377	5335	5335	0
Total	29645	6603	5384	0

Table 4.3. Contrasts of aqueous THg concentrations in treatments analyzed with the mixed model analysis. THg = total mercury, degrees of freedom in the numerator was 1, degrees of freedom in the denominator was 9, F value = is a ratio of the variability, Pr is the probability that there is no difference between treatments.

Contrasts THg	**F value**	**Pr**
Controls vs. Complete Burn	0.0	0.9874
Controls vs. Fresh	58.61	<.0001
Controls vs. Partial Burn	23.36	0.0009
Complete Burn vs. Fresh	58.70	<.0001
Complete Burn vs. Partial Burn	23.45	0.0009
Fresh vs. Partial Burn	58.61	<.0001

Table 4.4. Contrasts of aqueous MeHg concentrations in treatments analyzed with the mixed model analysis. MeHg = methyl mercury, degrees of freedom in the numerator was 1, degrees of freedom in the denominator was 9, F value = is a ratio of the variability, Pr is the probability that there is no difference between treatments.

Contrasts MeHg	**F value**	**Pr > F**
Controls vs. Complete Burn	1.43	0.2617
Controls vs. Fresh	67.76	<.0001
Control vs. Partial Burn	41.04	0.0001
Complete Burn vs. Fresh	49.48	<.0001
Complete Burn vs. Partial Burn	27.13	0.0006
Fresh vs. Partial Burn	67.76	<.0001

Table 4.5. Net MeHg production ($\mu g \cdot m^{-2} \cdot day^{-1}$) in experimental limnocorrals derived by the difference in concentrations. Net rates of change in MeHg concentrations was not applicable in Complete Burn treatments and Controls.

Treatments	**Before July 18th**	**After July 18th**
Fresh	+0.068	-0.091
Partial burn	+0.029	-0.003

FIGURES

Figure 4.1. Mean THg concentrations in surface water (ng L^{-1} +/- one standard error of the mean [SEM]). The first samples were collected on June 26th before treatments addition.

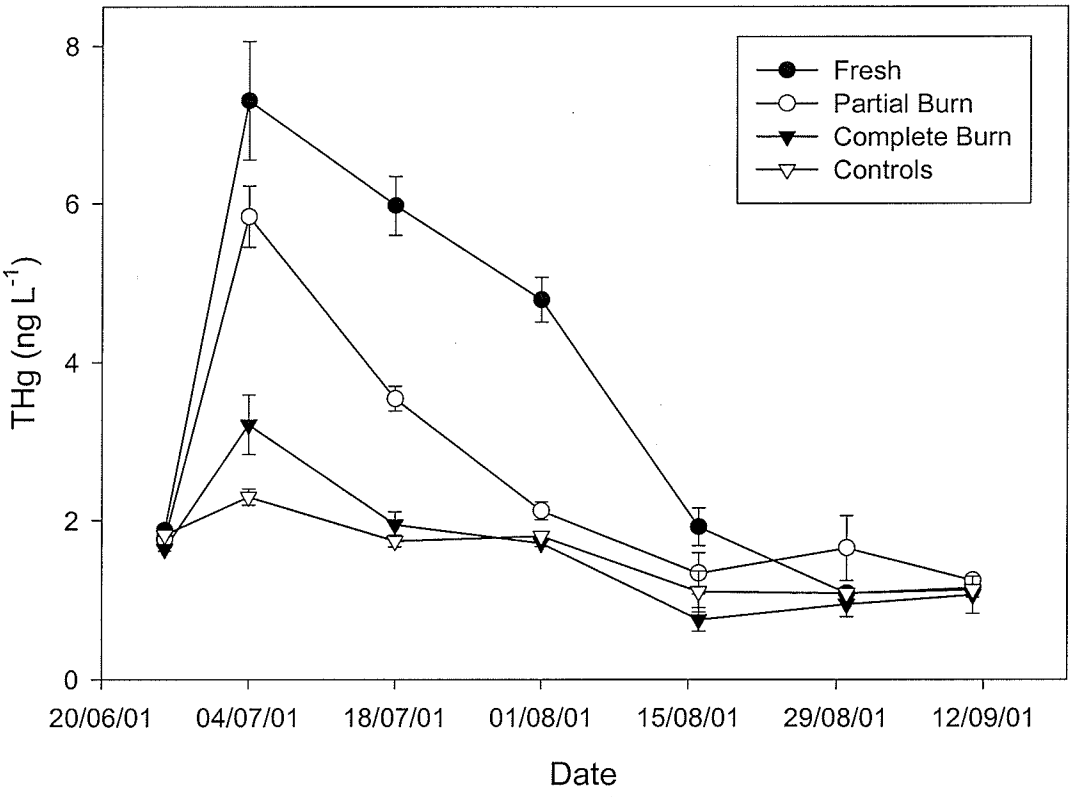


Figure 4.2. Mean MeHg concentrations in surface water (ng L^{-1} +/- one SEM). The first samples were collected on June 26th before treatments were added.

