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A Field and Modeling Assessment of Methyl Mercury Accumulation in an Engineered Retention Pond

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A Field and Modeling Assessment of Methyl Mercury Accumulation in
an Engineered Retention Pond

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A Field and Modeling Assessment of Methyl Mercury Accumulation in
an Engineered Retention Pond

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Abstract

The accumulation of methyl mercury (MeHg) in lakes during summer stratification has been demonstrated to affect biotic mercury (Hg) accumulation. However, small, shallow polymictic lakes can experience short-term stratification and mixing events that are largely unstudied in their abilities to affect Hg cycling and MeHg accumulation. Short-term stratification events and changing lake characteristics impact lake biogeochemical cycles, and therefore, MeHg production and transport. A field and modeling analysis was performed on a small suburban lake located on the University of Connecticut campus to determine the impact of lake characteristics on the potential for MeHg accumulation. MeHg concentrations ranged from non-detect – 0.095 ng L⁻¹ in daily outlet samples and non-detect – 0.104 ng L⁻¹ for samples collected from the water column during stratified conditions during the summers of 2009 and 2010. Laboratory methylation investigations using lake sediments demonstrated a potential adjusted MeHg accumulation rate in the hypolimnion of 0.00155 ng L⁻¹ hr⁻¹, sufficient to produce accumulation in the lake given appropriate conditions. A modeling analysis was performed to evaluate the impact of lake condition parameters on MeHg accumulation. Stratification length did not impact MeHg accumulation; and while the input rate and demethylation rate affected the long-term steady state concentration, the key parameter for increasing hypolimnetic accumulation was increased submerged aquatic vegetation. This research indicates that small, shallow lakes have the capacity for MeHg accumulation and should be evaluated when determining MeHg transport and export in a watershed.

Key words: anoxia, hypolimnetic accumulation, lake characteristics, mercury, methyl mercury, polymictic

Introduction

Mercury (Hg) is a toxic, global contaminant that occurs in terrestrial and aquatic ecosystems from natural and anthropogenic sources, with over 6,600 tons of mercury emitted to the atmosphere annually in the form of elemental, gaseous ionic and particulate Hg (Mason and Sheu, 2002). Upon delivery to ecosystems, Hg can form methyl mercury (MeHg), a particularly toxic chemical species due to the negative health effects and the potential for bioaccumulation in food chains (e.g., Driscoll et al., 2007; Morel, 1998; Evers et al., 2007). Remote freshwater systems such as dimictic lakes and wetlands have been studied extensively to determine the rates and processes that control mercury methylation, transport, and bioaccumulation (e.g., Grigal et al., 2002; Selvendiran et al., 2008; Wollenburg and Peters, 2009). However, developed aquatic systems and the impacts of anthropogenic changes to biogeochemical (BGC) and hydrologic cycles remain under-investigated (Segal et al., 2011)

Methylation, the addition of a methyl group to an inorganic Hg species (Hg^{2+}) generally is accepted to be mediated by sulfate reducing bacteria (SRB; e.g., Fleming et al., 2005; Gilmour et al., 1992), but can also be carried out by iron-reducers (Fleming et al., 2006). The association with anoxic conditions and need for an organic carbon source results in the majority of methylation and MeHg accumulation in wetland areas (Branfireun et al., 1998), lake sediments (Drott et al., 2007) and at the sediment water interface of aquatic systems (Morel et al., 1998). Lake studies that have focused on long-term stratification in dimictic lakes have indicated that MeHg accumulates during summer stratification in the anoxic hypolimnion (Watras et al., 1995; Regnell et al., 1997). Accumulation of MeHg in the anoxic zone of a lake increases the flux of MeHg to the rest of the water column and the atmosphere through advection and diffusion when a mixing event occurs (Morel et al., 1998; Wollenburg and Peters

2009). Research on dimictic lakes has demonstrated that MeHg hypolimnion concentrations can become elevated from 0.5 pM in May to 2.5 pM in September while epilimnion concentrations remain constant at approximately 0.5 pM for a forested lake (Regnell et al., 1997) and 40 pM for a polluted urban lake (Todorova et al., 2009). However, the majority of research studies on MeHg cycling in lakes has been conducted on large, deep dimictic lakes, particularly in remote forested ecosystems while small, urbanized lake ecosystems remain under investigated (Watras et al., 1995; Wollenburg and Peters, 2009).

