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Mercury inputs and outputs at a small lake in northern Minnesota

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Abstract Storages and cycling of total mercury (Hg_T), methylmercury (MeHg), and Hg^0 are described for Spring Lake, a small bog lake in the Marcell Experimental Forest in north-central Minnesota. We quantified photoredox transformations, MeHg photolysis, burial to the sediments, and internal and external loadings of Hg_T and MeHg. Atmospheric deposition was the main input of Hg_T; MeHg was supplied by a combination of atmospheric, near-shore wetland, and biotic (methylation) sources. Hg_T outputs were dominated by burial (67%), and Hg^0 evasion accounted for 26% of Hg_T outputs. The watershed of Spring Lake is small (3.7× lake surface area), and accordingly, bog and upland runoff were minor contributors to both Hg_T and MeHg inputs. Wet deposition was ~9% of total MeHg input, and other external inputs (runoff, sediment porewater) provided only an additional 7%, indicating that internal production of MeHg was occurring in the lake. Photolysis of MeHg, measured in the field and laboratory, removed ~3× the lake mass of MeHg (20 mg) annually, and was the dominant sink for MeHg. Residence times of MeHg and Hg_T in the lake were 48 and 61 days, respectively, during the open-water season, compared with only 8 days for the residence time of MeHg on settling particles (seston). Photoreduction of Hg^{2+} to Hg^0 was greater than the reverse reaction (Hg^0 photooxidation), and the residence time of Hg^0 in the photic zone was short (hours). Data from this study show active cycling of all the measured species of mercury (Hg_T, MeHg, and Hg^0) and the importance of MeHg photolysis and photo-redox processes.

Keywords Elemental mercury · Mercury · Methylmercury · Photodegradation · Photolysis · Sediment

Introduction

Mercury cycling in ecosystems involves a complicated set of chemical, biological, and physical transformations, including biotic and abiotic methylation and demethylation, volatilization, photoreduction, photooxidation, and adsorption. Some processes, such as phototransformations, have not been widely studied, and mass balance analyses seldom include site-specific data for these potentially important processes. Moreover, conclusions about the relative importance of sediments, atmospheric inputs, chemical transformations, and effects of landscape conditions on mercury fluxes and concentrations are not consistent among available mass balances for total mercury (Hg_T) and especially methylmercury

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(MeHg) in aquatic systems (Henry et al. 1995; Iverfeldt et al. 1996; Kotnik et al. 2002; Meili et al. 1991; Sellers et al. 2001; Sullivan and Mason 1998; Watras 1994). MeHg inputs to surface waters are thought to depend on catchment conditions (e.g., wetlands versus uplands) (Allan et al. 2001; St Louis et al. 1996, 1994), microbial activity (Gilmour et al. 1992; Compeau and Bartha 1985), hydrology (Branfireun et al. 1996), and geology (Siciliano et al. 2003). Lakes are thought not to be net generators of MeHg, but the bioaccumulative nature of MeHg nonetheless results in greatly elevated MeHg concentrations in biota compared to concentrations in lake water.

This study was aimed at improving our understanding of the source strengths and chemical transformations of mercury in lakes. We measured concentrations of Hg_T, MeHg, and elemental mercury (Hg^0_{aq}) in water, sediment, biota, near-shore wetlands, and the atmosphere of a small bog lake in a forested watershed in northern Minnesota and obtained site-specific rate data on various physical and chemical cycling processes for which information is sparse in the literature.

Site description

Spring Lake (47°31′ latitude and 93°28′ longitude), the focus of this study, is in the US Forest Service's Marcell Experimental Forest, ~30 km north of Grand Rapids, MN. Its surface area is 8.9 ha, mean depth is 2 m, and it has no well-defined inflow or outflow tributaries (Fig 1). Chemically, its water is highly dilute (conductivity = 19 μS cm^{-1}, Table 1), reflecting its hydrogeomorphic setting as a groundwater recharge system. The lake water is stained by humic material and has moderately high DOC (11 mg L^{-1}). Secchi depth is 1.1 m; light absorptivity is 0.30 cm^{-1} at 254 nm and 0.015 cm^{-1} at 440 nm. The lake is well mixed after ice-out, and although it does not stratify stably during summer, dissolved oxygen near the bottom (~10 cm from the sediment-water interface) often is <0.1 mg L^{-1} in summer. The surrounding forest is dominated by black spruce (*Picea mariana*), sphagnum moss (*Sphagnum magellanicum* and *S. angustifolium*), and ericacous shrubs (Verry and Urban 1992). The small drainage area (33 ha) has no human development. About 75% of the area adjacent to the lake is occupied by wetlands

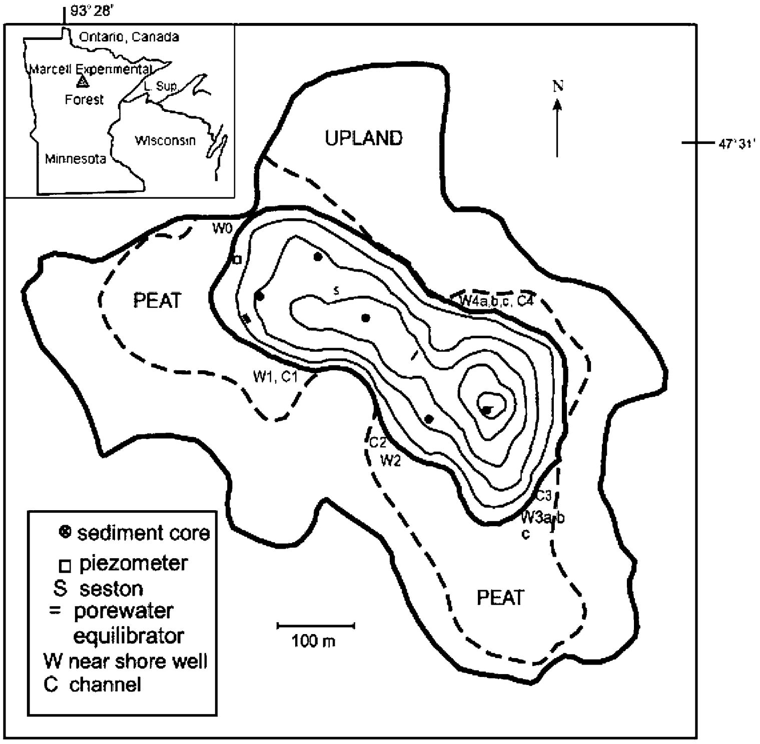

Fig. 1 Watershed and bathymetric map of Spring Lake in the Marcell Experimental Forest, MN; 1 m bathymetric contours. SE lake margin: area of diffuse inflow from near-shore wetlands; NW margin, also wetland: area of diffuse outflow. W_0–W_{4a-c}: areas where near-shore wetlands were sampled via shallow wells; C1–C4: small open channels where surface water samples were collected

Table 1 Morphometry and water chemistry of Spring Lake, 2001–2002, open-water season

Parameter	Mean value ± one SD or range (pH)
Maximum depth (m)	5.5
Mean depth (m)	2
Lake volume (10^5 m^3)	1.83
Lake area (ha)	8.9
Drainage area (ha)	33
pH	5.8 (5.2–6.5)
Alkalinity (meq L^{-1})	0.076 ± 0.0077
Conductivity (µS cm^{-1})	19 ± 1.6
Total suspended solids (mg L^{-1})	3.2 ± 1.2
Dissolved oxygen (% of saturated)	85 ± 15
DOC	11.0 ± 0.8
Total N (µg L^{-1})	641 ± 104
Total P (µg L^{-1})	18 ± 5
Fe (µg L^{-1})	85 ± 49
Mn (µg L^{-1})	5.9 ± 8.4
SO_4^{2-} (mg L^{-1})	0.87 ± 0.12
Cl^- (mg L^{-1})	0.30 ± 0.061

Chemical analysis by the Science Museum of Minnesota, St. Croix Watershed Research Station. Cations and anions were filtered and are reported as dissolved concentrations

and 25% by mineral soils; 26% of the entire watershed is wetland and 48% is upland mixed forest.

Methods

Lake water and biota sampling

Lake water was collected for Hg_T and MeHg from 2000 to 2003 using Teflon bottles cleaned in warm HCl (55°C; all HCl in this study was Baker Instra-analyzed™), stored with 1% HCl, and rinsed three times and transported to the field with high-resistivity deionized water. Water was collected facing into the wind from the bow of a non-motorized boat using polyethylene gloves. Samples were acidified with HCl (all samples = 0.8% HCl by volume) and refrigerated until analysis. Water samples at depth were collected using an acid-cleaned Teflon Kemmerer sampler (Wildco™). Samples for Hg_T and MeHg were collected during the ice-free season (March–November, 2000–2003) approximately monthly. Water samples were collected monthly for analysis of Hg^0 in 2001 and 2002.