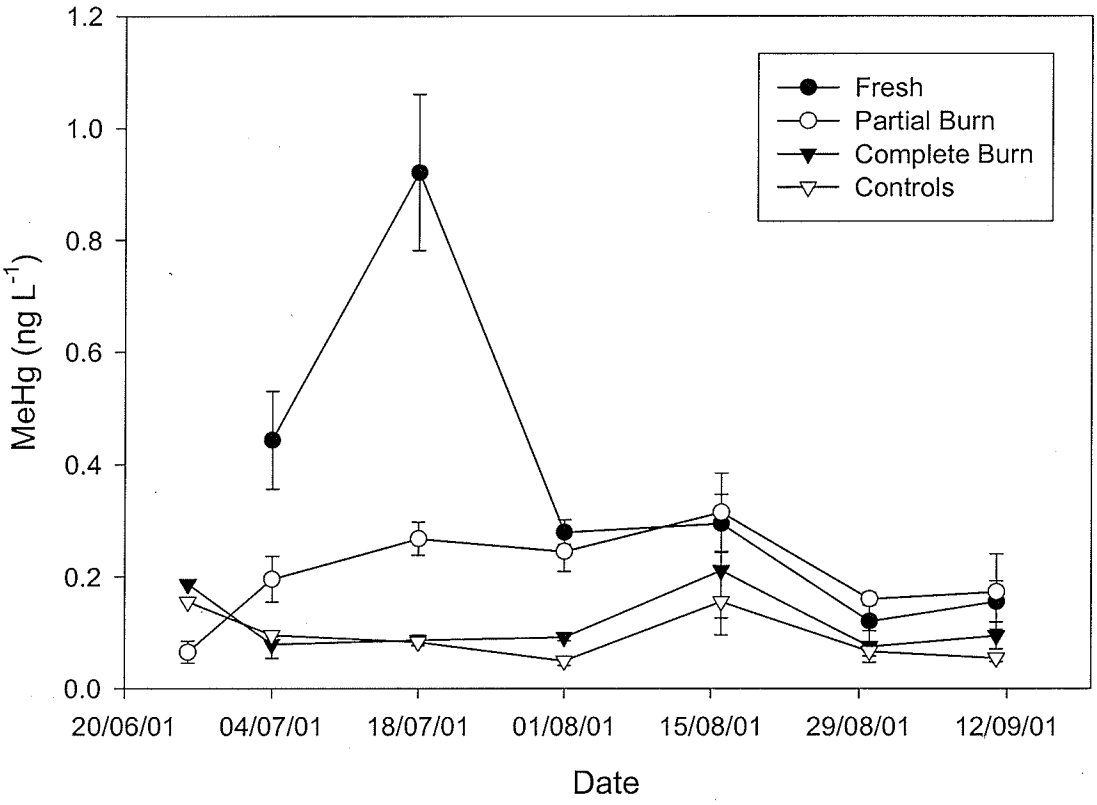


Figure 4.3. Mean MeHg concentrations in zooplankton (ng g^{-1} d. w. +/- one SEM).

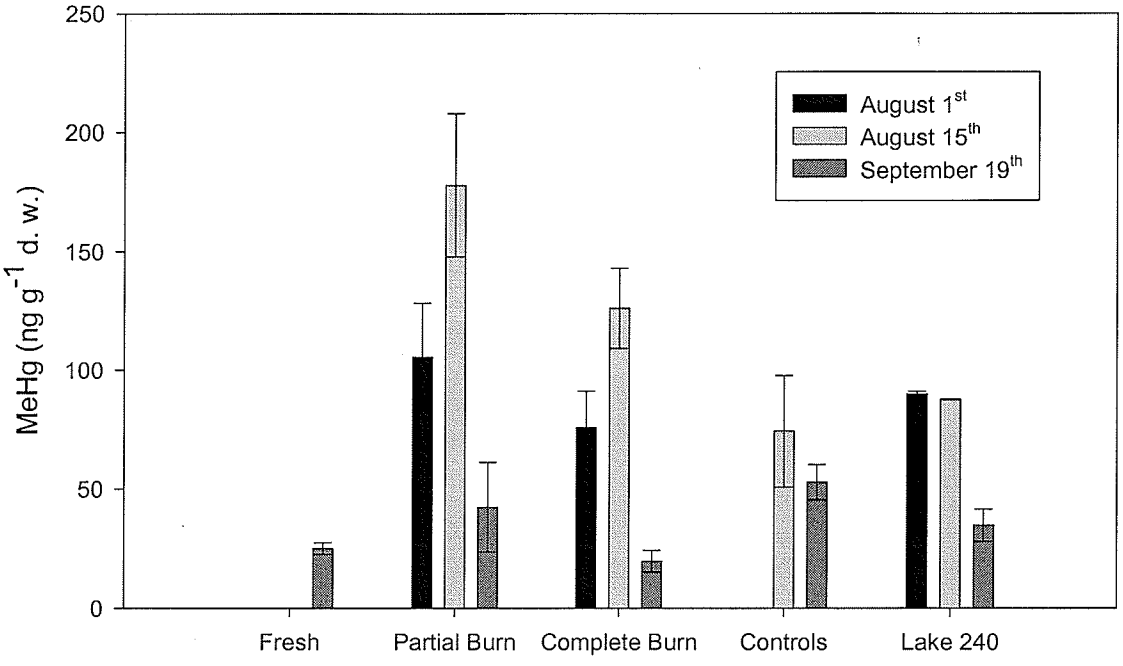


Figure 4.4. Mean MeHg concentrations (ng g^{-1} d. w. +/- one SEM) in Chironomid larvae for the week of September 19th, 2001.

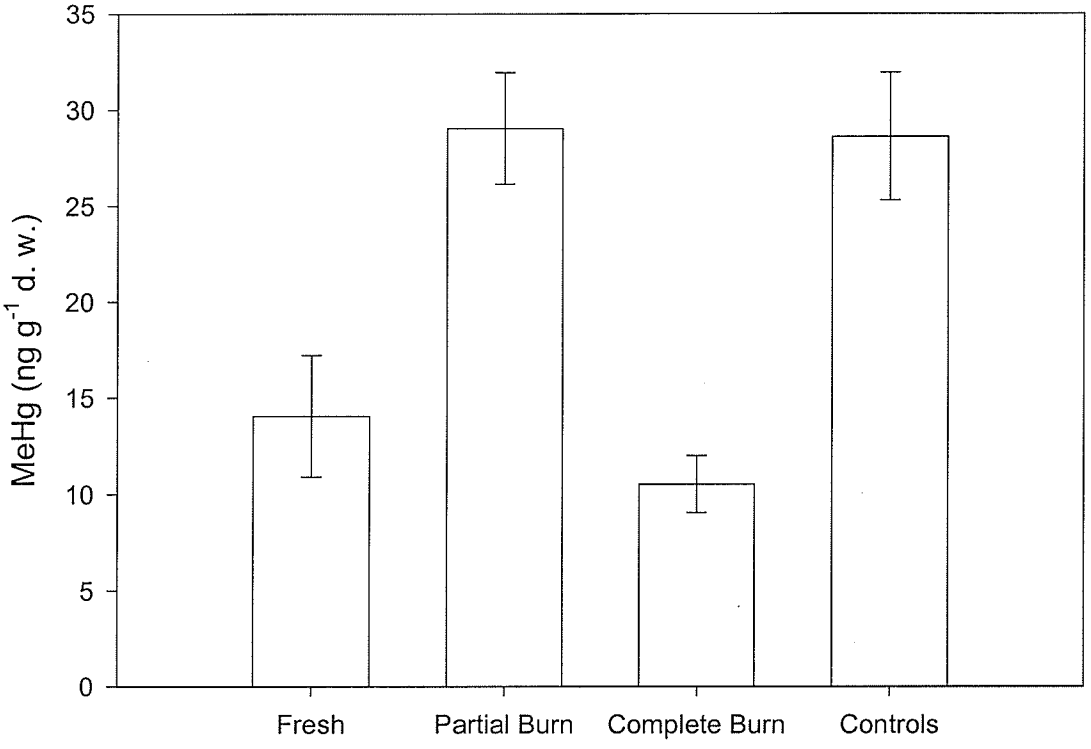


Figure 4.5. Mean MeHg concentrations in emerging insects (ng g^{-1} d. w. +/- one SEM).