Altered hydrologic and biogeochemical (BGC) cycles in developed systems may influence Hg methylation and transport, necessitating an understanding of Hg storage and export to accurately assess the impacts of engineered ponds and lakes on Hg fate and transport (Regnell et al., 1997; Ullrich et al., 2001). Shallow retention ponds are a common mechanism for mitigating impervious surface runoff and protecting water quality (Casey et al., 2005). An estimated 2.6 million and counting small, artificial lakes across the continental United States exist (Smith et al., 2002). Though these ponds are individually small in size, the sheer quantity can have a significant impact on ecosystem BGC cycling (Torgersen, 2008). Retention ponds can remain mixed throughout all seasons though some can experience short-term water column stratification that is polymictic in nature due to high eutrophication, daily temperature variation, and/or weather conditions such as wind and precipitation (Torgersen, 2008; Wetzel et al., 2001). Daily stratification and mixing has been demonstrated to alter the temperature, pH and dissolved oxygen dynamics (Torgersen, 2008; Torgersen and Branco, 2007) with the length and intensity of stratification and the hypolimnion water temperature to the rate of decrease of hypolimnetic oxygen (Wilhelm and Adrian, 2008). Prior research on our study site, Mirror Lake, was conducted in 2008 and demonstrated that stratification events may be linked to

elevated MeHg concentrations in the hypolimnion of a small suburban retention pond (Segal et al., 2011). MeHg concentrations ranged from 1.4 to 2.9 ng L⁻¹ in the hypolimnion and from 0.05 – 0.5 ng L⁻¹ in the epilimnion during low flow events. However, due to the lack of continuous sampling through the study stratification length and the occurrence of anoxic events cannot be linked definitively to elevated MeHg concentrations. Yet, the effect of short-term anoxic periods, decreased retention time and polymictic conditions on MeHg production and cycling in small, shallow, eutrophic engineered ponds remains under-investigated but is critical for assessing the impact of engineered solutions on Hg fate and transport.

To investigate Hg cycling and potential for methylation in a suburban retention pond we conducted a field, laboratory and modeling investigation. The objectives of our study were to establish whether polymictic conditions increase the accumulation of MeHg in retention ponds and to determine the long-term consequence of this accumulation on outflow concentrations of Hg and MeHg. Diurnal and multi-day stratification events were examined to assess the impact of mixing conditions on Hg processes, particularly methylation potential. Samples were taken for Hg, MeHg and ancillary chemistry over baseflow and storm conditions in the water column and outlet during the summers of 2009 and 2010. Short- and long-term sampling strategies were implemented to evaluate the direct impact of stratification as well as overall implications for Hg species fate and transport. These were supplemented by sediment methylation experiments to quantify the MeHg accumulation rate for system. The long-term outlet concentrations also were utilized in a simple stratified lake model to assess the potential long-term impact on MeHg flux.

Background

Hg sources and watershed cycling

Hg inputs to the environment are expansive, due to the long range transport potential of Hg^0 and the differing contributions from natural and anthropogenic sources (Driscoll et al., 2007; Mason and Sheu, 2002). Natural sources of mercury to the environment include erosion from rocks and soils and discharge from hydrothermal water sources, while anthropogenic sources include electrical utilities, land use changes, incinerators, industrial manufacturing, and wastewater treatment (Morel et al., 1998). Atmospheric deposition from point sources dictates the majority of Hg contamination in urban areas, as Mason et al. (2000) demonstrates that there is elevated wet deposition of THg in downtown Baltimore ($30 \mu\text{g m}^{-2} \text{yr}^{-1}$) relative to rural sites ($\sim 15 \mu\text{g m}^{-2} \text{yr}^{-1}$). Forested systems that are undisturbed by anthropogenic point sources are still subject to atmospheric deposition of Hg, though these systems typically have mercury concentrations at non-toxic levels (Driscoll et al., 2007).

Watershed characteristics such as size, location, geography, land cover and land use play a significant role in determining the concentration of Hg and MeHg that is mobilized within a system (Grigal et al., 2002). Two important drivers for Hg mobilization in surface water systems are dissolved organic carbon (DOC) and binding to suspended solids (Mason et al., 1998; Hurley et al., 1995). Hg watershed transport mechanisms are particularly important during high flow events when increased watershed saturation leads to higher DOC export from soils and elevated flow conditions mobilize sediments (Segal et al., 2011), demonstrating why areas rich in DOC such as wetlands have a high export of MeHg relative to upland and urbanized areas (Porvari and Verta, 2003; Regnell et al., 1997). Watershed characteristics

typically dominate Hg flux during storm events from forested ecosystems due to the necessity of wetlands and high DOC for enhanced Hg flux, as Hg mobility is positively correlated with DOC in forested ecosystems (St. Louis et al., 2004), where in urbanized areas particulate sorption dominates Hg storm flux (Mason and Sullivan, 1998). Urban THg yields (stream outlet flux relative to total atmospheric input) of 40-103% (Lawson et al., 2001; Mason and Sullivan, 1998) are higher than the 10-30% estimated for forested watersheds (Hurley et al., 1995; Mason et al., 1997), reflecting the enhanced susceptibility of developed watersheds to runoff.

