

Methyl mercury in pristine and impounded boreal peatlands, Experimental Lakes Area, Ontario¹

A. Heyes, T.R. Moore, J.W.M. Rudd, and J.J. Dugoua

Abstract: Methyl mercury (MeHg) concentrations were measured in peat and peat porewater of pristine wetlands and an impounded riparian wetland at the Experimental Lakes Area in northwestern Ontario, Canada. In pristine wetlands, MeHg concentrations in peat ranged from 0.1 to 60 ng·g⁻¹ and in peat porewater from 0.02 (the detection limit) to 7.3 ng·L⁻¹, with higher concentrations in wetlands that received upland runoff. Impoundment increased the average MeHg concentration in the near-surface peat porewater from 0.2 to 1.0 ng·L⁻¹. As the increase was most dramatic near the peat – surface water interface, we suggest that the elevated MeHg concentrations resulted from an increase in net MeHg production associated with the decomposition of inundated vegetation. Impoundment increases the area of potential Hg methylation by imposing anoxia over the entire wetland surface and by facilitating the exchange of nutrients and MeHg between the peat surface and the surface water. No clear chemical control on MeHg concentration was observed among the pristine wetlands or in the impounded wetland. However, in laboratory incubations of peat, porewater MeHg concentration increased upon the addition of sulfate. We propose that sulfate availability is an important variable in Hg methylation in pristine northern wetlands.

Résumé : Nous avons mesuré les concentrations de méthylmercure (MeHg) dans la tourbe et l'eau interstitielle de la tourbe de terres humides intactes et d'un marécage riverain endigué dans la Région des lacs expérimentaux, dans le nord-ouest de l'Ontario, au Canada. Dans les terres humides intactes, les concentrations de MeHg dans la tourbe allaient de 0,1 à 60 ng·g⁻¹, et dans l'eau interstitielle de la tourbe, de 0,02 (limite de détection) à 7,3 ng·L⁻¹, les concentrations les plus élevées se trouvant dans les terres humides qui recevaient le ruissellement des hauteurs environnantes. L'endiguement augmentait la concentration moyenne de MeHg dans l'eau interstitielle proche de la surface de la tourbe, qui passait de 0,2 à 1,0 ng·L⁻¹. Étant donné que l'augmentation était particulièrement marquée près de l'interface tourbe – surface de l'eau, nous posons que les concentrations élevées de MeHg étaient causées par une hausse de la production nette de MeHg, associée à la décomposition de la végétation inondée. L'endiguement augmente la superficie de méthylation potentielle de Hg en imposant une anoxie sur toute la surface de la zone humide et en facilitant l'échange de nutriments et de MeHg entre la surface de la tourbe et la surface de l'eau. Nous n'avons observé aucune influence chimique nette sur la concentration de MeHg parmi les terres humides intactes ni dans le marécage endigué. Toutefois, dans des travaux d'incubation de tourbe en laboratoire, la concentration de MeHg dans l'eau interstitielle augmentait avec l'ajout de sulfate. Nous posons que la disponibilité du sulfate constitue une variable importante dans la méthylation de Hg dans les terres humides intactes du Nord.

[Traduit par la Rédaction]

Introduction

In North America, the most common contaminant of fisheries is methyl mercury (MeHg) (U.S. Environmental Protection Agency 1997). Most lakes suffer from elevated atmospheric inputs of total Hg (T-Hg) (Fitzgerald et al. 1998), which is reflected in the fish (Bodaly et al. 1993; Driscoll et al. 1994). As little of the T-Hg falls as MeHg (St. Louis

et al. 1996), for Hg to appear as MeHg in fish, it must undergo methylation within the watershed (Choi and Bartha 1994; Gilmour and Riedel 1995). Significant contamination of fish stocks with MeHg is common in lakes that have been altered for use as reservoirs (Bodaly et al. 1984; Verdon et al. 1991; Schetagne et al. 1997). In this case, Hg deposition need not be elevated for levels of MeHg to increase in fish (Bodaly and Fudge 1999). Rather, Hg methylation is stimulated by the microbial decomposition of flooded plant material and material in organic soils (Hecky et al. 1991; Kelly et al. 1997; Heyes et al. 1998). However, an enhancement of the effect, caused by elevated T-Hg pools in soil and sediment resulting from increased levels of atmospheric Hg deposition over the decades prior to impoundment, cannot be ignored.

The presence of Hg in peat bogs has been well documented (e.g., Jensen and Jensen 1991; Grondin et al. 1995; Benoit et al. 1998), and in their natural state, wetlands retain the majority of atmospherically deposited Hg (St. Louis et al. 1994). However, catchments containing wetlands are important sources of MeHg to lakes (e.g., St. Louis et al. 1994; Hurley et al. 1995; Branfireun et al. 1996). Aside from wet-

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lands being identified as MeHg sources, little has been published about the cycling of Hg within wetlands. However, few measurements have been made of MeHg concentrations in peat or T-Hg and MeHg in porewater (Bishop et al. 1995; Branfireun et al. 1996; Gilmour et al. 1998). Therefore, little can be said about how MeHg is distributed within a wetland, how MeHg burdens vary among wetland types, or under what conditions Hg is methylated within a wetland. Since Hg methylation has been linked to sulfate-reducing bacteria (Choi and Bartha 1993), and other redox-dependent microbial processes, such as methanogenesis, are related to water table position in wetlands (Bubier 1995), we hypothesized that Hg methylation would also be related to water table position.

In occupying the lower levels of the landscape, wetlands are often flooded by reservoir construction. The Experimental Lakes Area (ELA) Reservoir Project was undertaken to examine what the impact of impounding a small wetland would have on MeHg production and uptake into fish. The results of the study would be used to help constrain a model of Hg cycling in reservoirs. We hypothesized that upon impoundment, Hg methylation would increase with the expansion of anoxic condition over the entire peatland, and the increase in net methylation rate would be reflected in the porewater. The Hg methylation would be initially fueled by the rapid decomposition of terrestrial plant matter, which is rich in nutrients and Hg (Andersson 1979; Hecky et al. 1991; Heyes et al. 1998). As the pool of new carbon was finite, we hypothesized that the duration of elevated MeHg production would be limited.

Nutrients supplied to microorganisms through the porewater influence the activity of both Hg-methylating organisms and substrate-competing nonmethylating organisms. Porewater chemistry also affects the speciation of Hg, which controls Hg bioavailability (Benoit et al. 1998). As sulfate-reducing bacteria are the most likely bacteria to methylate Hg in the environment (Gilmour et al. 1992), we hypothesized that porewater chemistry, in particular sulfate concentration, would affect net MeHg production in the wetland.

In this paper, we report MeHg concentrations in peat and porewater of seven undisturbed wetlands in the ELA. We describe how 3 years of impoundment affected the size and distribution of the MeHg pool in the porewater of a riparian wetland. Finally, by examining the porewater chemistry among the pristine wetlands and over time in the impounded wetland and by manipulating peat and its porewater chemistry in the laboratory, we discuss what biogeochemical factors influence MeHg production in boreal peatlands.

Methods

ELA

The ELA is located in northwestern Ontario, Canada (49°40'N, 93°43'W). The climate is continental, with mean July and January temperatures of 19 and -17°C, respectively. Over the 1969–1995 period, the mean annual precipitation was 678 mm (K. Beatty, Freshwater Institute, 501 University Crescent, Winnipeg, MB R3T 2N6, Canada, personal communication). The uplands at ELA comprise areas of exposed lichen-covered Precambrian granite, shallow moss-covered soils (<5 cm thick), and slightly deeper soils (generally <50 cm deep) found in pockets in the granite. The shallow soils support black spruce (*Picea mariana*) whereas the deeper soil pock-

ets are covered in extensive bryophyte mats and support black spruce and jack pine (*Pinus banksiana*). Wetlands occur in a variety of positions in the drainage network, such as headwater collection areas and beside lakes and streams. There is some variation in the wetland vegetation, but in general, it is typical of bogs. Black spruce and tamarack (*Larix laricina*) form open canopies, and the shrubs *Chamaedaphne calyculata* and *Ledum groenlandicum* cover the *Sphagnum fuscum* hummocks. *Sphagnum magellanicum* and *Sphagnum fallax* occupy the wetter hollows and lawns. The wetlands in this study have been named based on their location in the drainage network and vegetation assemblage.