Near-shore wetlands are a potentially important component of the mercury cycle of Spring Lake. The near-shore wetland area (8.5 ha) is almost equal to the lake surface area and occupies most of the shoreline margin. To sample this environment, nine shallow PVC wells (labeled W_0–W_{4a-c}) were pushed into the near-shore wetland sediments in mid-May, 2003 (Fig. 1). The wells consisted of concentric PVC cylinders: an outer casing of thin walled, 5-cm diameter open tubes 46 cm long with 30–40 evenly spaced 0.64 cm diameter holes which served to prevent large debris from entering the sampling well. The inner PVC cylinder was 2.5 cm diameter (O.D.), finely slotted (0.25 mm) at 0.5-cm intervals (Geoprobe™ screen). The PVC was acid-cleaned in warm 10% HCl and rinsed with high-resistivity deionized water. The outer casing was inserted 38 cm into the peat, and the inner casing, capped at the bottom, then was inserted. The outer casing was fitted with a loose fitting cap. After insertion into the peat, the well was allowed to equilibrate for ≥12 h before sampling. Peat porewater was sampled using a hand-held vacuum pump and Teflon tubing inserted into the inner casing. Water samples were acidified and then filtered (in this study, all filtered samples for Hg analysis were done using a 0.7 µm glass fiber, Whatman™ 1825-047) within 2 h of collection. Because of the acid-induced formation of floc, the samples were acidified prior to filtration.

Four channelized areas (C1–C4) in the peat also were sampled. Likely constructed by beavers, these areas are potential conduits from near-shore wetlands to the lake. They were <1 m in width and depth and continued 5–20 m from the shore into the peat/upland. Water samples from the channels did not show visibly high amounts of suspended material and therefore, were not filtered. Samples were preserved with acid and transported on ice to the laboratory.

Seston were collected at 1.4 m depth using Teflon tubing attached to a wooden rod and hand-operated pump connected in series to a reusable Teflon filter pack (Savilleux™). A site near the lake center (total water depth of 2.8 m) was sampled six times for seston in 2003 (May–October). For each sample, a pre-weighed 0.7 µm glass-fiber filter was used. Filters were previously baked at 550°C and handled with gloved hands. Five to seven filters were loaded with seston, and the corresponding volume of water (500–550 mL) was measured. Filters were stored in polyethylene bags and frozen within 30 min of collection. Seston-loaded filters were freeze-dried and weighed (0.001 mg) again to determine dry mass and then analyzed for Hg_T and MeHg. Eight blank filters were compared for consistency in mass by filtering high-resistivity, deionized water, drying, and re-weighing. The average change in filter mass was 0.22%, or 8.3% of the average freeze-dried seston mass (0.774 mg). Seston included some zooplankton, but microscopic inspection of filters showed no more than six zooplankton individuals on a filter. On a dry mass basis, seston, and zooplankton have similar concentrations of MeHg and Hg_T (Table 2). The zooplankton mass on the filters was assumed to be small relative to the total seston mass. Thus, most of the MeHg and Hg_T mass was attributed to detritus and phytoplankton.

Precision was determined by routinely collecting seston and zooplankton samples in triplicate. The coefficient of variation for seston averaged 40–45% for Hg_T and MeHg. Precision for zooplankton measurements was similar; average coefficients of variations were 35–40% for Hg_T and MeHg. The relatively high variability represents both sampling and analytical variability.

Zooplankton were collected monthly during the 2001 and 2002 ice-free seasons using a Wisconsin net with a 300-μm mesh (Wildco^{TM}). The net and bucket were towed in the upper meter of water for 100–200 m and emptied into a polyethylene bag. The procedure was repeated 5–6 times to obtain ~250 mL of concentrated organisms. Samples were frozen until analysis. Aliquots of 10–20 mL were withdrawn from the thawed sample using a glass syringe with a modified circular opening (5 mm) at the base and analyzed for Hg_T, MeHg, and dry mass.

Fish were collected on three dates in 2000–2002 using near-shore seines deployed for 8–12 h. Northern pike (*Esox lucius*) were collected in April, 2000; spot-tailed shiners (*Notropis hudsonius*) were collected in April, 2000 and July, 2002; and young-of-year yellow perch (*Perca flavescens*) were collected in April, 2000, June, 2001, and July, 2002. Individual fish were identified, measured for length, placed into polyethylene bags and frozen.

Table 2 MeHg and Hg_T concentrations in fish, zooplankton, seston, and water in Spring Lake, 2000–2003

Matrix	Mean	SD	*n*	Minimum	Maximum	Mean length (cm)	SD (cm)
Fish							
Northern pike (ng g^{-1})	1,684	554	10	1,211	2,863	53.6	2.6
Spot tailed shiner (ng g^{-1})	256	69	25	112	390	7.6	0.8
Yellow perch (ng g^{-1})	219	86	38	51	400	7.8	1.2
Zooplankton (>300 μm)							
MeHg (ng g^{-1})	60	48	47	20	197		
Hg_T (ng g^{-1})	387	261	47	97	1,083		
Seston							
MeHg (ng g^{-1})	62	49	7	17	144		
Hg_T (ng g^{-1})	550	205	6	350	950		
Lake water							
MeHg (ng mL^{-1})	0.00010	0.00014	80				
Hg_T (ng mL^{-1})	0.00143	0.00110	80				
BCF							
Northern pike	1.2×10^7						
Spot tailed shiner	1.8×10^6						
Yellow perch	1.6×10^6						
Zooplankton, MeHg	4.3×10^5						

Concentrations in biota are on a dry mass basis. Collection dates: northern pike, April 6, 2000; shiners, April 6, 2000 and July 16, 2002; yellow perch, April 6, 2000, June 1, 2001, and July 16, 2002; zooplankton, 17 dates during 2001 and 2002; seston, six dates in 2003

Sediment cores and sediment porewater

Sediment cores ~1 m long were collected by piston corer at five locations in the lake on April 6, 2000, just after ice-out. Analysis of ^{210}Pb was performed on each core at selected depths to determine age and sediment accumulation rates. Sediment porewater profiles were measured with porewater equilibrators constructed from acrylic, a relatively oxygen-impermeable material and deployed in early May and mid-September 2001 and April, August, and October 2002. Methods for analysis of sediment cores and sediment porewater were described by Hines et al. (2004).

Hydrology

Water budget information was obtained to enable calculation of mass budgets for Hg_T and MeHg in Spring Lake. These data were obtained from US Forest Service precipitation and water-yield records for two adjacent bogs and uplands (S-2 and S-6) covering two full years (2001–2002). The elevation of Spring Lake is slightly higher relative to the surrounding water bodies, and the bottom of the lake is ~1 m above the regional ground-water table. Evaporation was estimated by the Jensen–Haise method, which requires only air temperature and solar radiation. Daily information on these variables was available from the US Geological Survey for Williams Lake (z_{avg} = 5.2 m and area = 36 ha), a lake similar to and 100 km southwest of Spring Lake. The Jensen–Haise method was evaluated along with ten other equations for predicting evaporation at small lakes in the north-central United States and was found to be adequate for long-term estimates (years) when compared to a detailed energy budget approach (Winter et al. 1995). The primary water source for Spring Lake was found to be direct atmospheric deposition (rainfall plus snowfall), and the primary loss was evaporation.

Spring Lake does not have well-defined inflow or outflow tributaries, but it is obvious from its dilute chemistry that outflow (ground-water recharge) occurs. To estimate ground-water exchange between the lake and watershed, three independent methods were used. First, a piezometer at the northwest margin of the lake was used to measure the vertical hydraulic gradient across the 1.5 m peat layer at the lake bottom (underlain by compacted sand), and recharge was calculated from Darcy's Law using a hydraulic conductivity of 3.0×10^{-6} cm s^{-1}, estimated from nearby wetlands (E. Verry, US Forest Service, Grand Rapids, MN, personal communication, 2004). Measurements of hydraulic head were made on four dates from June to October, 2002, and all showed water levels that were lower inside the piezometer relative to the lake surface. The average recharge was 2.9 m^3 h^{-1}. There was increasing hydraulic head toward fall, implying greater potential later in the year for outflow (ground-water recharge) from the lake. Second, recharge was estimated by difference from the hydrologic budget; this yielded an average value of 2.3 m^3 h^{-1}. Third, recharge was estimated from the observed decline in lake level (13 cm) during 5 months of ice-cover from 2001 to 2002 by assuming negligible water input to the lake during this time. The estimated recharge rate from this method was 3.1 m^3 h^{-1}. The average recharge rate from the three methods (2.8 m^3 h^{-1}) was used for water budget purposes.

Photochemical transformations of Hg

Two field studies were conducted to measure MeHg photolysis. The first measured the depth profile of photolysis, and the second examined its time-course in two different seasons. For the first study, pairs of 250 mL Teflon bottles were suspended at water depths of 3, 10, 25, 40, and 60 cm; controls wrapped in foil were suspended at 1 m. Filtered lake water was spiked with MeHgCl at 8.3 ng L^{-1}. Bottles were incubated for 5 days (June 20–26, 2001) and then acidified (0.8% HCl) and analyzed. In the second study, 70 mL quartz bottles were filled with filtered lake water, spiked with 15 ng L^{-1} of MeHg, and then incubated near the lakeshore at 3 cm depth in July and October 2002. Care was taken to avoid shading by shoreline vegetation. MeHg degradation was monitored over 1 week by removing bottles at intervals of 1–2 days and placing them in a dark refrigerator. At the end of the week, the samples were preserved with acid and analyzed.

Rates of Hg^0 photooxidation were measured in the laboratory using a medium-pressure mercury arc lamp (Ace Glass^{TM} 7825, 450 W with a 390 mm borosilicate glass immersion jacket), high-resistivity deionized water, and lake water spiked with Hg^0.

