Speciation and transport of newly deposited mercury in a boreal forest wetland: A stable mercury isotope approach

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[1] As part of the Mercury Experiment to Assess Atmospheric Loadings in Canada and the United States (METAALICUS) the fate and transport of contemporary mercury (Hg) deposition in a boreal wetland was investigated using an experimentally applied stable mercury isotope. We applied high purity (99.2% ± 0.1) ^{202}Hg(II) to a wetland plot to determine if (1) the ^{202}Hg was detectable above the pool of native Hg, (2) the ^{202}Hg migrated vertically and/or horizontally in peat and pore waters, and (3) the ^{202}Hg was converted to methylmercury (MeHg) in situ. The ^{202}Hg was easily detected by ICP/MS in both solid peat and pore waters. Over 3 months, the ^{202}Hg migrated vertically downward in excess of 15 cm below the water table and traveled several meters horizontally beyond the experimental plot to the lake margin along the dominant vector of groundwater flow. Importantly, at one location, 6% of aqueous ^{202}Hg was detected as Me^{202}Hg after only 1 day. These results indicate that new inorganic Hg in atmospheric deposition can be readily methylated and transported lakeward by shallow groundwater flow, confirming the important role of wetlands as contributors of Hg to aquatic ecosystems.

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1. Introduction

[2] Elevated mercury (Hg) levels in fish and other higher organisms is a serious global environmental concern. In the absence of direct point or local geological sources, the dominant pathway of Hg entry into ecosystems is via atmospheric deposition [*Fitzgerald et al.*, 1998; *Schroeder and Munthe*, 1998]. Most of the Hg that is deposited from the atmosphere comprises inorganic species (dominantly Hg(II)), yet the majority of the Hg (>95%) in fish tissue is monomethylmercury (MeHg) [*Bloom*, 1992]. Compelling evidence is emerging that couples contemporary atmospheric Hg deposition and fish mercury concentrations in some environments [*Watras et al.*, 2000, 2002]. Although research implicates obligate-anaerobic sulphate-reducing bacteria (SRB) as the principal Hg methylators, both in the laboratory [*Compeau and Bartha*, 1985; *Benoit et al.*, 2001], and in the natural environment [*Gilmour et al.*, 1992; *Benoit et al.*, 2003], we still have no process-based information that demonstrates that contemporary inorganic Hg deposition is converted to MeHg in the terrestrial or aquatic environment, or bioaccumulated preferentially over the large existing pool of Hg in soils and sediments. Mercury is strongly adsorbed to the mineral and organic soil constituents [*Desauziers et al.*, 1997; *Hintelmann et al.*, 2002]. The strong retention of mercury by soils contributes to the considerable uncertainty surrounding the effects of industrial emission reductions. It is impossible to determine critical loads to ecosystems without the ability to discriminate between the reactivity of the very large pool of Hg stored in soils and lake sediments from new Hg derived from contemporary atmospheric deposition.

[3] Wetlands have been identified as sources of MeHg to the downstream aquatic ecosystem [*St. Louis et al.*, 1994, 1996; *Hurley et al.*, 1995; *Driscoll et al.*, 1998], and potentially important sites of MeHg production in some catchments [*Branfireun et al.*, 1999, 2001]. As important as wetlands may be as MeHg sources, we have no process-based information about the transformation of inorganic mercury to methylmercury in wetlands except in specific ecosystems such as the Florida Everglades [e.g.,,*Gilmour et al.*, 1998] or the mechanisms of transport to the downstream system [*Branfireun and Roulet*, 2002].

[4] The Mercury Experiment to Assess Atmospheric Loadings in Canada and the United States (METAALICUS) is an international, multiagency research project designed to investigate the relationship between the contemporary deposition of mercury from the atmosphere and mercury in fish by using stable mercury isotopes experimentally applied to an entire watershed. One of the specific project-

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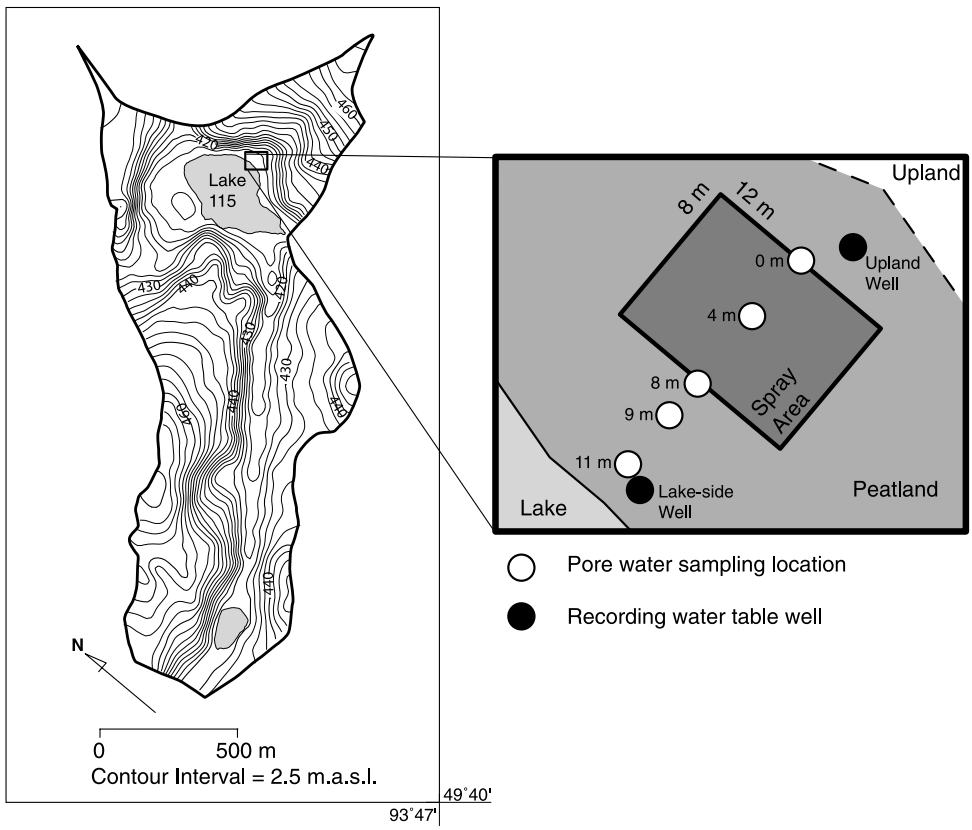

Figure 1. Topographic map of the experimental watershed. The location of the study plot and the instrumentation are presented on the inset map.

scale subobjectives is to better understand the role of upland and wetland in the transport and transformation of mercury species. A METAALICUS upland pilot study reported by *Hintelmann et al.* [2002] found that newly deposited Hg was more reactive than the native Hg, but that mobility was low, decreasing with time as the new Hg became incorporated into the soil pool. This decrease in initial mobility suggested that Hg amounts in terrestrial runoff may respond slowly to changes in Hg loading from the atmosphere. Here we report the results of a pilot study that was undertaken to isolate the behavior of the experimentally applied stable mercury isotope in boreal wetlands. The specific objectives of this study were to (1) determine if an experimental addition of ^{202}Hg in an amount only fivefold greater than 1 year's average atmospheric deposition is detectable above the large pool of native mercury in boreal peatland soils, (2) determine if experimentally applied ^{202}Hg(II) is transformed in situ into the more toxic methylmercury (Me^{202}Hg), (3) assess the mobility of ^{202}Hg in boreal peatland soils by sampling along the dominant hydrological gradient, and (4) use measured hydrological data to determine if the inferred movement (if any) of ^{202}Hg(II) and/or Me^{202}Hg is physically reasonable.