MeHg lake cycling

MeHg transport to and cycling within an aquatic system is complex and subject to a variety of transport processes. MeHg can enter a water system through runoff from wetlands, atmospheric deposition and in-situ production (Mason et al., 2006; Rudd, 1995). Once MeHg enters a water system it can be transported within or removed from a water column or a combination of the two processes. Transport to a water system is due to DOC complexation, particle sorption and resuspension and the degradation of biota while removal processes include particle settling, biotic uptake and demethylation.

Atmospheric deposition:

Though the majority of Hg in the atmosphere is in the form of Hg⁰ (<95%) (Driscoll et al., 2007), atmospheric deposition can also be a small source of MeHg to an aquatic system, generally in the form of litterfall as MeHg can accumulate on leaves, twigs and needles. The origin of MeHg on litterfall is unknown, and though it is most likely atmospheric in origin it can also be produced on the leaves (Rudd, 1995). However, the majority of lake systems do not

have a large input of litterfall due the fact that wind patterns would have to carry litterfall into a lake system.

Wetland runoff

Wetlands are classified as areas where the underlying soil is permanently saturated with water, which allow for high MeHg production due to prevalence of anoxia and reducing conditions. Wetlands can export high concentrations of MeHg to downstream aquatic systems, acting as a point source pollutant (Branfireun et al., 1996; Rudd, 1995). The concentration of MeHg that is export from wetlands depends on many factors, including the season and amount of precipitation (Rudd, 1995). MeHg is formed in wetlands due to high periods of anoxia and large amounts microbial activity, which indicates that the summer season produces the most MeHg (Selvendiran et al., 2008). The quantity of precipitation determines the amount of MeHg that is transported from wetlands into an aquatic system (Rudd, 1995). Summer season with extended drought periods and dry stream flow have almost half of the MeHg export from wetlands than a summer season with a continuous stream flow (Rudd, 1995).

In lake methylation

Hg methylation the most common way MeHg can be formed in an aquatic environment (Holmes and Lean, 2006). Mercury methylation is the addition of a methyl group to an inorganic Hg species (Hg^{2+}) (Gilmour and Henry, 1992). Microbial mediated methylation and abiotic methylation are possible in freshwater systems, but the total abiotic methylation is up to one order of magnitude lower than microbial methylation (Berman and Bartha, 1986). Anaerobic sulfate reducing microbes are the primary methylators in freshwater systems and

they mediate mercury methylation when sulfate is reduced to sulfide (Gilmour and Henry, 1992). Methylation typically takes place in lake sediment and at the sediment water interface where anoxia is common due to the lack of light penetration in sediments. Other microbes, such as iron reducers can methylate mercury but have a small impact on the net MeHg concentration in comparison to sulfate reducing bacteria (Fleming et al., 2006).

DOC complexation

DOC (dissolved organic carbon) can affect the transport and bioavailability of MeHg in an aquatic system (Porvari and Verta, 2003). DOC is generally comprised of decaying biotic material from plants and algae. MeHg forms strong complexes with DOC in oxic and anoxic waters when DOC concentrations are not limiting (Porvari and Verta, 2003). This strong complexation hinders MeHg bioavailability to other organisms, as the availability of MeHg to biota decreases with increasing DOC concentrations (Gorski et al., 2008). Low concentrations of DOC have variable consequences in the bioaccumulation of MeHg, where DOC can enhance MeHg uptake or have no effect (Gorski et al., 2008). Concentrations of MeHg increase with concentrations of DOC in water, which indicates that DOC facilitates transport of MeHg within a lake system and from other watersheds, such as a wetland, to a lake system (Porvari and Verta, 2003). Methylation of Hg(II) to MeHg is facilitated by DOC, as it acts as a substrate to methylating bacteria. However, DOC can also inhibit methylation due to the high binding potential of DOC-Hg^{II} (Miskimmin et al., 1992).

Particle settling and resuspension

Particle settling is an important removal process of MeHg from the water column. MeHg can sorb on to particles and complex with DOC (Gorski et al., 2008). The density and size of the particle as well as water column characteristics will determine the particle's settling velocity from the water column to the sediments (Gulliver, 2007). Settling of MeHg bound particles is considered a removal process from the water column, though particles can become resuspended into the water column. Mesocosm experiments have determined that sediment resuspension is not a significant source of MeHg to the water column (Mason et al., 2006), which would indicate that sediment resuspension is not contributing to high MeHg outflux in lake systems; though high flow events were not examined and can contribute to outflux of MeHg (Segal et al., 2011).

