

Methyl mercury dynamics in littoral sediments of a temperate seepage lake

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Abstract: The sites and rates of methyl mercury (MeHg) production and transport in littoral zone sediments were investigated at Palette Lake in northern Wisconsin. In littoral areas where groundwater inflow occurs, sulfate supply from groundwater creates profiles of electron acceptors (sulfate) and donors (methane, sulfide) that are reversed from those found in sediments whose sulfate supply is delivered from overlying water. The highest MeHg concentrations in porewaters and the maximal advective MeHg flux rates ($4.5\text{--}61.7\text{ ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$) were observed in the spring, while highest bulk phase concentrations occur later in the summer. These estimated MeHg fluxes are greater than the mean areal production rates estimated previously for the water column and are similar to the atmospheric flux. Gross MeHg production was measured using the addition of ^{203}Hg as a tracer to sediments. The depth at which maximal ^{203}Hg methylation occurred coincided with the observed maximums in solid-phase and porewater MeHg concentrations. Because input, advection, and accumulation of MeHg in these sediments were measured directly, an independent estimate of MeHg production could be made and compared with ^{203}Hg -derived rates. This comparison suggests that the ^{203}Hg tracer method provides reasonable estimates of gross methylation rates and that a substantial fraction of solid-phase Hg is available for methylation.

Résumé : On a étudié les sites et les taux de production et de transport du méthyl mercure (MeHg) dans les sédiments de la zone littorale au lac Palette, dans le nord du Wisconsin. Dans les zones littorales où il y a afflux d'eau souterraine, l'apport de sulfate provenant de l'eau souterraine crée des profils d'accepteurs (sulfate) et de donneurs (méthane, sulfure) d'électrons qui sont inversés par rapport à ceux observés dans les sédiments qui reçoivent l'apport de sulfate des eaux de surface. Les plus fortes concentrations de MeHg dans les eaux interstitielles et les taux maximaux des flux d'advection du MeHg ($4,5\text{--}61,7\text{ ng}\cdot\text{m}^{-2}\cdot\text{jour}^{-1}$) ont été observés au printemps, tandis que les plus fortes concentrations dans la phase solide des sédiments ont été observées plus tard dans l'été. Ces flux estimés du MeHg sont supérieurs aux taux moyens de production par unité de surface estimés antérieurement pour la colonne d'eau, et sont similaires au flux atmosphérique. On a mesuré la production brute de MeHg en ajoutant aux sédiments du ^{203}Hg à titre de traceur. La profondeur à laquelle a eu lieu la méthylation maximale du ^{203}Hg a coïncidé avec les maximums observés des concentrations de MeHg dans la phase solide et dans l'eau interstitielle. Étant donné que l'afflux, l'advection et l'accumulation du MeHg dans ces sédiments ont été mesurés directement, une estimation indépendante de la production de MeHg a pu être réalisée et comparée aux taux dérivés à partir de ^{203}Hg . Cette comparaison fait ressortir que la méthode utilisant le ^{203}Hg comme traceur fournit des estimations raisonnables des taux bruts de méthylation, et qu'une fraction substantielle du Hg de la phase solide est susceptible d'être méthyliée.

[Traduit par la Rédaction]

Introduction

As clean techniques have become standard practice in aquatic mercury (Hg) studies, investigators have focused efforts on important biogeochemical processes and cycling pathways of

Hg. Of particular interest has been an examination of external monomethyl mercury (MeHg) sources to aquatic ecosystems such as precipitation (St. Louis et al. 1995), runoff (Swain et al. 1992; St. Louis et al. 1994; Hurley et al. 1995), and groundwater (Krabbenhoft et al. 1995), as well as internal processes that result in MeHg production in the water column (Watras et al. 1995) and at the sediment–water interface (Gilmour et al. 1991; Krabbenhoft et al. 1995; Branfiren et al. 1996). Recent research emphasis placed on the production, transport, and fate of MeHg results from (i) the observation that virtually all Hg in fish tissue is MeHg (Bloom 1992) and (ii) the recent development of techniques for measuring MeHg concentrations (Horvat et al. 1993) and in situ Hg methylation rates (Gilmour and Riedel 1995).

Recent studies have shown that system-scale parameters such as lake size and depth, littoral zone area, and epilimnetic temperature, as well as profile measurements of methylation rates determined on incubated cores, all point to the sediment–water interface in littoral zones as an important site for MeHg production (Bodaly et al. 1993; Ramlal et al. 1993). These observations corroborate with previous findings that sandy

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littoral zone sediments are a key site for sulfate reduction (Rudd et al. 1986) and that sulfate-reducing bacteria are important Hg methylating agents in aquatic ecosystems (Gilmour et al. 1991). Littoral sediments are also the dominant MeHg production site in recently flooded reservoirs (Hecky et al. 1991; Rudd 1995; Kelly et al. 1997). Many of the previous studies, however, have not taken into account the role that groundwater plays in the aquatic Hg cycle, particularly in littoral zones of lakes where groundwater discharge is generally focused. Not recognizing the direction and mode of aqueous transport in sediments can lead to erroneous conclusions.

Groundwater has two potentially important functions in the MeHg production process in aquatic ecosystems: as a transport vector and as a solute source for many biogeochemical processes. Advective transport of solutes species that might stimulate methylation (e.g., sulfate) usually dominates over diffusion in sandy sediments (Berner 1980) and dictates the ultimate direction of flow, either upward discharge to the lake or downward recharge to the contiguous aquifer. Unless the direction of groundwater flow is determined in sediment-water exchange studies, the source or sink function of the sediment-water interface cannot be fully ascertained. Groundwater can also provide solutes that are essential for many biogeochemical processes operating near the interface, such as dissolved organic carbon (DOC), inorganic Hg, and sulfate for the methylation process (Krabbenhoft et al. 1995). However, there have been few detailed examinations of the littoral zone sediment-water interface as a MeHg generation site in places where there is appreciable groundwater flow. The challenge in conducting Hg studies at the groundwater-lake interface is twofold: difficulties in collecting contamination-free samples at small (centimetres) intervals in sandy sediments and quantifying the natural variability in groundwater flow rates that exists over relatively small areas.