2. Methods

2.1. Study Site

[5] This study was conducted in 1999 in a small peatland located in the Experimental Lakes Area (ELA) (49°40′N, 93°43′W) near Kenora, Ontario, Canada (Figure 1). The rectangular experimental plot is a 12 by 8 m (96 m^2) area of the wetland located at the base of a well-defined subcatchment. The wetland has a homogeneous, low-lying vegetation community, with no large vascular vegetation. The surface is dominated by living sphagnum mosses (*Sphagnum* spp.) with scattered pitcher plant (*Saracen purpurea*), cotton grass (*Eriophorum vaginatum*) and sedges (*Carex* spp.). The top 30–50 cm of peat soil is composed of poorly decomposed, fibrous sphagnum, with a total depth of 0.5 m at the hillslope side of the experimental plot, increasing to around 1.5 m at the lake margin. Nearer the lake margin, more humified peats are found below the floating mat of fibrous sphagnum peat. Underlying the sphagnum peat throughout the experimental plot is a layer of coarse unsorted gravel and cobbles of an indeterminate thickness, which is itself underlain by relatively impermeable granitic bedrock.

2.2. Mercury Isotope Application and Sampling

[6] We simulated atmospheric Hg deposition by applying enriched ^{202}Hg (99.2% ± 0.1; obtained from the Oak Ridge National Laboratory, Oak Ridge TN). To obtain the desired application of 25 μg m^{-2} (approximately 5 times the present annual average wet THg deposition rate [*St. Louis et al.*, 1996]), 43.2 mg of ^{202}Hg was dissolved in a small volume of 9N HCl, and serial dilutions were performed to arrive at a solution concentration of 75 μg mL^{-1}. The acid concentration of the final solution was 1% HCl by volume. This solution was applied to the wetland surface using acid-cleaned plastic pressurized hand sprayers in a one-time application on 13 July 1999.

[7] Pore water samples were drawn from either permanent shallow piezometers, or a portable peat pore water probe constructed from a pure Teflon® tube with a 1 cm perforated sampling interval that is inserted to the desired depth in the peat [*Krabbenhoft et al.*, 1998]. Pore water samples were filtered in line through 0.45 μm Meissner® filters into acid-cleaned 125 mL Teflon bottles and acidified with ultrapure HCl (0.5% by sample volume). Pore water sampling was performed prior to the isotope addition and at 1, 2, 8, 30, and 90 days post addition. Note that not all depths or locations were sampled on a given sampling day (no samples are indicated on the figures as described in the caption for Figure 3). Intact peat cores were extracted from the experimental plot using 10 cm diameter acid-cleaned polycarbonate core tubes 1, 2, and 90 days after the isotope addition. Peat samples were extruded, sliced into 4 or 5 sections (surface living vegetation, 0–3, 3–6, 6–10, and 10–13 cm) and frozen until analysis. Ultraclean field sampling protocols were followed at all times.

[8] Samples were analyzed for both the native Hg species and the added isotopic ^{202}Hg. Peat soil and vegetation samples were digested at 80°C using a 7:3 (vol/vol) mixture of concentrated HNO_3 and H_2SO_4 acid. After BrCl oxidation, THg content in the digests was determined by $SnCl_2$ reduction, gold trap preconcentration, and detection using flow injection cold vapor ICP/MS (Perkin Elmer Elan 6100). For THg analyses of filtered pore waters, samples were subjected to a BrCl oxidation, stannous chloride reduction and purging with Hg-free nitrogen onto gold traps, which were processed as described elsewhere [*Hintelmann et al.*, 1995, 1997; *Olson and DeWild*, 1999]. MeHg in water, soils, and vegetation was isolated from the sample matrix by atmospheric pressure water vapor distillation [*Horvat et al.*, 1993]. MeHg in the distillates was derivatized using sodium tetraethylborate and preconcentrated onto Carbo® traps. Quantification was achieved after thermodesorption, GC separation, and detection by ICP/MS [*Hintelmann et al.*, 1995; *Hintelmann and Evans*, 1997]. Typical limits of detection (LOD) for THg were 0.04 ng/L in water and 0.2–1 ng/g in vegetation and soils, and for MeHg they were 1 pg/L in water and 1–10 pg/g in soils. LOD for the ^{202}Hg isotope in the various samples are dependent on the concentration of native mercury in the respective sample. To precisely quantify the applied isotope concentration, it must be $\geq$0.5–1% in excess of the native mercury concentration. The exact LOD varied with the precision of the isotope ratio measurement that was achieved during each run.

2.3. Hydrology

[9] Precipitation data were obtained from a rain gauge located adjacent to the research site. The experimental plot was instrumented at its four corners and in a longitudinal profile with shallow piezometer nests that were used for pore water sampling and monitoring of hydraulic head (Figure 1c). Piezometers were constructed of ~1 cm I.D. PVC tubing with 5 cm slotted openings at depths ranging from 0.05 m to 1 m below the peat surface. The transverse and longitudinal boundaries of the plot area were instrumented with continuous water level recorders (Remote Data Systems WL-40), storing water table elevation at half-hourly intervals.

[10] The shallow peat layer in the experimental plot, coupled with its highly permeable open, fibrous structure made estimates of the distribution and magnitude of horizontal and vertical saturated hydraulic conductivity (K) impossible using typical hydrometric techniques such as a slug test. We decided to perform a simple analysis in order to determine that, if observed to do so, it was physically feasible that the ^{202}Hg was transported by lateral subsurface flow. Hydraulic conductivity (K) can be estimated by assuming that flow velocity was governed by the hydraulic drop of the water table across the 12 m width of the test plot (the distance between the upland and lakeside recording wells), and assuming Darcy flow. Two target cumulative flow distances (2 and 6 m over the period of measurement) were determined as the minimum and mean travel discharges between the experimental plot and the lake edge, respectively. The average linear velocity (m/s), is determined as:

$$v = \frac{K\left(\frac{h_1 - h_2}{L}\right)}{\phi} \quad (1)$$

where K is the hydraulic conductivity (m/s), h_1 is the head at the origin (m), h_2 is the head at distance L, the flow length (m), and ϕ is the porosity (conservatively set at 0.9). Porosities of poorly decomposed sphagnum peats have been determined to be as high as 0.97 [*Beckwith and Baird*, 2001]. The travel velocities and calculated hydraulic conductivities are for water, or elements conservatively moving with that water, exclusively. Although it is likely an unreasonable assumption that Hg of any species will be transported conservatively with water, this simple analyses will provide some evidence as to whether or not the transport of ^{202}Hg beyond the experimental plot is within the realm of physical possibility over the study period.

