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Importance of hypolimnetic cycling in aging of "new" mercury in a northern temperate lake

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HIGHLIGHTS

- Newly added mercury partitions more strongly than ambient mercury to lake particulate matter.
- The redox cycle in lakes plays a strong role in "aging" newly added mercury.
- New mercury is delivered to the sediment–water interface faster than ambient mercury.
- Particle partitioning and settling allow new mercury to be quickly delivered to zones of methylation.

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ABSTRACT

The aging of "new" mercury (Hg) was investigated in Experimental Lake 658 as part of the Mercury Experiment To Assess Atmospheric Loading In Canada and the United States (METAALICUS). Mercury enriched in ^{202}Hg was added to the epilimnion over a three-year period to simulate direct atmospheric deposition. We evaluated the aging of newly added mercury (Hg_{Lake}) in the water column using chemical methods and experiments to examine differences in phase partitioning and transport compared to the ambient pool, Hg_{Amb}. Aging was sufficiently slow to observe differences in the partitioning characteristics of Hg_{Lake} and Hg_{Amb}. Amended Hg_{Lake} initially partitioned to a greater extent to epilimnetic particulate matter (log Kd of Hg_{Lake} = 5.08; log Kd of Hg_{Amb} = 4.9). Hg_{Lake} was transported rapidly to the hypolimnion by settling particulate matter. Partitioning became more similar after amended Hg was recycled within the hypolimnion through redox processes. Experiments showed the removal of Hg from the aqueous phase by Fe and/or Mn oxyhydroxide–organic matter complexes. Separations using the anion exchange resin DEAE indicated that both Hg_{Lake} and Hg_{Amb} were associated mainly with dissolved organic matter (DOM) and with partial association with sulfide in anoxic waters, but the degree of association of Hg_{Lake} with DOM was higher in oxic (epilimnetic) waters. In the solid phase, chemical fractionation indicated greater association of Hg_{Lake} with organic matter, while Hg_{Amb} showed greater association with oxyhydroxide and inert phases. Overall, the results suggest that "new" Hg added from the atmosphere is initially more particle-reactive than ambient Hg in the epilimnion, where initial sorption/partitioning occurs mainly to plankton and detrital particles. Once Hg has been deposited at the sediment–water interface, extended equilibration time in combination with microbial and chemical redox processes "age" the "new" Hg, and particle partitioning becomes similar for the added isotope and ambient pools.

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1. Introduction

Direct atmospheric deposition is a major source of mercury (Hg) for surface waters — especially for seepage lakes and for those with large lake-to-watershed ratios (Engstrom et al., 1994). However, it is difficult to assess the short-term effects of direct atmospheric deposition to lakes because Hg is also delivered from the surrounding watershed. Additionally, it is difficult to distinguish "new" Hg (in both the lake and its watershed) from "old" Hg that has been present for years (decades or longer). To enable assessment of "new" versus "old" Hg in a lake–watershed system, separate stable isotopes of Hg(II) were added to a boreal lake (Lake 658) and the surrounding lacustrine wetland and terrestrial watershed in a project known as METAALICUS (Mercury Experiment To Assess Atmospheric Loading in Canada and the United States; Harris et al., 2007). Associated investigations focused on the fate and transport of amended inorganic Hg and, eventually, bioaccumulation of methylmercury (MeHg) in predatory fishes.

Previous research has provided insights into the transport and reactions of Hg in aquatic systems. Sedimentation of aquatic particles to the hypolimnion of a thermally stratified lake results in an environment of high microbial activity and large physical and chemical gradients. These conditions influence ligand assemblages which, in turn,

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influence Hg speciation, phase distribution, transport, and bioavailability (Babiarz et al., 2003a,b; Hurley et al., 1991; Benoit et al., 1999b; Chadwick et al., 2006). In the solid phase, it is generally accepted that important components of aquatic particles, with respect to sorption of Hg and subsequent removal from the water column by particle settling, include: thiols associated with natural organic matter (Amirbahman et al., 2002; Haitzer et al., 2002, 2003; Qian et al., 2002; Turner et al., 2004; Yoon et al., 2005; Aiken et al., 2011), hydrous Fe and Mn oxides (Gagnon et al., 1996; Bloom et al., 1999; Hammerschmidt et al., 2004; Chadwick et al., 2006), and solid-phase sulfides (Mikac et al., 2000, 2002; Bloom et al., 2003; Hammerschmidt and Fitzgerald, 2004). Transport to the hypolimnion is important because the hypolimnion and the sediment–water interface (SWI) of epilimnetic and metalimnetic sediments are important zones for methylation of Hg. The timing of the response of methylating bacteria to an amended spike of inorganic Hg is largely dependent on delivery of Hg to the SWI.

In the aqueous phase, speciation of Hg(II) is hypothesized to be controlled by dissolved organic carbon (DOC) and inorganic ligand (e.g., sulfide) speciation, thereby influencing the ability of Hg to partition to the solid phase (Hurley et al., 1994; Babiarz et al., 1998; Benoit et al., 1999b). In oxic environments, DOC is generally regarded as the dominant ligand controlling the speciation of Hg (Andren and Harriss, 1975; Amirbahman et al., 2002; Haitzer et al., 2002, 2003; Qian et al., 2002; Ravichandran, 2004). DOC depth profiles from lakes may be controlled by several factors including: planktonic production and dissolution, and bacterial assimilation in the water column (Maurin et al., 1997), allochthonous organic matter inputs from the watershed (Zumstein and Buffle, 1989), formation and dissolution of DOC-containing Fe and Mn oxides (Alberic et al., 2000; Chadwick et al., 2006), and decomposition of sedimentary organic matter (Tipping and Woof, 1983; Hamilton-Taylor et al., 1996; Chadwick et al., 2006). In anoxic environments, sulfide is thought to be the dominant ligand controlling Hg speciation (Benoit et al., 1999a,b; Wolfenden et al., 2005); however, recent evidence suggests that natural organic matter can compete with sulfide despite previous thermodynamic predictions to the contrary (Ravichandran et al., 1998a,b; Waples et al., 2005). The distribution of Hg between organic matter and sulfide may be controlled in part by kinetics, as trace metals (including Hg) may not be in equilibrium with sulfide (Morse and Luther, 1999; Hammerschmidt et al., 2004). Furthermore, the stability of sulfide is influenced by the presence of sulfide oxidizing species. For example, the presence of Fe(III) in acid-mine waters has been shown to release Hg through the oxidation of cinnabar (Burstaller et al., 1975; Skyllberg, 2008).

Here we investigate the "aging" of new Hg added directly to a lake (designated as Hg_{Lake}) by comparing it to ambient Hg (Hg_{Amb}) already present in the lake system. We use "aging" to refer to the changes in the phase distributions and associations of Hg following introduction of Hg(II) as an inorganic salt into the surface waters of the lake (Fig. 1). Following amendment to the lake, initial processes include partitioning between aqueous and solid phases (sorption–desorption reactions) and partitioning among components of the aqueous and solid phases. Association with the settling particulate matter leads to the transport of Hg from the epilimnion to the hypolimnion and eventually to the sediment–water interface. Particle diagenesis in the hypolimnion may result in the release of Hg into the aqueous phase, where binding to sulfides, DOC and other ligands may occur. In addition, iron (Fe) and manganese (Mn) mobilized from bottom sediments under anoxic conditions migrate upward toward the anoxic–oxic boundary zone where formation and settling of Fe(III) and Mn(IV) hydroxyoxides occur. Coupling of Hg to this "ferrous wheel" or "manganous wheel" may re-deliver Hg to the sediment–water interface (Campbell and Torgersen, 1980; Chadwick et al., 2006). These processes are expected to gradually age or homogenize "new" Hg (Hg_{Lake}) and "old" Hg (Hg_{Amb}), leading to similarities in reactivity and bioavailability. In this paper, we use several chemical methods to probe the aging of Hg during transport and exposure to biogeochemical processes in the water column of Lake 658.

The METAALICUS project offered a unique opportunity to follow the effects of recent additions of Hg to a lake system through the use of stable isotopes of Hg added at environmentally-relevant concentrations (Harris et al., 2007). Our subproject of the multidisciplinary METAALICUS study focused on particle–water partitioning and internal cycling of the amended isotopic spike (Hg_{Lake}) relative to the pool of ambient Hg (Hg_{Amb}) in the lake. Specifically, we asked the following questions:

— Do Hg_{Lake} and Hg_{Amb} show similar partitioning between solid and aqueous phases in the lake?

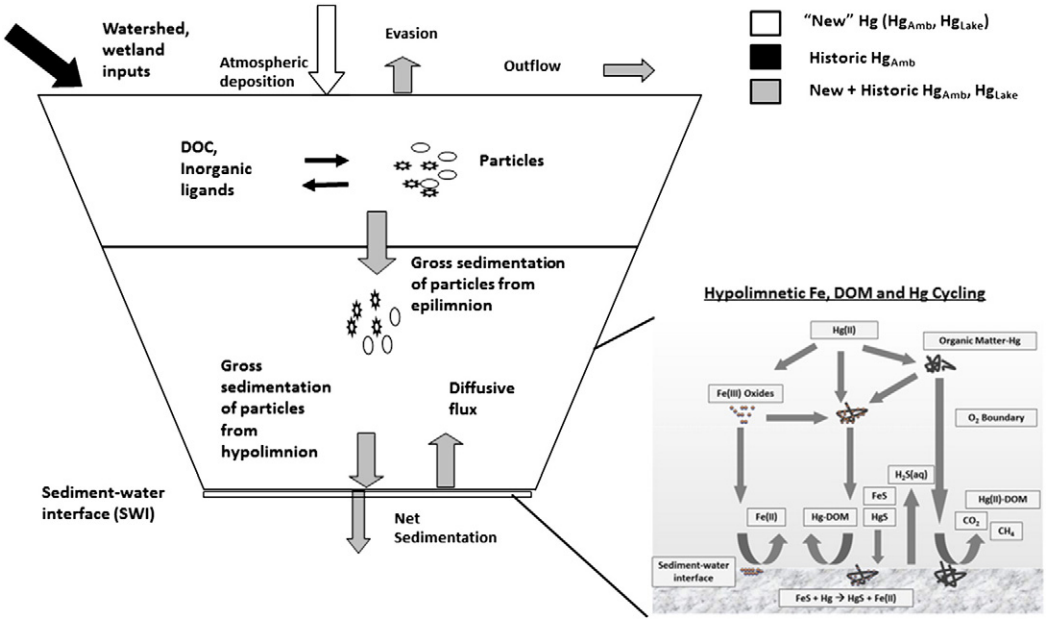


Fig. 1. Processes affecting Hg transport in Lake 658. Arrows represent fluxes and shading in arrows represents types of Hg delivered to and cycled through the lake. Inset depicts cycling processes at the sediment–water interface.