A stock solution of $Hg^0_{(aq)}$ was prepared by passing N_2 over a droplet of Hg^0 in a Teflon mixing jar and sparging the gas into a 4-L carboy filled with filtered lake water. Solutions of $Hg^0_{(aq)}$ up to 500 ng L^{-1} were prepared by mixing the stock solution with filtered lake water. One difficulty in measuring the kinetics of Hg^0 photooxidation is that the back reaction (photoreduction of Hg^{2+}) cannot be stopped. However, by spiking Hg^0 in excess and analyzing over fairly short times periods (minutes to hours), the back reaction was minimized. Samples were irradiated in 125-mL Teflon bottles 10 cm from the lamp on a merry-go-round reactor. Bottles were removed at intervals and analyzed for $Hg^0_{(aq)}$ or stored in the dark for <60 min until bubblers were available for purging. Amyot et al. (1997) found that Teflon bottles absorb little PAR (0.7%) and about 34% of the UV-B radiation. Chemical actinometry performed by measuring the loss rate of *p*-nitroacetophenone-pyridine (A. Khwaja, Department of Civil Engineering, University of Minnesota, personal communication, 2004) showed that this mercury lamp provided a light intensity ~6× greater than noon-time, mid-June radiation at 45°N. First-order loss rates thus were divided by six to estimate the maximum ambient photooxidation.

Loss rate coefficients of Hg^{2+} by photoreduction could not be measured accurately using the above methods because the concentration of photoreducible ionic mercury is unknown. Strong partitioning to organic matter renders a large fraction of ionic mercury unreactive, thereby making estimates of rate coefficients uncertain. Instead, we determined zero-order production rates of $Hg^0_{(aq)}$ (ng L^{-1} h^{-1}) using lake water incubated in 2.5 L borosilicate glass containers in full sunlight for 1–2 h. Lake water free of $Hg^0_{(aq)}$ was available from unfiltered 2.5 L samples that had been purged with N_2 for 1 h to determine the concentration of $Hg^0_{(aq)}$. No addition of Hg was made to the 2.5 L containers. For incubations, the containers were placed on their sides, partially submerged in a water bath at the same temperature as the lake. After incubation, the samples were purged with N_2 to capture the produced Hg^0 on gold traps that later were analyzed by thermal desorption and cold-vapor atomic fluorescence spectrometry (CVAFS) in the laboratory. Borosilicate glass attenuates solar radiation (Amyot et al. 1997), and so this method likely underestimates photoreduction.

Light intensity in the water column of the lake was determined on three dates (July 29, 2000, August 29, 2000, and October 16, 2002) using an IL 1700 radiometer. Wavelengths corresponding to UV-B (290–320 nm), UV-A (320–400 nm), and PAR (400–750 nm) were measured at 10-cm intervals and decreased exponentially with depth. The zone for photochemistry was considered to be from the surface to the depth at which radiation was 10% of the surface value. This yielded a depth of 15 cm for UV-A and 50 cm for PAR. UV-B radiation often was not detectable at 10 cm. The depth-averaged radiation for the top 10 cm for measured values at 0, 3, and 10 cm on July 29, 2000 (12:30 p.m.) was 0.038 E m^{-2} day^{-1} for UV-B, 1.58 E m^{-2} day^{-1} for UV-A, and 62 E m^{-2} day^{-1} for PAR.

Analysis of mercury forms

We measured total Hg (Hg_T) and MeHg in water, biota, and sediment samples, and elemental Hg (Hg^0) in water and air. Hg_T here refers to all forms of mercury oxidized by bromium monochloride (BrCl) and then reduced to Hg^0 by stannous chloride ($SnCl_2$). This includes organic mercury (mostly MeHg hydroxide), mercury bound to organic matter, Hg^0, and mercuric and mercurous species. The analytical procedure, EPA Method 1631, measures Hg^0 thermally desorbed from gold traps using CVAFS (EPA 1998) at 254 nm with a Tekran™ 2500 detector. Gold traps were quartz tubes packed with glass beads coated with a fine layer of gold (Brooks Rand™, Seattle, WA). Standard reference material (NIST 3133; $Hg(NO_3)_{2\ aq}$) was used to monitor analytical performance. The mean concentration was within 1.1% of the certified value (1,000 mg L^{-1}). Contamination from particulate matter and air was minimized by conducting analyses in a clean room equipped with a HEPA filter. All sampling was done using powder-free gloves, and samples were double bagged in clean, polyethylene bags.

Aqueous Hg_T was measured by digesting 35–120 mL of water with 1–2 mL of BrCl solution. Preparation of BrCl and other reagents was described by Claas (1995). After at least 24 h of digestion at room temperature, excess BrCl was neutralized with hydroxylamine hydrochloride solution (30 μL mL^{-1} of BrCl). The sample then was added to an

Erlenmeyer bubbler, reduced with 0.5 mL $SnCl_2$ solution, and analyzed as described above. Hg_T on glass-fiber filters containing seston or zooplankton was analyzed in 30 mL Teflon digestion bombs to which 25 mL of high-resistivity deionized water and 1.0 mL BrCl were added. Samples were sealed and heated at 35–40°C for 1 week. Five blanks were prepared for every 20 samples, and the entire volume of each bomb was analyzed as described above.

Sediment Hg_T was analyzed by the procedure of Fleck et al. (1999). Sediments were freeze-dried, and 100–300 mg aliquots were weighed and placed in acid-cleaned 30 mL Teflon digestion bombs to which 10 mL each of concentrated sulfuric acid and nitric acid were added. The bombs were sealed and placed in an oven at 50°C overnight. A ~0.5 mL aliquot of the digested sediment was added to an Erlenmeyer bubbler filled with high-resistivity deionized water. Nitric acid was neutralized using hydroxylamine. The high-resistivity deionized water in the bubblers was replaced after each set of samples because interferences and carryover were observed (J. Fleck, personal communication, 2001). Analysis by CVAFS was performed as described above. Standard reference materials from the National Research Council Canada, MESS-3 (marine sediment) and DORM-2 (dogfish muscle) were used to monitor analytical performance. The mean concentration of Hg_T for MESS-3 was within 4.3% of the certified value (91 ng g^{-1}). The mean concentration of Hg_T DORM-2 was within 7.5% of the certified value (4,640 ng g^{-1}).

Elemental mercury ($Hg^0_{(aq)}$) in lake water was measured by purging 1.6–2.2 L samples for 1 h with ultra-high purity N_2 (further purified with a gold trap) at 500 mL min^{-1}. Samples were collected in 2.5 L glass bottles previously containing only low-mercury HCl. Purge gas from the samples was passed through a soda lime trap to remove water vapor and then through a double-dimpled gold trap. Sample containers and traps were handled with powderless plastic gloves. The gold traps were closed with Teflon plugs and placed into N_2-purged plastic cylinders for transport to the laboratory. A Tekran^{TM} 2500 analyzer was used to measure fluorescence of Hg^0 vapor using argon as the carrier gas. Response curves were determined using four low-level standards of $Hg(NO_3)_2$ that were reduced to Hg^0 with acidic $SnCl_2$ solution in 250 mL glass bubblers equipped with Teflon valves and fritted glass ends. The standards included background concentrations of Hg^0 that produced a negative *y*-intercept (mass versus area); consequently, the relative response curve was used (slope only, no *y*-intercept), and blank traps were run with the same purge N_2 gas. The mass of Hg^0 from the blanks (14% of the average Hg^0 in samples) was subtracted from each sample. Samples collected and analyzed in duplicate had an average relative percent difference of 22% ($n = 52$).

Total MeHg was measured by the method of Horvat et al. (1993). Distillations were performed on 80–100 mL samples with KCl (0.5 mL of a 20% solution by mass), H_2SO_4 (1 mL of 8 M), and $CuSO_4$ (1 mL of 1 M) at 135°C for 4–6 h using a Teflon system and N_2 carrier gas. Seston and zooplankton samples were analyzed by distilling biota-loaded freeze-dried filters with the above reagents. Distillates were kept on ice and out of direct light to prevent MeHg photolysis. Sodium tetraethylborate, $NaB(Et)_4$ (Strem^{TM} Chemicals) was added to convert MeHg to volatile methylethylmercury. The optimum pH (4.9) for the reaction was obtained using sodium acetate–acetic acid buffer. Clean, Hg-free N_2 was passed through samples at 65 mL min^{-1} for 12 min using a fritted bubbler, and the outlet of the bubbler was attached to a Tenax TA trap to sorb the alkyl Hg. The trap then was placed on an analytical line with argon as carrier gas (25 mL min^{-1}) and thermally desorbed and quantified by CVAFS after passing through a GC column (15% OV-3 on Chromasorb W-AW-DMCS, 60/80 mesh; Supelco Inc., Tanfkirchen, Germany) to separate Hg species in the sequence: Hg^0, methylethylmercury, and diethylmercury (from ethylation of Hg^{2+}) (Liang et al. 1994). Peak areas were quantified as Hg^0 using a Hewlett Packard 3396-II integrator.

Sediment was analyzed for MeHg using a similar procedure. A mass of freeze-dried sediment (50–200 mg) was diluted with 90 mL of high-resistivity deionized water and distilled as described above (Bloom 1992). To monitor analytical precision, a reference material was prepared from a sample of Spring Lake sediment that was thoroughly mixed and freeze-dried. An aliquot of this sediment was distilled and analyzed with each set of samples. The average concentration of MeHg from the reference material was 1.06 ng g^{-1} (dry basis), SD 0.31, and $n = 39$. Sediment reference material was obtained from the

International Atomic Energy Agency (IAEA 356) in 2003. The measured mean concentration of MeHg was within 8.5% of the certified value (5.46 ng g^{-1}) using the distillation technique.