3. Results

3.1. Hydrology

[11] A major rain event 1 day after the ^{202}Hg application resulted in an increase in water table level across the plot and an equalization of the hydraulic gradient (Figure 2). As the water levels subsided from this event, water table measurements show a predominantly lakeward hydraulic gradient until 14 August (Figure 2). A dry period persisting for nearly all of August resulted in a reversal of the wetland horizontal hydraulic gradient, with inflow from the lake for nearly a month. Rain in early September reestablished an upland to lake flow path until the end of the measurement period in October.

3.2. Aqueous Phase Native and Isotopic Total Mercury

[12] Native pore water THg concentrations were variable over the study period (Figure 3). Concentrations ranged from 1.6 ng/L to over 25 ng/L, with no clear trend with depth. The mean native pore water THg concentration was 5.5 ng/L (SD = 4.1) for all sampling locations, 5.3 ng/L (SD = 3.3) inside the experimental plot (Figure 2, 0–8 m), and 6.4 ng/L (SD = 6.6) outside (Figure 3, 9 and 11 m). The mean and standard deviation for the concentrations found outside of the plot are skewed by a single high value of 25.2 ng/L at the 11 m profile at 90 days.

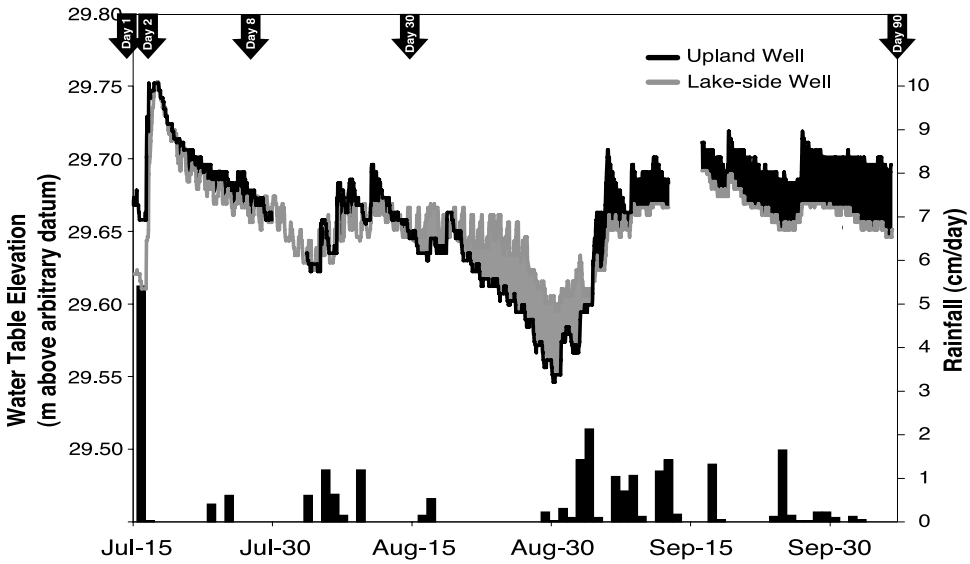

Figure 2. Rainfall and water table elevation at the upland (black) and lake (gray) ends of the experimental plot transect for the study period. The normal direction of flow is toward the lake (black line over gray) Flow is reversed from the lake toward the upland during a period of low rainfall (gray line over black). Sampling times are indicated by the arrows at the top.

[13] Pore water samples taken 1 day after the ^{202}Hg application clearly indicate the presence of the added ^{202}Hg in the surface and pore water within the experimental plot (Figure 4). At the surface ^{202}Hg concentrations averaged 1.78 ng/L, decreasing to an average of 0.51 ng/L at 10 cm below the peat surface. No ^{202}Hg was detected at >20 cm below the surface, nor at the 9 m profile outside of the experimental plot.

[14] After 2 days, the concentrations of ^{202}Hg in pore water had decreased markedly with concentrations at 5 cm below the surface averaging only 0.37 ng/L, with detectable levels of ^{202}Hg at 10 cm below the surface evident only at the 8 m profile. No ^{202}Hg was found outside of the experimental plot. After 30 days, the single profile taken inside of the experimental plot showed ^{202}Hg concentrations at 5 and 15 cm below the surface that were detectable (0.03 and 0.04 ng/L, respectively), but marginally below the conservative 1:100 detection confidence ratio of ^{202}Hg to native Hg concentration. Although the absolute concentrations must be viewed with caution, we are confident in the analytical detection of the presence of the ^{202}Hg at concentrations above background at these locations. In addition, ^{202}Hg was found at 30 cm below the peat surface (0.18 ng/L) in the middle of the experimental plot, and was evident in the near surface pore waters outside of the experimental plot (9 m profile; 0.06 ng/L at −5 cm) (Figure 4). Ninety days after the ^{202}Hg application, detectable levels of ^{202}Hg are still evident throughout the top 20 cm of peat pore waters in the experimental plot, and at the 11 m profile, which is 3 m outside of the experimental plot (Figure 4).

3.3. Aqueous Phase Native Methylmercury

[15] Aqueous pore water samples analyzed for native MeHg were taken at 1, 8, and 90 days after the ^{202}Hg application (Figure 5). Only samples from profiles 0, 4, 8, and 11 m were analyzed for native and Me^{202}Hg. At 1 day post application, ambient aqueous MeHg in the experimental plot averaged 0.71 ng/L at 5 cm below the peat surface. At 8 days, pore water samples from the surface had a slightly lower mean concentration (0.23 ng/L) while the mean concentration of samples from 5 cm was 0.64 ng/L, similar to that a week prior. One sample from 15 cm had a lower concentration of 0.18 ng/L.

[16] Pore water samples taken 3 months after the experimental application in October are much higher in MeHg concentration than July (overall mean of 1.83 ng/L). Pore water concentrations between 0 and −10 cm ranged closely about this mean concentration. At −20 cm within the experimental plot, concentrations decreased, averaging 1.20 ng/L, whereas at −20 cm at the 11 m profile, the MeHg concentration was notably higher (3.8 ng/L) than any other samples analyzed from this site (Figure 5).