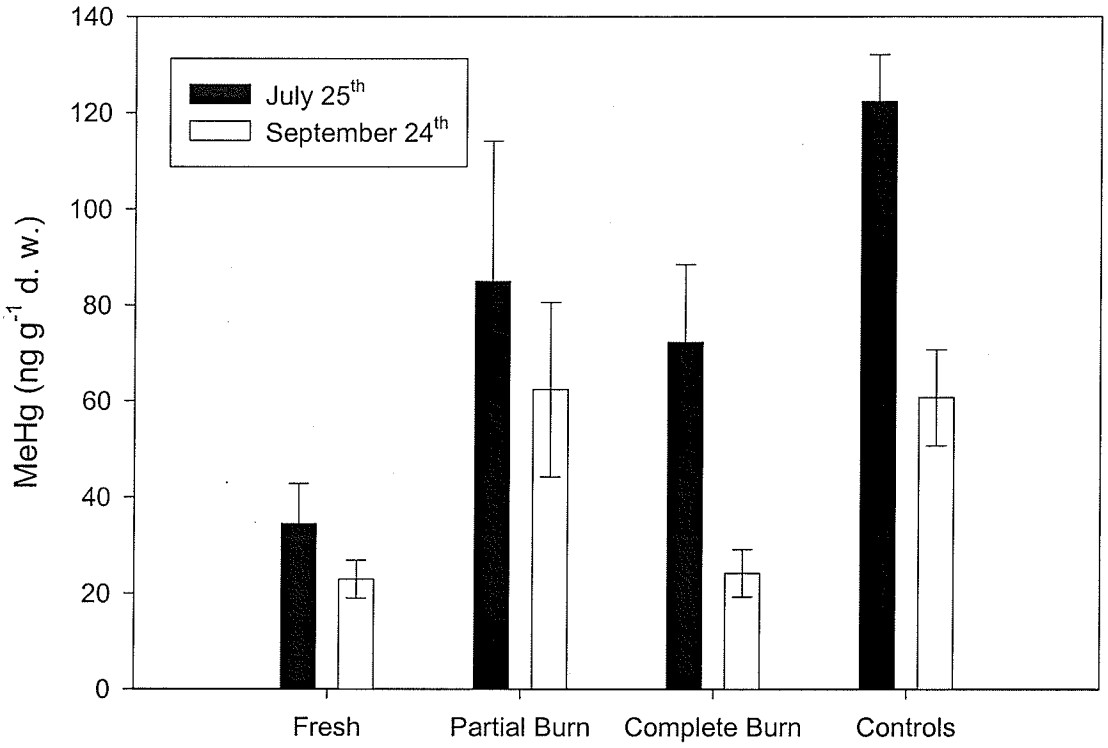


Figure 4.6. Bioaccumulation factors (log BAF; $[MeHg]_{zooplankton}$ /$[MeHg]_{water}$), of MeHg in zooplankton and Chironomid larvae for September. Bars represent maximum and minimum values.

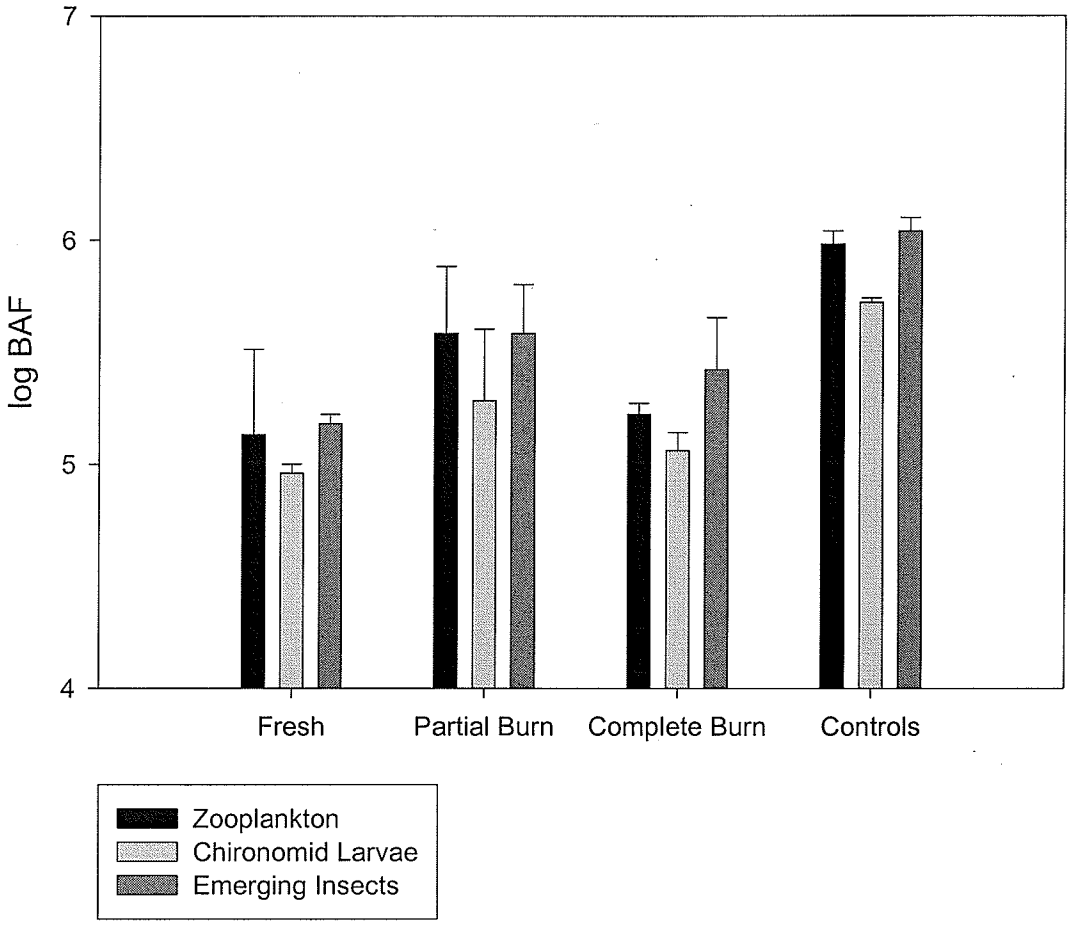


Figure 4.7. Mean dissolved organic carbon (DOC) concentrations in surface water ($\mu mol \cdot L^{-1}$ +/- one SEM).