In this paper, we investigate the processes controlling the production and flux of MeHg at the littoral zone sediment-water interface of Palette Lake, Wisconsin. We demonstrate a novel method for estimating net Hg methylation rates in sediments where MeHg profiles and groundwater flow rates have been measured and compare these rates with measured gross methylation rates determined by trace-level ^{203}Hg additions to intact incubated cores (Gilmour and Riedel 1995). Finally, we estimate MeHg production and flux in the context of other MeHg flux mechanisms for Palette Lake.

Study area

Located in the Northern Highland Lake District of northern Wisconsin, Palette Lake (46°04'N, 89°36'W) has no public vehicle access, and thus receives minimal human impact. It is a dimictic seepage lake; water enters by groundwater inflow and precipitation and leaves by groundwater outflow and evaporation. The lake has a surface area of about 0.70 km² and maximum and average depths of 19 and 10 m, respectively, and is situated in about 50 m of glacial outwash sediments that overlie Precambrian crystalline bedrock (Attig 1985). These deposits are primarily sand and gravel, which provide for effective hydraulic exchange between the groundwater system and lakes and streams. A neighboring lake 200 m to the east and about 2 m higher in elevation induces constant groundwater inflow along the northeast shoreline of the lake.

Materials and methods

Field sampling strategy

An established network of piezometers around the perimeter of Palette Lake documented the existence of an inflow zone along the northeast shoreline and revealed that porewater chemistry in groundwater inflow zones (10% of the shoreline) and outflow zones differs markedly, including total Hg (Hg_T) (Krabbenhoft and Babiarz 1992). Our general strategy for estimating mass fluxes of Hg_T and MeHg from the littoral sediments to the lake was to simultaneously collect porewater chemical profiles and groundwater discharge data over the course of about 2 years (1992–1994). The observed chemical profiles in porewaters, then, are reflective of the balances between upward advective flow through the sediments and the biogeochemical processes controlling chemical constituent concentrations. For comparison with the mass flux estimates of MeHg, gross MeHg production within the sands was also estimated in situ using ^{203}Hg as a radio-tracer. Methylation rate measurements were made in August 1993 at the lake's maximum temperature and in May 1994 about 2 weeks after ice-out. Concentrations of Hg_T and MeHg in sand cores were also measured at the same depth intervals that porewater and methylation rates were measured.

Estimating mass flux of Hg_T and MeHg

To calculate the mass loading rate of Hg_T or MeHg from groundwater discharge, we applied the following:

$$(1) \quad M = (C_{PW}) (q) (A) (t)$$

where M is the areal mass loading rate of Hg_T or MeHg, C_{PW} is the concentration of Hg_T or MeHg at the sampling interval closest to the interface (nanograms per litre), q is the groundwater flow rate (metres per day), A is the area of littoral zone with groundwater inflow (square metres), and t is time (days). Because we have never observed MeHg in groundwater at depths greater than about 0.5 m below the sediment-water interface, and we measure the vertical flow rate, this equation also provides an estimate of net MeHg production within littoral sediments. These estimates are compared against the ^{203}Hg -determined gross methylation rates.

Groundwater inflow measurements were made on 16 dates during ice-free periods from 1992 to 1994. On each occasion, two or three measurements were made in the same location as porewater sampling. Measurements were made using a variable-head infiltrometer, an adaptation of a constant-head permeameter (Means and Parcher 1963), to estimate the vertical hydraulic conductivity of the sediments (K_v , metres per day). The specific discharge rate, q , in eq. 1 is derived by multiplying K_v by the measured hydraulic gradient (metres per metre), which was determined by the use of minipiezometers that were installed at each site when groundwater flow rates were measured.

Porewater and sediment sampling methodologies

All sampling aspects of this research used ultraclean sampling and analytical techniques (Fitzgerald and Watras 1989). Samples were filtered using preashed, quartz-fiber filters (nominal 0.7- μm pore size). Hg_T samples were acidified to 1% HCl, while MeHg samples were put on dry ice in the field and kept frozen until analysis. Ancillary samples for pH, alkalinity, sulfate, and chloride were stored in polyethylene bottles, DOC and dissolved inorganic carbon (DIC) samples in glass vials, and CO_2 and methane samples in glass syringes. In a limited number of cases, samples were taken for oxygen-18 (^{18}O) analysis for determination of a porewater dilution factor.

In situ porewater samples were collected using two devices: one that used an applied vacuum and another that used free drainage by gravity. With either method, samples were taken at three to five depths between 0 and 10 cm. The applied-vacuum method involved the use of a borosilicate-glass frit which was connected by Teflon tubing to an inline filter and then to a Teflon transfer jar to which a

vacuum was applied. The frit was inserted vertically into the littoral zone sediments (about 0.2–0.5 m lake water depth) to the desired sampling depth and held in place. The only exception to this was when taking samples at the 1 cm depth interval, the frit was inserted at an acute angle to minimize leakage of lake water into the frit. A hand suction pump was used to apply a vacuum (about 40 kPa) to the transfer jar, which induced flow of porewater into the transfer jar. About 30–60 mL of sample was withdrawn for each insertion at a particular depth; this process was repeated three to five times at the same depth within about a 0.5-m quadrat to generate enough sample volume for all the analyses. The pooled sample from the transfer jar was then split among the various sample containers.

The free-drainage method for porewater sampling involved the use of a 30.5-cm-long, 2.54-cm (outside diameter) Teflon piezometer point, which has four slots (0.04 cm wide) over a 1-cm interval near its sharpened endpoint. The device was pushed into the littoral sediments to the desired depth and then evacuated using a Teflon sample line and a peristaltic pump. The pump was then set to a minimum speed so that the pumping rate approximately equaled the drain rate of porewater into the evacuated sampler.