Biotic uptake and degradation

The bioaccumulate nature of MeHg is due to its high solubility in lipids and tendency to bind to thiol groups attached to proteins. Bioconcentration (BCF) factors from 10^4 to 10^7 have been reported in aquatic biota, where:

$$BCF = \frac{C_A}{C_W}$$

C_A = Concentration of MeHg in biota

C_W = Concentration of Hg in water

Bioaccumulative MeHg concentrations in fish are not determined by the concentration of MeHg in the surrounding water, but rather the concentration of MeHg in the base of the food web, such as phytoplankton and algae (Mason et al., 1995). Increasing the concentration of phytoplankton can effectively decrease the concentration of MeHg transported to zooplankton

due to bloom dilution, which indicates that the bioaccumulative nature of MeHg is affected by more than the concentration of MeHg present in the water system (Pickhardt et al., 2002).

Degradation of biotic material will re-release previously bound MeHg to the water column, as seen in Segal et al., 2011 after a Cu algaecide application.

Biotic and photolytic demethylation

Biotic and photolytic demethylation are two mechanisms of removal of MeHg from the water column and sediments (Ullrich et al., 2001). Biotic demethylation is the most common form of demethylation and dominates MeHg removal in the sediments (Robinson and Tuovinen, 1984). Biotic demethylation can be mediated by abiotic and aerobic organisms, though the majority of demethylation is mediated by aerobic organisms (Ullrich et al., 2001). Photolytic demethylation is another mechanism of removal of MeHg from a water system and is linearly related to photosynthetically active radiation (PAR) (Hammerschmidt and Fitzgerald, 2006; Sellers et al., 1996), with a high radiation indicating a high demethylation rate. Though photolytic demethylation is dominant in freshwaters where there is high light penetration (Sellers et al., 1996), the end products of MeHg photolytic degradation have not been identified.

Site description

Mirror Lake is a small retention pond (20,500 m²) located on the University of Connecticut Storrs campus with an approximate volume of 14,640 m³ and a maximum depth of 1.5 m (Torgersen, 2008). The drainage basin of Mirror Lake encompasses rooftops, pavements, roads and small grassy areas, reflecting the developed land cover of campus. Six stormwater

drains input water into Mirror Lake while the outflow of the pond is discharged over a single concrete weir to form a small stream. The average residence time of water in non-storm events is approximately 10 days with an outflow of $1 \text{ m}^3 \text{ min}^{-1}$; but, in storm events the flow over the weir increases and the residence time of the lake can decrease to less than one day. Mirror Lake is eutrophic (Segal et al., 2011) and has high turbidity and light extinction coefficients of 1 m^{-1} to 5 m^{-1} (Torgersen, 2008, Torgersen and Branco, 2007). Although relatively shallow, Mirror Lake undergoes a diel stratification cycle with vertical temperature gradients of up to 8°C m^{-1} due to increases in air temperatures from May to September (Torgersen and Branco, 2007). This thermal stratification inhibits vertical mixing during the daytime. Decreasing temperatures at night allow for vertical convective mixing and a vertical redistribution of heat. However, in the summer months, nighttime air temperatures do not always decrease which prevents surface cooling and results in vertical stratification periods that persist for many days (Segal et al., 2011; Torgersen, 2008; Torgersen and Branco, 2007).

Oxygen and carbon fluxes from the pond indicate a significant microbial community influence that typically releases CO_2 to the atmosphere but can also release O_2 for extended periods of time (Torgersen and Branco, 2007). Previous research has indicated that Mirror Lake's microbial community does not always follow the traditional Redfield photosynthesis/respiration reaction ratio and O_2 and CO_2 dynamics can vary from very short (daily) to much longer (seasonally) time scales (Torgersen and Branco, 2008). During time periods where Mirror Lake stratifies and mixes on a daily cycle, the entire water column may have decreased DO in the nighttime due to microbial respiration. Prolonged stratification periods will allow anoxic conditions to develop in select stratified layers at night due to the lack of O_2 inputs from surface waters and microbial respiration.

Further influencing the mixing and oxygen conditions is the eutrophic nature of the pond. Mirror Lake is characterized by excessive algal and submerged aquatic vegetation (SAV) growth and a very turbid water column (Torgersen, 2008; Torgersen and Branco, 2007). Such dominance of cyanobacteria (blue green algae) is common in eutrophic water systems (Smith et al., 1999). Before 2009, SAV had formed a deep mat of biotic material on the sediments and exacerbated stratification (Segal et al., 2011). However, during our two-year study SAV was minimal likely due to suction harvesting in August 2008 and 2009. Additional management of the lake includes copper algaecide applications approximately three times per summer season for algal growth.