3.4. Aqueous Phase Methylated Isotopic Mercury

[17] ^{202}Hg was added to the experimental plot exclusively in an inorganic form. The only mechanism by which excess Me^{202}Hg could appear in this wetland would be through in situ methylation. Me^{202}Hg was detected in the experimental plot 1 day following the ^{202}Hg application (Figure 6). At 5 cm below the peat surface, 43 pg/L was found in the 0 m profile at the upland edge of the experimental plot representing 6% of the ^{202}HgT found at that location. Me^{202}Hg was also detected at −5 cm at the 4 m profile. After 8 days, Me^{202}Hg was found in surface pore water (3.8 pg/L), with the highest concentrations found at −5 cm (mean = 22 pg/L). Me^{202}Hg was also found (2.3 pg/L) at −15 cm at the 8 m profile.

[18] Ninety days after the isotope addition, Me^{202}Hg was found in pore waters throughout and beyond the experimental plot. At the upland edge of the experimental plot the Me^{202}Hg concentration at −5 cm was 17 pg/L and was below the LOD at −10 and −20 cm. At the 4 m profile, concentrations at the surface and at −5 cm were 9 and 19 pg/L respectively and were below the LOD at −10 and

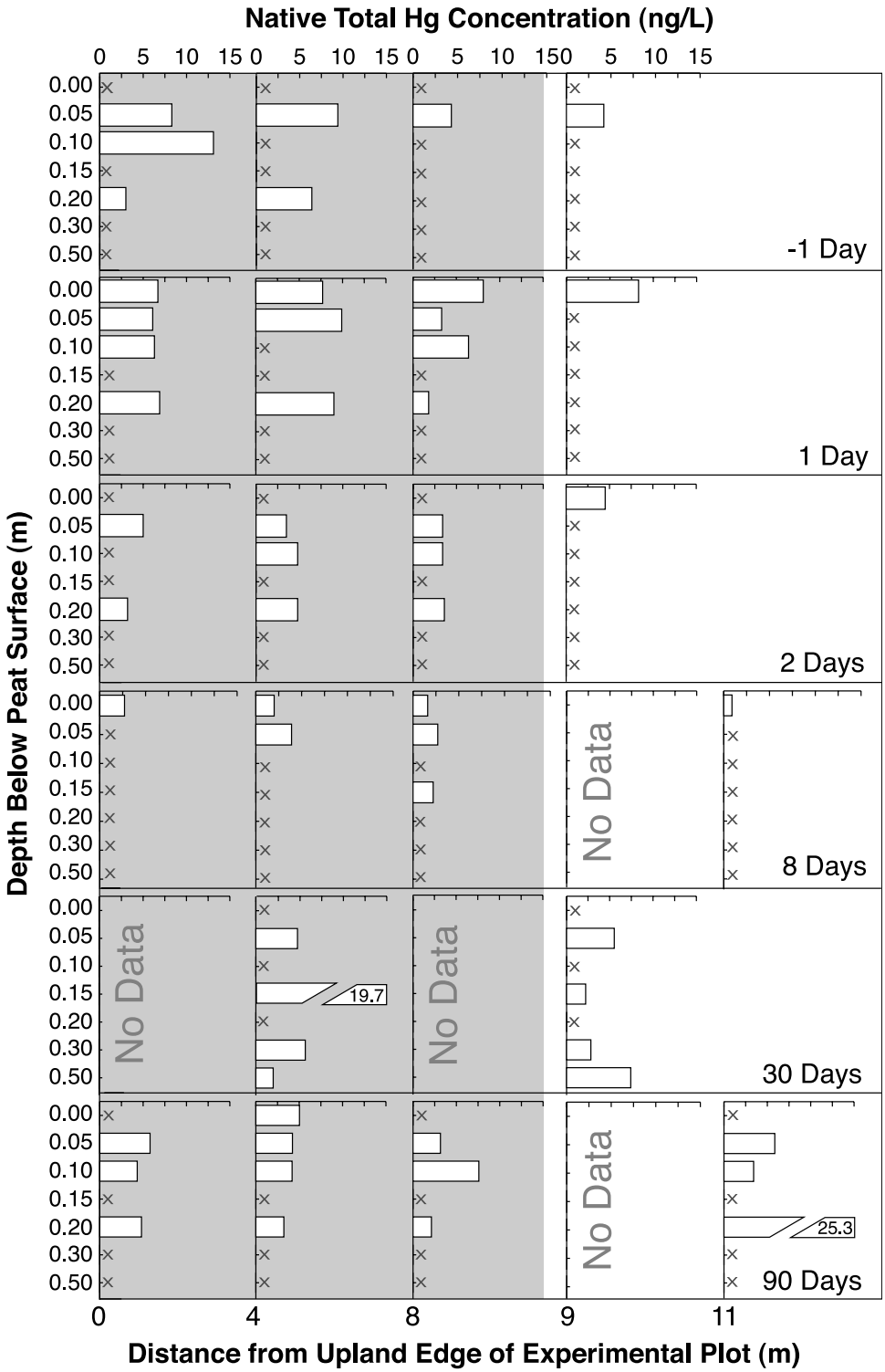

Figure 3. Native total mercury concentrations in wetland pore water. For all of the graphical results in this paper presenting native and ^{202}Hg data, open bars or symbols represent native Hg concentrations, and solid bars or symbols represent ^{202}Hg concentrations. Individual graphs show THg concentrations in ng/L versus depth. Each row of graphs represent a transect through the experimental plot from the upland edge (left) to the lakeshore (right) with the relative distance indicated on the x axis. Each row presents the concentrations at each sample location and depth over time relative to the Hg isotope application date. The gray box delimits the section of the transect that received the experimental isotope application. Since sampling location and depth varied over time and by species, all sampling depths and locations are shown in each figure for ease of comparison and interpretation. Where no sample was taken or analyzed, "No Data" or "X" are indicated at that location or depth, respectively.