Both porewater sampling methods described above are potentially susceptible to sample dilution by lake water in response to the imposed downward hydraulic gradient. This was especially true for the sampling intervals closest to the interface (0–2 cm). For temperate lake systems, stable isotopes of water (^{18}O and deuterium) can be used to detect the presence of lake water in porewater samples and to estimate the dilution factor for individual porewater samples (Krabbenhoft and Webster 1995). Here, we use a separation quotient similar to that of Krabbenhoft et al. (1990):

$$(2) \quad \frac{\delta^{18}\text{O}_L - \delta^{18}\text{O}_S}{\delta^{18}\text{O}_L - \delta^{18}\text{O}_{\text{GW}}} = X$$

where X is the fraction of groundwater in the porewater sample and $\delta^{18}\text{O}$ are the ^{18}O results expressed in per mil (‰) notation relative to V-SMOW for lake water (L), groundwater (GW), and the porewater sample (S). By obtaining the dilution factor, and the concentration of Hg (Hg_T or MeHg, nanograms per litre) in the sample and lake water, we can estimate the Hg concentrations in those samples where dilution may be significant using the following:

$$(3) \quad X[*\text{Hg}_S] + (1 - X) [\text{Hg}_L] = \text{Hg}_{\text{obs}}$$

where Hg_{obs} and Hg_L are the concentrations of Hg_T and MeHg in the analyzed porewater and lake water samples, respectively, and $*\text{Hg}_S$ is the estimated dilution-corrected concentration of Hg_T or MeHg at the sampling interval of interest.

Intact sediment cores for the ^{203}Hg -determined gross methylation rates were sampled by hand into acid-leached 4.8-cm-diameter PVC tubes. Sediments were extruded and sectioned within a few hours of collection. For each sampling date and site, one or two cores were sectioned into 2- to 4-cm segments with depth to about 10 cm, plus three 0- to 4-cm sections were collected from separate cores. All sediment samples were immediately frozen.

Analytical methods

Hg_T in aqueous samples was determined by cold-vapor atomic fluorescence spectroscopy (CVAFS) following oxidation with BrCl , reduction by SnCl_2 , and purge and trap of the evolved Hg^0 onto gold-coated sand columns (Gill and Fitzgerald 1987; Bloom and Fitzgerald 1988). MeHg was analyzed using the distillation and aqueous-phase ethylation method of Horvat et al. (1993) and detection by CVAFS. Quantification limits for Hg_T and MeHg for surface waters are about 0.06 and 0.02 ng/L, respectively; porewater samples have higher quantification limits, about 0.4 ng Hg_T /L and 0.1 ng MeHg/L, due to their inherently smaller volumes. Solid-phase MeHg and Hg_T analyses were performed as described above. Modifications, SRM analyses, and spike recoveries are described in Gilmour and Riedel (1995).

Ancillary parameters were determined by the following methods: alkalinity by potentiometric Gran titration, sulfate and chloride by high-performance liquid chromatography, DIC and DOC by a carbon analyzer that uses acidification and persulfate–UV oxidation, and methane and CO_2 by gas chromatography with an inline methanizer and flame ionization detection. Reduced sulfur concentrations were measured by cold-acid distillation (AVS, acid-volatile sulfides) and chromium reduction (CRS, chromium-reducible sulfides) (Fossing and Jorgensen 1989). Dissolved sulfide in porewaters was preserved in sulfide antioxidant buffer (Brouwer and Murphy 1994) and measured electrochemically using a selective ion probe.

Gross MeHg production from inorganic $\text{Hg}(\text{II})$ within sediments was estimated using custom-synthesized high specific activity ^{203}Hg as a radiotracer, as described in Gilmour and Riedel (1995). The goal of this method is to use ^{203}Hg of specific activity sufficient to act as a tracer in natural sediments and waters. In short-term experiments, this should provide gross methylation rates (Xun et al. 1987). Rates estimated using greatly elevated Hg concentrations may not reflect rates at ambient Hg concentrations and speciation (Gilmour et al. 1991). Since the specific activity of commercially available ^{203}Hg is not sufficient to be used as a tracer in natural waters or in uncontaminated sediments, high specific activity $^{203}\text{HgCl}_2$ was produced for this work by custom synthesis from ^{202}Hg . Two batches were used in this work, with specific activities of 1.03×10^9 Bq/mg (August 1993) and 6.18×10^8 Bq/mg (May 1994).

Methylation within sediments was estimated by injection of $^{203}\text{HgCl}_2$ into intact sediment cores at 1 cm depth intervals. The $^{203}\text{HgCl}_2$ solution was preincubated with sediment porewaters for an hour before injection into cores to allow formation of dissolved Hg complexes. Sealed cores were incubated in situ for a period of hours to 2 days and then cut with depth into 2.5-cm slices and immediately frozen. Injections of ^{203}Hg were generally made to 10 cm depth. Information on the time course and substrate concentration dependence of Me^{203}Hg production in these sediments is given in Gilmour and Riedel (1995).

Me^{203}Hg was extracted from aliquots of thawed sediment, as described in Gilmour and Riedel (1995), and assayed using a 3-in. (7.6-cm) NaI-well gamma detector. The ambient methylation rate was calculated by multiplying the fraction of added ^{203}Hg methylated per day by the ambient Hg_T concentration in the horizon of interest. This calculation assumes that ^{203}Hg is added as a tracer and that the speciation and sediment–water partitioning of added Hg mimic those of ambient Hg. Concentrations of Hg_T in Pallette inflow sands average about 1 ng/g (dry weight), and our additions increased the Hg_T concentrations by 2.7 ng/g (August 1993) and 0.8 ng/g (May 1994).