The Hg_T in fish was analyzed similar to that in sediment using modified methods of Bloom (1992). Wet tissue samples (~1 g) were digested in 30 mL Teflon digestion bombs with 7 mL concentrated sulfuric : nitric acid (5:2, v:v). Bombs were wrench tightened and placed in a 900 W microwave oven at 30% power for 20 s, vented, and subjected to microwave irradiation again. After cooling, 23 mL of high-resistivity deionized water and 1.0 mL of BrCl were added to the samples. The bombs were sealed tightly, double bagged, and placed in an oven at 40°C overnight. An aliquot (~0.5 mL) of the acid-digested sample was analyzed for Hg_T, which was assumed to exist as MeHg in the fish (Bloom 1992).

Results and discussion

Hg and MeHg concentrations in Spring Lake

Lake water

No strong seasonal or inter-annual trends were evident for Hg_T in the lake water over the ice-free season (March–November) over the years 2000–2003 (Table 3; Fig. 2). Concentrations were relatively stable around a mean of 1.43 ng L^{-1}, and annual average concentrations varied by only 17% from the highest (1.57 ng L^{-1}; 2000) to the lowest (1.31 ng L^{-1}; 2003). The highest individual measurement (4.4 ng L^{-1}) occurred on June 1, 2001 during a 1.3 cm rain storm and probably reflects new Hg loading. MeHg exhibited greater relative variability over the study period; annual average concentrations varied from 0.083 ng L^{-1} in 2003 to 0.17 ng L^{-1} in 2000. The percent of samples with detects was high (94% for Hg_T and 76% for MeHg) and zero was substituted for all non-detect data. An increase in the MeHg/Hg_T ratio (Fig. 2, panel C) was observed each year for MeHg based on depth-averaged water concentrations (usually 0–4 m, analyzed at 1 m intervals). Surface and near-bottom samples were collected on seven dates from 2001 to 2002 near the deepest part of the lake (depth = 5.5 m). Detectable concentrations of MeHg at the two depths were found on four dates (Table 3, see minimum and maximum columns). Applying a paired *t*-test resulted in a statistically significant difference in MeHg concentration (p = 0.025 and n = 4). In contrast, enrichment of Hg_T in bottom waters was not significant (paired *t*-test, p = 0.13; n = 7).

Concentrations of Hg^0_{aq} (Fig. 2, panel D) did not show long-term increasing or decreasing trends over the measurement period (2001–2002), but lower concentrations were observed early (May) and late (November) in the ice-free season as illustrated by the dotted lines in Fig. 2, panel D. With a few exceptions, Hg^0_{aq} concentrations were in the range 0.02–0.10 ng L^{-1} (1.4–6.9% of Hg_T), and the average concentration over the 2 years of measurements was 0.050 ± 0.038 ng L^{-1} (SD). Diel trends were examined because sunlight has been shown to photoreduce Hg^{2+} to Hg^0 (Amyot et al. 1994; Krabbenhoft et al. 1998; Siciliano et al. 2002; O'Driscoll et al. 2006). Consistent diel trends were not observed, but a weak positive relationship was

Table 3 Concentrations of Hg forms in Spring Lake, 2000–2003

	Mean	Median	SD	n	% Detect	Minimum	Maximun
$Hg^0_{(aq)}$ (ng L^{-1})	0.050	0.043	0.038	52	100	0.00060.0	0.161
Hg_T (ng L^{-1})	1.43	1.31	1.10	80	94	nd	4.4
MeHg (ng L^{-1})	0.10	0.072	0.14	80	76	nd	0.42
6/1/2001[a]						0.067[a]	0.13[a]
8/14/2001[a]						0.11[a]	0.17[a]
7/17/2002[a]						0.15[a]	0.31[a]
9/25/2002[a]						0.037[a]	0.15[a]

[a] MeHg concentrations on dates when surface and depth samples were available; for these dates, minimum = near surface depth (0–1 m), maximum = bottom concentration (3–4 m), nd = not detected

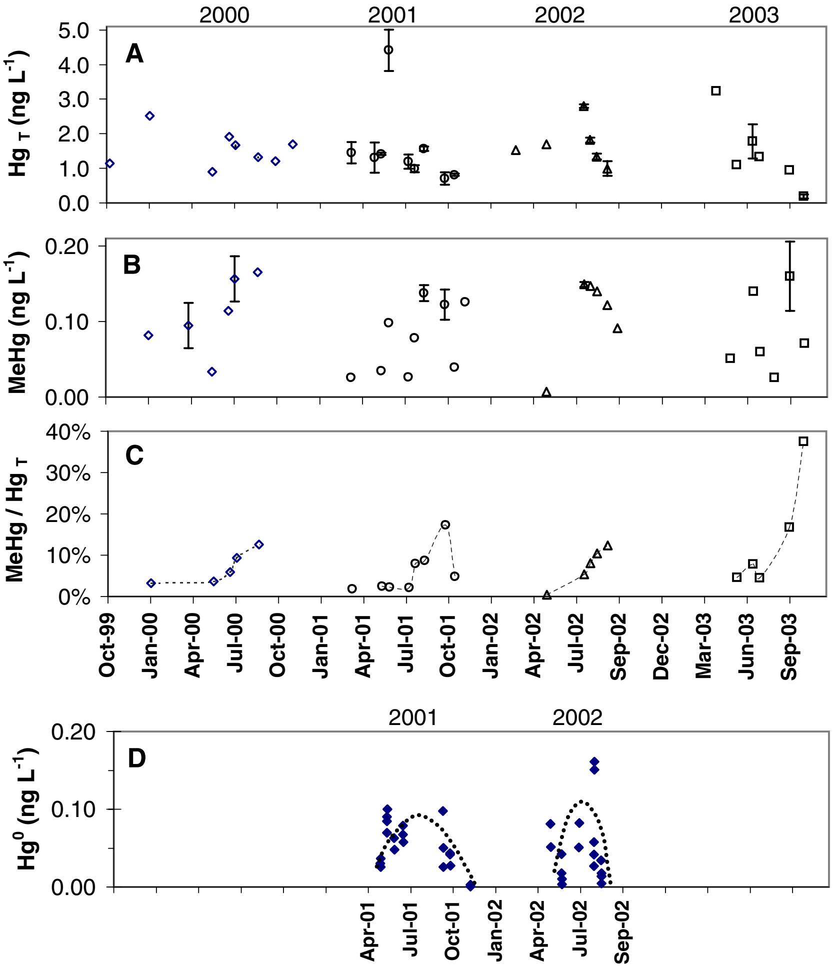

Fig. 2 Concentrations of unfiltered water from Spring Lake, MN: Hg_T (**A**), MeHg (**B**), MeHg/Hg_T (**C**), and $Hg^0_{(aq)}$ (**D**). Concentrations are depth averaged at 1 m intervals except for $Hg^0_{(aq)}$ which was collected right at the lake surface. The *dotted lines* illustrate annual trends in: (1) lakewide MeHg/Hg_T toward late summer and fall, (2) higher concentrations of $Hg^0_{(aq)}$ during the sunnier months resulting from net photoreduction. *Error bars* are the relative percent difference of duplicate samples times the average of the duplicate-pair

found between Hg^0 and short wave radiation (Hines and Brezonik 2004). The lake usually was highly supersaturated in Hg^0_{aq} (up to 2,900%), and fluxes of Hg^0_{aq} were almost always from water to air. Together, this information suggests net photoreduction of Hg in the surface water of Spring Lake during the daytime.

Sediment and sediment porewater

The bottom sediment in Spring Lake is highly organic with small amounts of coarse woody debris. For the five sediment cores, the depth-averaged water content was 95.3 ± 0.7%, and the depth-averaged organic content was 54.4 ± 5.1% (0–60 cm and $n = 203$). Concentrations of Hg_T and MeHg at the sediment surface (0–1 cm) were 153 ng g^{-1} ± 21 (SD) and 2.4 ng g^{-1} ± 1.8 (s.d,) ($n = 5$ and dry mass), respectively. Hg_T increased toward the sediment-water interface starting at ~20 cm sediment depth, corresponding to the late 1800s; MeHg increased above ~12 cm sediment depth, corresponding to the late 1950s. Concentrations of Hg_T and MeHg in sediment porewater showed large variations with depth, and concentrations generally were higher than in the water column. In spring 2001 and late summer 2002, porewater was a source of MeHg to the lake, but vertical profiles at other times of the year indicated that porewater was not a source. Further analysis of Hg_T and MeHg cycling is provided in the section Rates of mercury cycling processes in Spring Lake and by Hines et al. (2004).

Seston, zooplankton, and fish

Concentrations of Hg_T in seston (Fig. 3) were fairly stable during the ice-free season (mean

550 ng g^{-1} ± 205 (SD), $n = 6$, and dry mass basis), with a minimum of 350 ng g^{-1} in early July and a maximum of 950 ng g^{-1} in mid-July. MeHg concentrations in seston (2003) varied seasonally, declining from >100 ng g^{-1} (dry mass) in May and June to 17 ng g^{-1} in September and October. The fraction of sestonic Hg_T present as MeHg was high (22%) early in the year (May) but declined to 3.1% by fall. The high fraction of sestonic MeHg early in the year may reflect inputs of MeHg on particles from near-shore wetlands but the seston data are limited. Several studies have found that wetlands provide high inputs of MeHg to surface waters (Branfireun et al. 1996, 1998; St Louis et al. 1996). However, dissolved MeHg concentrations in near-shore wetlands generally were low (<0.3 ng L^{-1}), suggesting that these wetlands may not supply the bulk of the MeHg to the lake. It is interesting to note that Hg_T and especially MeHg were higher in seston than in surficial (0–1 cm) sediments (seston/surficial sediment = 3.6 for Hg_T; 26 for MeHg). A two to fourfold enhancement of sestonic Hg_T relative to sediment also was found at Little Rock Lake in northern Wisconsin (Hurley et al. 1994).