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- What factors influence phase partitioning of Hg_{Lake} and Hg_{Amb} in the lake?
- Is Hg_{Lake} recycled between anoxic and oxic zones above the sediment–water interface and what is the role of recycling in the aging of Hg_{Lake}?

Further research by our group (Chadwick et al., 2006; Chadwick, 2006) examined the recycling of both total and methyl Hg in the hypolimnion and at the sediment–water interface, while other METAALICUS investigators have focused on microbial methylation, bioaccumulation, evasion, terrestrial inputs, and other processes (Hintelmann et al., 2002; Amyot et al., 2004; Poulain et al., 2006; Harris et al., 2007; Graydon et al., 2009).

2. Site description

Lake 658 (49° 43.95′ N, 93° 44.20′ W) is an 8-hectare first-order boreal lake located within the Experimental Lakes Area (ELA) in northwestern Ontario. Dimictic Lake 658 is separated into two basins with each having a seasonally anoxic hypolimnion (Fig. 1). The maximum depths of the west and east basins are 13.4 m and 10.9 m, respectively. The lake is connected to Lake 660 (Lake Winnange), and hydrological flows were measured continuously during the ice-free season. The long-term average water residence time of Lake 658 is approximately 5.5 years (Sandilands et al., 2005; Chadwick et al., 2006). The terrestrial catchment of the watershed is dominated by jack pine (*Pinus banksiana*), black spruce (*Picea mariana*), white birch (*Betula papyrifera*), and trembling aspen (*Populus tremuloides*). Mineral soils within the watershed are thin (usually 1 m or less in depth) and discontinuous over pink Precambrian granodiorite. Soils and bedrock are typically covered with moss (*Spagnum* sp.), club moss (*Lycopodium* sp.), and lichens. Moss (*Spagnum* sp.) reaches depths greater than 0.5 m in the wetland and low-lying areas. Intermittent stream flow drains the uplands and the wetland adjacent to the lake.

3. Materials and methods

3.1. Stable isotope addition

To simulate direct atmospheric deposition, Lake 658 was dosed every two weeks (nine times between early June and mid October) with Hg enriched in stable ^{202}Hg (Hg_{Lake}). The additions occurred during each summer from 2001 through 2003 to give a loading of 20 μg m^{-2} $year^{-1}$ ~4 to 5 times the annual wet deposition (Sandilands et al., 2005). In addition, ^{200}Hg and ^{198}Hg were applied annually at similar loading rates to the 42-hectare upland and 2-hectare wetland portions of the adjoining watershed, respectively. The total doses over the 2001–2003 period were 67 μg m^{-2} to the upland, 76 μg m^{-2} to the wetland, and 66 μg m^{-2} to the lake (Harris et al., 2007). Prior to spiking the lake, the isotope was pre-mixed with adjacent Winnange Lake water in individual 20-L carboys. The lake spiking procedure used two boats (one for each basin) that were powered with electric trolling motors. Operators on each boat slowly dispensed the spike into the wake of the motor. The spike solution was administered at dusk to minimize photo-reduction and evasion. The spike generally resulted in a doubling of the mercury concentration (2 to 3 ng L^{-1}) in the epilimnion of the lake (Chadwick et al., 2006; Harris et al., 2007).

It must be noted that Hg_{Amb} combines historic Hg in the lake, Hg naturally delivered from the watershed, and Hg naturally delivered from direct atmospheric deposition. Additionally, we cannot differentiate between newly added Hg_{Lake} and internally-recycled Hg_{Lake} after the initial spike year, 2001.

3.2. Field sampling methods

All sampling, sample processing, and analysis for Hg followed accepted clean techniques to minimize contamination of samples (US EPA, 1996; Olson et al., 1997). Individual water samples were collected 2, 5, 7, and 9 m from the water surface and 80, 40, 20, 10, and 5 cm from the sediment–water interface (SWI). Vertical water column profile samples for filterable and particulate Hg, major ions, dissolved organic carbon (DOC), sulfide, and E2:E3 ratios of the DOC were obtained on the day before each spike addition (13 days after the previous spike). Redox potential, dissolved oxygen, temperature, pH, and specific conductance were measured in the field using a multi-parameter sonde (Hydrolab™ Scout II).

Here we present water column profiles in June and September from the 2001, 2002, and 2003 sampling years to compare spring conditions to late stratification. Water column samples were obtained using an all Teflon sampling line and weight connected to a peristaltic pump mounted on a clean boat dedicated to mercury sampling. Samples near the sediment–water interface were collected using a close interval sampler (CIS) constructed of trace-metal compatible materials that allowed us to sample at these fixed depths above the sediment–water interface (Colman, 1979; Babiarz et al., 2003a; Hurley et al., 1994).

The samples for filterable ("dissolved") Hg measurement were collected from acid-cleaned in-line polyethersulfone filtration capsules rated at a 0.45 μm pore size (Meissner™ Filtration Products). Particulate Hg samples were collected in-line on quartz fiber filters in acid-cleaned Teflon® housings (Hurley et al., 1994; Mason and Sullivan, 1997; Babiarz et al., 1998). Filters had a nominal pore size of 0.7 μm (Whatman QMA) and were ashed at 700 °C. The volume of water passed through each filter housing was measured with a graduated cylinder (typically 0.5 to 2.0 L).

Settling particulate matter was collected using sediment traps deployed in the hypolimnion of Lake 658. Sediment traps were constructed of acrylic and Teflon® components with a 14.6 cm diameter and a 5:1 aspect ratio (Hurley et al., 1991, 1994). Sediment traps were deployed in duplicate at depths of 7 and 13 m in the west basin from a surface float to limit sediment resuspension during deployment and retrieval. The positions of sedimentation traps were below the thermocline; therefore, limiting the influence of strong eddy currents present in the epilimnion. Sediment traps were collected and deployed the morning before each lake spike. Prior to deployment, sediment traps were filled with water from their suspension depth using a bilge pump secured to an anchored rope. The traps were not poisoned to minimize potential contamination of samples, and trapping intervals were kept short (~2 weeks) to minimize complications from decaying matter.

At the end of a trapping period the contents of each sediment trap were transferred into large (2L) Teflon® bottles. Sediment trap samples for Hg analysis were collected in duplicate on ashed 0.7 μm quartz fiber filters using a Teflon® filter tower (Savillex) attached to an acid-cleaned desiccator held under vacuum using a small piston pump. Suspended particulate matter (SPM) samples were collected in duplicate for each sediment trap sample by filtering a known aliquot of water through a pre-weighed 0.45 μm, 47 mm polycarbonate track etched filter. Results reported in this paper represent the average between replicate samples and traps.

All natural water samples and speciation experiments (below) were processed immediately after collection in a field laboratory equipped with HEPA air filtration at the Experimental Lakes Area (Ontario, Canada). Sulfide samples were preserved with sulfide antioxidant buffer (SAOB). Samples for Hg analysis were preserved to 1% acid using 50% trace metal grade (TMG) HCl. Major ion samples were collected in acid cleaned PTFE-lined bottles, preserved to 1% acid using 50% TMG HNO_3. DOC samples were collected in 125 mL amber bottles. Water samples were stored at 4 °C until analysis.

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SPM, particulate Hg and sediment trap samples were transferred to Petri® dishes and frozen until analysis.

3.3. Batch reactor experiment

Batch reactor experiments were performed with water collected from the hypolimnion to explore the influence of Fe and Mn oxidation on the redelivery of Hg_{Amb} and Hg_{Lake} to the sediment–water interface. Reactors consisted of individual 5 L Teflon® bottles filled with filtered (0.45 μm) water collected just above the sediment–water interface (5 cm) using the close interval sampler (CIS; Babiarz et al., 2003a). A group of identical reactors were prepared and one bottle was sub-sampled in series for each incubation time point. Before use, each bottle was purged with high-purity argon to remove oxygen and limit potential oxidation artifacts from oxygen adsorbed to the Teflon® walls. Once filled with lake water, the reactors were held open to the atmosphere in the dark at 4 ± 0.3 °C to mimic the conditions at the oxic–anoxic boundary; i.e.: diffusion of Fe(II) and Mn(II) into the oxic zone and subsequent oxidation that results in the formation of particulate Fe(III) and Mn(IV) oxyhydroxides. The reactors were kept static to promote particle formation processes similar to those found in the hypolimnion of Lake 658. Transmission electron microscopy (TEM) experiments performed by other researchers found that batch reactors stirred or sparged with oxygen yield particles of different morphologies and larger iron oxide aggregates than particles generated in the absence of stirring (Taillefert et al., 2000).