Pristine sites

The porewater chemistry and distribution of T-Hg and MeHg were examined in seven wetlands or wetland areas covering a range of wetland types at the ELA. Three of the wetlands, the Eagle Marsh, an upland bog, and a riverine wetland, were located in different watersheds and named for their most prominent feature. The Eagle Marsh was dominated by *Carex*, the upland bog had formed around a small stream, and the riverine wetland had formed by accretion of mosses along the lakeshore (Heyes 1996). The headwater wetland surrounding Lake 632 and the riparian wetland surrounding Lake 979 had hydrologically distinct areas within each wetland. The headwater wetland surrounding Lake 632 was classified as ombrotrophic bog except for the area around the inflow stream, which contained clusters of *Carex* and was classified as a poor fen (Branfireun et al. 1996). The area surrounding Lake 979 is hydrologically distinct from the NE arm, as the latter was not influenced by water flowing through the central pond (Fig. 1). The area surrounding Lake 979 was assigned the name riparian bog and the NE arm was named the NE bog. In the summers of 1992 and 1993, peat porewater profiles were taken from four sites in the riparian bog, two sites in the NE arm, two sites in the poor fen, three sites in the ombrotrophic bog, two sites in the riverine wetland, three sites in the upland bog, and three sites in the Eagle Marsh. The depths from which porewater samples were taken varied among the wetlands and depended on the depth of peat and our ability to extract porewater. Water table positions were measured on the day of sampling using polyvinylchloride (PVC) wells at all wetlands except the Eagle Marsh, where the water was above the surface of the peat.

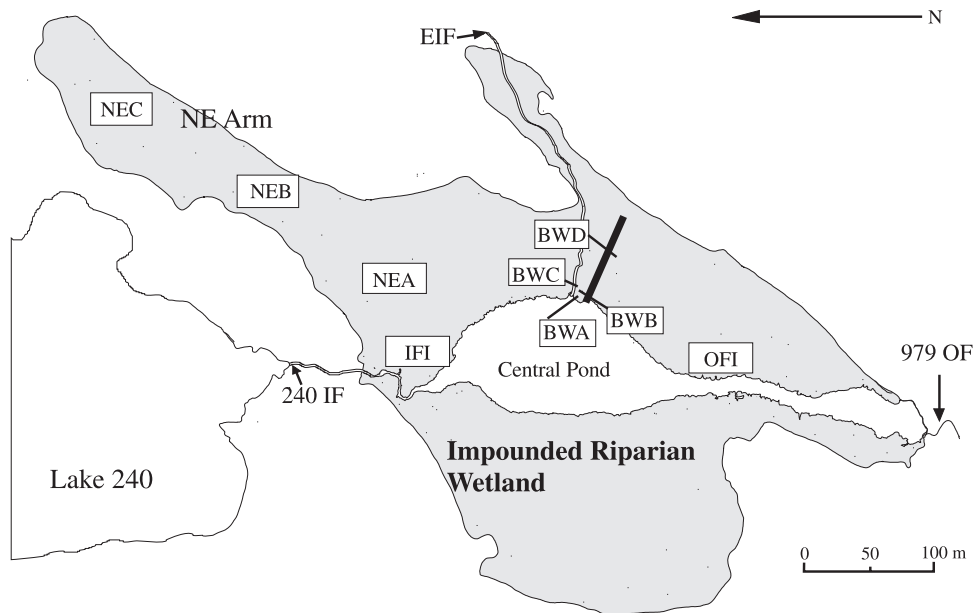
Impounded wetland

To examine the impact of impoundment on net MeHg production in a wetland, we flooded the entire wetland surface surrounding Lake 979. Water from an upstream oligotrophic lake (Lake 240) was used to flood the wetland beginning in July of 1993 and June of subsequent years. Impoundment increased the water level in the old pond by 1.2 m and the maximum depth to 2.5 m. While flooded, the depth of water above the peat surface ranged from 1.8 m adjacent the pond to only a few centimetres at the wetland margin.

The water was drained to near the preimpoundment level each October and refilled in the spring. While controlling water storage in our experimental reservoir, we did not set out to mimic the complex operation of a hydroelectric reservoir. Reservoirs are drawn-down and refilled on varying cycles, some of which cover many years. We wanted to simulate the exposure and reimpoundment of peat surface and include its impact in our study.

In September of 1993, approximately 10% of peat at the periphery of the old pond floated. In each subsequent year, the amount of floating peat increased and peat islands (approximately 1 m thick) ringed the central pond. About half of the entire peat surface in the experimental reservoir was floating by the end of the 1995 impoundment season. While floating of peat has occurred in a number of small reservoirs in Finland (covering approximately 5% of

Fig. 1. The Lake 979 catchment at the ELA, northwestern Ontario, Canada, showing the location of wells in the riparian wetland and the NE arm (NE bog). The shaded area was impounded in 1993.



93° 44' 00" +
49° 37' 30"

+ 93° 44' 00"
49° 36' 30"

the basin) (Rönkä and Uusinoka 1976) and Wisconsin, the proportion of floating peat in our system is extraordinarily high because of our high wetland to old lake ratio. The floatation of peat results from the buildup of gases such as methane that expand with increased temperature, thereby increasing the buoyancy of peat (Rönkä and Uusinoka 1976).

Seven permanent sites for sampling peat porewater were established along boardwalks traversing two of the main hydrogeochemical gradients in the wetland portion of the catchment (Fig. 1). Four sampling sites were established at 0.4 m (Boardwalk site A or BWA), 2.2 m (BWB), 5.4 m (BWC), and 56.5 m (BWD) in an eastward line from the old pond edge. The stratigraphy of this transect comprises a silt bed, up to 2 m thick, overlain by *Sphagnum* peat. The *Sphagnum* unit increases in depth from a few centimetres at the wetland margin to 2 m at the pond edge. A layer of gyttja and limnic peat, up to 2 m thick and extending about 20 m from the pond edge, forms a wedge between the peat and the silt (B. Warner, Department of Geography, University of Waterloo, Waterloo ON N2L 3G1, Canada, personal communication). Three sampling sites were chosen along the central axis of the NE arm approximately 30 m (NEA), 90 m (NEB), and 150 m (NEC) from the old pond. A silt layer that can exceed 1 m in depth in some areas is situated between the peat and bedrock. The peat layer is approximately 3 m deep at site Northeast A (NEA), 1.5 m deep at NEB, and 2.0 m deep at NEC. The shallowing of the peat around NEB is the result of a bedrock shelf. To characterize the porewater chemistry in floating peat islands, we added two temporary sampling sites located near the inflow (IFI) and outflow (OFI) of the reservoir (Fig. 1).