Results and discussion

Porewater profiles

Porewater samples were acquired from the center of the groundwater inflow zone to avoid sampling in areas where the direction of flow may reverse occasionally due to transient hydrologic conditions. On three occasions, we sampled using both the applied-vacuum and gravity-drain methods to test the efficacy of these methods for sampling in sandy littoral sediments. The results of each method show similar overall concentration ranges for Hg_T , as well as similarly shaped profiles with subsurface maxima (Fig. 1).

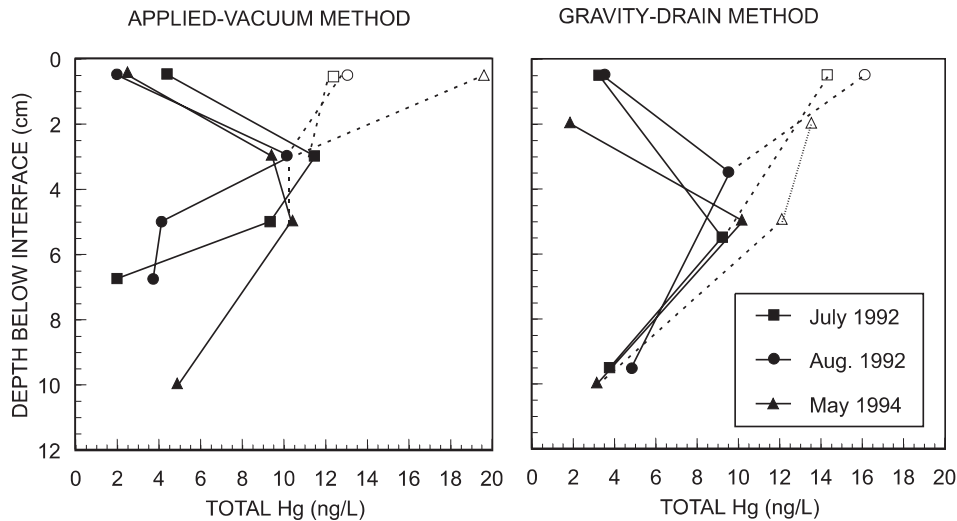
^{18}O analytical results show that the subsurface maxima in the porewater profiles are due to sample dilution by lake water. During each sampling period, and for both sampling methods, the deepest porewater samples have $\delta^{18}\text{O}$ values very similar to those observed previously (range -11.0 to -11.7‰) for groundwater at Pallette Lake (Krabbenhoft and Babiary 1992) and are very distinct from lake water which averages about

Table 1. Results of Hg_T and ^{18}O analyses on porewater samples, and calculated values of groundwater fraction and dilution-corrected Hg_T in near-surface porewater samples.

Method	Date	Depth (cm)	$\delta^{18}O$	GW fraction ^a	Hg_T obs. (ng/L)	Hg_T calc. (ng/L) ^b
Applied vacuum	July 1, 1992	0.5	-6.07	0.30	4.42	12.4
	Aug. 24, 1992	0.5	-4.39	0.08	1.96	13.0
	May 9, 1994	0.5	-4.76	0.08	2.49	19.6
	May 9, 1994	3.0	-10.52	0.89	9.45	10.5
	May 9, 1994	5.0	-11.44	1.02	10.37	10.2
	May 9, 1994	6.75	-11.58	1.04	4.97	4.81
Gravity drain	July 1, 1992	0.5	-5.14	0.17	3.26	14.3
	July 1, 1992	10.0	-11.10	1.00	3.81	3.81
	Aug. 24, 1992	0.5	-4.96	0.16	3.43	16.1
	Aug. 24, 1992	6.75	-11.01	1.00	4.85	4.85
	May 9, 1994	2.0	-4.70	0.07	1.88	13.5
	May 9, 1994	5.0	-10.09	0.83	10.25	12.1
	May 9, 1994	10.0	-11.21	0.99	3.21	3.23
	May 9, 1994	91	-11.30	1.00	na	na

^aCalculated groundwater fraction using eq. 2 and the $\delta^{18}O$ results for the deepest sampling interval for a given date and measured lake water $\delta^{18}O$ values of -3.92, 3.82, and -4.20‰ on July 1, 1992, August 24, 1992, and May 9, 1994, respectively.

^bEstimated porewater Hg_T concentration using eq. 3.

Fig. 1. Comparison of sample collection methods for Hg_T porewater profiles from the inflow zone. Solid symbols show the actual sample Hg_T concentration; open symbols show the corrected Hg_T concentration after the results of the ^{18}O analysis were used in eqs. 3 and 4 to correct for lake water dilution.

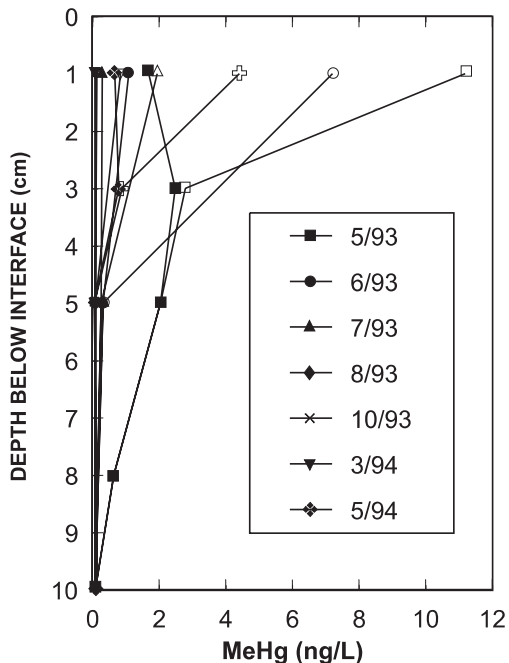
-4.0‰. If we assume conservative mixing of a two-endmember system (lake and groundwater), we can calculate the fraction of groundwater present in our samples (Table 1). These calculations show that shallow porewater samples (<2 cm depth) are dominantly lake water (70–93% lake water), but that the samples from about 3 cm depth or more are representative of porewater (83–100% groundwater). By using the average lake water concentration of 1 ng Hg_T/L and the calculated lake water fraction for the shallow samples, corrected Hg_T concentrations were derived. The corrected Hg_T values show a more linear trend with the samples collected at depth, especially the profiles from the gravity-drain method (Fig. 1). The corrected Hg_T concentrations at 1 cm depth in this figure are very similar to the values observed by Krabbenhoft and Babiarz (1992), who also sampled porewaters from the littoral zone of Palette Lake, but extracted porewaters from intact