The Hg_T in zooplankton was moderately variable but lacked seasonal trends (Fig. 3); values were similar to those found in other studies using nets with a similar mesh size (300 µm) (e.g., Monson 1997). MeHg concentrations in zooplankton showed moderate increases in early summer 2001 and small increases in late summer 2002. These trends contrast with the results for seston, which showed peak concentrations in May and a steady decline toward fall. MeHg averaged 19% of the Hg_T in zooplankton in 2001 and 11% in 2002. Uptake of MeHg in *Daphnia magna* is primarily from food (Monson and Brezonik 1999), but water represents an important source and sink for Hg^{2+} (Tsui and Wang 2004). Variables that influence zooplankton uptake of mercury include water color and pH (Westcott and Kalff 1996), DOC and salinity (Barkay et al. 1997), dissolved humic substances (Monson and Brezonik 1999; Sjoblom et al. 2000), and zooplankton size and habitat (Kainz et al. 2002). Considerable uncertainty exists regarding the mechanisms of Hg uptake by biota (Benoit et al. 1999; Golding et al. 2002).

Table 2 summarizes MeHg and Hg_T concentrations in biota (fish, zooplankton, and seston) of

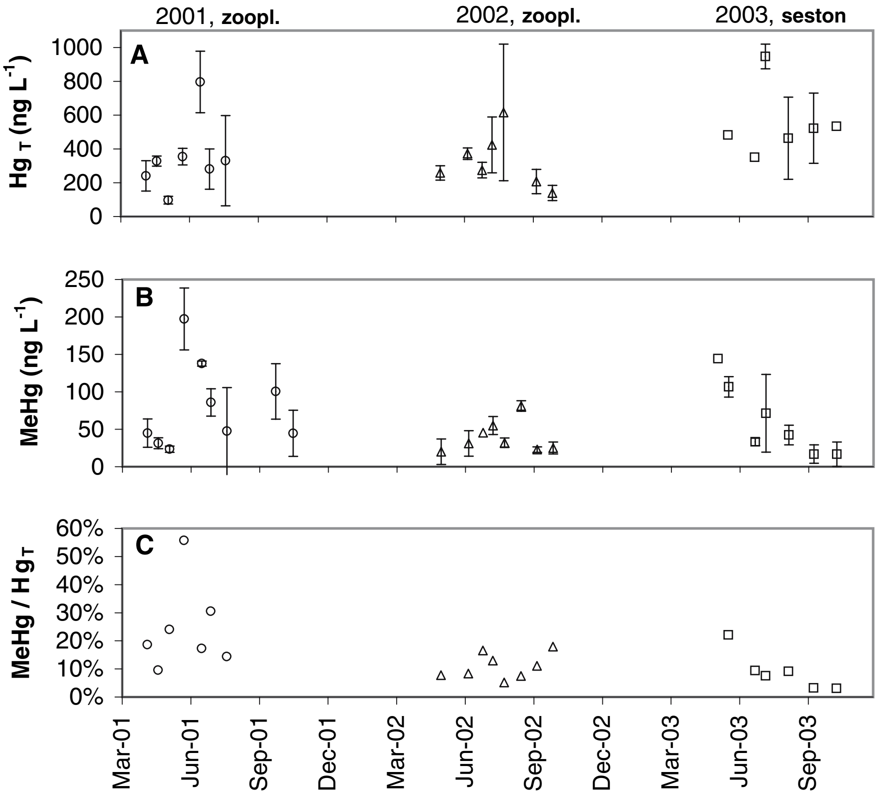

Fig. 3 Zooplankton >300 µm (2001–2002, vertical tows) and seston (2003, 0.7 µm glass fiber filter) collected at Spring Lake, MN: Hg_T (**A**), MeHg (**B**), MeHg/Hg_T (**C**). *Error bars* are the SD of three replicate samples

Spring Lake, along with bioconcentration factors (BCFs), where BCF = [concentration in biota (dry mass basis)] : (concentration in water). Northern pike are highest in the food web, and they had the highest MeHg and BCF values. Based on wet weight, Hg in northern pike averaged 0.34 ppm (80% of the fish wet mass was water). The concentrations of MeHg in northern pike of Spring Lake are consistent with results from fish surveys throughout Minnesota (Sorenson et al. 1990). Zooplankton and seston in Spring Lake had lower MeHg concentrations than fish, but when the data for biota are compared with lake water concentrations, it is apparent that most of the bioaccumulation occurs low in the food web.

Rates of mercury cycling processes in Spring Lake

Photolysis of MeHg

Photolysis of MeHg measured during June 20–26, 2001 showed a decrease with water depth up to ~60 cm (Fig. 4). The depth at which UV-A was 10% of incident was 15 cm, and the depth at which PAR was 10% of incident was 50 cm. This suggests that PAR is at least partly responsible for MeHg photolysis. Sellers et al. (2001) measured MeHg photolysis at 0.5 m depth intervals at ELA Lake 240 and calculated rates as the difference between the loss of MeHg in light-incubated samples and dark controls:

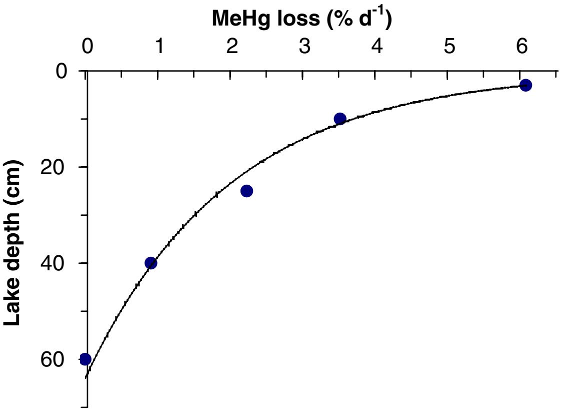

Fig. 4 Depth profile of MeHg photolysis, June 20–26, 2001 in Spring Lake. Initial MeHg concentration spiked to 8.3 ng L^{-1}. See Eq. 1 for calculation of MeHg loss

$$\text{MeHg loss}\ \left(\%\ \text{day}^{-1}\right) = \frac{(\Delta C - \Delta B)}{C_0}, \qquad (1)$$

where ΔC is the change in MeHg concentration between the time-zero and the in situ-incubated bottles (ng L^{-1} day^{-1}), ΔB is the loss of MeHg in the dark control (ng L^{-1} day^{-1}), and C_0 is the initial concentration of MeHg (8.3 ng L^{-1}). Loss rates presented by Sellers et al. (2001) from ELA ranged from −3 to 27% per day for 0–50 cm. Similar values were found at Spring Lake although the depths were slightly different (3–60 cm; Fig. 4).

A second set of experiments measured the loss of MeHg in surface water (3 cm) over time in July and October, 2002. Pseudo first-order rate constants calculated from slopes of semi-log plots were 0.41 day^{-1} for July (r^2 = 0.77 and n = 6) and 0.042 day^{-1} for October (r^2 = 0.98 and n = 3). Because the loss of MeHg in the foil-wrapped bottles over 1 week was within range of the SD of measurements, no correction was made for losses from processes other than photolysis, such as biotic or abiotic demethylation.

The depth profile of MeHg photolysis shows that the zone for this process was ~50 cm. A depth-averaged rate constant was calculated from the values at 3 cm depth as follows. Data were plotted as depth versus pseudo first-order rate constant using two time points [$\ln(C/C_0)$ versus time], June 20 and June 26, 2001 at each depth. From this plot, the relationship for k versus depth was determined

$$k = -\ln(z/56.78)/26.53 \qquad (2)$$

to interpolate pseudo first-order rate constants at 1-cm intervals from 1 to 50 cm (Fig. 5). The calculated rate constants then were normalized to 3 cm to produce a depth-correction factor. The normalized depth-correction factor was multiplied by the pseudo first-order rate constants for 3 cm in July and October, and rate constants depth-averaged to 50 cm were computed (0.15 and 0.015 day^{-1}, respectively) (Fig. 5). This approach may overestimate photolysis in spring and fall because the angle of incidence for sunlight during these seasons is smaller (less light intensity) compared to June.

To compare the ratio of photolysis from summer to winter, we used the program GCSOLAR (EPA 1999). For the latitude of Spring Lake (47°N), the ratio of

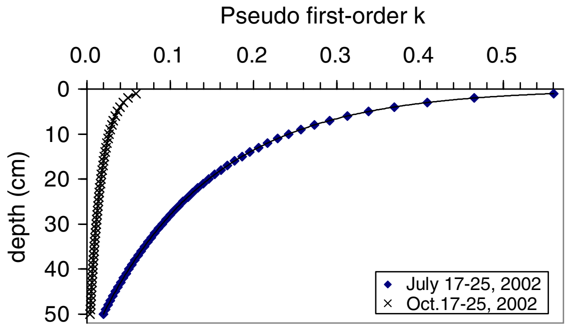

Fig. 5 Pseudo first-order rate constants for MeHg photolysis, estimated according to depth based on loss rates at 3 cm in July and October, 2002

summer to winter photolysis in water is 8.2, according to GCSOLAR, which is similar to the ratio of field-observed photolysis rates (~10). Monthly depth-averaged photolysis rate constants were estimated by fitting the July and October rates to a sine function assuming a peak at summer solstice and a 12-month period.