Individual water samples were collected after incubation periods of 0.5, 1, 2, 4, 6, 8, 10, 15, 20, and 30 h after collection. At each time step, a batch reactor was gently mixed and sacrificed for sampling of Hg_{Lake}, Hg_{Amb}, Fe, Mn, and DOC. Samples were filtered using a Teflon® filter tower attached to an acid-cleaned desiccator held under vacuum using a small piston pump in a HEPA lab hood. A bottle in the desiccator collected the filtrate. Particulate Hg_{Lake}, Hg_{Amb} Fe, and Mn concentrations were calculated by the difference between the total and filterable fractions. The pH (± 0.1 unit) and temperature (5 ± 0.1 °C) did not change significantly during the course of the experiment (data not shown). Similarly, the concentrations of total (unfiltered) Fe (mean = 19.91 ± 0.05 mg L^{-1}), Mn (mean = 1.23 ±

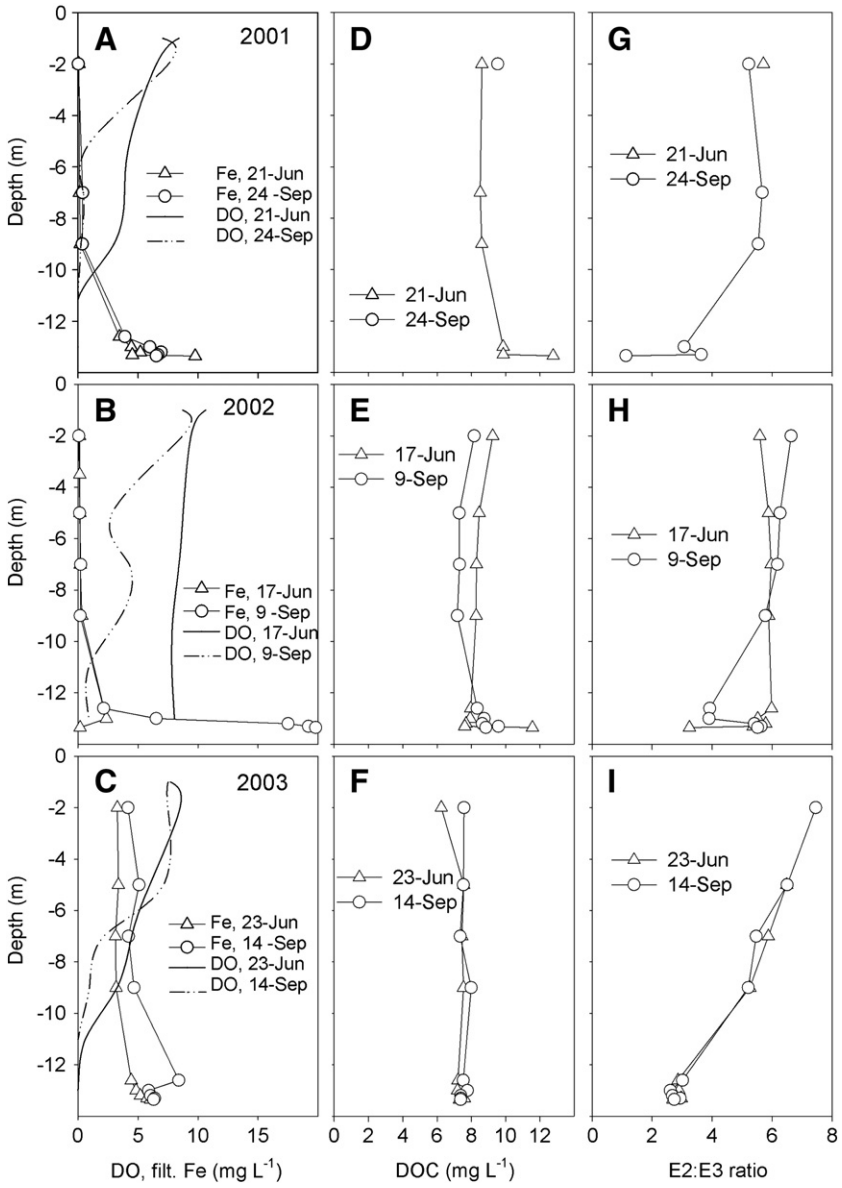


Fig. 2. Water column profiles during early summer and late fall in Lake 658 through the first three years of isotope addition. A–C: dissolved oxygen (DO) and filtered iron (Fe); D–F: dissolved organic carbon (DOC). G–I: E2:E3 ratio of dissolved organic carbon. J–L: filterable ambient Hg (Hg_{Amb}); M–O: filterable lake isotope Hg (Hg_{Lake}); P–R: ratio of lake isotope Hg to ambient Hg.

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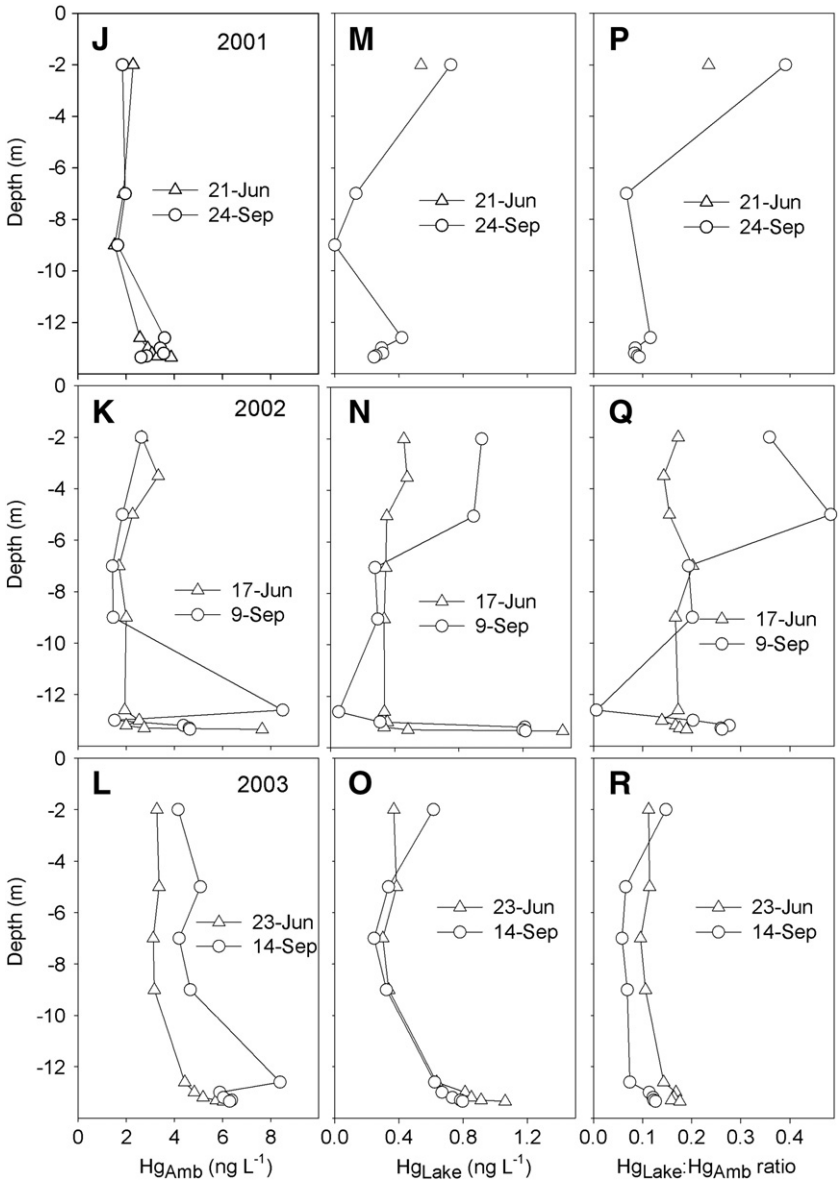


Fig. 2 (*continued*).

0.01 mg L^{-1}), Hg_{Amb} (mean = 7.73 ± 0.09 ng L^{-1}), and Hg_{Lake} (mean = 1.67 ± 0.02 ng L^{-1}) in each reactor varied little during the experiment.

3.4. Sequential extraction of Hg in suspended particulate matter

To explore the solid-phase associations of Hg_{Lake} and Hg_{Amb} contained in SPM, an analytical scheme of selective chemical extractions was adopted. Three sequential extractants were used to isolate three extractable fractions of Hg: (1) 1 M KOH-extractable Hg, (2) 1 M HCl-extractable Hg, and (3) 12 M HNO_3-extractable Hg. The solid phase components extracted by these reagents are discussed below (see Discussion section).

The sequential chemical extraction scheme was applied to suspended particulate matter collected from three zones within the water column of Lake 658: (1) the oxic epilimnion where the particles are primarily organic (i.e., biogenic) in character; (2) the oxic–anoxic interface which is a zone of Fe(II) oxidation and formation of Fe(III) oxyhydroxides; and (3) the sediment–water interface which is an anoxic zone of possible $FeS_{(s)}$ formation. To obtain the suspended particulate matter, unfiltered water was collected in individual 5-L Teflon® bottles. Particles were harvested using ashed quartz fiber filters housed in a Teflon® filter tower attached to an acid-cleaned desiccator held under vacuum using a small piston pump in a nitrogen glove box. The volume of water passed through each filter was measured gravimetrically. Following filtration, particle-laden filters were immediately transferred into 125-mL Teflon® bottles in a nitrogen atmosphere. Approximately 30 mL of reagent was used for each extraction. A 10-mL deionized water rinse was used between the 1 M KOH and 1 M HCl extraction steps. After adding each reagent or rinse, the bottles were capped, shaken vigorously to immerse the filters, mixed on an orbital table (150 rpm) for 12 h, and centrifuged at 5000 rpm for 15 min. Each extractant or rinse was then decanted into a separate bottle and diluted to approximately 100 mL.