Methods

A field, laboratory and modeling investigation was completed to assess the potential influence of polymixis and water chemical conditions on MeHg cycling in a suburban retention pond. Field samples were collected under mixed, stratified, and storm conditions in Mirror Lake during the summers of 2009 and 2010. Sampling to assess the potential for daily short term variability was conducted in the water column and from the outlet of the weir whereas long-term variability and storm conditions were assessed through collection of samples from only the outlet. Discharge from the lake was calculated in August 2010 from water level measurements collected using a pressure transducer (Solinst; Georgetown, ON) deployed at the weir. Weather data including air temperature, solar radiation and wind speed were obtained from a weather station located approximately 2 km from the lake. Real-time measurements were collected hourly for temperature, DO, specific conductivity and pH via an in-situ profiler system, BORIS

(Branco et al., 2005), to provide an accurate description of water column conditions. BORIS operates by drawing water sequentially through sets of horizontal plates at heights of 20, 45, 80 and 100 cm above the sediments and pumping the samples through a flow cell that is connected to an YSI 6200 Sonde (YSI; Yellow Springs, OH; Branco et al., 2005). During 2009, water column data for temperature, DO, specific conductivity and pH is available for the stratified sampling as well as select outlet sampling periods. However, only temperature data is available from the summer of 2010 due to complications with the remaining BORIS probes.

Water column samples were collected with a separate apparatus in Mirror Lake deployed less than 10 m from BORIS by pumping lake water through sets of plates placed at 15 and 55cm above the sediments and connected to the surface via Teflon tubing. A third grab sample was collected from the water surface (approximately 110 cm above the sediments). Sets of water column samples were taken 2-4 times per day from 7:00 to 19:00 DST from 03 – 07 August 2009 and 22 – 26 July 2010. Sampling dates were chosen to represent the lake during stratified conditions which typically occur during hot, dry weather. Daylight sampling from 7:00-19:00 DST allowed the capture of possible water chemistry fluctuations that may occur from the daytime increase in thermal stratification due to rising air temperatures.

Outlet samples were collected approximately 5 meters downstream from the weir in the morning when the lake was most likely to experience mixed conditions so the outlet sample could be assumed to represent the chemistry of Mirror Lake. Outlet samples were collected daily to weekly from June to October in 2009 and daily from June to August in 2010. Additionally, seven outlet samples were collected across the hydrograph of a small storm that deposited 2.85 inches of rainfall from 30 September – 01 October 2010. Hydrograph outlet

samples represent a well-mixed, low residence time situation with contributions from impervious surface runoff and overland flow.

Lake water column samples were pumped into acid-washed glass bottles and then transferred into Teflon or borosilicate glass containers using trace clean techniques for Hg species and LDPE for ancillary chemistry. All mercury samples were collected according to trace-clean protocols (Method 1669; EPA 1996) and were frozen in the dark until processing. Once thawed, samples were processed within one week. Half of each sample was filtered through a 0.45 μm PES filter (Millipore; Billerica, MA) prior to acidification with 0.4% trace metal-grade HCl (v/v). Acidified samples were stored at 4°C until analysis. After collection, ancillary samples were stored in the dark at 4°C until filtration and analysis.

Methylation rate

MeHg accumulation experiments were performed to determine a MeHg net accumulation rate specific to Mirror Lake sediment and water chemistry. A series of sediment mesocosms were prepared using processed sediment and lake water collected from Mirror Lake. Sediment was collected on 17 May 2011 using a box dredge, sieved (1 mm), and allowed to settle in the dark at 4°C for two weeks. Standing water was siphoned from the collected sediment regularly until the majority of standing water was eliminated. Grab samples of lake water were collected from the surface of Mirror Lake on 27 May 2011, filtered (0.45 μm PES) and frozen. Lake water was defrosted on 30 May 2011 and bubbled with N_2 (g) less than 2 hrs in advance of mesocosm preparation to remove oxygen and promote the development of anoxic conditions in the sediment. Mesocosm samples were prepared by adding 50 mL of collected wet sediment and 200 mL of filtered lake water to 250-mL borosilicate bottles with Teflon lined

caps. MeHg accumulation samples (3 replicates for each time point) were spiked with 5 ng L^{-1} HgCl_2 . Two sets of control samples were prepared; a sterile control spiked with 0.1% sodium azide (m/v) used to assess molecular diffusion of MeHg from the sediments and a natural production control that was prepared without a Hg spike. Following preparation, the samples and headspace were purged with $\text{N}_2(\text{g})$ and all samples ($n = 29$) were incubated in the dark at 27°C . Three MeHg accumulation replicates and the sterile control were sampled at 0, 12, 24, 48, 120 and 288 hrs, while three replicates of the non-spike control were collected at 120 and 288 hrs. After removal from the incubator 100 ml of liquid was decanted into vials and centrifuged for 15 minutes at 2000 rpm to remove remaining sediment. The supernatant was decanted, acidified with 0.4% HCl (v/v) and stored at 4°C in the dark until MeHg analysis.