Sampling

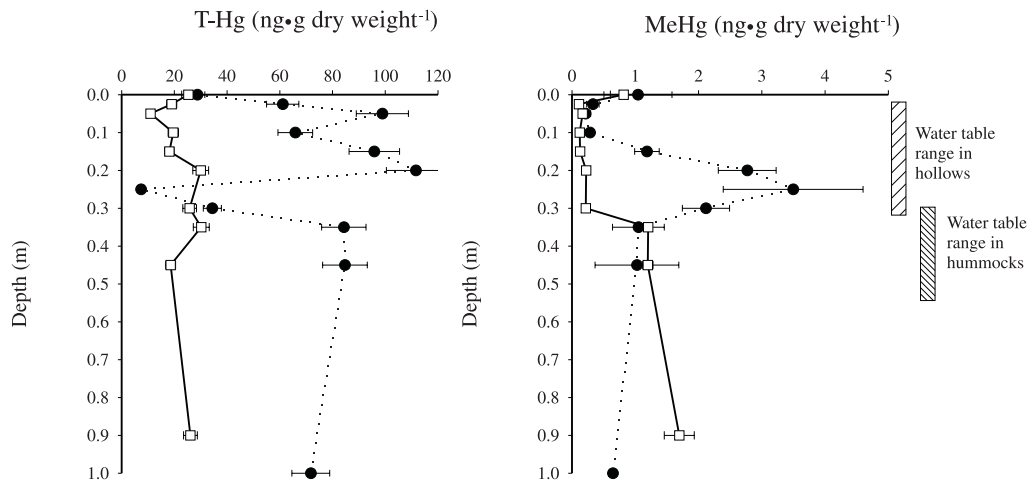
To establish the concentrations of T-Hg and MeHg in peat of the pristine ELA wetlands, peat was collected at 10-cm intervals from a hummock and hollow in the riparian wetland and three hollow sites in the upland bog. All peat handling was conducted using

clean-room grade PVC gloves and samples were stored frozen in plastic bags until analysed.

We chose peat porewater as the primary substrate in which to assess the distribution of MeHg in the pristine and impounded wetland because it is the transportable fraction of MeHg produced in wetlands that can be exported to lakes for uptake into fish. Porewater sampling is also easier than coring the peat; it can also be repeated and is less damaging to the wetland. Two methods of porewater sampling were employed. In the headwater bog and the riparian wetland (later to be impounded), PVC wells, screened with 400- μ m Nitex[®] mesh, were placed in the wetland 1 year prior to sampling to allow the PVC surfaces to equilibrate with the peat and avoid contamination (Branfireun et al. 1996; Heyes 1996). Footpaths and boardwalks were constructed to minimize disturbance. Each site consisted of wells and piezometers installed in nests at depths from 0.50 m to a maximum of 6.0 m. Using a peristaltic pump, stagnant water was pumped from the wells through Teflon[®] tubing prior to sampling. Sample water was pumped from the wells into a Teflon[®] transfer case (flask with inlet and outlet ports) to prevent contamination from the peristaltic pump. The second method of sampling employed a Teflon[®] "sipper." The sipper was used to sample water between the peat surface and a depth of 0.50 cm at all sites and at all depths in the poor fen, upland bog, Eagle Marsh, and riverine wetland (Fig. 2).

The porewater for MeHg analysis was filtered in the field. Water collected in the transfer case was poured through a 0.45- μ m cellulose nitrate filter, housed in a disposable Nalgene[®] filter case, into a Teflon[®] bottle and frozen until analysis. The pristine wetlands were sampled once in the summer of 1993 and the impounded wetland was sampled at five sites (BWA, BWC, BWD, NEA, and NEB), once after its impoundment in 1993 and twice in 1994 and 1995. Samples were also collected for pH, dissolved organic carbon (DOC), total dissolved phosphorus, nitrite, ammonium, nitrate, and sulfate analyses. Nitrate and sulfate were determined only on samples from the impounded wetland, the poor fen, the ombrotrophic bog, the riparian wetland, and the NE bog. To collect water

Fig. 2. T-Hg and MeHg in hollow (●) and hummock (□) peat of the riparian wetland. Error bars indicate 1 SD around the mean of duplicate or triplicate analyses. The position of the water table is indicated beside the profile label.



for pH analysis, C-flex[®] tubing was fixed in-line and the porewater withdrawn using a syringe to avoid degassing. MeHg, pH, and DOC concentrations were collected from peat island sites in the fall of 1994 (only IFI) and July and September of 1995 (Fig. 1). Samples for Hg analyses were handled using ultraclean protocols described in St. Louis et al. (1994). A strict acid-washing protocol was followed for all sampling equipment and bottles.

Experimental methods

As we were going to use changes in porewater MeHg concentration to determine responses of net MeHg production to manipulations, we first had to understand how MeHg in porewater partitioned between itself and peat. The partitioning of MeHg between peat and porewater was determined on samples collected from the poor fen, the ombrotrophic bog, and the riparian wetland. In the poor fen, peat was collected from a depth of 10–25 cm (referred to as poor fen peat in the experiment) and the surface (black peat) of hollows. Peat was also collected from a depth of 10–25 cm in the ombrotrophic bog (ombrotrophic peat). In the impounded wetland, peat was taken from the surface (black peat), a depth of 10–20 cm (brown peat), and a depth of 1 m (deep peat). Peat was collected in acid-washed sealable containers and transported to the laboratory where it was homogenized in a glove bag. Twenty grams (wet weight) of peat was placed in 150-mL acid-washed Pyrex[®] volumetric flasks along with 100 mL of oxygen-stripped deionized water or peat porewater. Although this peat to porewater ratio is smaller than in situ, the larger amount of water was required for MeHg analyses. Each flask was capped with a Suba Seal[®] and incubated at 17°C, typical of summer temperatures in near-surface peat. The flasks were swirled approximately every 8 h to mix the flask water. Replicate flasks of each type were sampled destructively and the water passed through a 0.45- μ m filter after 24, 72, 120, and, in some cases, 240 h.

To investigate the factors controlling MeHg production, additions were made to peat sampled from the poor fen and incubated as above. To prevent nutrient depletion and minimize variability between flasks because of the heterogeneous nature of peat, a sequential addition experiment format was followed. Subsamples of MeHg were removed and chemical additions made using a syringe and Teflon[®]-coated needle. After a 72-h equilibration period, sulfate was added to four replicate flasks at 24-h intervals for 6 days. The sulfate was equilibrated with porewater and added with the intention of increasing the sulfate concentration by 60 mg·L⁻¹ at each addition. In supporting experiments, aspects of HgS chemistry and microbiology were examined. Inhibition of Hg methylation by the

potential formation of mercury sulfides was examined by increasing the sulfur concentration in 20 mg·L⁻¹ steps, thus paralleling the increase in sulfur in the sulfate addition flasks. To inhibit sulfate reduction, molybdate (MoO₄²⁻ added as Na₂MoO₄·2H₂O) was added to a final concentration of 8 mg·L⁻¹. To test if carbon quality was limiting Hg methylation, pyruvate (NaCH₃COCOOH) was added, increasing the carbon concentration by 1.3 mg·L⁻¹, which is 10 times the carbon dioxide respiration rate observed in earlier control flasks. Finally, peat porewater was exchanged for unaltered peat porewater in four control flasks. All flasks were sampled prior to the additions (day 3) and again 24 h after the additions (day 4). On these two occasions and the final sampling day, a 40-mL aliquot was taken from each flask for MeHg and general chemistry analyses. On days 5–8 only, 20-mL aliquots were taken and MeHg and water chemistry were determined on alternate days. Concentrations of carbon dioxide and methane in the headspace were determined on days 4 and 6.

Analytical methods

The T-Hg concentrations in peat and porewater were determined using cold-vapour atomic fluorescence (Bloom and Fitzgerald 1988) and MeHg concentrations by cold-vapour atomic fluorescence after distillation (Horvat et al. 1993) and aqueous ethylation (Bloom 1989). Analyses of T-Hg and MeHg concentration of peat were performed on wet samples, and the concentrations were converted to dry weight using a correction factor derived by oven drying (50°C) samples of peat taken from the same homogenate. Samples were analysed in duplicate or triplicate. The MeHg extraction efficiency was 90 ± 15% as monitored by standard additions. The analytical error for T-Hg in peat was 10% and in water was 5% and for MeHg was <20%. The absolute detection limit for T-Hg was 12 pg and for MeHg was 9 pg. All MeHg concentrations are quoted as nanograms per litre or nanograms of Hg per litre. No evidence of a distillation artefact was observed (Bloom et al. 1997). Both methods are described in detail in Heyes et al. (1998).