sediment cores using suction. That method is considerably more laborious but not as susceptible to sample dilution by lake water. Based on these results, we conclude that subsurface maxima in Hg_T concentration are the result of a sampling artifact and that concentrations of Hg_T actually increase nearly linearly toward the sediment–water interface.

Porewater samples for MeHg analysis were taken using the applied-vacuum method on seven occasions from May 1993 to May 1994 (Fig. 2). Three observations can be made from these data: (i) many samples fall at or below the quantification limit of 0.1 ng MeHg/L, (ii) those profiles where MeHg is above the quantification limit generally show subsurface maxima, and (iii) those profiles where MeHg is appreciably above the quantification limit were all sampled in spring and early summer.

On three occasions (June 1993, August 1993, and May

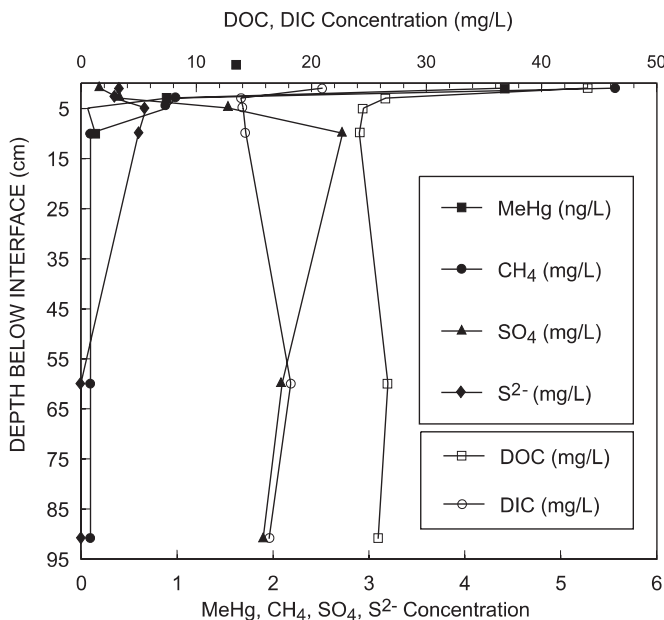
Fig. 2. Porewater MeHg profiles from the inflow zone at Palette Lake using the applied-vacuum method for sampling. Solid symbols show the actual sample MeHg concentration; open symbols show the corrected MeHg concentration after the results of the ¹⁸O analysis were used in eqs. 2 and 3 to correct for lake water dilution.



1994), we used a 15-mL portion of the porewater samples from 1 and 3 cm depth for ¹⁸O analysis and found similar dilution ratios as those presented above. The three samples taken at 1 cm depth averaged 5.05‰ (range -4.76 to -5.65‰) whereas the three samples from 3 cm depth averaged -10.31‰ (range -10.22 to -10.64‰). Lake and groundwater samples were not taken for ¹⁸O analysis in June 1993 and August 1993. Considering that these two endmember waters show very little variability in ¹⁸O results, we calculated the fraction of groundwater in these samples using the observed averages of -3.98 and -11.1‰ for lake and groundwater, respectively. Using these data and eq. 4, we corrected MeHg concentrations at the 1 and 3 cm depths (Fig. 2). The corrected profiles show that the greatest MeHg concentrations occur at the shallowest sampling depth (1 cm), and the greatest values are observed in spring and early summer. The porewater samples with high MeHg concentrations (>2 ng/L) all show a high proportion of Hg_T as MeHg, ranging from about 30 to 50%, which is reflective of rapid rates of Hg methylation in littoral sediments.

Ancillary measurements on porewater samples demonstrated the dynamic character of biogeochemical processes near the sediment-water interface and the fine scale (centimetres) at which large changes in critical constituents occur (Fig. 3). These data were also corrected for lake water dilution. The most rapid rate of change for all the constituents occurs in the upper 10 cm. Between 60 and 90 cm depth, sulfate, sulfide, methane, DOC, and DIC show little or no change, and, with the exception of sulfide, only modest changes were observed between 10 and 60 cm depth. About 98% of the sulfate advecting upward is lost between 0 and 10 cm. Sulfide

Fig. 3. Ancillary porewater chemistry data for samples collected in May 1994 from the groundwater inflow zone. CH₄, methane; SO₄, sulfate; S²⁻, sulfide.