Concentrations of Hg in field filter blanks were generally low. The concentration of Hg in the KOH, HCl, and HNO_3 extractants ranged from 0.1 to 0.5, 0.1 to 0.4, and 0.1 to 0.5 ng L^{-1}, respectively. Mass balances for Hg_{Amb} and Hg_{Lake} ranged from 87% to 108% and 86% and 106%, respectively. Overall, this mass balance approach had

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essentially complete recovery of all Hg from the sequential extraction process.

3.5. DEAE fractionation of aqueous-phase Hg

Aqueous phase Hg fractionation was performed using a diethylaminoethyl cellulose resin (Toyopearl® DEAE-650M). To clean the DEAE resin, we poured it into a clean Teflon® bottle with 0.25 M NaOH and mixed it for 1 h on an orbital shaker table at 100 rpm. The base was removed by vacuum filtration using a 47 mm diameter 0.45 μm Teflon® filter (Savillex) secured to a Teflon® filtration tower. While still in the tower, the resin was rinsed twice with 500 mL of deionized water (Milli-Q, Millipore®). After transferring the resin to a clean Teflon® bottle with 0.5 M TMG HCl + 0.1 M TMG HNO_3, it was mixed for 1 h on a shaker table. The acid was removed by vacuum filtration using the Teflon® filtration tower assembly. The resin was then placed in the original Teflon® bottle where it was mixed again with 0.5 M TMG HCl + 0.1 M TMG HNO_3 for 1 h on a shaker table. The resin was filtered again to remove the acid and flushed with MQ water until the final pH of the filtrate was 6. Lastly, fine grains were removed by suspending the resin in a 2 L Teflon® vial (Savillex) filled with Milli-Q-water for 1 h and removing the supernatant. Clean DEAE was stored in Milli-Q water prior to use in the field.

Columns used for the separations consisted of Teflon® tubing (6.3 mm I.D. × 9.5 mm O.D.) and 6.4 mm Teflon® frits (Savillex). All solutions and samples were delivered to the column and eluted through the resin using a four-channel peristaltic pump equipped with acid cleaned C-flex (1/8″ I.D. × 1/4″ O.D.) and Teflon® (1.7 mm I.D. × 3.2 mm O.D.) tubing. Sample delivery tubing was attached to the column using Teflon® reducing compression fittings (Savillex). Approximately 3.0 g of clean DEAE resin was placed into each column by resuspending a known amount of resin in purified water, pouring the resin into the column, and removing the excess water using the peristaltic pump (i.e. packing the column). Prior to all speciation experiments, approximately 100 mL of purified water was passed through each column and discarded. Next, a known volume (50 to 125 mL) of sample was passed through the DEAE column at a flow rate of approximately 7 mL min^{-1} using a peristaltic pump. The DEAE column was then quantitatively eluted at approximately 7 mL min^{-1} with a volume of acid similar to the original sample volume. The acid used in all Hg separations was a solution of 0.5 M TMG HCl + 0.1 M TMG HNO_3. We then measured the amount of Hg passing through the DEAE column (permeate) and the amount retained (retentate).

Complete details of the separation scheme used in all Hg DEAE speciation experiments are presented in Chadwick (2006). Anoxic samples were stored in an anoxic glove box prior to separation and were processed under continuous nitrogen flow to limit potential oxidation artifacts. In addition, Teflon® bottles for anoxic speciation were purged with high-purity argon prior to sampling. During the course of a separation, the ultraviolet (UV) absorbance at 254 nm was monitored to determine if there was breakthrough of DOC during the separation.

3.6. Analytical methods

All isotopic analyses of Hg were performed at the laboratory operated by the United States Geological Survey in Middleton, WI. Total mercury concentrations were determined using the bromine monochloride (BrCl) oxidation technique followed by stannous chloride ($SnCl_2$) reduction, nitrogen purging, gold trap pre-concentration, and thermal desorption (Gill and Fitzgerald, 1987). Samples were analyzed via inductively coupled plasma-mass spectrometry (ICP-MS) on a Perkin Elmer ELAN 6100 (Hintelmann et al., 2002; Babiarz et al., 2003b). The analytical detection limit (three times the standard deviation of the blank) averaged 0.1 ng L^{-1} Hg.

Dissolved organic carbon (DOC) was determined using high temperature (680 °C) catalytic oxidation (Shimadzu TOC-5000) with an analytical uncertainty of ±0.1 mg L^{-1}. The E2:E3 ratios of the samples followed the methodologies of Chin et al. (1994) and are summarized in Weishaar et al. (2003). Major ion composition (Fe, Mn, Ca, Mg, S, K, and Na) was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES; Perkin Elmer Optima 4300 DV) with an analytical uncertainty typically under 5%. Uncertainties in measurements of dissolved oxygen and temperature were ±0.1 mg L^{-1} and ±0.1 °C, respectively. Preserved total sulfide samples were analyzed within hours using a specific ion electrode (Benoit et al., 1999a,b). The analytical detection limit for this method was 0.1 μmol L^{-1}. The mass of SPM was determined gravimetrically after drying the filter at 105 °C.

4. Results

4.1. Lake 658 water column profiles during stratification

As a dimictic lake that is well-sheltered by steep basin walls and tree cover, Lake 658 exhibits strong thermal stratification with subsequent oxygen depletion in the hypolimnion. The degree of anoxia in the hypolimnion varied over the three study years. In 2002, full mixis in early spring was clearly evident in the June thermal profile and filterable ("dissolved") Fe was barely detectable near the sediment–water interface (SWI; Fig. 2B). In 2001 and again in 2003, it appears that hypolimnetic turnover was incomplete during spring (Fig. 2A, C). Oxygen levels near the SWI were low, and the amounts of redox-sensitive constituents (e.g. Fe, Mn) were elevated in the overlying water during both early and late stratification. This lack of mixing in the spring allowed continuous anoxia at the SWI and a corresponding greater flux of redox-sensitive constituents into hypolimnetic waters.

Dissolved organic carbon (DOC) concentration (Fig. 2D–F) also showed differences over the study period that are related to both watershed input (the main source of most DOM) and redox conditions in the hypolimnion. In general, DOC concentrations decreased in the water column over the course of the study, with higher levels in the water column in 2001 and near the SWI during 2001 and 2002. Major differences, however, were observed in the type of DOC observed near the SWI, especially in 2003. Decreasing E2:E3 ratios near the SWI (Fig. 2I), suggest that dissolved organic matter near the SWI is enriched in high molecular weight (HMW) aromatic compounds (Chin et al., 1994). This change occurred at depths of increased Fe cycling, suggesting that particulate Fe may preferentially sorb HMW DOC and carry it into the hypolimnion where the DOC is released upon dissolution of the redox-sensitive Fe.

Profiles of Hg_{Amb} were related to thermal stratification of the lake (Fig. 2J–L). In all three years, filterable Hg concentrations were highest in the region of the SWI. Early stratification profiles show that filtered Hg was 3 to 4 ng L^{-1} for most of the water column and increased to >4 ng L^{-1} in the deep hypolimnion during stratification. Interestingly, total Hg levels in the lake increased substantially from 2001 to 2003. This occurred even though 2003 was a dry year, and watershed inputs were the lowest of the three study periods (Hg_{Amb} loadings for 2001–2003 were 1.64, 1.48 and 0.51 g $year^{-1}$, respectively; Harris et al., 2007).

The 2001 sampling year was the only period when hypolimnetic Hg_{Lake} could be attributed solely from that year. In subsequent years, the Hg_{Lake} signal likely included ^{202}Hg added in previous years due to the potential for recycling of Hg_{Lake} from bottom sediments. During stratification in 2001 (Fig. 2M), filterable Hg_{Lake} profiles show that Hg_{Lake} isotope added to the epilimnion appeared in the aqueous phase near the SWI. Filterable Hg_{Lake} was observed in the hypolimnion two weeks after addition of the first spike (Chadwick, 2006). This confirms that Hg_{Lake} added to the epilimnion was partially transported to the hypolimnion within the year of

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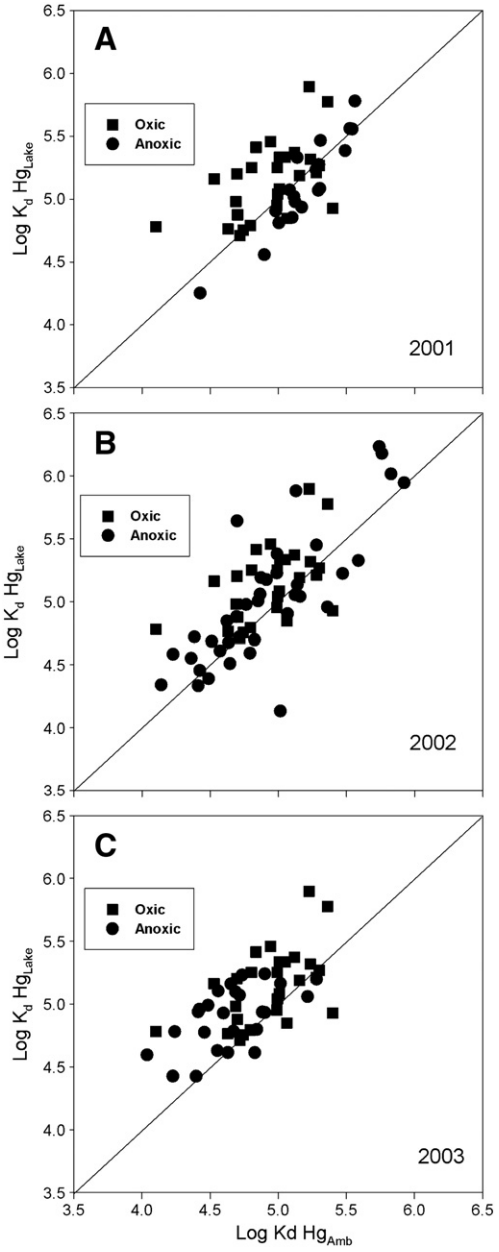


Fig. 3. Distribution coefficients for Hg_{Lake} and Hg_{Amb} in Lake 658. Samples that were obtained from anoxic portions of the hypolimnion are shown as circles. Samples from oxygenated portions of the hypolimnion, metalimnion and epilimnion are indicated by squares. A: 2001; B: 2002; C: 2003.

addition to the lake. Similar to Hg_{Amb}, the Hg_{Lake} profiles show higher concentrations near the SWI in all three years (Fig. 2M–O). In 2003, however, the gradient extended much further into the water column due to significant anoxia in the hypolimnion.