Ammonium, nitrate, nitrite, dissolved phosphorus nitrogen, and total dissolved phosphorus were analysed using the methods described in Stainton et al. (1977) and sulfate by suppressed ion chromatography. pH was measured in a closed vessel using a Fisher pH meter and Ag/AgCl miniature glass body combination electrode. The DOC concentration was measured by high-temperature combustion on a platinum catalyst using a Shimadzu TOC-5050 analyser. Methane and carbon dioxide were determined using a Varian[®] gas chromatograph with methanizer.

Table 1. MeHg concentrations and SD around the mean of triplicate measurements in pristine wetland peat.

Site	Depth (m)	MeHg (ng·g ⁻¹)	SD
Upland bog site A	0.10	28.6	8.1
	0.25	11.2	3.8
	0.40	34.8	7.1
Upland bog site B	0.10	2.6	0.2
	0.25	8.5	1.4
	0.40	13.1	3.0
Upland bog site C	0.10	0.30	0.1
	0.25	0.44	0.1
	0.40	13.1	1.4
Poor fen	Surface pool	53	9.6
	0.15	14.3	1.0
Ombrotrophic bog	0.10	8.1	3.1

Results

MeHg and T-Hg concentrations in peat and porewater of pristine wetlands

T-Hg concentrations in riparian bog peat ranged from 3 to 120 ng·g⁻¹ and were higher in hollows (68 ± 31 ng·g⁻¹) (mean \pm SD) than in hummocks (22 ± 6 ng·g⁻¹) (Fig. 2). Concentrations of MeHg were also generally greater in the hollows (2.1 ± 0.9 ng·g⁻¹) than in the hummocks (0.16 ± 0.05 ng·g⁻¹) (Fig. 2). In the top 10 cm, the MeHg concentrations in hollows and hummocks were similar. Over the next 20 cm, and coincident with the position of the mean annual water table, the MeHg concentration in the hollow peat increased dramatically to approximately 3.5 ng·g⁻¹ at 25 cm and then decreased to approximately 1 ng·g⁻¹ at 35 cm. In the hummock, the water table was positioned at 30 cm, where MeHg concentrations increased to approximately 1.0 ng·g⁻¹. In other wetlands, MeHg concentrations ranged from 0.16 ng·g⁻¹ in the hummocks of the ombrotrophic bog to 53 ng·g⁻¹ in the pools of the poor fen (Table 1).

For the seven wetlands, peat porewater MeHg concentration averaged 0.48 ± 1.0 ng·L⁻¹ ($n = 71$), ranging from below the detection limit (0.02 ng·L⁻¹) to 7.26 ng·L⁻¹ (Fig. 3). Within individual profiles, the largest MeHg concentrations occurred near the top of the profile. The concentration and distribution of MeHg concentrations in the porewater of these wetlands are similar to those of a Swedish riparian wetland (0.3–1.5 ng·L⁻¹) (Bishop et al. 1995), despite differences in sampling methods. Peat–porewater MeHg partition coefficients, determined from sites where peat and porewater were collected together, covered two orders of magnitude, from 10^3 to 10^5 . Where measurements of the T-Hg concentration in porewater were made ($n = 8$), the T-Hg concentration ranged from 1.95 to 8.63 ng·L⁻¹, of which between 1 and 26% was MeHg.

Changes in concentration and distribution of MeHg and T-Hg concentrations in peat and porewater following impoundment

External inputs of MeHg and T-Hg to the Lake 979 catchment varied little over the duration of the impoundment (V. St. Louis, Department of Biological Sciences, University of Alberta, Edmonton, AB T6G 2E9, Canada, unpublished data),

indicating that changes in MeHg concentration were the result of within-catchment processes. MeHg concentrations in the preimpoundment peat averaged 1.0 ng·g⁻¹, ranging from 0.1 to 3 ng·g⁻¹ ($n = 20$). In July 1995, the MeHg concentration in the majority of the peat averaged 3.3 ± 2.7 ng·g⁻¹ ($n = 26$). Peat that was predominantly black in colour was found in patches along the wetland–pond margin and on the surface of submerged peat and had MeHg concentrations that exceeded 50 ng·g⁻¹ ($n = 3$).

Prior to impoundment, the mean MeHg concentration in porewater of the upper 1 m of peat was 0.27 ± 0.22 ng·L⁻¹ ($n = 22$), ranging from 0.02 to 1.0 ng·L⁻¹. Beneath 1 m, the mean MeHg concentration was 0.10 ± 0.05 ng·L⁻¹ ($n = 8$), ranging from 0.05 to 0.2 ng·L⁻¹. The distribution of MeHg in these peat profiles is typical of that of other ELA wetlands, with the maximum concentration occurring just beneath the water table (Fig. 3). The MeHg concentration in unfiltered water from the Lake 979 pond averaged 0.1 ng·L⁻¹ (Kelly et al. 1997), indicating that the wetland was as a source of MeHg to the pond.

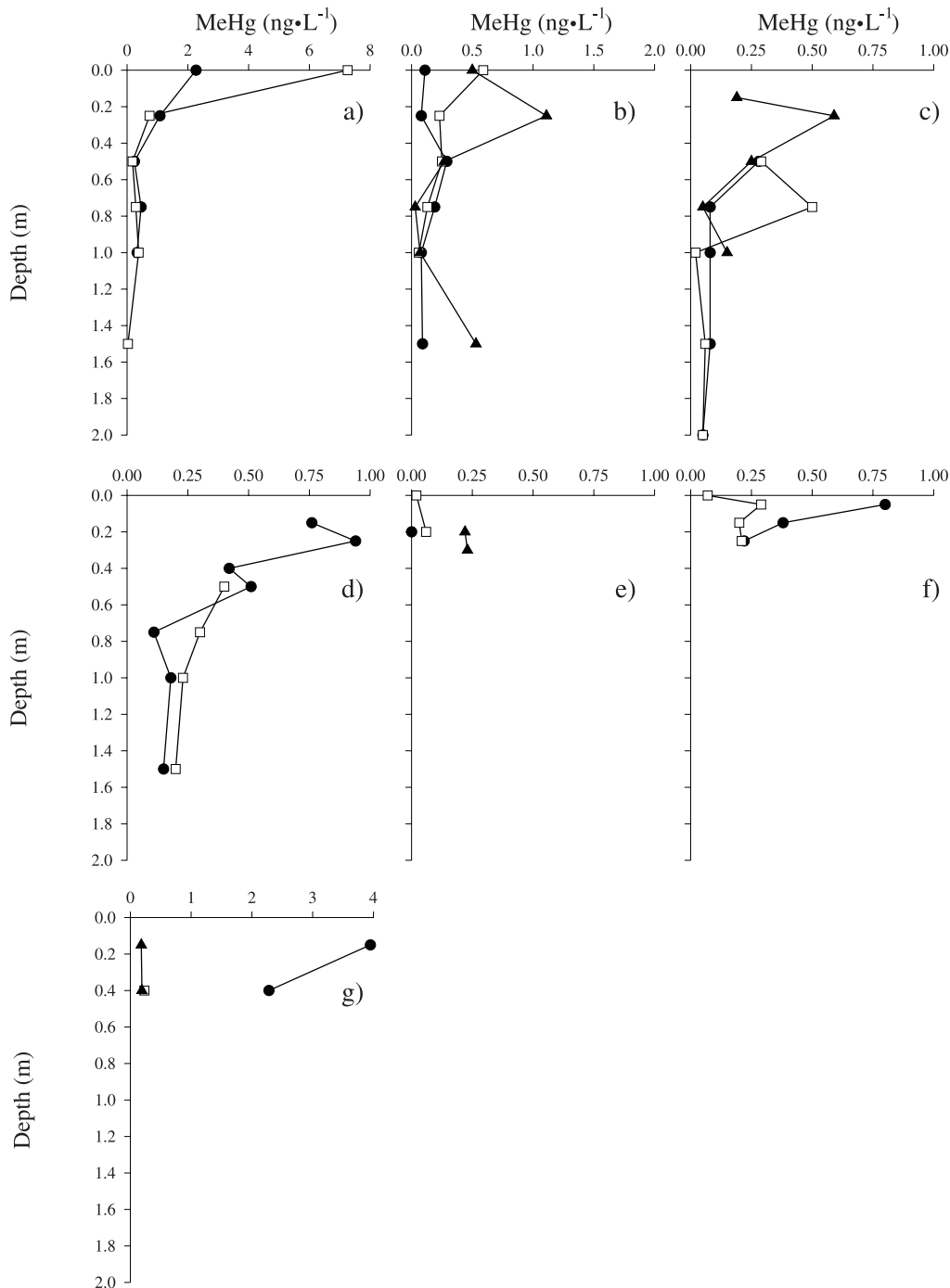
Following impoundment, the mean MeHg concentration in peat porewater was 0.90 ± 0.83 ng·L⁻¹ ($n = 121$) and ranged from 0.02 to 6.7 ng·L⁻¹. The highest MeHg concentrations occurred in the upper 0.5 m of peat and most often near the peat–water interface (Fig. 4). Shortly after impoundment, the MeHg concentration profile maxima shifted from the preimpoundment location of just beneath the water table to near the peat–water interface (Fig. 4). A typical profile from 1 year after impoundment showed a decrease in MeHg concentration with depth. Two years after impoundment, sites BWC, BWD, and NEA had peaks in the MeHg concentration profiles at the peat–water interface and at a depth of 1.0 m whereas MeHg concentrations were generally low and profiles uniform at sites BWA and NEB (Fig. 4).