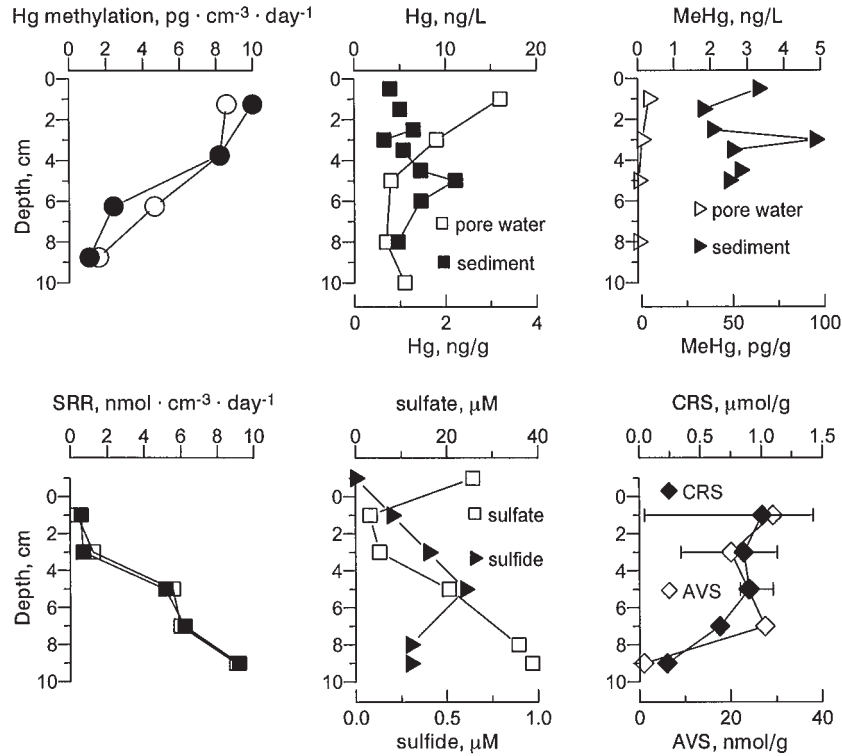


concentrations increase from less than detectable at 60 cm to a subsurface maximum of 0.8 mg/L at 5 cm. The decrease in porewater sulfide at depths less than 5 cm may be due to precipitation with iron, as iron hydroxide is visible in the near-surface sediments, or less sulfide is formed above 5 cm depth. In littoral sediments of the groundwater inflow zone, sulfate reduction is driven by groundwater sulfate advecting upward through sediments. These concentration profiles of major constituents are reversed from patterns seen in nonadvecting areas or where lake water and transport downward is the ion source (Rudd et al. 1986). Methane, DIC, and DOC all show dramatic increases over the upper few centimetres. During three other sampling periods (including March 1994 when the lake was ice covered) the same suite of ancillary parameters were measured and similar profiles were observed, suggesting that these processes operate continuously.

Details of biogeochemical processes in the top 10 cm, where microbial activities are highest, are shown in Fig. 4 for August 1993 and May 1994, within 2 weeks of ice-out. Gross MeHg production, measured using ²⁰³Hg as a tracer, was maximal at or near the sediment surface. In both spring and summer, sulfate was depleted as groundwater was advected toward the sediment surface, and sulfate reduction rates decreased concomitantly. Sulfate reduction rates were about twice as high in August as in April. Solid-phase sulfur (AVS and CRS) accumulated over the summer, and dissolved sulfide increased somewhat as well. However, the low sulfate concentrations in Palette Lake and the low organic content of these sandy littoral sediments are reflected in overall very low sulfide concentrations in all phases. Hg methylation rates were maximal just above the zone of maximum sulfate reduction in both May and August. While bulk and dissolved Hg_T concentrations remained similar, MeHg accumulated in bulk-phase sediments from May to August. However, porewater MeHg concentrations were much higher in the spring, as discussed above.

Fig 4. Sediment depth profiles of Hg methylation rates and sulfur and Hg chemistry in Palette Lake littoral sediments in the groundwater inflow zone for May 9, 1994, and August 26, 1993. Hg methylation rates were measured using ^{203}Hg as a radiotracer and calculated using total sediment Hg as substrate. Each profile represents an individual sediment core. AVS (acid-volatile sulfides) and CRS (chromium-reducible sulfides) profiles shown are averages of at least three cores, with standard deviations shown as error bars. Sulfate, sulfide, Hg, and MeHg in porewaters were taken from pooled replicate samples, and sulfate concentrations are shown for above the sediment–water interface.

August 1993



May 1994

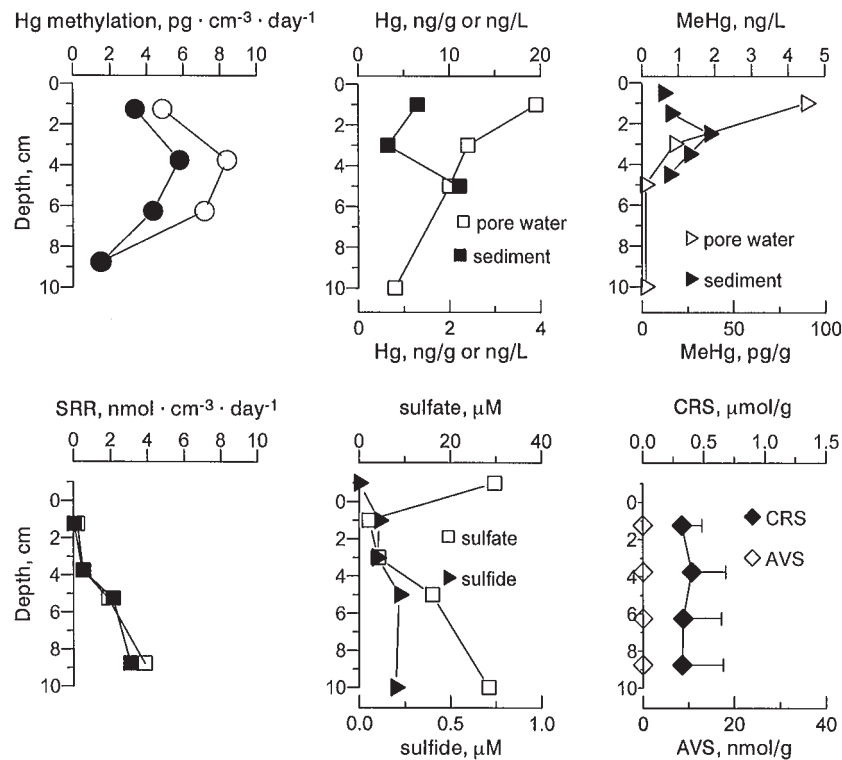


Table 2. Calculated seasonal mass-flux rates of MeHg and Hg_T for Palette Lake.