Analytical techniques

Samples were analyzed for DOC (2010), anions (NO_3^- , PO_4^{3-} , Cl^- , SO_4^{2-}), Hg species (THg, THgD, MeHg) and TSS. DOC was analyzed via persulfate-UV oxidation with an Apollo 9000 TOC combustion analyzer (Teledyne Tekmar Company, Mason, OH), with anions (NO_3^- , PO_4^{3-} , Cl^- , SO_4^{2-}) analyzed via ion chromatography (IC) according to Method 9056A for the determination of inorganic anions by ion chromatography (EPA 2007). Unfiltered (THg) and dissolved (THgD) total Hg were analyzed via oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry (CVAFS) as detailed in EPA Method 1631 Revision E (EPA, 2002). MeHg was analyzed by distillation, ethylation, purge and trap, desorption, and CVAFS according to EPA Method 1630 (EPA, 2001). Quality assurance was assessed via continuous calibration verification ($\pm 10\%$) and a 10% rate for lab duplicates, field duplicates and matrix spikes. Recovery of spikes was $\pm 10\%$ for DOC, IC and THg and $\pm 20\%$ for MeHg. The

detection and quantification limits for THg and MeHg are 0.2 ng L^{-1} and 0.02 ng L^{-1} , respectively.

Model development

A model was developed to further evaluate processes affecting MeHg concentration in Mirror Lake. MeHg lake cycling is complex, as many mass transfer processes affect MeHg cycling. Potential inputs include in situ MeHg production, particle resuspension, neighboring wetlands, atmospheric deposition, and biotic degradation. Potential removal processes include abiotic and biotic demethylation, volatilization, biotic uptake, particle settling and flushing (Driscoll et al., 2007; Grigal, 2002). The processes to include in the model were determined by evaluating the relative importance of each relative to MeHg in our particular lake system. In situ production was assumed to be the dominant input given a lack of particle resuspension during dry flow (Mason et al., 2006), the lack of watershed wetland area, relatively low MeHg precipitation inputs (1%; Knight, 2008), and the minimal biomass existing in Mirror Lake during 2009 and 2010 due to an active lake treatment including suction harvesting initiated in 2008. Abiotic demethylation and flushing were assumed to control removal given that volatilization of MeHg is over 1000 times lower than that of Hg^0 (Knights, 2008), the low measured TSS in Mirror Lake during dry conditions, and the minimal biomass present during the study.

A simplified two-compartment model was constructed from Schwarzenbach et al. (2003) to describe MeHg concentration changes in the epilimnion (Equation 1) and hypolimnion (Equation 2) over time for a stratified lake (Schwarzenbach et al., 2003). The pair of coupled, first-order linear differential equations were solved using matrix techniques to

evaluate the potential for MeHg accumulation in the lake with time given specific water chemical, mixing and photolytic conditions (Schwarzenbach et al., 2003). Model assumptions included that the system in question was a two compartment system, the flushing rate does not deplete V_E , the accumulation of MeHg is not prohibited by V_H and MeHg accumulation only occurs if the hypolimnion is anoxic.

$$\frac{dC_1}{dt} = J_1 - (k_F + k_{DE} + k_{exE})C_1 + k_{exE}C_2 \quad (1)$$

$$\frac{dC_2}{dt} = J_2 + k_{exH}C_1 - (k_{DH} + k_{exH})C_2 \quad (2)$$

where:

- C_1 = concentration of MeHg in the epilimnion [ng m^{-3}]
- C_2 = concentration of MeHg in the hypolimnion [ng m^{-3}]
- J_1 = MeHg input to the epilimnion from the watershed [$\text{ng m}^{-3} \text{ s}^{-1}$]
- J_2 = accumulation of MeHg in the hypolimnion [$\text{ng m}^{-3} \text{ s}^{-1}$]
- k_F = flushing rate of the epilimnion [s^{-1}]
- k_{DE} = demethylation rate in the epilimnion [s^{-1}]
- k_{DH} = demethylation rate in the hypolimnion [s^{-1}]
- k_{exE} = exchange rate from the epilimnion to the hypolimnion [s^{-1}]
- k_{exH} = exchange rate from the hypolimnion to the epilimnion [s^{-1}]
- t = time [s^{-1}]

The model differential equations include two MeHg net flux terms into the system, J_1 and J_2 . J_2 represents MeHg accumulation assumed to occur in the sediments and at the sediment-water interface and is included as an input function into the hypolimnion. J_2 was estimated via laboratory methylation experiments with Mirror Lake sediments and scaled to the Mirror Lake water column. Although expected to be relatively minor, input to the epilimnion due to watershed atmospheric deposition (J_1) was assumed to be constant throughout the modeling and was estimated initially as per Knights et al. (2008) according to watershed surface composition.