Hammerschmidt and Fitzgerald (2006a) measured photolysis rates of MeHg at Toolik Lake in the Alaskan Arctic and found a first-order response with respect to MeHg concentration. The photolysis pathway has been found to be indirect (Chen 2003) and first-order loss rates near the water surface from three studies are similar (Lake 240 at ELA ~0.2 day^{-1}, Toolik Lake = 0.23 day^{-1}, this study = 0.41 day^{-1}). The higher loss rate at Spring Lake might be due, in part, to the lower latitude relative to the other two lakes.

Photooxidation and photoreduction

Studies of Hg^0 photooxidation in freshwater found that UV-A radiation drives the process, with rate constants ranging from 0.06 to 0.7 h^{-1} (Lalonde et al. 2004). The depth of 90% attenuation of UV-A radiation for Spring Lake is 15 cm (volume = 13,400 m^3) and this depth was set as the zone for photoredox processes in Spring Lake. Photooxidation of Hg$^0_{(aq)}$ measured in the laboratory using a mercury arc lamp was divided by 6 to adjust the light intensity to ambient, yielding first-order rate constants (k_{ox}) of 0.39–0.76 h^{-1}. The average rate constant, 0.58 h^{-1}, multiplied by the average lake concentration of Hg$^0_{(aq)}$ from May to July, 2001 to 2002 (0.050 ng L^{-1}), is 0.029 ng L^{-1} h^{-1} (range of 0.0049–0.067 ng L^{-1} h^{-1} based on the range of k_{ox} and SD of Hg$^0_{(aq)}$ concentrations). This represents a maximum rate of photooxidation because the light adjustment for the mercury arc lamp was relative to mid-day, mid-June light conditions.

Although production rates of Hg^0 (photoreduction of Hg^{2+}) were measured throughout the year, only values from mid-day late May, June, and July were used to compare to photooxidation, measured under similar light intensity. The average rate of photoproduction of Hg$^0_{(aq)}$ in the photic zone of Spring Lake over this period in 2000 and 2001 was 0.054 ng L^{-1} h^{-1}, n = 7. Few data are available on rates of Hg^0 photoproduction in freshwaters, but Amyot et al. (2000) reported rate constants of 1–2 h^{-1} in the St. Lawrence River and Lake Ontario based on laboratory experiments using spikes (40 ng L^{-1}) of Hg^{2+}. O'Driscoll et al. (2006) found gross rates of photoreduction of roughly 0.3 h^{-1} (for both UV-A and UV-B radiation) for lakes throughout Nova Scotia and Central Quebec.

On average, the rate of Hg^0 photoproduction was 1.9 times its rate of photooxidation. These rates were calculated for the zone of photoredox transformations at Spring Lake (z = 15 cm) at mid-day during the months of maximum solar radiation (late May, June, and July). The net result is production of Hg$^0_{(aq)}$ in the water column (0.025 ng L^{-1} h^{-1} at mid-day). The program GCSOLAR (US EPA 1999) was used to adjust the mid-day net photoproduction rate to an integrated full-day rate for spring, summer, and fall for the purpose of modeling the Hg cycle. This reduced the mid-day rate by factors of 3.85, 3.49, and 4.96, respectively.

Sediment accumulation and exchange

For mass balance purposes, the accumulation of Hg$_T$ was calculated by decade to compare accumulation rates for similar time-stratigraphic units. Based on the average of the five cores, the accumulation of Hg$_T$ from 1990 to 2000 was 21.4 µg m^{-2} year^{-1} ± 7.9 (SD), n = 5. There was a sharp down-core decline in MeHg concentrations, but as discussed by Hines et al. (2004), the profiles most likely reflect diagenesis (resulting in net demethylation) rather than historic changes in MeHg deposition to the sediment. The shape of the decline suggests a first-order decay process. Because of diagenetic loss, MeHg accumulation (net deposition) was based only on the top sections (0–1 cm) of the cores for the mass balance. On an areal basis, this yielded a flux of 0.32 μg m^{-2} $year^{-1}$ ± 0.23 (SD), $n = 5$, or a total lake-to-sediment loss of 17.2 mg $year^{-1}$. Because the ^{210}Pb accumulation rates did not indicate a high degree of sediment focusing, accumulation rates were not focus-corrected. The depositional area was assumed to be defined by the 2 m bathymetric contour, yielding a depositional zone of 53,600 m^2 (~60% of the lake surface area).

Two of the five measured profiles of MeHg in sediment porewater showed a small diffusive flux from the sediment to the water column. Peaks of MeHg (up to 2.2 ng L^{-1}) were found deeper in the porewater on other dates, but there was no MeHg gradient near the sediment-water interface (Hines et al. 2004). The deep MeHg peaks in September 2001 were correlated roughly with maxima in sulfate-reducing activity (5 and 15 cm) (Johnson 2004). The MeHg porewater profile from August, 2002 showed distinct MeHg peaks of 1.4–1.5 ng L^{-1} at depths of 7, 12, 19, and 29 cm. Piezometer measurements showed a small hydraulic head (lower water level inside the piezometer relative to the lake level) indicating seepage from the lake. The average MeHg diffusive flux from the sediment calculated by Fick's first law using the two profiles that had concentration gradients from sediment to water (May, 2001 and August, 2002) was 0.005 μg m^{-2} mo^{-1} (D_w of MeHg = 0.5 × 10 cm^2 s^{-1}). This value is 20% of the MeHg sediment accumulation and was considered to be a minor input of MeHg to Spring Lake.

Loss of MeHg from seston as it was deposited to the sediment was estimated from the difference between seston and sediment MeHg concentrations multiplied by the gross sedimentation rate (r_{sed}) and lake surface area (A_l):

$$\begin{aligned}\text{Loss of MeHg}\left(\text{mg mo}^{-1}\right) &= \\ &[(\text{MeHg}_{\text{seston}}) - (\text{MeHg}_{\text{sed}}])]r_{\text{sed}}A_l,\end{aligned} \tag{3}$$

where $r_{sed} = 0.013$ g cm^{-2} $year^{-1}$ is the average from the top 3 cm of the five sediment cores and $A_l = 8.9$ ha. The average loss rate for two measurements in May–June, 2003 was 122 mg mo^{-1} and from five measurements from July to October, 2003 was 33 mg mo^{-1} (SD = 23). To estimate the MeHg residence time, these rates were divided into the respective lakewide seston mass of MeHg (May–June = 33 mg and July–October = 9.3 mg), yielding a residence time of 8.3 days for May–June and 8.6 days for July–October. Although seston concentrations vary throughout the year, the similar residence time of MeHg on seston implies that degradation of MeHg is steady. The settling time of seston from the water column is short (~10 days based on the average sedimentation rate and average suspended solids of 1.5 mg L^{-1}) compared to the time spent in the sediment phase, suggesting that most of the demethylation occurs in the sediment. Figure 6 shows the percent of Hg_T that is MeHg over four matrices (porewater, lake bottom water, seston, and sediment) and demonstrates that roughly 10% of Hg_T in the lake is MeHg, and this declines to 1% or less at depth in the sediment environment.

The Hg_T concentration in surficial sediment (153 ng g^{-1}) is lower than that of seston (550 ng g^{-1}), and by calculations analogous to those for MeHg, this yields a residence time of 11 days for Hg_T in settling seston particles. The decreases in Hg_T and MeHg concentrations from seston to sediment could be explained by several processes (in addition to demethylation for MeHg): (1) clastic sedimentary material from the near-shore land may be lower in mercury, essentially diluting sediment concentrations relative to seston; (2) uptake and/or production of MeHg by biota would contribute to a greater decline in MeHg from seston to sediment than for Hg_T, as

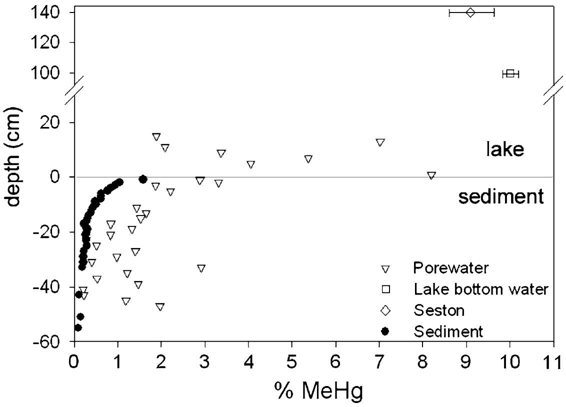

Fig. 6 Sediment depth (0 = sediment-water interface) versus MeHg as percent of Hg_T for four matrices. Sediment and porewater concentrations are averaged from all available data. *Error bars*: one SD for six measurements (includes all data for seston and lake bottom water)

observed; and (3) a decrease in concentration or strength of Hg binding sites (or both) from seston to sediment.