	Flow rate (m ³ /day)	Days	Concentration range (ng/L)	Mass flux (ng·m ⁻² ·day ⁻¹)	Whole-lake flux (mg)
MeHg					
Springtime	196	76	0.8–11.2	4.5–61.7	12–164
Summer–fall	126	130	0.0–1.9	0–7.0	0–32
Total for ice-free period (mid-April to early November)					12–196
Hg_T					
Springtime	196	76	12.4–19.6	69–109	184–292
Summer–fall	126	130	12.4–19.6	44–71	203–321
Winter	126	159	12.4–19.6	45–70	248–392
Total for ice-free period (mid-April to early November)					387–613
Annual flux					635–1005

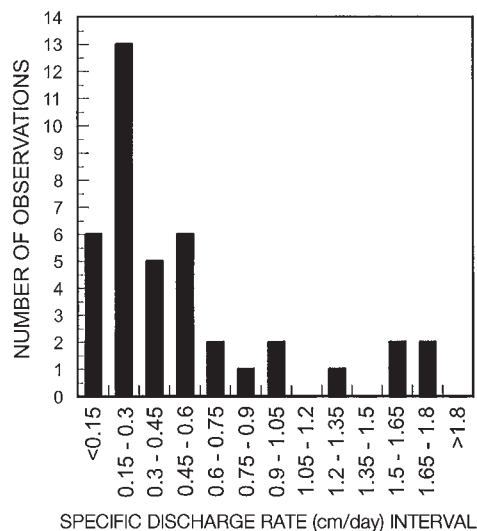
Mass flux of Hg_T and MeHg to Palette Lake

Groundwater discharge rates at Palette Lake show a lognormal distribution (Fig. 5), a common observation for natural sediments. The average discharge rate of all 40 measurements was 0.48 ± 0.42 cm/day, but springtime measurements were greater than those made in summer and fall: 0.56 ± 0.59 cm/day (April–June, N = 21) versus 0.36 ± 0.34 cm/day (July–November, N = 19). Given that the area of lakebed contributing groundwater discharge to Palette Lake was essentially constant during this study (3.5 × 10⁴ m²), we can convert these seasonal vertical discharge rates to volumetric flow rates of 196 m³/day (springtime) and 126 m³/day (summer–fall). This seasonal difference is due to greater hydraulic gradients in spring, resulting from recharge of melting snow and rainy periods during spring and early summer.

Using the volumetric flow rates described above and the corrected Hg_T and MeHg concentrations from Table 1 and eq. 1, mass flux rates for the ice-free period at Palette Lake were estimated (Table 2). Because MeHg porewater data and groundwater discharge rates show significant differences between the spring and summer–fall periods, we calculated MeHg flux rates for both periods. These calculations show that the majority of MeHg advected from the littoral zone sediments at Palette Lake occurs in the spring; the average rate for spring is 11.1 ng·m⁻²·day⁻¹ (range 1.1–23.5) compared with 0.5 ng·m⁻²·day⁻¹ (range 0–1.4) for summer–fall. For the 76-day spring period, this equates to a production rate of 3–62 mg MeHg for the groundwater inflow area compared with 0–6 mg MeHg for the 130-day summer–fall period. If we had based our calculations on a diffusive transport model, and neglected advection, the estimated MeHg flux from the littoral zone would be insignificant.

The large range in calculated MeHg flux estimates (12–196 mg over the ice-free period) is reflective of the observed range of MeHg concentrations in porewaters and the variability in flow rates. When compared with the estimated atmospheric MeHg deposition rate to Palette Lake of 49 mg/year (Lamborg et al. 1995), the efflux from littoral sediments can be an important (or dominant) source of MeHg to Palette Lake. This is especially true in early spring when up to 164 mg of MeHg effluxes from the littoral sediments and about 15 mg is contributed by atmospheric deposition. The springtime efflux rate of MeHg (4.5–61.7 ng·m⁻²·day⁻¹) is as much as three times the estimated rate for the water column

Fig. 5. Groundwater discharge velocities measured from the groundwater inflow zone using the infiltrometer test method.



during a stratified period when sulfate reduction was occurring (10–20 ng·m⁻²·day⁻¹, Watras et al. 1995).

For Hg_T, we did not have enough data to detect seasonal differences in the observed range of Hg_T concentrations at the top of individual profiles, and the data we have are not as disparate as the MeHg profiles. Thus, we use only one concentration range in our flux estimates (Table 2). These calculations show that about 387–613 mg Hg_T is contributed to Palette Lake during the ice-free period. Of this Hg_T flux, 2–50% is MeHg. If we extend these calculations by assuming that the summer–fall flow and concentration data are representative of winter conditions, an estimated annual littoral zone Hg_T flux of about 600–1000 mg is derived. This range of Hg_T flux values compares favorably with the estimate of Krabbenhoft and Babiarz (1992), who used different methods for acquiring porewater samples and estimating the groundwater flux rate, and estimated an annual flux rate of 700 mg. About 30–40% of this Hg flux is new Hg from groundwater flow; the remainder is presumably recycled Hg from the epilimnion (including MeHg) brought to littoral sediments by particle settling and released to porewaters by mineralization. When compared with the estimated annual atmospheric flux of about

Table 3. Gross MeHg production rates estimated from ^{203}Hg methylation, and advective MeHg efflux from sediments.

Date	Gross MeHg production ($\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$)					MeHg advection ($\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$)
	Based on solid-phase Hg		Based on porewater Hg		N	
	Average	SD	Average	SD		
Aug. 1993	596	55	0.91	0.25	6	0.58
May 1994	449	84	1.00	0.20	4	46.6

7000 mg, we conclude that, unlike the MeHg flux estimates, the littoral zone sediments are not a dominant Hg_T source.