4.2. Partitioning of Hg between solid and aqueous phases in the water column

The partitioning of Hg between particles and water was examined by calculating a distribution coefficient (Kd) as follows:

$$Kd = C_{Part}/C_{Filt} \quad \left(L\ kg^{-1}\right) \tag{1}$$

where C_{Part} is the concentration of Hg associated with particulate matter (ng kg^{-1}) and C_{Filt} is the concentration of Hg (ng L^{-1}) in the filter-passing (0.45 μm) aqueous phase. Thus, a high Kd value reflects a high affinity of Hg for particulate matter.

The log Kd values ranged from 4.04 to 5.92 ($\bar{x} = 4.90 \pm 0.38$, $n = 178$) for Hg_{Amb} and from 4.13 to 6.31 ($\bar{x} = 5.08 \pm 0.37$, $n = 178$) for Hg_{Lake} over the entire sampling period, from 2001 to 2003 (Fig. 3A–C). The lower Kd values were for samples collected from the deepest portion of the anoxic hypolimnion. The Lake 658 Kd values compare well with other studies; log Kd values for total Hg ranged from 4.5 to 5.7 in Wisconsin lakes (Hurley et al., 1994), from 5.5 to 5.8 for open water areas of Lake Michigan (Mason and Sullivan, 1997), and 4.8 ± 0.1 in the open water of Lake Superior (Rolfhus et al., 2003). Log Kd values of about 4.3 for sediments from Lake 239 of the Experimental Lakes Area (Ontario, Canada) were measured using the stable isotope $^{200}Hg(II)$ as a tracer (Hintelmann and Harris, 2004).

The relationships between Hg_{Amb} and Hg_{Lake} in partitioning to particles are shown in Fig. 3. Deviations from the 1:1 line indicate differences in the partitioning behaviors of Hg_{Amb} and Hg_{Lake}. Importantly, log Kd values were higher for Hg_{Lake} than for Hg_{Amb}, especially for oxic waters (Fig. 3; Table 1), indicating that Hg added to the lake recently was more particle-reactive than Hg which had been in the lake longer.

When the Kd data are further separated into samples from the oxic portion of the water column as compared to samples from the anoxic hypolimnion, further differences are apparent for the summed data and for annual means from 2001 to 2003 (Table 1). With the exception of the anoxic hypolimnion at the initial stages of the experiment in 2001, mean annual Kd values were higher for Hg_{Lake} than Hg_{Amb}. Log Kd values of both Hg_{Lake} and Hg_{Amb} decreased in anoxic zones and to a much greater degree during 2003, when anoxia persisted during the entire stratified period (Fig. 2C).

4.3. Partitioning of Hg in the aqueous phase

To explore partitioning of Hg among components of the aqueous phase (Hg complexing ligands in the filtered phase), a DEAE fractionation scheme was applied to filtered water samples from Lake 658. As described in the Materials and methods section, measurements were made of the amount of Hg passing through the DEAE column (permeate) and the amounts retained by the column (retentate). Neutral and positive complexes of Hg should pass through the column, while complexes of Hg carrying a negative charge should be retained (see Discussion section). Because this approach for speciation is operational, we refer to the fractions as Hg-permeate and Hg-retentate, respectively. Because DOM is negatively charged, Hg–DOM complexes should be present in the retentate. Even so, neutral complexes with trace-level components of DOM could be present in the permeate. We also note that neutral complexes of sulfide species should be eluted in the permeate fraction.

Samples for aqueous phase fractionation were collected at several depths in the water column on 23 June and 18 August 2003, one day

Table 1
Mean distribution coefficients (log Kd values) and statistically significant difference between Hg_{Amb} and Hg_{Lake} for particle–water partitioning of Hg in whole lake, and oxic and anoxic water column compartments in Lake 658 from 2001 through 2003.

Year	Whole lake		Oxic epilimnion and hypolimnion		Anoxic hypolimnion	
	Hg_{Amb}	Hg_{Lake}	Hg_{Amb}	Hg_{Lake}	Hg_{Amb}	Hg_{Lake}
2001	5.04	5.13	4.94	5.15**	5.19	5.11
2002	4.94	5.08*	4.95	5.15**	4.82	4.84
2003	4.68	5.03***	4.72	5.18***	4.66	4.99**
2001–03	4.90	5.08***	4.92	5.17***	4.88	4.95***

* $p<0.05$.
** $p<0.01$.
*** $p<0.001$.

Table 2
Comparison of pH, Dissolved oxygen, filtered Fe and sulfide in profiles from Lake 658 during 2003. Modeled $Hg(HS)_2$ based on predictions following Benoit et al. (1999a,b). Mass balances for Hg_{Amb} and Hg_{Lake} are sums of retentate and permeate from DEAE column separations compared to total sample prior to resin separation.

Sampling location depth	Date	pH	DOC mg L^{-1}	Filtrate Fe mg L^{-1}	Filtrate sulfide μmol L^{-1}	Modeled $Hg(HS)_2$ %	Mass balance Hg_{Amb} %	Mass balance Hg_{Lake} %
West basin, Lake 658								
2 m (oxic)	23 Jun 03	7.3	6.2	0.06	<DL	NA	95.7	110.0
7 m (oxic)	23 Jun 03	6.3	7.4	0.17	<DL	NA	106.3	91.6
40 cm above SWI (anoxic)	23 Jun 03	6.0	8.4	7.40	0.81	73.2	109.9	90.7
5 cm above SWI (anoxic)	23 Jun 03	5.7	9.8	12.2	2.31	81.1	105	97.8
West Basin, Lake 658								
2 m (oxic)	18 Aug 03	7.3	7.1	0.01	<DL	NA	116.3	95.2
5 m (oxic)	18 Aug 03	6.4	7.2	0.06	<DL	NA	96.6	116.8
7 m (oxic)	18 Aug 03	6.1	7.1	0.20	<DL	MA	101.3	103.9
9 m (oxic)	18 Aug 03	6.1	7.3	0.25	<DL	NA	105.5	98.4
40 cm above SWI (anoxic)	18 Aug 03	5.8	8.8	8.34	8.3	74.2	101.5	102.1
5 cm above SWI (anoxic)	18 Aug 03	5.6	10.4	8.83	8.5	82.4	105.3	103.5

after routine spiking of the lake with the Hg_{Lake} isotope. We included samples from the epilimnion and from the anoxic zone, near the SWI. Each zone differed in water chemistry. The concentration of DOC was higher and pH was lower in the near-bottom, anoxic zone samples (Table 2). The concentration of Fe increased with depth and ranged from about 0.06 to 0.25 mg L^{-1} in the oxic zone and 7.4 to 12.2 mg L^{-1} in the anoxic zone, for the two sampling dates. Sulfide was detectable at 40 and 5 cm above the sediment–water interface and ranged from about 0.8 to 8 μmol L^{-1}. Modeled $Hg(SH)_2^0$ concentration, expressed as a percent of "dissolved" Hg , following Benoit et al. (1999b), ranged from 73 to 82% in the near-bottom samples. Similar to epilimnetic samples, the Hg_{Amb} and Hg_{Lake} in hypolimnetic samples were associated mainly with the retentate fraction, representing 60 to 92% of Hg_{Amb} and 70 to 98% of Hg_{Lake} on the two sampling dates (Fig. 4). The percent of filterable Hg in the retentate tended to be lower in the anoxic zone where sulfide was present.