Demethylation in the epilimnion was assumed to be photolytic due to the shallow average depth of the lake (1 m), the high visibility in the water column throughout the sampling events, and the dominance of photolytic demethylation in epilimnetic freshwaters (Branfireun et al., 1998; Sellers et al., 1996). Biotic demethylation in the sediments was incorporated in the generation term, J_2 , as conditions in the laboratory mesocosms represented a net accumulation rate. Abiotic demethylation in the hypolimnion and epilimnion was estimated by first converting surface solar radiation data to the solar radiation in the epilimnion and hypolimnion (Equation 3; Hondzo et al., 1991) using an attenuation coefficient typical of eutrophic lakes (2.5 m^{-1} ; Knightes, 2008). Solar radiation at the surface (s) of Mirror Lake is related to the solar radiation at depth (z).

$$H_{sol(z)} = H_{sol(s)} e^{-\eta(s-z)} \quad (3)$$

where:

$H_{sol(z)}$ = solar radiation at depth z [$\text{cal s}^{-1} \text{m}^{-2}$]

$H_{sol(s)}$ = solar radiation at the surface [$\text{cal s}^{-1} \text{m}^{-2}$]

η = attenuation coefficient [m^{-1}]

s = height of surface of water from the sediments [m]

z = height of depth z from the sediments [m]

Solar radiation at the depth of the epilimnion and hypolimnion was converted from $\text{cal s}^{-1} \text{m}^{-2}$ to W m^{-2} and then to PAR units; $\text{E m}^{-2} \text{s}^{-1}$ using an experimentally determined conversion factor ($2.02 \text{ } \mu\text{mol photons m}^{-2} \text{s}^{-1}$ of PAR = 1 W m^{-2} of global radiation; Mavi and Tupper, 2004), where $1 \text{ E} = 1 \text{ mol photons}$ (Hammerschmidt and Fitzgerald, 2006). Solar radiation data from the hypolimnion ($6.6 \text{ E m}^{-2} \text{d}^{-1}$) and epilimnion ($37.5 \text{ E m}^{-2} \text{d}^{-1}$) were used to scale an experimentally determined rate constant calculated by Hammerschmidt and Fitzgerald (2006), $2.6\text{E}^{-3} \text{ m}^2 \text{E}^{-1}$. The epilimnion photolytic demethylation is rate constant was calculated to be $1.12\text{E}^{-6} \text{ s}^{-1}$, while the hypolimnion is $2.0\text{E}^{-7} \text{ s}^{-1}$ (Hammerschmidt and Fitzgerald, 2006).

The flushing rate (k_F) was estimated using Equation (4) and represented the reciprocal of the lake retention time. We assumed that the outflow only depletes the epilimnion volume due to the high vertical height of the outflow weir (100 cm above the sediments). Previous research (Torgersen and Branco 2008; 2007) determined a dry period outflow of 0.0166 m³/s. The volume of the epilimnion was assumed to be constant (13309 m³) given the focus on dry conditions.

$$k_F = Q/V_E \quad (4)$$

where:

$$Q = \text{outflow [m}^3/\text{s]}$$

$$V_E = \text{volume of epilimnion [m}^3\text{]}$$

Vertical exchange rates between the epilimnion and hypolimnion were determined from Mirror Lake temperature profiles. Thermocline depth in the model and in the eddy diffusion calculations was assumed to be between 20 cm – 45 cm (height above the sediments) with the eddy diffusivity calculated at 32.5 cm. The vertical exchange rate was calculated by relating the vertical velocity of exchange to the compartment volume (Equation 5; Schwarzenbach et al., 2003).

$$k_{exi} = v_{ex}A_{th}/V_i \quad (5)$$

where:

$$k_{exi} = \text{the vertical exchange rate of layer } i \text{ [s}^{-1}\text{]}$$

$$V_i = \text{the volume of layer } i \text{ [m}^3\text{]}$$

$$A_{th} = \text{the surface area of the thermocline [m}^2\text{]}$$

$$v_{ex} = \text{the exchange velocity [m s}^{-1}\text{]}$$

The vertical exchange velocity, v_{ex} , is related to the thickness of the thermocline and the eddy diffusivity through the thermocline (Equation 6; Schwarzenbach et al., 2003).