Some of the differences in MeHg concentration profiles can be explained by the floatation of the peat, which promoted the mixing of pond water and peat porewater at the edge of the wetland, producing a similarity in MeHg concentration between the pond water and near-pond peat porewater (Fig. 4). The porewater MeHg concentrations of the peat islands averaged 0.72 ± 0.56 ng·L⁻¹ ($n = 29$, range 0.06–2.51 ng·L⁻¹), with the highest MeHg concentrations occurring at both the surface and base of the peat island. By midsummer 1995, the area of floating peat had expanded to include sites BWC, BWD, and NEA. Like the peat islands, high porewater MeHg concentrations were recorded at a depth of 1 m as well as near the peat surface at these sites.

Postimpoundment peat porewater MeHg concentrations were generally lowest in the NE arm. This may be attributed to lower peat temperatures (N.T. Roulet, Department of Geography, McGill University, 805 Sherbrooke St. W., Montreal, QC H3A 2K6, Canada, personal communication) under the forest canopy and isolation from the central pond in Lake 979.

While an increase in the porewater concentrations is apparent, statistically testing aspects of the effect, such as its duration, is difficult because the variability in the data and the sample size combine to limit the extent to which data can be tested with statistical rigor. Therefore, we will outline the case for impoundment increasing porewater MeHg concentrations and the sustainability of this increase. On every

Fig. 3. Porewater MeHg concentrations in the pristine wetlands: (a) poor fen, (b) ombrotrophic bog, (c) riparian wetland, (d) NE bog, (e) riverine wetland, (f) Eagle Marsh, and (g) the upland bog at the ELA.



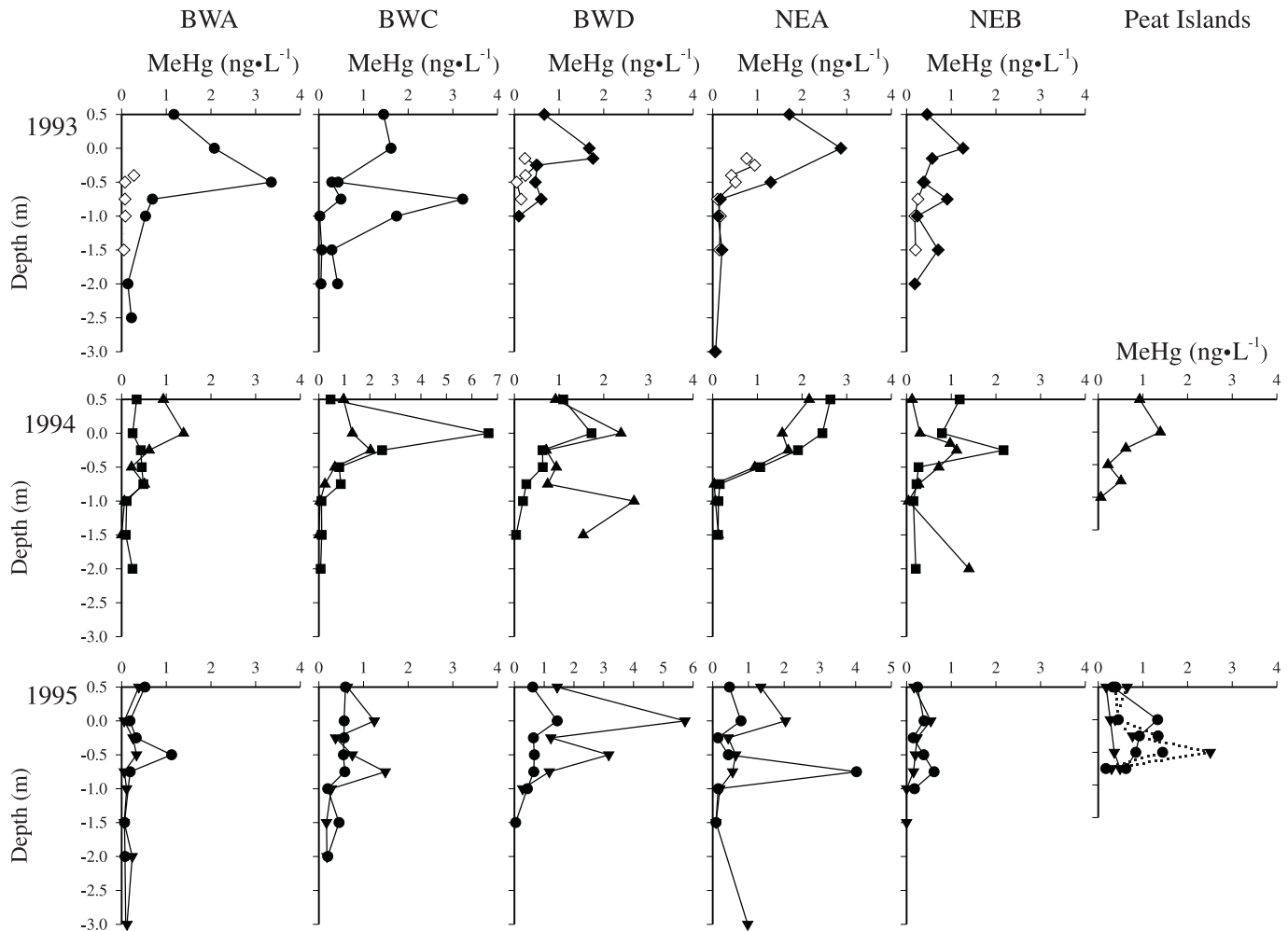
postimpoundment sampling date, the average MeHg concentration was higher than at the preimpoundment sampling or the average from among the pristine wetlands (Fig. 5). The preimpoundment median MeHg concentration was lower than any of the postimpoundment lower quartile boundaries. Also, the average postimpoundment MeHg concentration is significantly greater than the preimpoundment and pristine porewater concentrations ($p = 0.01$, t test). However, the data are poorly distributed and we cannot statistically test the differences between individual sampling dates and thus whether the impact of impoundment is diminishing over time. The

median MeHg concentration in September 1995 was similar to the median in the four previous sampling periods, but the maximum MeHg concentrations clearly decreased over time. This leaves us to surmise that while the effects of impoundment were still apparent after 2 years, the magnitude of the impact appears to have diminished.