4.4. Batch reactor experiment

We examined the influence of redox processes on the distribution of Hg between solid and aqueous phases by mimicking lake processes at the redoxcline using a batch reactor, whereby anoxic water samples were incubated in open air. The reactor simulated conditions at the boundary where diffusion of Fe(II) and Mn(II) into the oxic zone results in particle formation via oxidation (Campbell and Torgersen, 1980; Chadwick et al., 2006). In these initially anoxic systems, the concentration of dissolved oxygen increased from non-detectable to approximately 4.5 mg L^{-1} during the first 10 h, but then remained relatively constant, reaching 4.9 mg L^{-1} after 30 h (Chadwick, 2006). The "plateau" oxygen concentration was well below the saturation concentration for dissolved oxygen. Since Fe(II) and sulfide concentrations were also below their detection limits during the oxygen concentration plateau period, this plateau

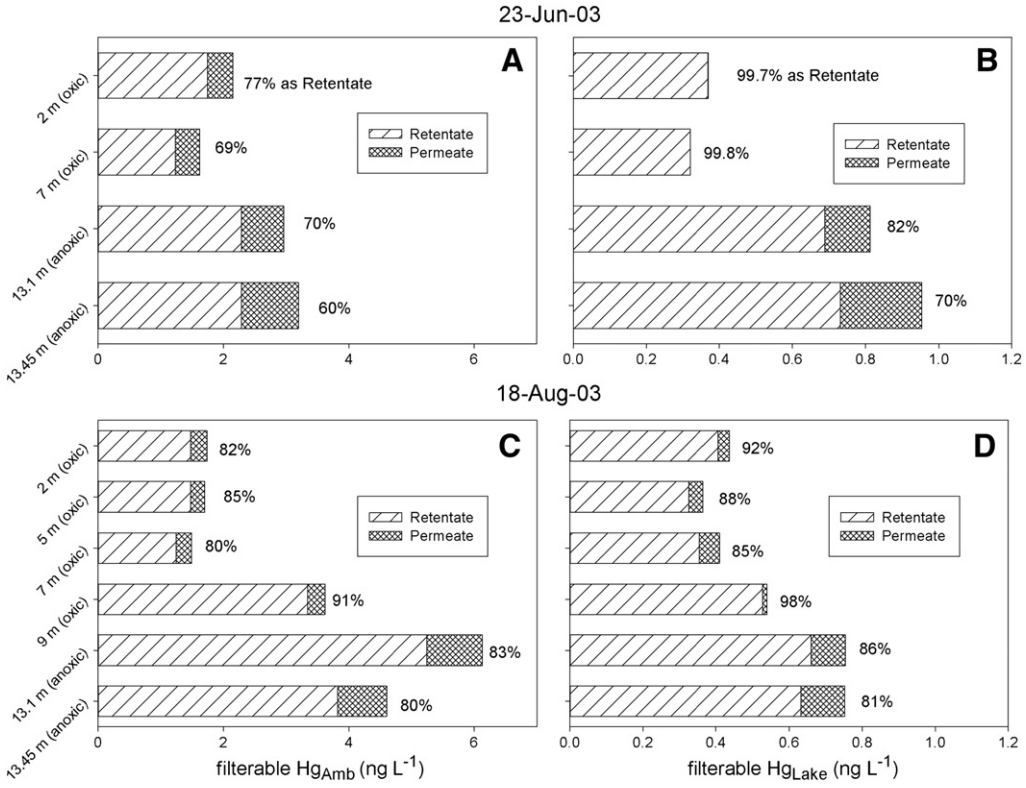


Fig. 4. Experimental (DEAE resin) speciation of HgT in filtered Lake 658 oxic and anoxic water column samples. A. 23-Jun-03 — Hg_{Amb}; B. 23-Jun-03 — Hg_{Lake}; C. 18-Aug-03 — Hg_{Amb}; D. 23-Jun-03 — Hg_{Lake}.

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likely reflected a balance between the rate of oxygen uptake from the atmosphere and consumption of oxygen by microbial respiration and geochemical oxidation. In addition, oxygen gradients may have existed in each batch reactor because they were static systems. Therefore, the apparent unsaturated oxygen concentration likely represents a weighted average of waters saturated with oxygen near the air–water interface that were homogenized prior to sampling with unsaturated waters at the bottom of the incubation bottles. The lack of Fe(II) during the oxygen plateau period suggests that the majority of filterable iron was colloidal Fe(III) (Chadwick et al., 2006).

Other changes in chemical constituents occurred during the first 10 h of incubation (Fig. 5). Filterable Fe and Mn concentrations decreased to about 43% of their initial concentrations. In comparison, DOC decreased by about 58%, while filterable Hg_{Amb} and Hg_{Lake} concentrations decreased to 66% and 72%, respectively, from their initial concentrations. The decrease in DOC concentration observed in the batch reactor experiment reflects the influence of Fe and Mn oxidation on DOC distributions within the hypolimnion. As previously reported, a strong linear relationship was found between DOC concentration and the concentrations of both filterable Fe ($r^2 = 0.97$, $n = 15$, $p < 0.001$) and [Mn] ($r^2 = 0.96$, $n = 15$, $p < 0.001$), indicating a close linkage of DOC to the cycles of Fe and Mn (Chadwick et al., 2006).

The fraction of Hg removed with time was generally greater (3 to 12%) for Hg_{Lake} than Hg_{Amb} in the batch reactor experiment (Fig. 5). This observation suggests that differences existed in the physical and/or chemical speciation of Hg_{Amb} versus Hg_{Lake} shortly after exposure of anoxic waters to oxygen, and the subsequent formation of Fe and Mn oxyhydroxides, and removal of DOC by the oxyhydroxides.

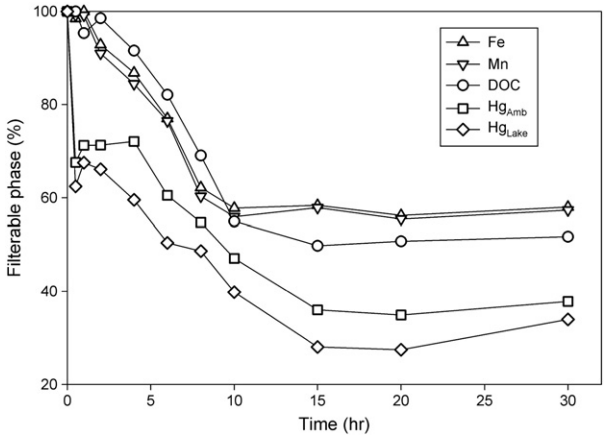


Fig. 5. Fraction of filterable component remaining versus time for Hg_{Lake},Hg_{Amb}, DOC, Fe, and Mn in the batch reactor experiment.

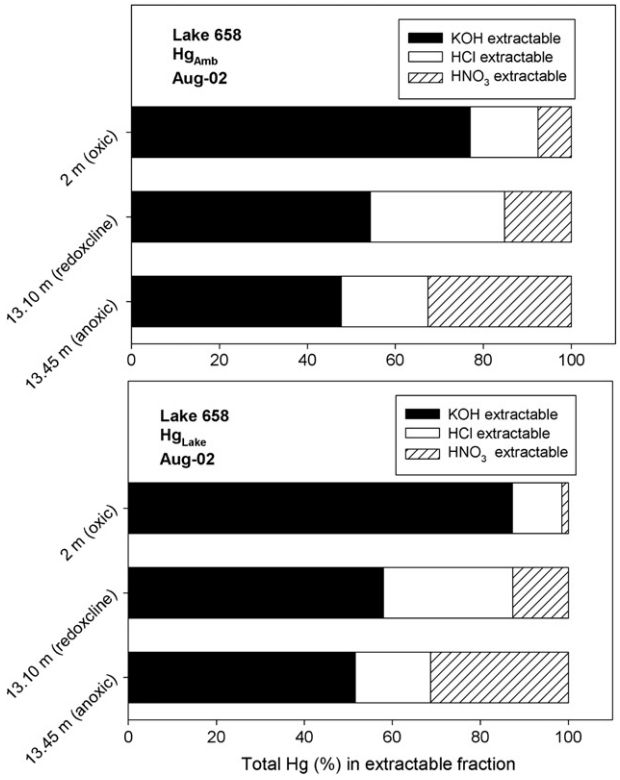


Fig. 6. Sequential extraction of water column particulates isolated from the west basin of Lake 658 in July 2002.

4.5. Examination of Hg association with components of the solid phase using sequential extraction

A sequential extraction technique was used to fractionate the major components of settling particulate matter in Lake 658 and the apparent association of Hg with these components. The components extracted by the KOH, HCl, and HNO_3 reagents are presented below in the Discussion section. The KOH extractant solubilized the largest fraction of Hg in all samples (Fig. 6), representing 48 to 85% of particulate Hg_{Amb} and 52 to 89% of particulate Hg_{Lake}. The KOH-extractable fraction was highest in the epilimnion and decreased with depth in the water column. The decreasing percentage of KOH-extractable Hg with depth indicates that association with components extracted by the HCl and HNO_3 reagents became more important in the anoxic hypolimnion. Importantly, differences between Hg_{Lake} and Hg_{Amb} were observed in their associations with the KOH-extractable fraction (Fig. 6). The percentage of KOH-extractable Hg was significantly ($p = 0.034$) greater for Hg_{Lake} than Hg_{Amb}, especially in the epilimnion.

4.6. Settling of particulate material and associated Hg

Settling particulate matter was collected using sediment traps. Here we show data for traps positioned at 7 and 13 m below the lake surface, just below the thermocline and near the sediment–water interface, respectively (Fig. 7). Measurements of Fe and Al in the trap material, shown as the Fe:Al ratio, were used to examine the influence of Fe(III) reduction in anoxic zones on settling of particulate Fe. The higher Fe:Al ratios in the 13 m traps are evidence of the "ferrous wheel" (Campbell and Torgersen, 1980; Chadwick et al., 2006), whereby Fe(III) is reduced in the anoxic zone, migrates upward to the oxycline, undergoes oxidation, and is re-deposited as Fe oxyhydroxide. Temporal variations were observed in the within-year patterns of Fe:Al ratios. In the 13 m traps, highest Fe:Al ratios were usually observed in mid- to late-summer periods of prolonged anoxia, in association with the release of Fe from anoxic bottom sediments (Fig. 2; Chadwick et al., 2006). In 2001 and 2003, Fe:Al ratios in 7 m traps increased with time, which is indicative of the transport of Fe from the hypolimnion into the lower epilimnion.