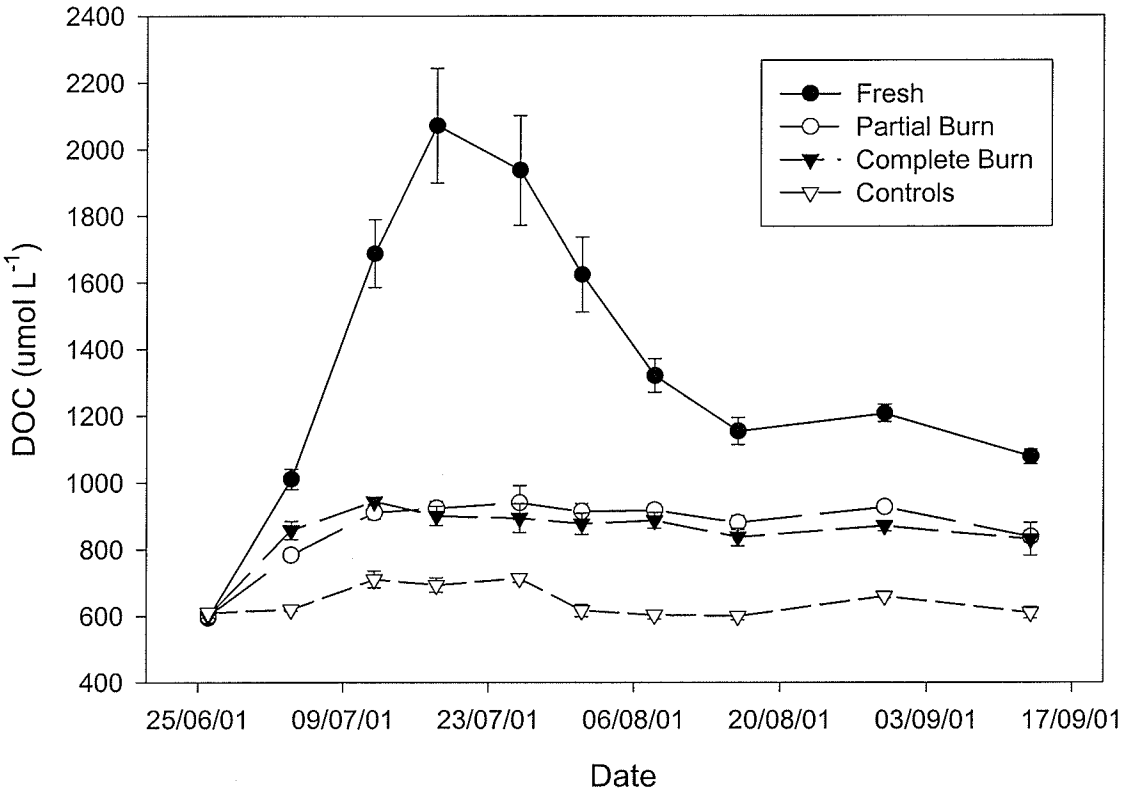


Figure 4.8. Linear regressions of the bioaccumulation factor (log BAF) of MeHg in zooplankton, Chironomid larvae, and emerging insects versus dissolved organic carbon (log DOC). r^2 is the variability in the log BAF that is explained by log DOC.

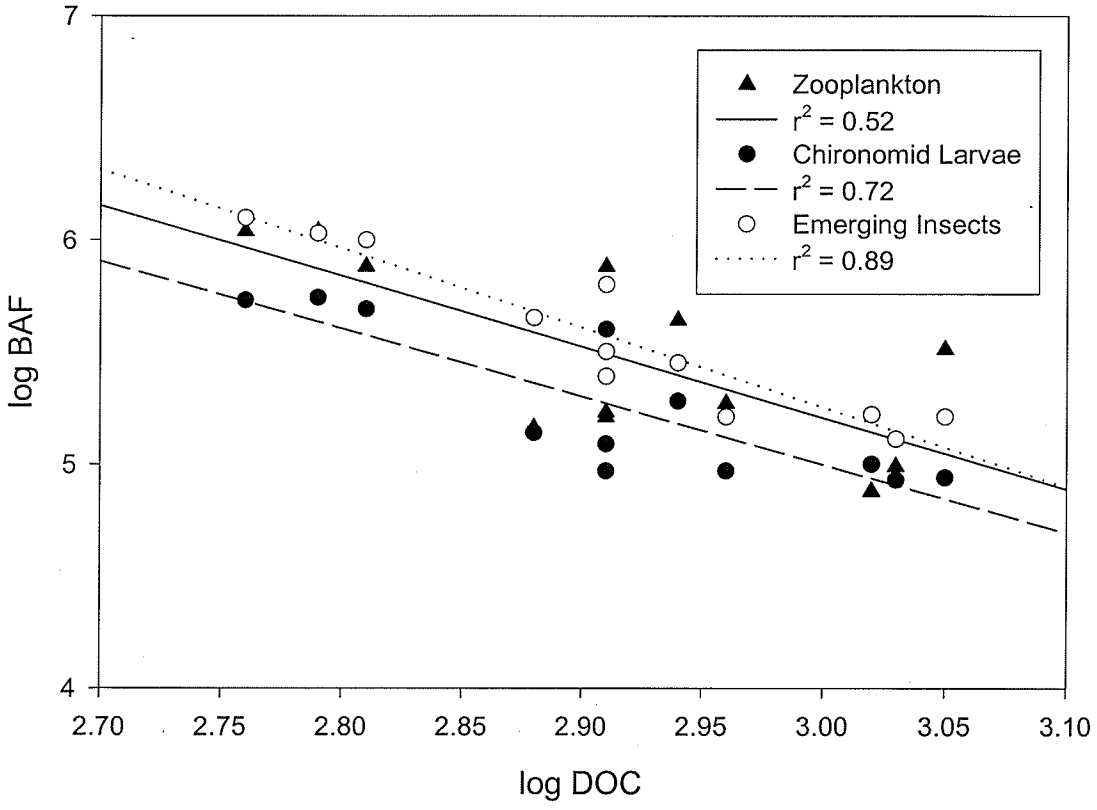


Figure 4.9. Mean concentrations of MeHg in periphyton (ng g^{-1} d. w. +/- one SEM).