Mass budgets for Hg_T and MeHg

Water budget

Direct atmospheric deposition accounted for 65% of the annual water input to Spring Lake (2001–2002), and evaporation accounted for 84% of the water loss (Table 4). The average rate of ground-water recharge calculated by three independent methods (2.8 $m^3 h^{-1}$; see Hydrology section under Methods) extrapolates to a recharge of 24,500 m^3 $year^{-1}$ (26% of total water loss). Ground-water recharge calculated by difference (20,100 m^3 $year^{-1}$) indicates that Spring Lake is a net ground-water recharge lake. Sandy parent material is visible at the northern and southern shoreline, and this is probably where most of the outflow occurs. These margins were assumed to represent 75% of the outflow; the lake bottom was assumed to account for the rest. The lake volume (183,000 m^3) divided by the sum of water losses (38,000 m^3 $year^{-1}$, excluding evaporation) yields a residence time of 4.8 years for conservative substances (so-called chemical residence time) in the lake.

Mercury storages

Based on concentrations of Hg_T and MeHg in seston and unfiltered lakewater (Table 5), we conclude that more than half of the mass of both Hg_T and MeHg in the lake was in seston. Relatively little Hg_T and MeHg resides in large-bodied zooplankton (>300 µm), but because only large-bodied zooplankton were collected, this may simply reflect the collection method. The amount of MeHg in fish was estimated by multiplying MeHg concentrations in fish by the fish mass in the lake, which was estimated for Spring Lake from general lake productivity rates for Minnesota lakes: 30 kg (wet) for northern pike and 80 kg (wet) each for yellow perch and spot tailed shiners (E. Swain, MN Poll. Contr. Agency, St. Paul, personal communication, 2004). Although these values are only estimates, Table 5 demonstrates that most of the MeHg (82%) in the lake is in biota. However, the sediments are the largest reservoir of both Hg_T and MeHg. Even at the shallow depth of 0–1 cm in the sediment, there is more Hg_T (5.6 times) and MeHg (1.1 times) than there is in the entire unfiltered lakewater.

Mercury inputs

The average wet deposition of Hg_T from 1998 to 2003 was 8.5 µg m^{-2} $year^{-1}$ ± 1.6 (SD), and wet deposition of MeHg for 2003 was 0.10 µg m^{-2} $year^{-1}$ [data from the Mercury Deposition Network (MDN) site MN16, 1.5 km north of the lake; http://nadp.sws.uiuc.edu]. Other studies at forested sites in similar latitudes of North America and Scandinavia have reported wet deposition rates of 5.1–10 µg m^{-2} $year^{-1}$ for Hg_T and 0.08–0.12 µg m^{-2} $year^{-1}$ for MeHg (St Louis et al. 2001). The MDN data for Marcell fit near the midpoint of these ranges.

Dry deposition was estimated following the approach of Lindberg et al. (1994) and Munthe et al. (1995), who used net throughfall as a surrogate for dry deposition. Net throughfall is the difference between throughfall (all precipitation falling through the forest canopy) and wet deposition. Based on their findings, we estimated that dry deposition of Hg_T was half the annual wet deposition. Dry deposition represents the greatest uncertainty for Hg_T sources. It should be noted that at some sites, dry deposition may even exceed wet deposition (Miller et al. 2005). Three studies reported MeHg in net throughfall (St Louis et al. 2001; Lindberg 1996; Lee et al.

Table 4 Water budgets for Spring Lake, 2001 and 2002

	Precipitation (mm)	Lake level change (mm)	Evaporation transpiration Jensen–Haise (mm)	Bog runoff (mm)	Upland runoff (mm)	GW, by difference (mm)
5/1/2001–12/11/2001	570	−115	911	368	41	−47
4/30/2002–12/3/2002	554	−24	876	161	42	−143

Table 5 Mass storage and burial of Hg_T and MeHg in Spring Lake

	Hg_T (mg)	MeHg (mg)	$MeHg/Hg_T$ (%)
Lake mass			
Unfiltered lake water	272	20	7.2
Seston	147	13	9.0
Zooplankton	0.14	0.013	9.3
Yellow perch[a]	4		
Spot tailed shiners[a]	4		
Northern pike[a]	10		
Sediment mass (0–1 cm)[b]	1,530	22	1.4
Sediment mass (0–10 cm)[c]	26,100	188	0.72
Burial (mg year^{-1})	859	12.9	1.5

[a] Analyzed for Hg_T and assumed to be present as MeHg

[b] Corresponds to 2–4 years of sediment accumulation (collected 4/6/2000)

[c] Corresponds to 25–80 years of sediment accumulation

2000). In each case, there was little difference between MeHg in throughfall and wet deposition, implying that dry deposition of MeHg is very low (<0.09 µg m^{-2} year^{-1}). In the model, dry deposition of MeHg was set to zero.

Estimating mass loads from the lake's surrounding wetlands required both hydrologic and chemical measurements. Hydrologic information was available for 2003 from two adjacent wetlands (S-2 and S-6) at the Marcell Experimental Forest, providing water yields (runoff volume per area) from upland and bog landscapes similar to those at Spring Lake. The US Forest Service maintains daily records of upland runoff from subsurface collectors, as well as total flow from v-notch weirs in landscapes of known area. Thus, water yields are available for both upland and bog landscapes by subtracting the upland yield from the total water yield.

Concentrations of MeHg from six sets of samples collected in 2003 from nine shallow wells in the near-shore wetlands (Fig. 1) were fairly stable (MeHg mean ± SD = 0.26 ± 0.14 ng L^{-1} and $n = 6$). MeHg concentrations in shallow ground water from two wells at the toe slope of separate upland areas adjacent to Spring Lake were similar (0.27 ± 0.15 ng L^{-1} and $n = 6$). Concentrations of filtered Hg_T in the near-shore wetlands were measured in three of the nine wetland wells; six wells ($W_{3a\text{–}c}$ and $W_{4a\text{–}c}$) did not yield sufficient sample volume for Hg_T analysis. Concentrations of Hg_T in the three wells (W_0, W_1, and W_2) averaged 3.8 ng L^{-1}. Concentrations of Hg_T were not measured in upland runoff, but monthly sampling by Kolka et al. (2001) near wetland S-2 (500 m west of Spring Lake) yielded a mean concentration of 17 ± 3.8 ng L^{-1} ($n = 8$) for May–October 1995.

The mean Hg_T concentration from Kolka et al. (2001) was multiplied by upland flow to estimate the mass load of Hg_T from upland runoff at Spring Lake. To compute mass loads of MeHg from the wetland and upland subsurface flows, MeHg concentrations from the respective well samples were multiplied by flow estimates over a time period mid-way between sampling dates. Daily loads were summed over 1 month. The mass load for March to November from the wetlands was 72 mg for Hg_T (0.84 µg m^{-2} year^{-1}) and 4.4 mg for MeHg (0.052 µg m^{-2} year^{-1}) (Fig. 7). Loads from the upland area were much lower: 9.3 mg for Hg_T (0.51 µg m^{-2} year^{-1}) and 0.12 mg for MeHg (0.0068 µg m^{-2} year^{-1}) (Fig. 7). The wetland areal mass load for Hg_T is near the low end of reported values from similar landscapes (0.2–4.4 µg m^{-2} year^{-1}) (Kolka et al. 2001; Lee et al. 1995; Mierle 1990; St Louis et al. 1994). For MeHg, the bog areal load is also near the low end of values from similar landscapes (0.03–0.22 µg m^{-2} year^{-1}) (Porvari and Verta 2003).

Losses of Hg_T and MeHg

The average ground-water recharge rate from three estimation methods (2.8 m^3 h^{-1}) was multiplied by average concentrations of Hg_T or MeHg in the lake water to obtain their losses by ground-water recharge (Tables 6, 7). Over the 9-month ice-free period (March–November) these losses were only 10% of

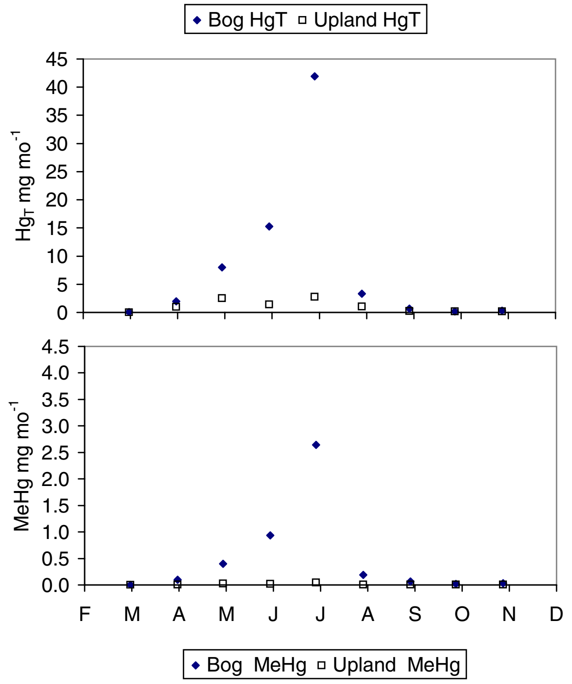

Fig. 7 Mass loads of Hg_T and MeHg from bog and upland watershed to Spring Lake, 2003

the lake storages of Hg_T or MeHg. Hydrologic outflow thus was not a large sink for either Hg_T or MeHg.