The 7 m and 13 m traps collected both Hg_{Lake} and Hg_{Amb}, shown as the Hg_{Lake}:Hg_{Amb} ratio data in Fig. 7. Hg_{Lake} was present in the 13 m sediment trap material six days after addition of the first spike, indicating rapid particle partitioning and transport near the sediment–water interface (Chadwick, 2006). The Hg_{Lake}:Hg_{Amb} ratio was usually higher in the 7 m trap and tended to increase with time (especially in 2001), which is consistent with the addition of Hg_{Lake} to the epilimnion and subsequent association with epilimnetic particulate matter. Temporal patterns varied among years. Occasional periods of relatively low Hg_{Lake}:Hg_{Amb} ratios in the 13 m traps during 2002 and 2003 occurred when Fe:Al ratios were high, indicating enhanced transport of Hg_{Amb} into the hypolimnion in association with Fe transport (dissolution) from anoxic sediments.

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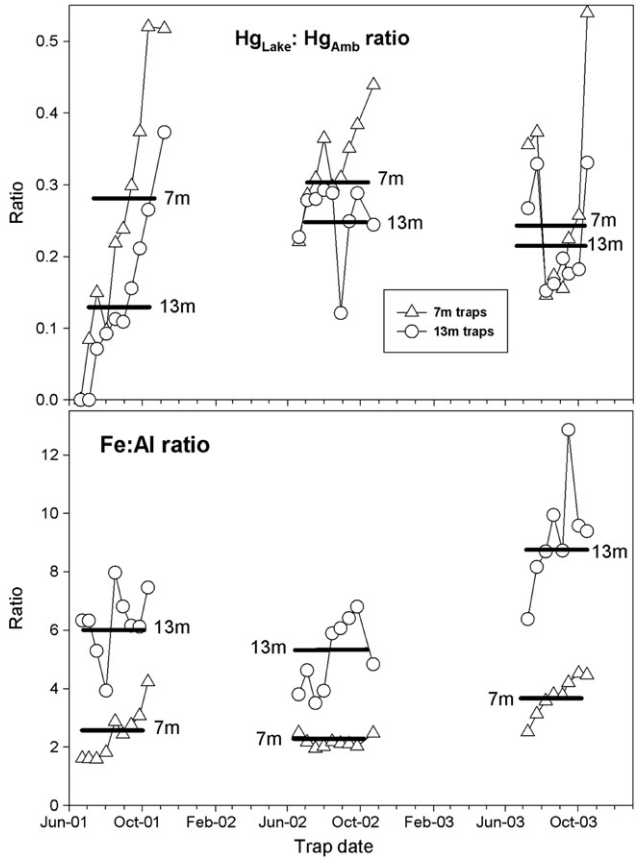


Fig. 7. Sediment trap particulate matter composition from shallow (7 m–base of thermocline) and deep (13 m–0.5 m above SWI) in Lake 658. The upper graph plots the Hg_{Lake}:Hg_{Amb} ratio of sedimenting particulates versus time. The lower graph shows the iron to aluminum ratios of the sedimenting particulate matter. Solid lines represent annual mass-weighted means.

5. Discussion

5.1. Probes of Hg partitioning behavior

We used several approaches to probe the properties of Hg_{Lake} and Hg_{Amb} in Lake 658. These measurements of partitioning and phase associations are based on experimental separations, which necessarily result in operational definitions of the phase associations of Hg. Here, we briefly discuss how we interpret the meaning of data collected with these techniques.

The Kd was used to probe the relative affinities of Hg for the aqueous and solid phases. The Kd is a distribution coefficient, based on measured concentrations of Hg in the aqueous (filterable) and solid (particulate) phases (see Eq. 1). In addition to phase affinity, other factors may influence the Kd, including slow partitioning kinetics, and the presence of Hg associated with colloidal or microparticulate matter in the filterable fraction. The Kd values tend to decrease as strong ligands (such as DOC) increase in concentration and draw Hg into the aqueous phase (Hurley et al., 1994; Babiarz et al., 1998; Benoit et al., 1999b; Chadwick, 2006).

Separations by diethylaminoethyl cellulose (DEAE) resins were used to probe differences between Hg_{Lake} and Hg_{Amb} in their association with ligands in the aqueous phase. Similar techniques have been used for other metals in natural water samples (Wang and Benoit, 1996; Taillefert and Gaillard, 1999). We applied this approach to filtered water samples from Lake 658. Measurements were made of the amounts of Hg passing through (permeate) and retained (retentate) by the DEAE column. The resin carries a positive charge and, in principle, neutral and positively-charged complexes of Hg pass through the column, while negatively-charged complexes are retained (Chadwick, 2006). Because this approach for speciation is operational, we refer to the fractions as "retentate" and "permeate". Complexes of Hg with DOC should be present in the retentate because the major components of DOC carry a net negative charge, but other negative complexes could also be present in this fraction. Neutral complexes with sulfides, a dominant ligand for Hg in anoxic waters, should be found in the permeate fraction, but other neutral or positive complexes could also be present in this fraction.

A sequential dissolution approach was used to probe differences between Hg_{Lake} and Hg_{Amb} in their associations with different components of the solid phases in suspended particulate matter. Extractants were chosen based on procedures used by other researchers. A five-step sequential extraction protocol (water, acetate/HCl (pH = 2), 1 M KOH, 12 M HNO_3, and aqua regia) had been developed to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils (Bloom et al., 2003). This method was verified qualitatively using X-ray absorption fine structure spectroscopy (Kim et al., 2003). Leaching of sediment with 1 M HCl has been found to solubilize trace metals associated with Fe and Mn hydrous oxides, amorphous Fe monosulfides, hydrous aluminosilicates, and carbonates (Huerta-Diaz and Morse, 1990, 1992; Hammerschmidt and Fitzgerald, 2004). Furthermore, a 1 M HCl extraction was found to have limited the ability to solubilize pure HgS (Mikac et al., 2000, 2002). We adopted a modified three-step procedure involving sequential extraction with 1 M KOH, 1 M HCl, and 12 M HNO_3. Based on the above investigations, 1 M KOH-extractable Hg, should represent organic matter-associated Hg. The 1 M HCl-extractable Hg fraction should represent a "reactive inorganic" Hg fraction, including Hg associated with Fe and Mn oxyhydroxides, amorphous monosulfides, aluminosilicates, and carbonates. The 12 M HNO_3-extractable Hg is an "inert" Hg fraction, not involved in biological or biogeochemical processes. Because the fractions are operationally-defined, we refer to them as KOH-extractable, HCl-extractable, and HNO_3-extractable Hg.

5.2. Aging of Hg in the lake system

The use of isotope-enriched Hg was a unique opportunity to evaluate the behavior of Hg added to Lake 658 as a simulation of direct atmospheric deposition. In the multi-purpose METAALACUS experiment, ^{202}Hg-enriched Hg (Hg_{Lake}) was added semi-continuously over the ice-free season (rather than a single "slug" dose). Thus, our strategy for evaluating the aging of Hg was to compare the forms and distribution of Hg_{Lake} and ambient Hg (Hg_{Amb}) as the Hg moved from the epilimnion to the hypolimnion and sediment–water interface. We did not focus on changes with time because that type of analysis is more appropriate for a slug-dose experiment. We expected aging to be reflected by differences between Hg_{Lake} and Hg_{Amb} in partitioning behavior. Initially, Hg_{Lake} might partition differently than Hg_{Amb}. However, with extended equilibration time and exposure to biogeochemical processes (aging), increasing similarities in partitioning behavior would be expected. As discussed below, several observations indicate that aging was sufficiently slow to allow observation of initial differences in the behavior of Hg_{Lake} and Hg_{Amb} in Lake 658.

5.2.1. Preferential partitioning of Hg_{Lake} to particulate matter

As compared to Hg_{Amb}, newly-added Hg_{Lake} partitioned preferentially, from the aqueous to the solid phases (filterable to particulate phases), especially in the epilimnion. This behavior is shown by the significantly higher Kd values for Hg_{Lake} than for Hg_{Amb} in oxic zones (Fig. 3; Table 1). The difference in Kd values was maintained over the three-year experiment, even though the Hg_{Lake} added in 2001 and 2002 had aged for one or two annual cycles by 2003. Similarly, during exposure of anoxic waters to oxygen in batch experiments and concurrent formation of oxyhydroxide Fe and Mn solid phases, removal of filterable Hg was more rapid for Hg_{Lake} than for

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Hg_{Amb} (Fig. 5). The preferential association of Hg_{Lake} with particulate matter is important for two reasons: First, Hg_{Lake} exhibits a greater affinity than Hg_{Amb} for binding sites on the surfaces of lake particles — which could be indicative of greater association with aquatic biota (bioavailability). Second, the higher Kd values could lead to preferential scavenging of Hg_{Lake} by particulate matter, thereby enhancing transport from the epilimnion by the settling of particulate matter.

The preferential binding of Hg_{Lake} to particulate matter may be due to kinetically-controlled differences between Hg_{Lake} and Hg_{Amb} in their associations with aqueous phase (filterable) ligands, such as DOC, which tends to lower Kd values (Babiarz et al., 2003b; Hurley et al., 1994). DEAE fractionation of filterable Hg in 2003 showed that epilimnetic Hg_{Lake} was almost entirely associated with the retentate fraction in June, shortly after the first-of-the-year addition of Hg_{Lake}, while Hg_{Amb} was partly associated with the permeate (neutral species) fraction (Fig. 4). Association of Hg_{Lake} with the permeate fraction increased with depth (anoxic zones) and time (August sampling). The greater degree of association with permeate ligands may account for the lower Kd values for Hg_{Amb} in the June epilimnion. As association of Hg_{Lake} with permeate-fraction ligands increased, the Kd values for Hg_{Lake} decreased, becoming more similar to the values for Hg_{Amb}. Slow kinetics for binding to the permeate ligands could account for the lower importance of permeate fraction for Hg_{Lake}, leading to a lower proportion of Hg_{Lake} in the filterable fraction and thus higher Kd values for Hg_{Lake} in the epilimnion. As discussed above, the permeate ligands may include neutral sulfide species, produced in anoxic (hypolimnetic) zones. The retentate fraction should contain negatively-charged DOC species.