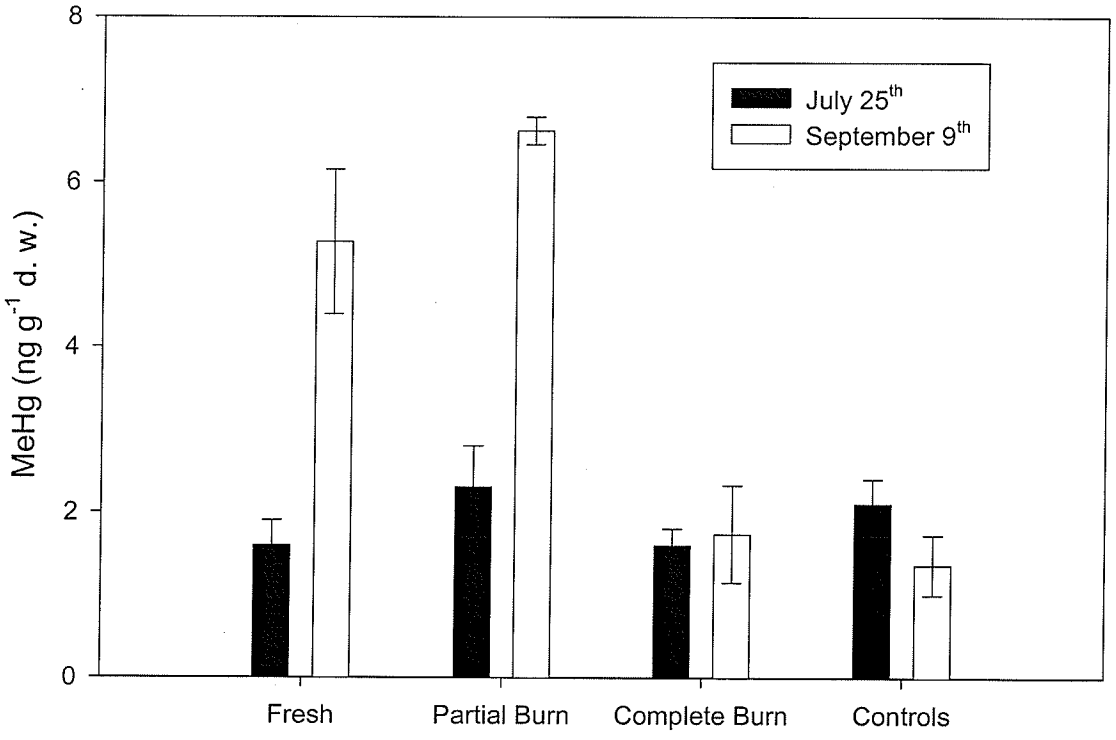


Figure 4.10. Bioconcentration factors (BCFs; $[MeHg]_{periphyton}$ /$[MeHg]_{water}$) of MeHg in periphyton. Bars represent maximum and minimum values on September 9th, 2001.

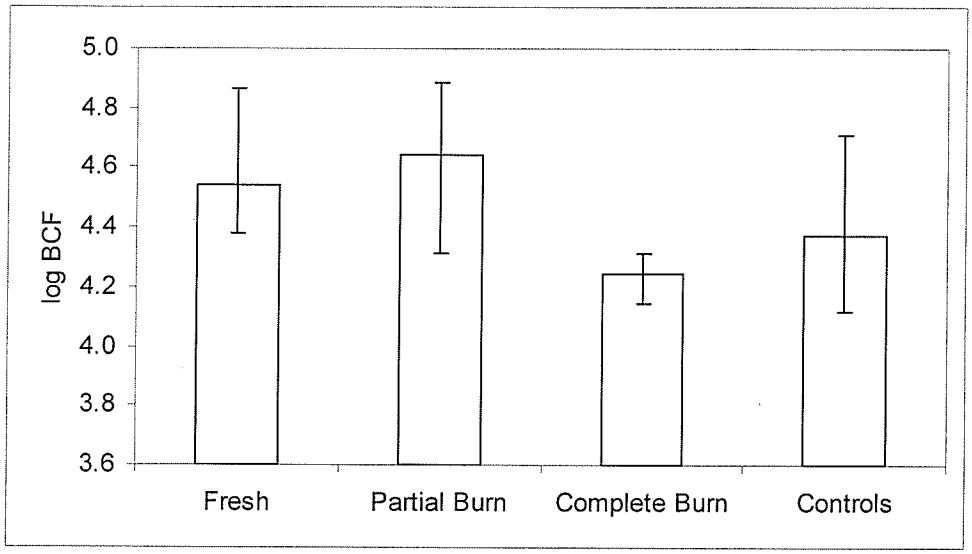


Figure 4.11. Biomass of periphyton (μg·cm^{-2} +/- one SEM).