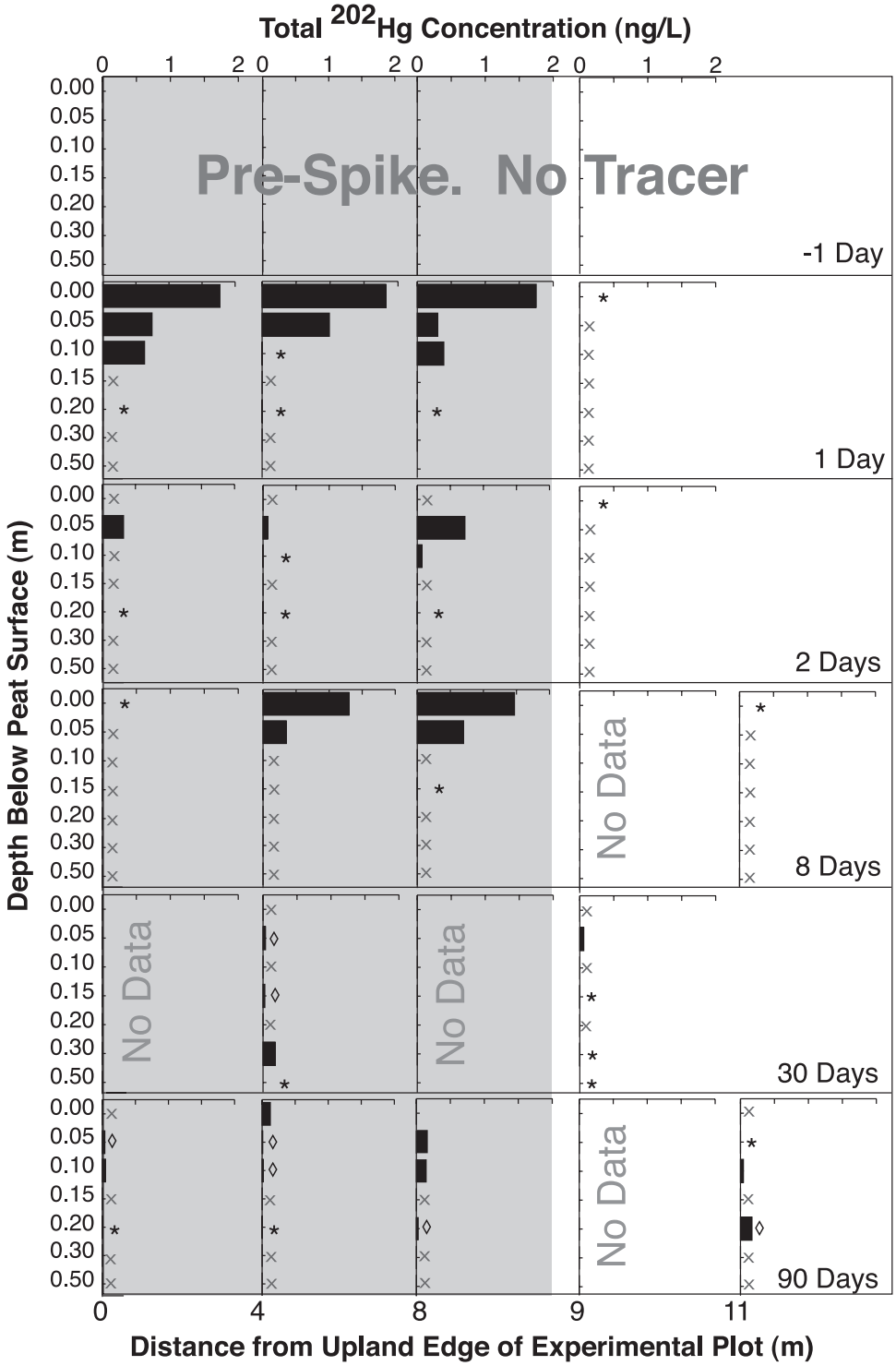

Figure 4. Total ^{202}Hg concentrations in wetland pore water. See Figure 3 for full explanation of figure presentation. An asterisk beside a sample depth indicates that a sample was taken and analyzed but no ^{202}Hg was detected. A diamond beside a sample depth indicates that ^{202}Hg was detected but is marginally below the conservative 1:100 ratio of isotopic to native mercury.

−20 cm. At the 8 m profile concentrations were 24, 15 and 22 pg/L at −5, −10, and −20 cm, respectively. Most significantly, Me^{202}Hg concentrations at the 11 m profile (outside of the experimental plot) were 21 pg/L at −5 cm and 28 pg/L at −10 cm depth. Even at −20 cm, Me^{202}Hg was detected (14 pg/L) but given the relatively high native MeHg concentration at that location, the enriched isotope concentration cannot be reported with full confidence as it is below the 1% confidence ratio.

3.5. Solid Phase Native and Isotopic Total Mercury

[19] Triplicate peat cores at 1 and 2 days, and a single core at 90 days after the isotope application were taken inside the experimental plot. The mean native THg concen-

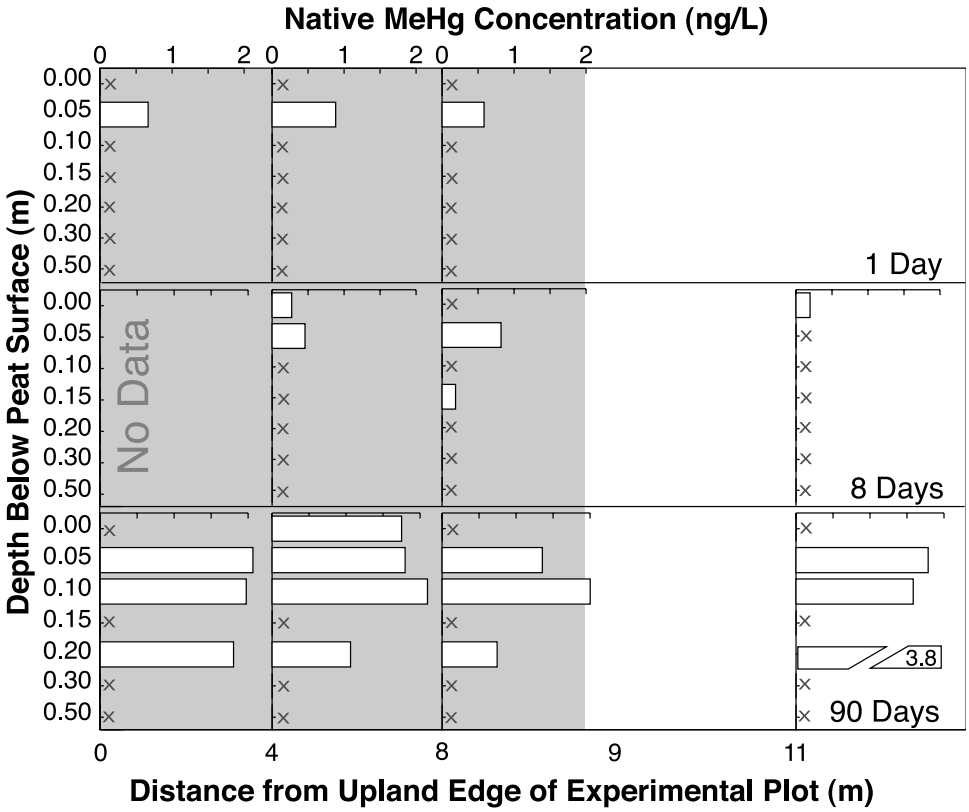

Figure 5. Native MeHg concentrations in wetland pore water. See Figure 3 for full explanation of figure presentation.