Evidence for porewater chemistry influencing MeHg production

The porewater chemistry of the pristine and impounded wetlands was screened for relationships with MeHg (Fig. 6).

Fig. 4. Porewater MeHg concentrations in the riparian wetland before and after impoundment. Preimpoundment in June 1993 (◇) and postimpoundment in August 1993 (◆), July (■) and September (▲) 1994, and July (▼) and September (●) 1995. The peat islands are separated into inflow (solid line) and outflow (dotted line).



Only one relationship was found among the seven wetlands, that being a weak but significant negative correlation between ammonium and MeHg ($r^2 = 0.152$, $p = 0.004$). In stepwise multiple regressions of two or more variables (n always being 10 times the number of variables), a significant negative correlation was found only between MeHg and pH in combination with ammonium ($r^2 = 0.216$, $p = 0.002$). However, within single wetlands, significant negative relationships were found between MeHg and pH (ombrotrophic bog: $r^2 = 0.621$, $p = 0.035$; poor fen: $r^2 = 0.595$, $p = 0.015$) and MeHg and ammonium (NE bog: $r^2 = 0.741$, $p = 0.006$; riparian wetland: $r^2 = 0.477$, $p = 0.009$). A significant positive relationship was found between MeHg and sulfate (poor fen: $r^2 = 0.765$, $p = 0.005$; NE bog: $r^2 = 0.865$, $p = 0.022$). In the impounded wetland, no correlations between any of the nutrient and MeHg concentrations were found.

Partitioning of MeHg between peat and porewater

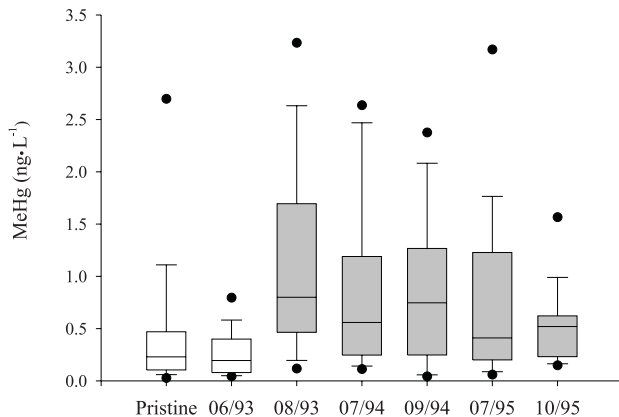
To manipulate the peat, we first had to understand how the MeHg would partition when the peat and porewater would be combined, but we also wanted to know what would happen when porewater rich in MeHg encountered peat containing relatively low concentrations of MeHg and vice versa.

Upon combining peat with porewater or deionized water, partitioning of MeHg to a quasi equilibrium was rapid, occurring in less than 24 h. While little MeHg is released from peat to deionized water (0.1 MeHg ng·L⁻¹, data not shown), MeHg can be released to or adsorbed from DOC-rich water (20–50 mg·L⁻¹) depending on their relative MeHg concentrations (Table 2). In these experiments, peat-porewater MeHg partition coefficients had the same 10³–10⁵ range as observed in the pristine wetlands. The results of these experiments helped set the equilibration time for the incubation experiments described below. More importantly, these experiments demonstrate how porewater chemistry influences MeHg partitioning and the dependence of porewater on peat MeHg concentration.

Examining net MeHg production in peat through incubation experiments

To investigate factors that might control rates of Hg methylation in peat, we made four different additions to peat samples that we hypothesized would either stimulate (sulfate, pyruvate) or retard (sulfide, molybdate) the net production of MeHg. In preliminary batch experiments that were similar to partition experiments in sampling design (not reported here),

Fig. 5. MeHg concentrations in peat porewater of the impounded wetland relative to the pristine and preimpoundment wetland. The horizontal line in the boxes is the median, the ends of the boxes are the lower quartiles, and the whiskers are 1.5 times the upper and lower quartiles.



some flasks receiving small one-time additions of sulfate ($6 \text{ mg}\cdot\text{L}^{-1}$) showed increased MeHg concentrations in flask water but others did not. We employed the repeated additions approach to minimize the sampling bias caused by the heterogeneous nature of peat. As hypothesized, the addition of molybdate decreased MeHg concentrations slightly (Fig. 7c), and we may have seen net demethylation. Additions of pyruvate and sulfide did not appear to affect MeHg concentrations relative to the controls (Figs. 7a, 7b, and 7d). Only in the flasks receiving sulfate did MeHg concentrations increase (Fig. 7e). On the ninth experimental day, the MeHg concentrations uniformly decreased by $1.8 \pm 0.7 \text{ ng}\cdot\text{L}^{-1}$ in samples amended with sulfate. On days 10 and 12, the MeHg concentrations returned to levels similar to those on day 8 ($1.6\text{--}46 \text{ ng}\cdot\text{L}^{-1}$). The decrease in the incubation water MeHg concentration is unlikely to be an analytical artefact but rather the result of a sampling problem created by the inadvertent exposure of the porewater to oxygen during filtration.

The sulfate concentration maximum of $217 \pm 10 \text{ mg}\cdot\text{L}^{-1}$ occurred on day 9. Sulfate was removed from the porewater at a rate of $1.25 \text{ mg}\cdot\text{g peat}^{-1}\cdot\text{day}^{-1}$ during sulfate addition and to $2.8 \text{ mg}\cdot\text{g}^{-1}\cdot\text{day}^{-1}$ after sulfate was no longer added (Fig. 7e). A substantial decrease in carbon dioxide production occurred only in the flasks receiving sulfide relative to the controls. The amount of methane produced during the incubations with molybdate, pyruvate, sulfate, and sulfide additions was 15–75% of that produced in the controls.

Discussion

MeHg concentrations in boreal peats ranged from 0.1 to $60 \text{ ng}\cdot\text{g}^{-1}$ and in peat porewater from less than 0.02 to $7.3 \text{ ng}\cdot\text{L}^{-1}$. The highest MeHg concentrations occurred in hollows, where anoxic conditions prevail close to the surface and the nutrient and Hg supply is potentially greater than in hummocks (Heyes et al. 1998). Among wetland types, the poor fen and upland bog had the highest MeHg concentrations. These sites are periodically connected to adjacent uplands. Mercury and nutrients delivered from these uplands in storm runoff may promote Hg methylation in the wetland

(Branfireun et al. 1996, 1997). However, there was no clear relationship between MeHg concentration and porewater chemistry, making it difficult to predict MeHg concentration from other chemical variables.

Impoundment dramatically increased peat porewater MeHg concentrations in the experimental system. Prior to impoundment of the peatland, the mean concentration of MeHg in the upper 1 m of peat porewater was $0.2 \text{ ng}\cdot\text{L}^{-1}$, equivalent to 0.02 g of MeHg in the upper 1 m of peat in the wetland portion of the catchment (14.3 ha). This preimpoundment pool of MeHg in peat porewater was only 2% of the 1.32 g exported from the impounded wetland in 1993. Using a porewater MeHg concentration typical of the upper 1 m of peat ($1.0 \text{ ng}\cdot\text{L}^{-1}$), we estimate that the typical postimpoundment porewater MeHg pool was 0.12 g , which is equivalent to 10, 14, and 39% of the 1.32, 0.92, and 0.33 g of MeHg exported from the flooded wetland in the three impoundment years, respectively (Kelly et al. 1997). Therefore, the post-impoundment porewater contained a significant amount of MeHg that could be transferred to the lake.