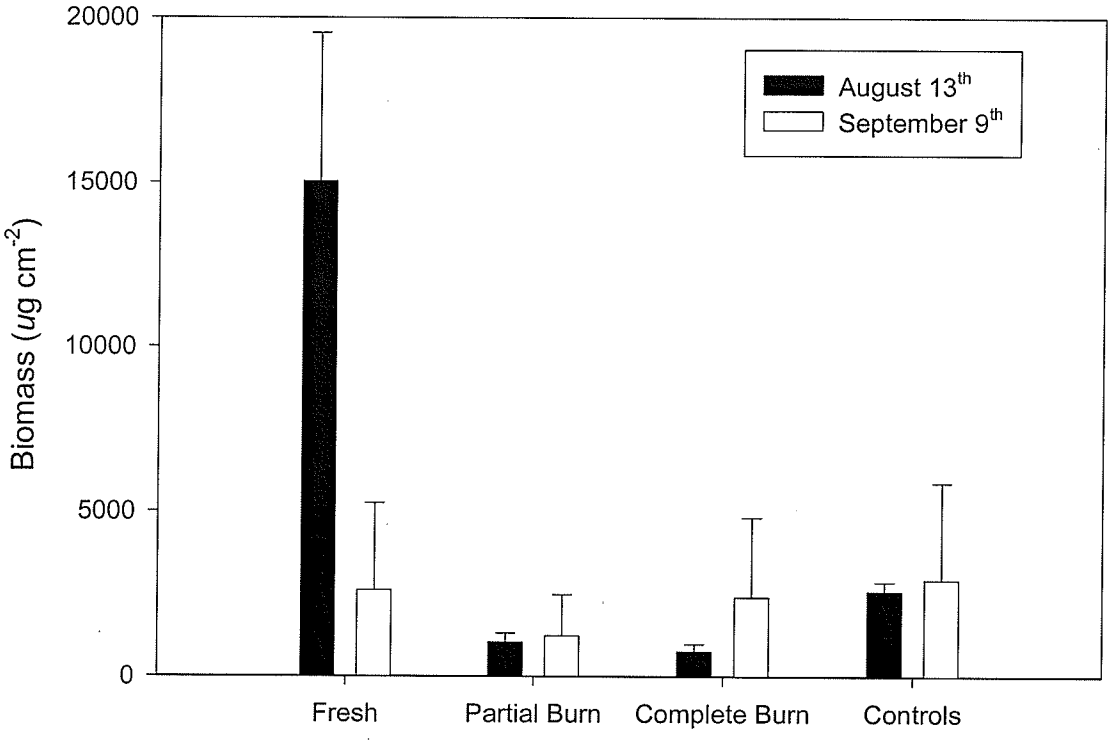


Figure 4.12. Biomass of bacteria (μg·cm^{-2} +/- one SEM).

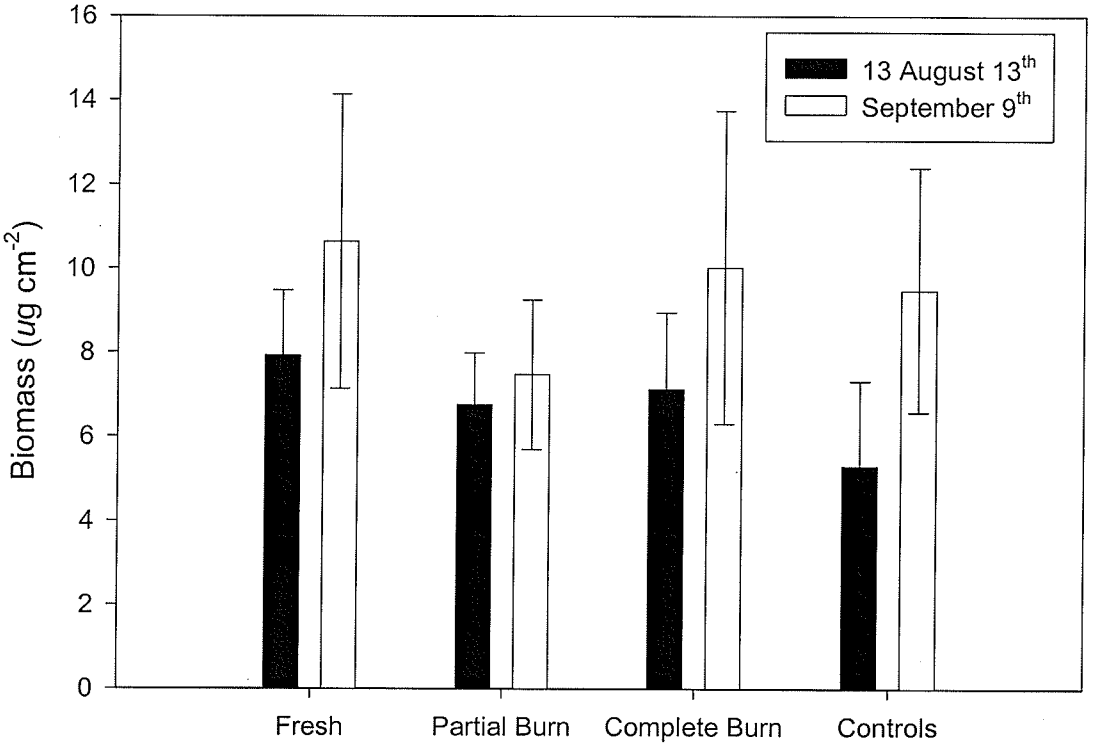


Figure 4.13. Mean water temperature in Partial Burn treatments, for example, (^{o}C +/- one SEM). Bars represent one standard error of three replicates.

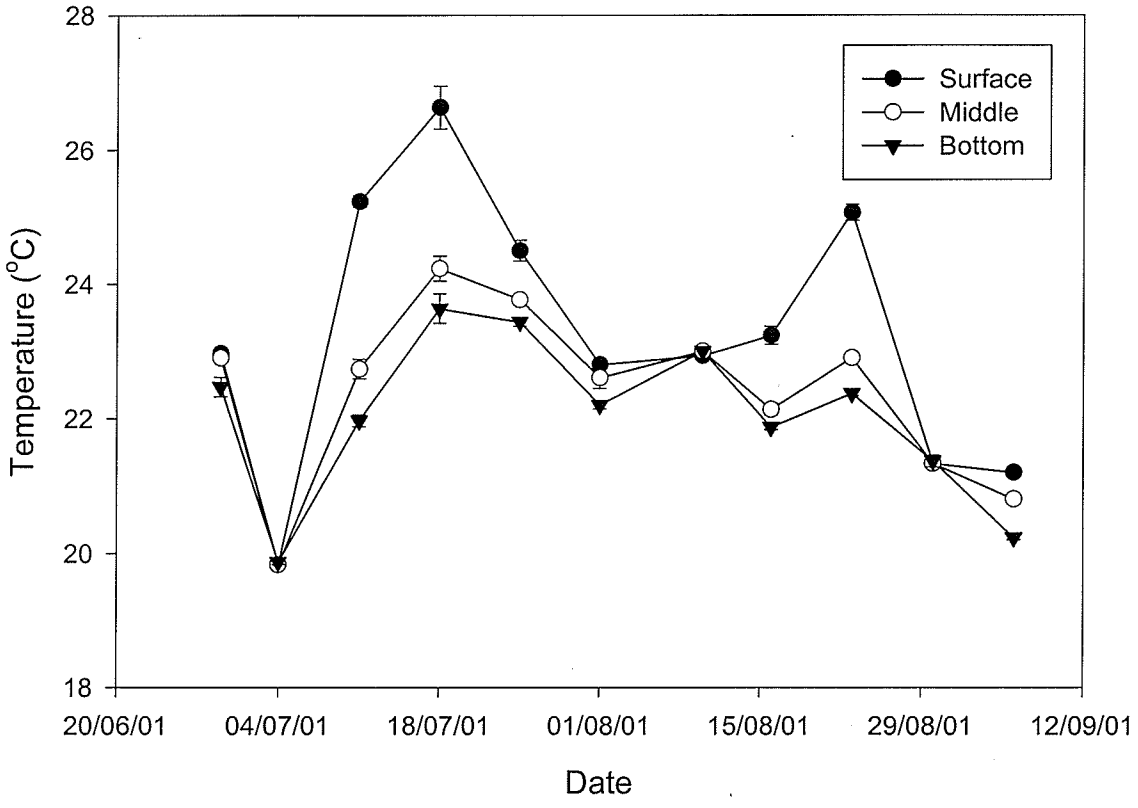


Figure 4.15. Mean partial pressure of carbon dioxide (pCO_2) (µatms +/- one SEM) in surface water.