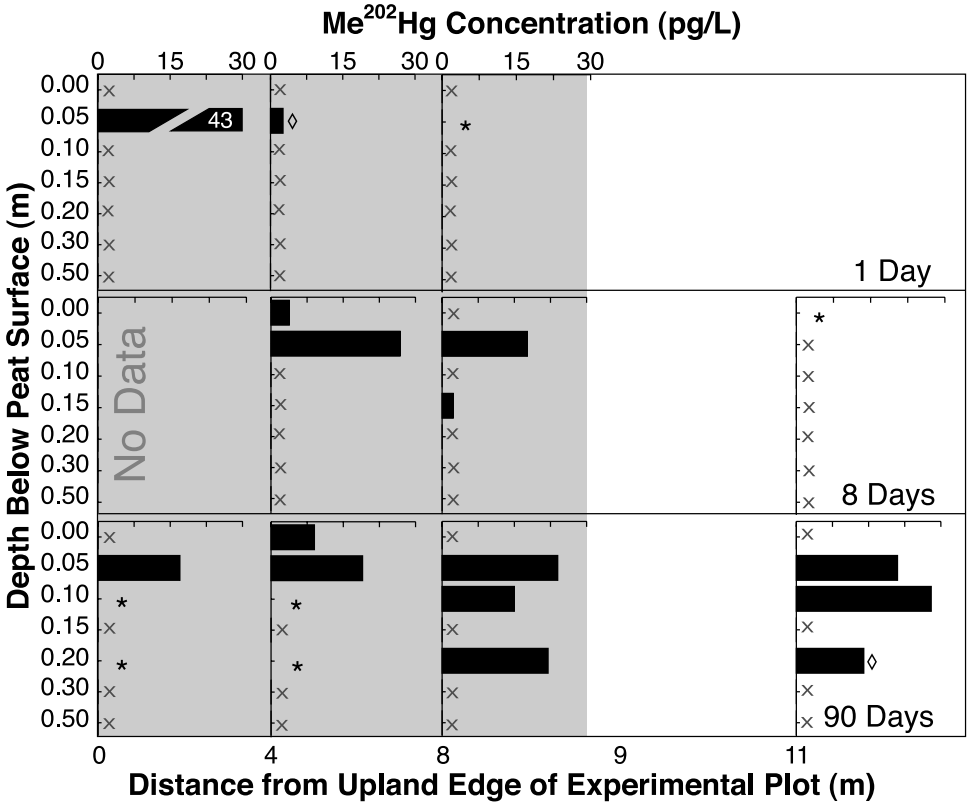

Figure 6. $Me^{202}Hg$ concentrations in wetland pore water. See Figures 3 and 4 for full explanation of figure presentation.

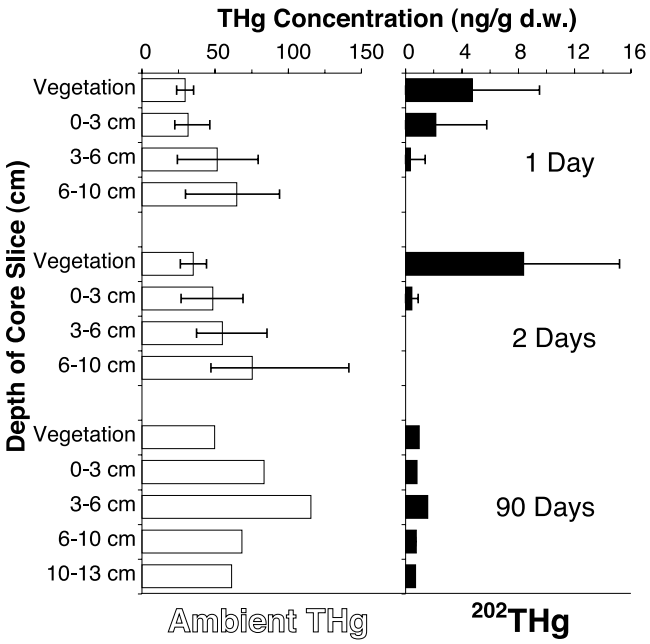

Figure 7. (left) Native THg and (right) $T^{202}Hg$ in wetland surface living moss and peat soil. N = 3 for samples taken at 1 and 2 days post application. Bars are the mean concentration, and error bars are the range. Only one core was taken at the 90 day sampling time. All $T^{202}Hg$ concentrations were above the 1:100 confidence ratio of native to isotopic mercury.

tration in the solid peat was 60 ng/g (dw), with a range of 24 to 141 ng/g (dw) (Figure 7). The cores extracted in July, 1 and 2 days post application show a trend of increasing solid phase THg concentration with depth. The single core taken in October 90 days post application shows a decrease in concentration below 6 cm.

[20] ^{202}HgT was also readily detected in the vegetation and peat in the 1, 2, and 90 day peat cores (Figure 7). One day after the isotope application, the mean concentration of ^{202}Hg in the surface vegetation layer was 4.75 ng/g dw, with detectable levels of ^{202}Hg found as far down as 6 cm in the peat core. After 2 days, the ^{202}Hg concentration was higher in the surface vegetation layer (8.37 ng/g dw), and lower at subsequent depths. By 3 months, the ^{202}Hg had evenly distributed throughout the top 13 cm of the soil core, with an average concentration of 0.97 ng/g dw.

[21] Distribution coefficients ($\log K_d = \log ([Hg]_{particle}/[Hg]_{aq})$; L kg^{-1}) were calculated for overall mean aqueous and soild phase native and isotopic THg for the top three depth intervals sampled (Table 1). The distribution coefficient for the native THg was remarkably consistent over the depth intervals, averaging 4.12 overall. For the ^{202}THg, the overall mean was slightly lower (3.19), increasing slightly with depth, indicating a higher proportion in the dissolved phase relative to the native Hg.

3.6. Solid Phase Native and Isotopic Methylmercury

[22] Native solid phase MeHg was determined from single peat cores taken at 1, 2, and 90 days after the ^{202}Hg addition (Figure 8). The core at 1 day shows little variation with depth between the surface vegetation and 6 cm below the surface, with concentrations averaging 2.4 ng/g dw. The 6–10 cm interval had a higher concentration of 3.4 ng/g dw. The MeHg concentrations decrease are similar in the day 2 core, but without the increase in concentration at the 6–10 cm layer. The October core, 90 days after the experimental addition, shows lower surface concentrations with a pronounced increase in concentration with depth, ranging from 0.43 to 3.96 ng/g dw from the surface to the 10–13 cm interval, respectively.

[23] Isotopic MeHg concentrations were only assessed in the solid phase for the October (90 day) core sample only (Figure 8). As with $Me^{202}Hg$ in pore waters, the enrichment of $Me^{202}Hg$ in the solid phase can only be a consequence of particle partitioning of the methylated inorganic ^{202}Hg that was experimentally applied. There is clear evidence of $Me^{202}Hg$ enrichment in the single core sample that was taken, with the maximum concentration occurring in the 0–3 cm slice (0.039 ng/g dw). This contrasts with the native solid phase MeHg that shows an increase in MeHg concentration with depth. Distribution coefficients were not calculated for MeHg as there was insufficient solid phase data.