In the impounded wetland, concentrations of MeHg are generally greater in the upper 1 m of peat porewater than in the overlying water column, implying that MeHg moves from the peat to the overlying water. Measuring or calculating the exchange of MeHg across the peat – surface water interface is nontrivial, as the instability of the peat surface and changing hydraulic conductivity of the peat make it difficult to determine the extent of any advective flux. By assuming no advective flux, we can at least estimate a minimal MeHg exchange. The MeHg complex that is released from the peat is unknown, but by choosing chloride and a 5000-dalton molecular weight organic ligand to represent end members, we can estimate the flux of MeHg from peat to overlying water (Gill et al. 1999). Using porewater MeHg concentrations from a depth of 1 cm beneath the peat–water interface and MeHg concentrations from the middle of the water column, the application of a one-step Fickian diffusion calculation yields estimated MeHg fluxes at sites BWA and BWD of 0.09 ± 0.36 and $1.23 \pm 1.02 \text{ ng}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively, if the complex is MeHg–DOC and 0.59 ± 2.36 and $8.03 \pm 6.61 \text{ ng}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively, if the complex is MeHg–chloride. With an impoundment period of approximately 3 months, the amount of MeHg released from the peat to the overlying water could range from 0.03 to 2.6 g , depending on which site and Hg complex is more representative. This range brackets the observed net fluxes from the impounded catchment of 1.32, 0.99, and 0.33 g in 1993, 1994, and 1995, respectively (Kelly et al. 1997).

It is clear that short-term impoundment resulted in increased MeHg concentrations in porewater, but the variability of the postimpoundment porewater MeHg concentration prevents a quality assessment of the 3-year trend. Therefore, from the porewater data, we can only say that impoundment impact was still present 3 years after impoundment but nothing on how long the impact is likely to be felt. Furthermore, without replicate reservoirs, we cannot assess the effect that a different impoundment regime may have had.

We did not measure in situ Hg methylation directly; thus, there are several possible explanations for the increase in porewater MeHg concentrations. The most plausible explanation is that either the in situ net Hg methylation rate in-

Fig. 6. Scatter plots of porewater chemistry and MeHg concentrations in the pristine and impounded wetlands.

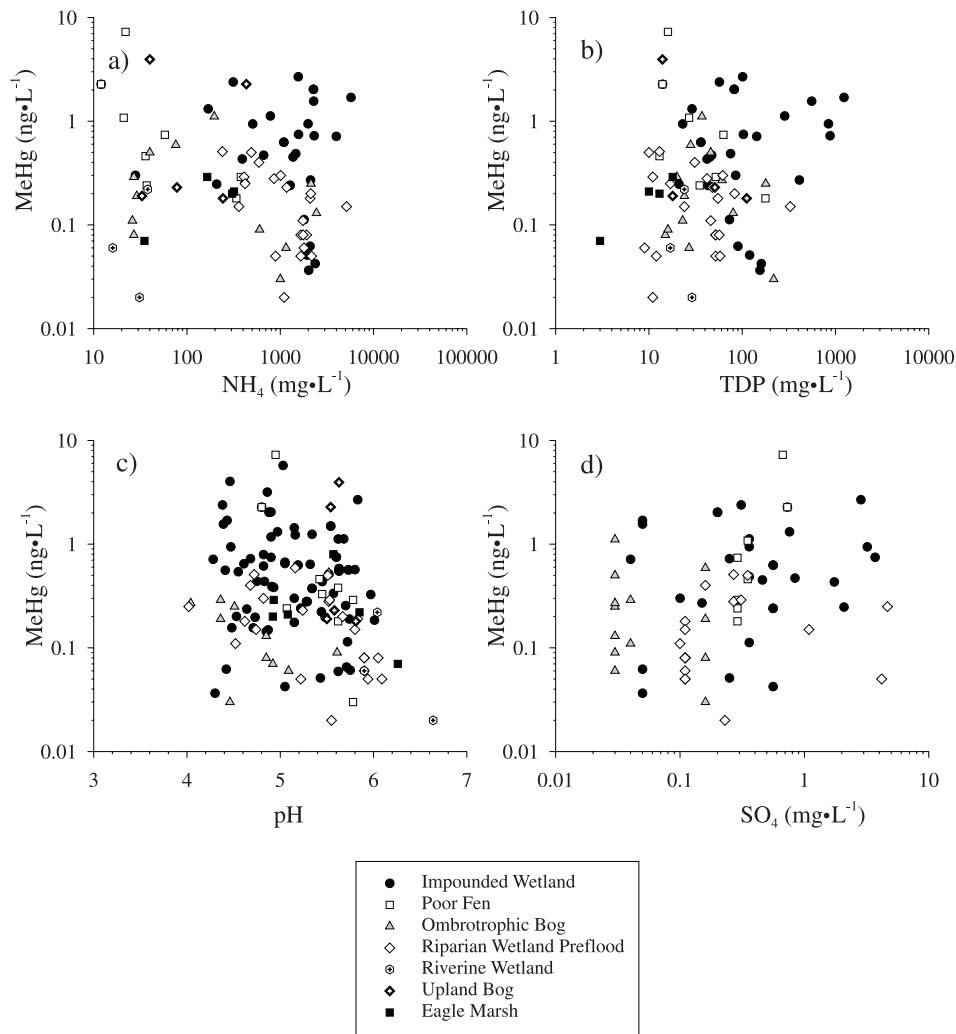


Table 2. Partitioning of MeHg between peat and porewater in incubation experiments.

Medium	Time (h)	Peat type				
		Poor fen	Ombrotrophic	Deep	Reservoir black	Poor fen black
Peat (ng·g ⁻¹)	0	21±13	8.3±1.0	4.4±0.3	50±8.9	53±9.7
Porewater (ng·L ⁻¹)	0	1.73±0.03	0.43±0.02	0.93±0.11	0.93±0.11	0.38±0.07
	24	1.29±1.16	0.27±0.07	0.02±0.02	8.75±2.47	7.56±0.76
	72	0.47±0.15	0.41±0.15	0.02±0.02	9.18±2.11	6.85±3.35
	120	0.85±0.20	0.50±0.05			9.84±1.83