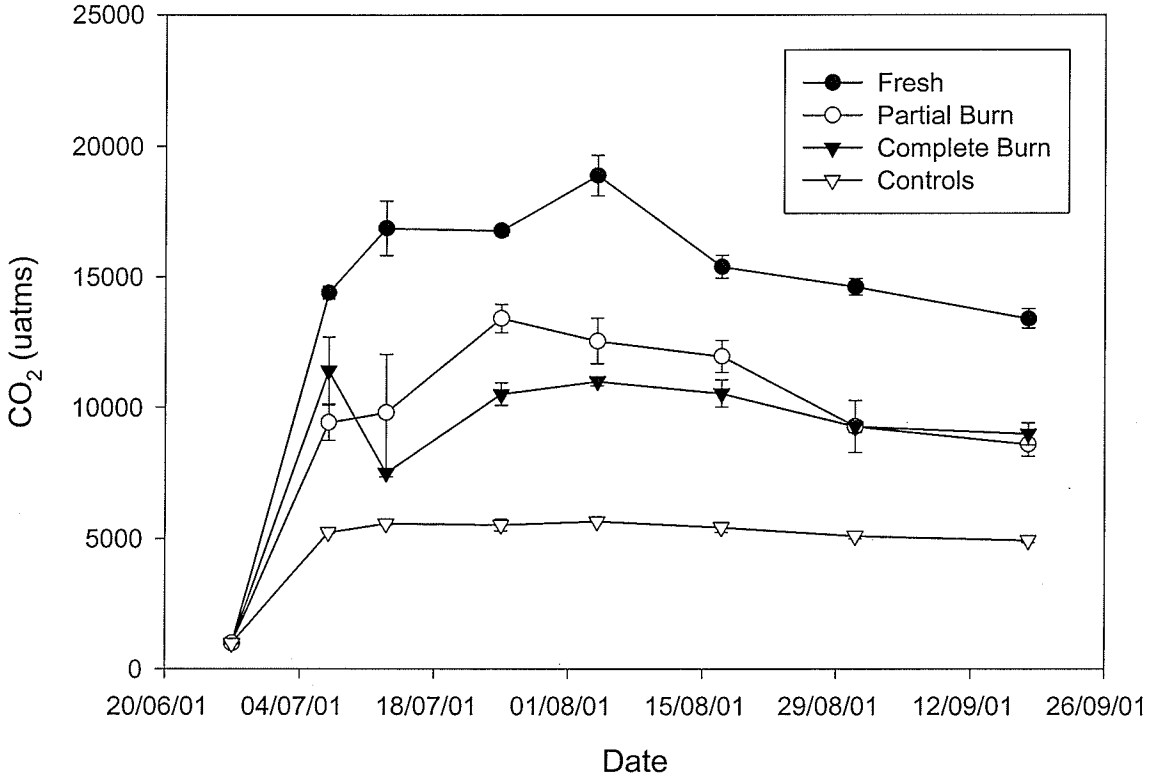


Figure 4.16. Mean partial pressure of methane (pCH_4) in surface water (µatms +/- one SEM). Bars represent one standard error of three replicates.

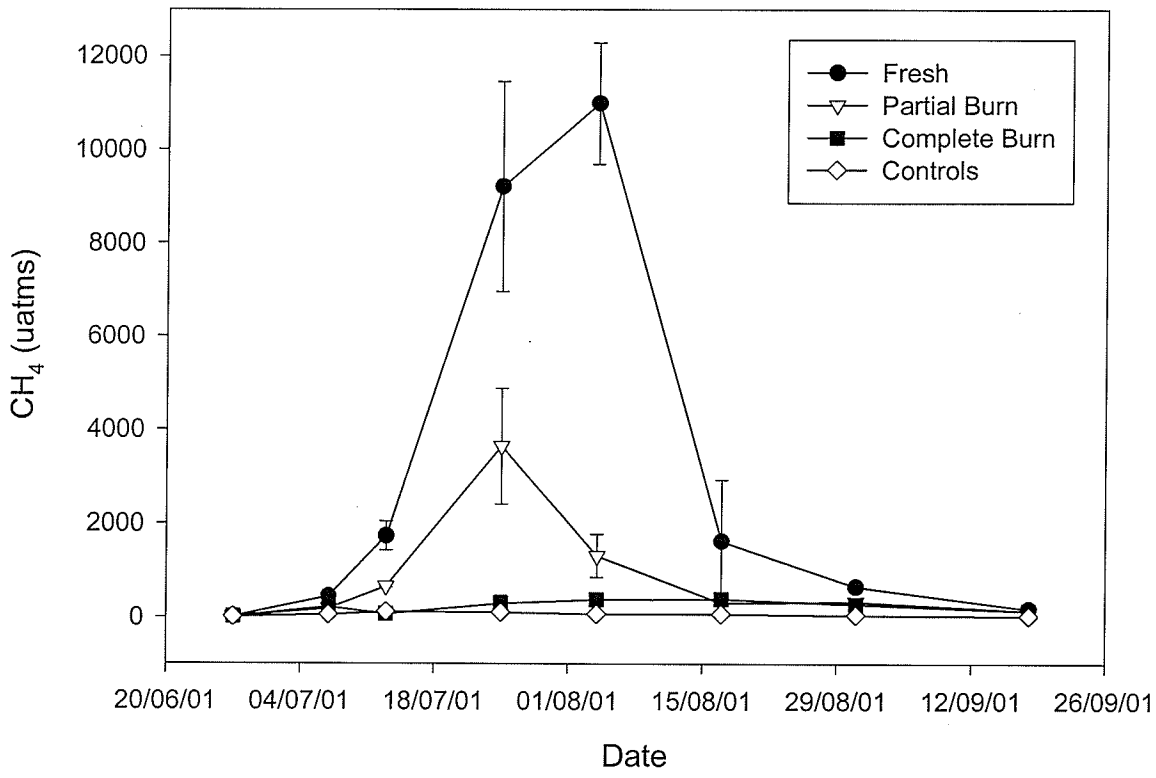
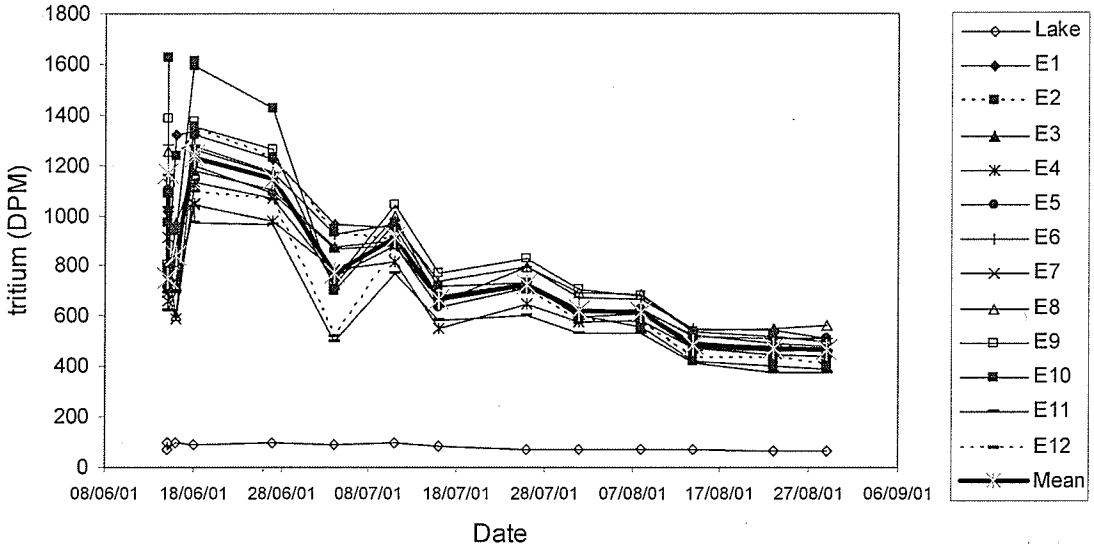