4. Discussion

[24] We believe that spatial and temporal variability in native THg concentrations in pore water and solid peat (Figure 3 and 7, respectively) are the result of a nonuniform and nonstatic pool of Hg in the peat soils. Variability in peat pore water solute concentrations (Figure 3) has been demonstrated elsewhere [*Hunt et al.*, 1997; *Branfireun*, 2004], and is particularly notable in the near-surface peats and zone of water table fluctuation. Differences in native aqueous THg concentrations may be due to numerous factors including differential Hg accumulation caused by variation in plant tissue types and decomposition rates [*Heyes et al.*, 1998], hydrological heterogeneities, and localized changes in pore water chemistry that affect the solid-liquid phase distribution. The high pore water native THg concentration found at −30 cm at the 11 m profile after 90 days (25.3 ng/L) strongly suggests accumulation along preferential hydrological flow

Table 1. Mean Peat and Pore Water Native HgT and ^{202}HgT Concentrations[a]

Depth, cm	Peat HgT, ng g^{-1} dw	Pore Water HgT, ng L^{-1}	HgT log Kd, L kg^{-1}	Peat ^{202}HgT, ng g^{-1} dw	Pore Water ^{202}HgT, ng L^{-1}	^{202}HgT log Kd, L kg^{-1}
0–3	54.5 (3, 26.5)	4.35 (10, 2.07)	4.09	1.14 (3, 0.90)	1.49 (6, 0.36)	2.88
0–6	74 (3, 36.0)	5.26 (18, 1.19)	4.14	0.64 (3, 0.83)	0.29 (13, 0.17)	3.34
6–10	69.6 (3, 5.41)	5.4 (9, 1.93)	4.1	0.25 (3, 0.44)	0.12 (7, 0.11)	3.34
Mean	66.0 (9, 24.17)	5.01 (37, 1.69)	4.12	0.68 (9, 0.76)	0.63 (26, 0.64)	3.19

[a]Means are calculated from all sample concentrations taken at the depth interval specified over the 3 month study period. Number of samples, standard deviation are given in parentheses. Pore water samples were not spatially or temporally coincident with the peat cores, and as such, the data must be interpreted cautiously.

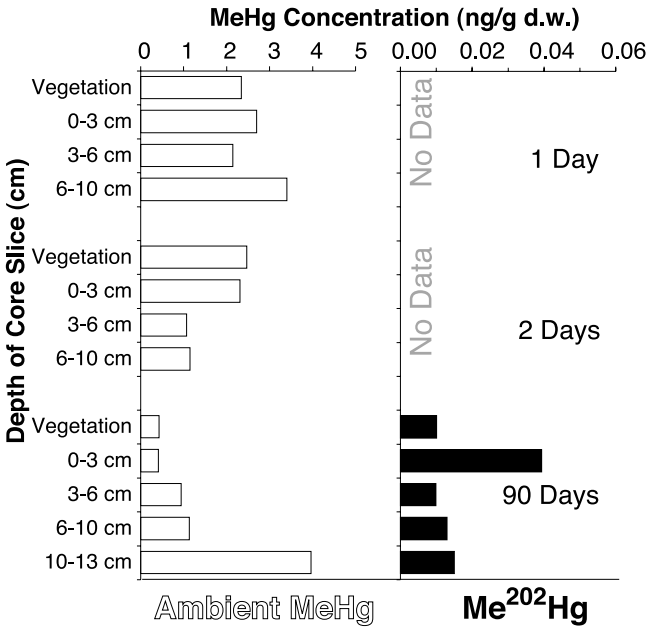

Figure 8. (left) Native MeHg and (right) $Me^{202}Hg$ in wetland surface living moss and peat soil. N = 1 for all samples.

path, driven by the strongest, most persistent lakeward hydraulic gradient measured during the study period (Figure 2). Solid phase native THg in these saturated peat soils have generally lower concentrations than those of upland mineral soils, and lack the clear pattern of near-surface enrichment [*Hintelmann et al.*, 2002].

[25] We detected the added ^{202}Hg in the aqueous phase 1 day after the application, demonstrating that an addition of a high-purity enriched stable isotope is detectable above the large pool of native THg, and thus can serve as a tracer of important environmental processes. The detection of the aqueous ^{202}Hg up to 10 cm below the peatland surface indicates that "new" mercury interacts in solution with a substantial volume of peat under saturated conditions, consistent with the results of *Branfireun et al.* [1999].

[26] The much lower aqueous ^{202}Hg concentrations 2 days after the application may be due to spatial heterogeneity in the ^{202}Hg distribution or particle partitioning, but are more likely the result of dilution as a result of a significant rainfall event that delivered 54 mm on July 15, earlier in the day that the samples were acquired. The observed decrease in the native aqueous THg concentrations support this conclusion, however the decrease in native THg concentrations are not as pronounced as that for ^{202}Hg. This may be a consequence of the higher proportion of particle-associated THg in the native Hg pool, lessening the effects of aqueous dilution.

[27] The ^{202}Hg was evident after 1 month, both below the surface (−30 cm) and beyond (9m profile) the experimental plot. Moreover, we are confident that the detection of ^{202}Hg at depth in the 11 m profile after 3 months irrefutably demonstrates advective transport of the ^{202}Hg tracer down the wetland hydraulic gradient to the lake margin.

[28] ^{202}Hg solid phase concentrations indicate a very rapid particle partitioning process; however migration and accumulation at depth after only 1 day indicates a much higher mobility of recently deposited inorganic mercury than we expected. After 90 days, the almost uniform vertical distribution of ^{202}Hg throughout the peat core is indicative of a dynamic partitioning of newly deposited mercury throughout a hydrologically active surface peat layer. *Hintelmann et al.* [2002] observed the vertical migration of an applied ^{202}Hg tracer into a forest soil, but determined that more than 50% of the added ^{202}Hg remained in the vegetation layer. Distribution coefficients (Table 1) suggest a difference in particle partitioning between native and amended ^{202}Hg, with the ^{202}Hg being present in higher concentrations in pore water than peat. The values of the coefficients all fall within the range of those reported for sediments, particles and waters in Lake Superior and other Great Lakes [*Rolfhus et al.*, 2003] and for MeHg in peat and peat pore water [*Heyes et al.*, 2000]. These data must be used cautiously as the samples were not taken from the same location, however we suggest a number of possible explanations for this difference in the distribution coefficient between the native Hg and ^{202}Hg. The distribution coefficient it is based on the total Hg concentration in the particle phase. It is our belief that there is a considerable pool of native Hg in solids that is not exchangeable; although this fraction is analyzed because of the digestion method, it functionally does not play into the phase distribution, thus skewing the distribution coefficient in favor of the particle phase. This is not the case for the amended ^{202}Hg, which is added in the aqueous phase and is likely not in equilibrium with the particle phase, although it clearly shows evidence of partitioning over the time period of the experiment. There may also be a difference in the ligand associations between the ^{202}Hg (or all recently deposited Hg) and older native Hg, or a difference in the reaction kinetics, however we have no specific evidence to demonstrate these differences from these data.