MeHg production rates

To estimate MeHg production using the tracer-level ^{203}Hg method, the specific activity of the Hg available for methylation must be known. The pool of Hg available to microbes for methylation in natural sediments is presently unknown, however, and remains a key to understanding and quantifying in situ methylation rates. We used two methods to calculate specific activity in sediments. Gross MeHg production from ^{203}Hg methylation was calculated by multiplying the methylated fraction of the added ^{203}Hg by either the concentration of solid-phase Hg_T or the porewater Hg_T concentration in sediments on the sample date (Table 3). Using solid-phase Hg plus added ^{203}Hg as the available Hg pool gives methylation rates that are between two and three orders of magnitude higher than rates derived using porewater Hg as the sole substrate. The time required to generate the observed MeHg pool in the littoral sediments would be on the order of 10–30 days using the methylation rate estimated with solid-phase Hg_T as substrate (Table 3). However, using the porewater-based calculation, turnover times would be decades. MeHg production using porewater Hg_T concentration was insufficient to support MeHg advection in May but not in August (Table 4). This calculation implies that some of the solid-phase Hg is available for methylation, either directly or through rapid dissolution. However, methylation rates estimated using the entire solid-phase pool exceeded the estimated MeHg advection.

Sources and sinks for MeHg in the groundwater inflow sands

The groundwater inflow zone at Pallette Lake offered a unique opportunity to make independent estimates of MeHg production. High MeHg concentrations and a steep gradient of MeHg in porewaters suggested that MeHg production was fairly rapid in these sediments. Low organic carbon content of the sands results in a relatively low affinity of Hg and MeHg for solids. As a result, porewater is a more important component of the Hg budget in this location than for most sediments. Because input, advection, and accumulation of MeHg could be directly measured, a budget could be constructed allowing independent estimation of MeHg production (Table 4). The budget could then be used to constrain our estimates of the $\text{Hg}(\text{II})$ substrate pool for methylation.

Advection is not the only potential sink for MeHg produced within the littoral sediments at Pallette Lake. The mass of MeHg in the groundwater inflow area sands increased over the course of the summer, but Hg_T did not. The increase in MeHg

Table 4. Budget for MeHg in Pallette Lake sediments in the groundwater inflow zone, 0–10 cm depth.

	May	August
Sources ($\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$)		
Gross MeHg production, ^{203}Hg based	449	596
Sinks ($\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$)		
Buildup of MeHg in solid phase (July–Aug. 1992)	187	187
Buildup of Hg in solid phase	0	0
MeHg advection	47	1
Sum of MeHg loss terms	234	188
MeHg pool size (ng/m^2)	3000	10 200

in bulk sediment was estimated from the increase in the average concentration in the top 10 cm during July–August 1992, when the most intensive sampling of sediments was performed. Average MeHg concentrations increased from 0.16 to 0.57 ng/g . This in situ accumulation of MeHg appears to be a larger sink for MeHg produced in the littoral sediments than advective transport to the overlying lake (by a factor of 10–100). The sum of accumulation and advection represents a lower bound on net MeHg production, assuming that deposition of particulate MeHg to littoral sediments is insignificant. Demethylation is also a potentially important loss term for MeHg, but this process was not measured directly in this study. Although the MeHg sediment accumulation data were only collected during summer, we assume here that the estimated accumulation rates are applicable to the spring as well.

For both May and August, the sum of the MeHg advection and solid-phase accumulation equaled one third to one half of the gross MeHg production rate estimated using ^{203}Hg addition (Table 4). Advection of MeHg from sediments appears to account for a small percentage of gross methylation at this site, especially in summer when flow rates are lower. Based on this rough budget, our estimates of gross MeHg production made using near-tracer-level ^{203}Hg addition appear to overestimate net methylation rates by less than a factor of 2, although there are significant uncertainties in the budget.

We have also examined the accuracy of the radiotracer method by comparison with sediment incubation methods (Gilmour and Riedel 1995) using no added Hg. In Pallette Lake littoral sediments outside the inflow zone, the incubation method yielded $90 \text{ ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ in June 1992 whereas the ^{203}Hg method yielded $350 \text{ ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ in May 1994. We also found reasonable agreement between these methods in another Wisconsin Lake (Gilmour and Riedel 1995). Taken together, these comparisons suggest that a substantial fraction of solid-phase Hg is available for methylation and that use of tracer additions of ^{203}Hg to sediments provides a reasonable estimate of gross in situ methylation rates.

Seasonality of MeHg production and flux

The general patterns of gross MeHg production and MeHg efflux from sediments were not the same, nor was the change in the magnitude of each of these processes across seasons. Gross MeHg production was only slightly higher in August at 25°C than in May at 8°C . We speculate that the rapid resupply of microbially available substrates, including Hg, might account for the relatively high rates of methylation observed in spring. However, advection of MeHg from sediments was

about 100 times higher in spring than in summer. MeHg concentrations in porewaters in the summer were quite low. If gross MeHg production rates are relatively constant over the ice-free season, much lower MeHg concentrations in summer might be attributed to increased rates of demethylation, or a change in the partition coefficient for MeHg onto solids. Other researchers using nontracer methods (Xun et al. 1987) have observed that demethylation rates in epilimnetic sediments are highest in spring to early summer, while the methylation/demethylation ratio is highest in late summer at maximum sediment temperature (Korthals and Winfrey 1987; Ramlal et al. 1993). The discrepancy between gross MeHg production and MeHg advection is more likely explained by increased partitioning of MeHg onto the solid phase. MeHg partition coefficients are low in these sands compared with organic sediments, about 100–1000 L·kg⁻¹. Partition coefficients for both Hg and MeHg were lowest in surface sediments and were lowest in the spring. In Pallette Lake sands, the concentration of solid reduced sulfides (a product of microbial sulfide reduction) does increase over the summer (Fig. 4), possibly providing a larger surface area and possibly more ligands for MeHg binding. However, the relative importance of kinetic and thermodynamic control over porewater Hg and MeHg concentrations is not known.

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