Figure 4.17. Tritium activity in surface water of each limnocorral (enclosure denoted by "E").



GENERAL CONCLUSION

Vegetation lost 96.6 and 94.2% of their THg and MeHg from burning. The loss of THg and MeHg in vegetation correlated with the loss of plant mass. After burning, soil lost 78.8 and 81.8% of its THg and MeHg. According to biomass surveys of forest and wetland areas in northwestern Ontario, and assuming the wetlands constitute approximately 12% of the boreal ecoregion, I estimate that fires in the Canadian boreal region could emit 20 ng of $Hg \cdot ha^{-1}$ and $56*10^6$ g of $Hg \cdot y^{-1}$. This is within the range of global estimates of Hg released from fires. I suspect that the global estimate of Hg emission from fires may be low because the amount of Hg stored in plants and the efficiency of Hg released from combustion of vegetation has not been well documented until recently.

In my limnocorral experiment, burning before flooding lowered THg and MeHg concentrations in water, but not in biota. Uptake of MeHg in zooplankton, Chironomid larvae, and emerging insects was modified by DOC as their BAFs correlated significantly with DOC. Since fish receive the majority of their MeHg through their food (Hall *et al.* 1997), I suspect that burning before flooding will not lower MeHg accumulation in fish.

Burning before flooding has an interesting influence on the carbon cycle. Before flooding forests are sinks for CH_4 and neutral with regard to CO_2 cycling. After flooding CH_4 is produced from anaerobic decomposition of organic carbon and emitted to the atmosphere, along with CO_2. CH_4 is more effective at trapping heat in the atmosphere than CO_2. During fires relatively little CH_4 is produced. Burning before flooding substantially decreased the partial pressure of CH_4 that I observed in my limnocorrals.

On the other hand, burning will mineralize most of the carbon, whereas flooding may degrade a much smaller portion of the total stored carbon. As a result, burning before flooding would probably contribute more CO_2 to the atmosphere than flooding alone.

Controlled burning before flooding is clearly not a suitable strategy to mitigate MeHg contamination in fish of hydroelectric reservoirs. Although there are some benefits to burning before flooding such as lowering the amount of THg and MeHg in the system, lowering aqueous concentrations of THg and MeHg, and lowering concentrations of CH_4, in one season of experimentation it did not fulfill the desire to lower MeHg bioaccumulation. If governing institutions and hydroelectric companies are to fulfill their goal of finding a method to ameliorate MeHg contamination in reservoirs, further investigations of mitigation methods will be necessary.

Unfortunately, many of the mitigation options being investigated do not consider the effects to wildlife. For example, if controlled burning before flooding were implemented to lower MeHg concentrations in fish to levels safe for human consumption, further ecological disturbances may result such as accumulation of incomplete combustion products or by-products of combustion, habitat loss, and atmospheric pollution. Another mitigation option being considered is addition of selenium to lower MeHg uptake in fish. The mechanisms by which selenium lowers MeHg in fish muscle tissue is unclear, however, there are some indications that it may cleave MeHg from sulphur proteins in muscle tissue and redistribute it to the kidneys and liver. This may benefit the fish consumer that consciously eats only the muscle tissue, but piscivorous fish, raptors, and other fish predators will not benefit from this method. In fact, this method may compound the risk for toxicity by exposure to selenium, another toxin.

Although intensive fishing seems labour intensive because of the requirement to repeatedly over fish the system, it seems to me that this is the most benign mitigation option. Application of intensive fishing, in combination with another mitigation method, may also be a suitable solution. For example, it is unknown if selenium can lower MeHg concentrations in fish without causing toxicity. A well-planned and controlled field experiment will test this possibility next summer at ELA. If safe concentrations of selenium effectively lower concentrations of MeHg in fish, then this method may be implemented in a whole ecosystem experiment. Selenium addition would be an extremely easy and inexpensive method to lower MeHg contamination if it works and is applied conscientiously. During the initial 10 to 30 years of flooding when fish MeHg concentrations are highest in reservoirs, additions of selenium may be supplemented with periodic intensive fishing events, which could also generate employment for local people.