[29] Sampling for native MeHg and $Me^{202}Hg$ was limited relative to THg, however native pore water MeHg concentrations reveal a seasonal trend, with the highest concentrations observed in October. The presence of aqueous $Me^{202}Hg$ demonstrates that the applied inorganic Hg isotope was rapidly methylated in situ. Concentrations of $Me^{202}Hg$ do not show the same seasonal trend as native MeHg, with a similar range of concentrations observed over the entire study period. This methylated 'new' mercury is also more mobile than expected, with detection outside of the experimental plot after 90 days. The fraction of $T^{202}Hg$ that is $Me^{202}Hg$ averaged 21% over all depths where $Me^{202}Hg$ was detected (n = 8) with a maximum of 65%, while the fraction of native THg as MeHg averaged 36% (n = 12) with a maximum of 50%. We conclude that the inorganic ^{202}Hg was at least equally available for methylation as the native inorganic Hg in the aqueous phase.

[30] Elevated solid phase $Me^{202}Hg$ concentrations after 90 days corroborate the aqueous $Me^{202}Hg$ concentrations, demonstrating methylation of the newly applied Hg (Figure 8). The fractions of THg that is MeHg for both the isotopic and native Hg are identical (2%), indicating that the solid phase speciation is not as dynamic as the aqueous phase. The isotopic and native mercury behave similarly in the solid phase, suggesting that this fraction does not participate as fully as the liquid phase in the dynamic net methylation/demethylation balance.

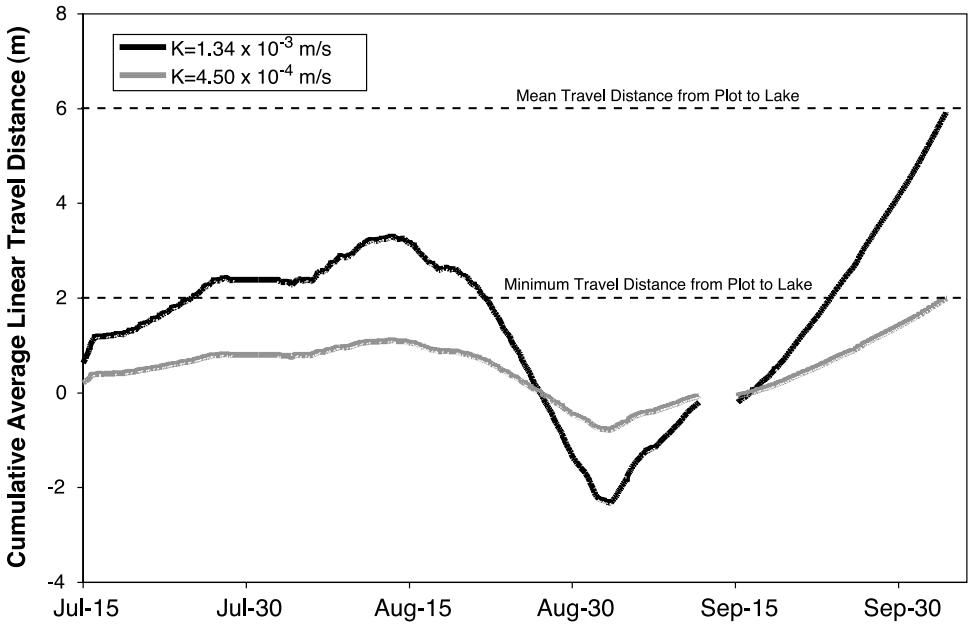

Figure 9. Cumulative average linear travel distance over the study period using the hydraulic conductivities (K) calculated from the required travel distances and measured hydraulic head differences. The gray line is the cumulative specific discharge determined for the minimum travel distance required (edge of plot). The black line is for the mean travel distance (middle of plot).

[31] The mechanisms of the MeHg production in these wetland sediments are almost certainly dominated by bacterial biomethylation. Sulfate-reducing bacterial groups have been implicated as principle methylators in anaerobic environments [see *Benoit et al.*, 2001], and dose-response experiments in boreal peat mesocosms have demonstrated an increase in pore water MeHg concentrations in response to the addition of sulfate [*Branfireun et al.*, 1999]. There is evidence of a sulfate reduction/methylation relationship in other wetland types where anaerobic processes are dominant [e.g., *Gilmour et al.*, 1998]. Certainly, sulfate reduction is an important process in the peatland that we studied here, as shown by other recent work [*Mitchell and Branfireun*, 2005].

[32] The feasibility of the transport of isotopic Hg tracer through the saturated surficial peat is supported by hydrological analyses. A value for K of 4.5×10^{-4} m/s is required to move water from the experimental plot to the lake edge for the minimum travel path (Figure 9). For the mean travel distance, this value must increase to 1.3×10^{-3} m/s (Figure 9). For a highly fibrous, undecomposed surficial peat, the calculated hydraulic conductivities in the range of 10^{-4} to 10^{-3} m/s represent a reasonable order of magnitude value, although accurate measures of such values are few [*Verry and Boelter*, 1979; *Hoag and Price*, 1995]. Although it is unlikely that the ^{202}Hg moves conservatively in groundwater, the simple analysis provides sufficient evidence of the feasibility of a groundwater driven transport vector for the applied ^{202}Hg in the absence of other direct measures.

5. Conclusion

[33] This pilot-scale study of the mobility and reactivity of an experimentally applied mercury isotope in a boreal wetland has provided valuable evidence that a relatively small addition (5 times annual natural deposition) is readily detectable above the native Hg pool, at least in the short term. After 90 days, decreasing ^{202}Hg concentrations in the both solid and liquid phases suggest ^{202}Hg concentrations may diminish through net sorption into larger sediment pools, evasion to the atmosphere as Hg(0) and discharge to adjacent waters. Experimentally applied ^{202}Hg was converted into detectable levels of Me^{202}Hg, demonstrating that 'new' mercury is available to methylation reactions, and rapidly enters this pool of mercury that biomagnifies up the food chain. When we couple the biogeochemical dynamics with the evidence of a surface hydrologic transport mechanism, we conclude that wetlands can be very dynamic environments for the transport and transformation of recently deposited Hg, contributing significantly to the total load to adjacent aquatic ecosystems in some watersheds. Future studies of wetland mercury dynamics must include more detailed assessments of the spatial and temporal variability of mercury methylation, the physical characteristics of flow in surficial high hydraulic conductivity peats, and the effects of changes in ancillary chemistry such as sulphate and pH, both of which are known to affect mercury methylation.

[34] The results of this investigation, combined with the findings of *Hintelmann et al.* [2002] demonstrated that the application of ^{202}Hg in an amount approximately 5 times the total annual deposition received at the ELA would provide measurable results for assessing the contemporary Hg cycle at the catchment scale. The METAALICUS whole ecosystem manipulation was initiated in 2000, and will provide an integrated picture of the response of biota, uplands, wetlands and lakes [see *Babiarz et al.*, 2003a, 2003b] to increased Hg input, in addition to detailed process-oriented data concerning the within-catchment dynamics of changing Hg loads.

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