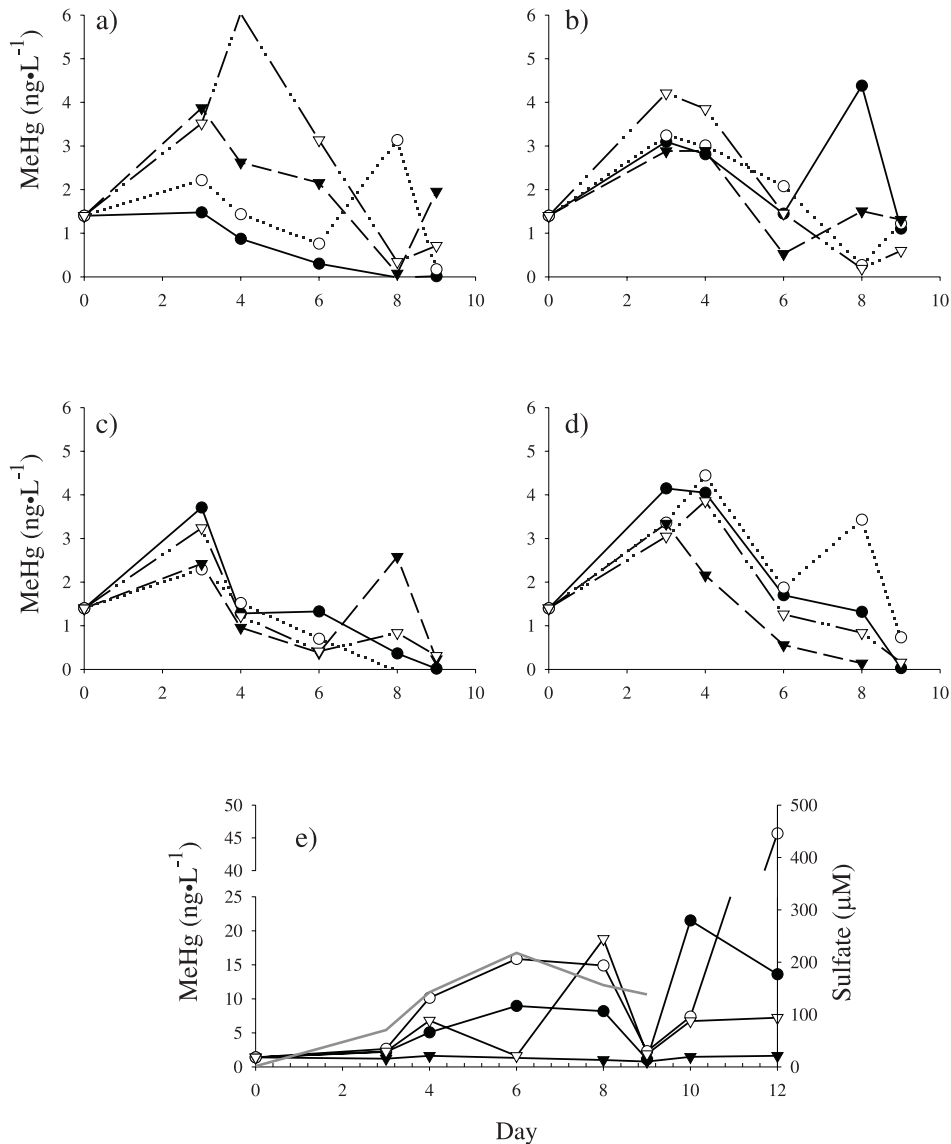
Note: Peat MeHg concentrations were determined at the start of the experiment.

creased following impoundment or the MeHg in the peat or vegetation incorporated prior to impoundment was released from plant matter and (or) peat (Moore et al. 1995; Heyes et al. 1998).

By estimating the size of the MeHg pools in the vegetation and peat, we can evaluate the importance of the preexisting MeHg stores. Moore et al. (1995) estimated the amount of MeHg in above-ground biomass of the impounded catchment to be 0.4 µg·m⁻², or a total of 0.062 g of MeHg, which is small compared with the measured annual exports (Kelly

et al. 1997). Furthermore, if MeHg accumulated in the living plant is, upon death, the major source of MeHg, the pool of MeHg in the decomposing tissues should decrease over time, but the mass of MeHg in decomposing tissues increased or remained unchanged (Heyes et al. 1998). Therefore, simply leaching MeHg that existed in plant tissue prior to impoundment contributes little to the postimpoundment porewater MeHg. However, the tissue is important through supplying Hg and stimulating microbial activity including the methylation process.

Fig. 7. Concentrations of MeHg in flask water of the (a) control, (b) pyruvate, (c) molybdate, (d) sulfide, and (e) sulfate repeated additions experiments. The average head space concentration and SD of carbon dioxide and methane in the replicates after 6 days was (a) 0.94 ± 0.14 and 0.33 ± 0.13 , (b) 0.93 ± 0.15 and 0.17 ± 0.07 , (c) 0.65 ± 0.09 and 0.13 ± 0.06 , (d) 0.13 ± 0.04 and 0.05 ± 0.01 , and (e) 0.92 ± 0.14 and 0.09 ± 0.06 $\text{mg}\cdot\text{L}^{-1}$, respectively. The flask water sulfate concentration is also plotted in Fig. 7e. Also note the scale break in MeHg concentration between 25 and 40 $\text{ng}\cdot\text{L}^{-1}$.



With the data collected in this study, we cannot quantify a change in the pool of MeHg in peat. The laboratory experiments demonstrate that MeHg can readily exchange between peat and porewater, but the wide range in MeHg partition coefficients (10^3 – 10^5) precludes the prediction of solid-phase MeHg concentrations from porewater concentrations. However, other observations indicate that the MeHg concentrations in peat are unlikely to have decreased. Concentrations of MeHg in some impounded peat, such as the black peat used in the partition study, were far greater (>50 $\text{ng}\cdot\text{g}^{-1}$) than in any pre-flood peat, and the mass of MeHg in *Sphagnum* moss placed in the impounded peat increased following impoundment (Heyes et al. 1998). It is possible that the elevated porewater MeHg concentrations result from changes other than an increase in the Hg methylation rate, such as a change in porewater chemistry causing MeHg to repartition

from the substantial pool of MeHg in the peat to the porewater. However, the postimpoundment MeHg export rate would eventually outstrip the preimpoundment rate of MeHg production.

In the broadest sense, the increased Hg methylation in the impounded wetland is the result of an increase in anoxic ecosystem decomposition. However, the factors that control Hg methylation, through influencing Hg bioavailability or microbial activity, are more difficult to identify. Acidity, temperature (Winfrey and Rudd 1990), DOC (Miskimmin 1991), and sulfate (Gilmour et al. 1992) have been shown to influence inorganic Hg bioavailability and the microbial activity related to MeHg production. However, relationships between peat porewater MeHg concentration and water chemistry in the ELA wetlands are weak. It appears that the controls on MeHg production, transport, and consumption are too com-

plex to allow simple empirical relationships to be developed for these systems.

From the laboratory incubations of ELA peat, it appears that net MeHg production in boreal wetlands is limited by sulfate and perhaps Hg. This sulfate limitation was corroborated by in situ sulfate additions (Branfireun 1999). The importance of sulfate in Hg methylation has also been established experimentally in estuaries and the Florida Everglades (Choi and Bartha 1994; Gilmour et al. 1995, 1998). While experimental data suggest that sulfate availability limits Hg methylation, porewater sulfate concentration is a poor indicator of MeHg concentration (Benoit et al. 1999). It is possible that one consequence of wetland impoundment is to facilitate the transfer of sulfate to the peat surface and thereby enhance Hg methylation.

More important than sulfate concentration to Hg methylation is the concentration of sulfide (Benoit et al. 1999). Ombrotrophic wetlands have rapid sulfate reduction rates (e.g., Bayley et al. 1986; Wieder and Lang 1988). Although we made no measurements of sulfide, the sulfide produced during sulfate reduction was either readily incorporated into the solid organic phase or rapidly reoxidized, as no sulfide odour was observed (Brown 1986; Rudd et al. 1986; Wieder and Lang 1988). Mercury is most available for methylation when sulfide concentrations are low ($<10^{-6}$ M), which likely occurs in both the impounded and pristine wetlands (Benoit et al. 1999). The importance of sulfide in northern wetlands and reservoirs certainly needs more investigation.

The scenario that we propose to explain the high levels of MeHg in our experimentally impounded wetland is twofold. First, the aerial extent of MeHg production increases. Impoundment creates a biogeochemical environment analogous to a wetland hollow over the entire riparian peatland. Anoxic microbial processes now dominate over the entire wetland, as indicated by a dramatic increase in methane efflux from the catchment (Kelly et al. 1997). Second, the rate of net MeHg production increases, as indicated by the higher MeHg concentrations in peat porewater. The mass of MeHg in the vegetation decomposing at the surface and at a depth of 10 cm increased rapidly and remained elevated over pre-impoundment concentrations (Heyes et al. 1998). Although we do not know whether the increase in MeHg in the decomposing vegetation resulted from adsorption and methylation of Hg released elsewhere in the impounded wetland or from methylation of Hg contained in the plant tissue, we propose that decaying vegetation and near-surface peat are important sites of MeHg production.

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