To calculate evasion of Hg^0, a two-layer gas-transfer model (Schroeder et al. 1992; Liss and Slater 1974) (Eq. 4) was used. O'Driscoll et al. (2003) showed that this approach correlated well with in situ data measuring Hg^0 evasion from lakes. From the aqueous concentration of Hg^0 in the photic zone, C_w, and the concentration in air, C_a, this flux may be estimated as follows:

$$F\left(\mathrm{ng\ m^{-2}h^{-1}}\right) = K_{ol}(C_w - C_a/H'), \qquad (4)$$

where K_{ol} is the overall mass transfer coefficient

$$1/K_{ol} = 1/K_{water} + 1/(K_{air} \times H') \qquad (5)$$

and H' is the dimensionless Henry's Law coefficient. Schroeder et al. (1992) assumed $K_{ol} \approx K_{water}$ = 0.09 m h^{-1}, which is within range of K_{water} values reported for small lakes (0.015–0.2 m h^{-1}); (Cohen et al. 1978; Mackay and Yeun 1983; Wanninkhof et al. 1991). Temperature correction of H' was made using the relationship of Sanemasa (1975):

$$H' = 0.0074(T) + 0.1551, \qquad (6)$$

where T is water temperature in °C. At T = 20°C, H' = 0.30, and at T = 10°C, H' is 0.23. Detailed surface water temperatures were obtained from

Table 6 Inputs, outputs, and masses of Hg_T for Spring Lake, March–November 2003

	Hg_T (mg)	% Of total inputs or output	Variable, constant, or modeled parameter
Inputs, 1,067 mg total			
Bog runoff	72	6.7	Monthly input
Upland runoff	9.3	0.87	Monthly input
Wet deposition	614	57.5	Monthly input
Dry deposition[a]	307	28.8	Constant
Photolysis of MeHg	65	6.1	Monthly input
Outputs, 1,290 mg total			
Burial	859	66.6	Constant
Outflow (GW seepage)	23	1.8	Modeled[d]
Evasion[b]	333	25.8	Monthly output
Methylation[c]	75	5.8	Modeled[d]
Lake mass, Hg_T	272		

[a] Assumed equal to half of wet deposition

[b] K_w = 0.09 m h^{-1}

[c] Average = 0.001; range: 0.0002 day^{-1} (March and November) to 0.002 day^{-1} (June–September)

[d] Modeled using STELLA (Version 8.0) as described by Hines (2004)

Table 7 Inputs, outputs, and masses of MeHg for Spring Lake, March–November, 2003

	MeHg (mg)	% Of total inputs or output	Variable, constant or modeled parameter
Inputs, 91 mg total			
Bog runoff	4.4	4.8	Monthly input
Upland runoff	0.12	0.12	Monthly input
Wet deposition	8.9	9.8	Monthly input
Dry deposition[a,b]	0	0	Constant
Methylation[c]	75	82	Modeled[d]
Porewater[e]	2.3	2.5	Monthly input
Outputs, 109 mg total			
Burial	12.9	11.8	Constant
Outflow (GW seepage)	1.1	1.0	Modeled[d]
Photolysis	65	59.6	Modeled[d]
Uptake by fish[f]	30	27.5	Modeled[d]
Lake mass, MeHg	20		

[a] Lee et al. 2000

[b] St Louis et al. 2001

[c] Average = 0.001; range: 0.0002 day^{-1} (March and November) to 0.002 day^{-1} (June–September)

[d] Modeled using STELLA (Version 8.0) as described by Hines (2004)

[e] Assumed input for May–September based on porewater equilibrator data

[f] Modeled using Trudel and Rasmussen (2001)

Williams Lake in west-central Minnesota (Parkhurst USGS Shingobee Headwaters Aquatic Ecosystem Project, unpublished data 2002). Less frequent measurements in Spring Lake (12 ice-free dates over 2 years) agreed well with values for Williams Lake (relative difference = 0.8%). Because H' is high, most of the resistance to Hg^0 mass transfer (>99%) lies in the water phase (Poissant et al. 2000). To calculate Hg^0 evasion we assumed a constant concentration of Hg^0 in the air phase of 1.5 ng m^{-3}, consistent with estimates of global atmospheric concentrations of Hg^0 (Poissant et al. 2000). An average Hg^0 concentration of 1.34 ng m^{-3} ± 0.18 was measured above Spring Lake (October 3–4, 2000) using a Tekran 2537 sampler. The lake usually was supersaturated in $Hg^0_{(aq)}$ (up to 29-fold); consequently, the flux usually was from water to air. The average evasion rate for Spring Lake during 2001–2002, based on day-time field measurements of C_w and calculated using Eq. 4, was 1.1 ng m^{-2} h^{-1} (74 mg mo^{-1} and $n = 38$). Day-time field observations likely are higher than night-time values because of net photoproduction of Hg^0 in the photic zone during the day. To estimate the 24-h rate of evasion, the observed rate of evasion was divided by a factor of 2, yielding 37 mg mo^{-1}, providing 26% of the Hg outputs, a value that is similar to that calculated by Fitzgerald et al. (2005) for Alaskan lakes (20%).

Summaries of the inputs and outputs are presented in Table 6 for Hg_T and Table 7 for MeHg. Some results presented in these tables were obtained from model simulations using the program Stella^{TM}, and they are described elsewhere (Hines 2004). The largest input for Hg_T was atmospheric deposition, and the greatest output was burial, followed by evasion to the atmosphere. The inputs and outputs for Hg_T were within 20% of each other. For MeHg, an in-lake source of MeHg was invoked to provide enough MeHg to balance (within 17%) the inputs and outputs of MeHg. The largest sink of MeHg was photolysis (71% of MeHg inputs), a finding consistent with MeHg mass balances of four lakes (photolysis accounting for 66–88% of MeHg inputs) in the Alaskan arctic (Hammerschmidt et al. 2006b).

The average photic zone mass of Hg^0 (0.67 mg) divided by the average loss rate of Hg^0 (by evasion plus photooxidation) yields a residence time of 1.5 h for elemental mercury. Residence times of Hg_T and MeHg were calculated by dividing the average lake mass by the average for total monthly output (for March–November). These residence times, 61 and 48 days, respectively, are much shorter than the water residence time of Spring Lake (4.8 years), which indicates that removal by outflow of water (i.e., ground-water recharge) is minimal. In comparison, the calculated residence time of MeHg from seston (based on loss to sediment) is roughly 8 days, which indicates that the turnover rate of MeHg in seston is quite rapid. The former residence time is similar to that calculated by Hintelmann et al. (2000) of 1.7 days for native MeHg in sediment. It is evident that Hg_T and MeHg are actively cycled in freshwater environments.

Summary and conclusions

Field measurements showed fairly stable Hg_T concentrations in the unfiltered lakewater of Spring Lake during ice-free periods of 2000–2003; MeHg concentrations were more variable. Seston had the highest MeHg concentrations, and even the lowest seston concentrations (17 ng g^{-1}, September, and October) were higher than those at the sediment surface (2.4 ng g^{-1}). Seston and zooplankton had similar concentrations of Hg_T and MeHg, but the highest concentrations in seston occurred in May and June, whereas the highest concentrations in zooplankton occurred from late June to August. Because concentrations and loads of MeHg from near-shore wetlands were low (generally <0.3 ng L^{-1}; 4.8% of MeHg inputs to the lake), the high-MeHg concentrations in seston suggest in-lake production of MeHg.

Concentrations of $Hg^0_{(aq)}$ in Spring Lake averaged 0.050 ± 0.038 ng L^{-1}, only 3.3% of the average Hg_T concentration. Although Hg^0 concentrations are low, they control loss of mercury by evasion to the atmosphere. Evasion of $Hg^0_{(aq)}$ (333 mg $year^{-1}$), was roughly one-third of the loss of Hg_T from burial (859 mg $year^{-1}$). Both photooxidation of Hg^0 to Hg^{2+} and photoreduction of Hg^{2+} to Hg^0 occur, but overall there is net production of Hg^0 in the photic zone. Consistent diel surficial trends in Hg^0 were not observed, possibly because of daily turnover of the surface mixed layer driven by diel temperature changes and wind-driven mixing.

The largest input for Hg_T was wet deposition (58% of total inputs), followed by estimated dry deposition (29% of total inputs). There is a high degree of uncertainty associated with estimating dry deposition. Bog and upland runoff contributed only 7.6% of the total Hg_T inputs and 4.9% of MeHg inputs. The watershed area of Spring Lake is small, and the wetland area of the watershed is about the same size as the lake surface area. Although wetlands may be the dominant input of MeHg at other sites (Branfireun et al. 1998; St Louis et al. 1994), the mass balance data for Spring Lake suggest that in-lake methylation is the largest input and photolysis of MeHg is the largest output. In addition, the lake is shallow and polymictic, allowing for high turnover of MeHg to the photic zone, which then may be photolyzed. Because the lake's watershed is small and there are no direct inflow and outflow tributaries, water discharge is low, resulting in a fairly long water residence time (4.8 years). The relatively low-areal bog runoff of Hg_T (0.84 μg m^{-1} $year^{-1}$) is consistent with these observations. Burial of Hg_T was 93% of the estimated wet plus dry deposition, indicating that atmospheric deposition is effectively balanced by sedimentation. Hg_T outputs are dominated by burial (67%); evasion accounted for 26% of Hg_T output. The chemical residence time for elemental mercury is short (hours) and for Hg_T and MeHg is much longer (61 and 48 days, respectively). Together, these data show active cycling of mercury and a need for addressing photolysis and photo-redox reactions in mass balanced studies.

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