Although DOM was the apparent predominant ligand controlling the speciation of Hg in the filterable phase, the decrease in the percent retained by DEAE suggests that sulfide complexes contributed to Hg speciation in the anoxic zone. However, the calculated speciation in the anoxic hypolimnion indicates that approximately 70–80% should be present as the neutral $Hg(SH)_2^0$ complex and appear in the permeate. While the fraction in the permeate was higher in anoxic samples, the fraction in the retentate (likely as DOM complexes) remained predominant. This observation supports the hypothesis that Hg and other trace metals are not in equilibrium with sulfide (Morse and Luther, 1999; Hammerschmidt et al., 2004). It further supports the hypothesis that DOM competes with sulfide in anoxic environments despite previous thermodynamic predictions (Ravichandran et al., 1998a,b; Waples et al., 2005). Similar results were observed by Clarisse et al. (2009) in Lake 658 for methyl-Hg complexes as measured using a diffusive gradient thin-film technique. This lack of thermodynamic equilibrium may contribute to the aging process.

The percent of Hg in the retentate (Fig. 4) over the water column ranged about 2 to 20% lower for Hg_{Amb} than for Hg_{Lake}, possibly indicating more extensive sulfide complexation of Hg_{Amb}. Previous research has suggested that sulfide complexes can persist in oxic waters (Wolfenden et al., 2005; Luther and Rickard, 2005). If neutral sulfide complexes dominate the DEAE permeate speciation of Hg in the oxic and anoxic portions of the water column, these results may reflect aging. This is because Hg_{Amb} has been in the system longer, and the time required for Hg sulfide complexes to diffuse from the anoxic hypolimnion is relatively long. This potential difference in speciation may explain the enhanced reactivity of Hg_{Lake} relative to Hg_{Amb} because Hg_{Lake} may be initially coordinated to weaker binding sites on DOM or physically positioned on the DOM to make it more available for exchange. Furthermore, the greater importance of sulfide species for Hg_{Amb} supports the hypothesis that sulfide may serve as a sink for Hg in freshwater lakes (Wolfenden et al., 2005).

5.2.2. Rapid delivery of Hg_{Lake} to the sediment–water interface

"New" Hg_{Lake} added to the epilimnion was found to be delivered rapidly to the hypolimnion and sediment–water interface (SWI). Transport to the hypolimnion is shown by several observations. First, after the initial addition of Hg_{Lake} to the epilimnion in June 2001, filterable Hg_{Lake} was observed in the hypolimnion within two weeks after the first amendment (Chadwick, 2006) and as evidenced in the profile from September 2001 (Fig. 2M). With further additions, the concentration and amount of filterable Hg_{Lake} in the hypolimnion increased (Fig. 2M–O), especially in 2003 when there was significant hypolimnetic buildup (see also Chadwick et al., 2006). Secondly, the profiles for DEAE-fractionated Hg in the filtered phase show higher concentrations of both Hg_{Lake} and Hg_{Amb} in the hypolimnion than in the epilimnion (Fig. 4). Third, sediment traps positioned at 7 m and 13 m collected both Hg_{Lake} and Hg_{Amb} (Fig. 7). Hg_{Lake} was observed in the sediment trap material 6 days after the first amendment indicating rapid particle partitioning and transport to the SWI (Chadwick, 2006). In 2001, the Hg_{Lake}:Hg_{Amb} ratio increased with time, reflecting the continued additions of Hg_{Lake} to the epilimnion over the summer. Finally, the batch experiment showed that Fe and Mn oxyhydroxides formed at the oxic–anoxic interface would preferentially remove filterable Hg_{Lake}, enhancing retention in the anoxic zone (Fig. 5). Overall, these results are consistent with a pattern of preferential binding of Hg_{Lake} to biogenic particulate matter in the epilimnion and removal to the hypolimnion with settling particulate matter.

5.2.3. Rapid delivery of Hg_{Lake} to zones of methylation

The preferential partitioning of Hg_{Lake} to biogenic particulate matter in the epilimnion (Fig. 3) and subsequent transport to the hypolimnion by particle settling (Fig. 7) may have led to enhanced methylation of Hg_{Lake} as compared to Hg_{Amb}. Methylation occurs in anoxic zones, often associated with biological sulfate reduction (Compeau and Bartha, 1985; Graham et al., 2012), and these conditions are found near the SWI. Thus, preferential transport of Hg_{Lake} to anoxic zones may contribute to the observations of enhanced methylation (see Chadwick et al., 2006, Fig. 8) and bioaccumulation (Harris et al., 2007) of Hg_{Lake} in Lake 658.

5.2.4. Redox processes enhance aging of Hg_{Lake}

The redox cycle, involving reduction–oxidation of Fe and Mn at anoxic–oxic boundaries, likely played an important role in the aging of Hg_{Lake} by aiding retention and biogeochemical cycling of Hg_{Lake} near the sediment–water interface. Aging is reflected in the increased similarities in the behaviors of Hg_{Lake} and Hg_{Amb} in anoxic zones. Although the Kd values for Hg_{Lake} were consistently and significantly different than Hg_{Amb} in the oxic portion of the water column, this difference decreased, and sometimes became insignificant following recycling in the anoxic hypolimnion (Fig. 3). Also, DEAE fractionation of filterable Hg showed greater similarities between Hg_{Lake} and Hg_{Amb} in anoxic waters, especially in late summer (Fig. 4). In addition, the increases in filterable Hg concentrations for both Hg_{Lake} and Hg_{Amb} near the sediment–water interface (Figs. 2 and 4) are indicative of the release of Hg from solid phases in anoxic zones.

Our results indicate that several biogeochemical processes contributed to the aging of Hg_{Lake} in anoxic zones. First, reductive dissolution of particulate Fe and Mn oxyhydroxides resulted in the release of reduced Fe and Mn and associated DOC and Hg into the aqueous phase (Fig. 2; Chadwick et al., 2006). Partial biological decomposition of biogenic particulate organic matter may have contributed to the release of Hg into the solution. The association of Hg with Fe oxyhydroxides likely results from binding of Hg to organic matter incorporated into the oxyhydroxide particles (Chadwick et al., 2006). After dissolution, the Hg and other solutes are transported toward the epilimnion, but upon reaching the anoxic–oxic zone boundary, the oxyhydroxide particles are re-formed, transporting particulate oxyhydroxides back toward the sediment–water interface, as illustrated in Fig. 1. The removal of Hg and DOC during formation of Fe oxyhydroxides is also demonstrated in Fig. 5. This association of Hg

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with the ferrous wheel (Campbell and Torgersen, 1980) and perhaps manganous wheel, plays an important role in extending the retention of Hg in anoxic zones, thereby enhancing aging. Mn cycling occurs higher in the water column than Fe due to the relatively slow oxidation rate and high redox potential for Mn. This results in complex oxidation–reduction "wheels" operating in different portions of the water column (Davison and Woof, 1984; Taillefert et al., 2000) that ultimately have a profound effect on Hg cycling (Chadwick, 2006).

The cycle of formation and dissolution of oxyhydroxides also allowed extended interaction of Hg with aqueous ligands (Fig. 4) and solid phases (Fig. 6). DEAE fractionation of the aqueous (filterable) phase indicated that negatively-charged complexes (retentate fraction) were dominant (Fig. 4). This fraction includes Hg associated with negatively-charged DOC. The permeate fraction, which includes neutral sulfide complexes, increased in importance in anoxic zones. The presence of sulfide complexes is consistent with the appearance of sulfide in anoxic zones (Table 2), which could occur either through sulfate reduction or sulfide release from anoxic bottom sediments (Chadwick et al., 2006). Fractionation of the solid phase by sequential extraction showed that the KOH-extractable fraction (attributed to association with organic matter) was the dominant fraction in the oxic zone, especially for Hg_{Lake} (Fig. 6). However, the HCl- and HNO_3-extractable fractions became more important in anoxic zones. The differences between oxic and anoxic zones could reflect the initial association of Hg_{Lake} with particulate biogenic organic matter after initial addition to the epilimnion, then partial movement to inorganic phases which are more important in the hypolimnion. Overall, the cycling between phases and species in association with redox-mediated processes is expected to "homogenize" Hg_{Lake} and Hg_{Amb}, thereby contributing to the aging of Hg_{Lake}.

6. Conclusions

"New" Hg_{Lake} and "old" Hg_{Amb} are influenced similarly by biogeochemical processes in Lake 658, including binding to particulate matter, transport from the epilimnion to the hypolimnion by particle sedimentation, and methylation in anoxic zones. However, after addition to the epilimnion by simulated direct atmospheric deposition, Hg_{Lake} initially exhibited greater particle affinity than Hg_{Amb}, as shown by higher Kd values for epilimnetic Hg_{Lake}. Upon transport to the hypolimnion, aging (through extended equilibration time and aided by redox-mediated processes), led to a more similar partitioning behavior of Hg_{Lake} and Hg_{Amb}. Aging appears to be sufficiently slow to allow enhanced methylation of Hg_{Lake}, as indicated by a higher fraction of methyl-Hg_{Lake} in the hypolimnion (Chadwick et al., 2006). Hypolimnetic buildup of methylmercury is important in the uptake of mercury into food webs (Slotton et al., 1995; Herrin et al., 1998). Our conclusions are consistent with the finding that recent amendments of Hg are more reactive towards methylation (Harris et al., 2007), volatilization (Amyot et al., 2004), and ligand-exchange (Hintelmann and Harris, 2004) than native Hg in aquatic ecosystems.

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