$$v_{ex} = E_{th} / \delta_{th} \quad (6)$$

where:

E_{th} = turbulent diffusivity over the thermocline [$\text{m}^2 \text{s}^{-1}$]

δ_{th} = vertical thickness of the thermocline [m]

Turbulent diffusivity (E_{th}), also known as eddy diffusion, is caused by shear forces within a water system that result in turbulent eddies (Gulliver et al 2007). Eddy diffusion coefficients can be difficult to estimate due to the 3-D nature of the diffusion field (Hondzo et al., 1991); though simplistic estimations of eddy diffusion can be made by substituting E_{th} in Fick's first law for the molecular diffusion coefficient. The concentration gradient can be represented through temperature differences that correspond to a density gradient within a lake (Benoit and Hemond., 1996; Hondzo et al., 1991; Jassby and Powell et al., 1975). An eddy diffusion coefficient was estimated from the discretized equation in Hondzo et al. (1991; Supplemental Information).

Small disruptions in the stratification are implicitly accounted for in the estimation of E_{th} as unlike Hondzo et al. (1991), eddy diffusion coefficients were estimated over 6-minute time intervals and averaged hourly instead of multi-day averaging. The sediment heat flux term H_{sed} was not considered due to a lack of data on sediment temperature, which may lead to errors in the energy budget on which the estimation of E_{th} is based.

The base model condition represented a 5-day period for Summer 2010 during which water temperature, solar radiation and water chemical data were collected. The objective modeling the base conditions was to examine the ability of the model to predict lake MeHg concentrations. As methylation in the sediments was assumed to occur only if the hypolimnion were anoxic, J_2 was set to zero for the entire 5-day base condition simulation of Mirror Lake

conditions and significant accumulation of MeHg was not expected. While the lake stratified during the day, algal photosynthesis maintained a high oxygen content in the hypolimnion and mixing at night replenished oxygen from the epilimnion to prevent the development of anoxic conditions. Additional simulations were performed to assess the potential for MeHg accumulation in the hypolimnion during 1-night, 4-night and 29-night stratified anoxic periods. In these simulations, the lake was assumed to remain stratified at night leading to the development of anoxic conditions that favor MeHg accumulation. During the 1-night, 4-night and 29-night simulations E_{th} , J_1 , J_2 , k_{DE} and k_{DH} were adjusted to reflect the changing lake conditions (Table 1).

Results and Discussion

Lake conditions

Temperature data collected using BORIS from 01 July 2009 to 29 August 2009 and from 15 July 2010 to 10 August 2010 (Figure 1) were used to assess the occurrence and strength of stratification present in Mirror Lake. Knowledge on stratification location and stability is limited by thermistor quantity and placement; therefore thermal stratification may be more complex than described in this study. Diel stratification and mixing events occurred except during select rain events, high wind events and air temperature cooling. Occasionally, thermal stratification extended over several days in select layers while other layers mixed nightly. Extended stratification events where at least one layer was permanently stratified occurred three times in 2009 with a maximum stratification length of three days and four times in 2010 with a

maximum of five days (Figure 1). Precipitation events of 1.78 cm on 23 July 2010 (12:20 – 21:00) and 0.56 cm on 19 July 2010 (11:30 – 13:30) mixed the lake where an event of 2.24 cm on 24 July 2010 (15:00 - 15:30) did not induce mixing which indicates that thermal mixing is dependent on total precipitation, the length of the precipitation event and the pre-event water temperature (Figure 1).

DO in 2009 generally reaches a maximum of 11 mg L^{-1} in the late afternoon in the 100-cm layer due to photosynthetic activity and a minimum of $0\text{-}5 \text{ mg L}^{-1}$ at night in the 20 cm layer due to microbial respiration. During nighttime mixing events, DO concentrations are constant throughout the lake. Stratification events that persist for more than one day experience a stratified DO pattern with a decrease in nighttime DO concentration in the stratified layers (80, 55, 45 and 20 cm above the sediments) the longer thermal stratification persists (Figure 2). DO concentrations follow a pattern similar to temperature stratification, typically with the lowest DO concentration in the 20-cm layer and the highest DO concentration in the surface layer. The exception was elevated DO present in the 20, 45 and 80 cm layer in 2009 after a suction harvest event due to disturbance of the sediment layer (data not shown). Unfortunately, difficulty with the DO sensors prevented the collection of DO data during 2010. We assumed that the DO cycle was similar to the temperature cycle from May to October in 2010 relative to 2009 trends. Temperature data from both years suggests that Mirror Lake has a polymictic cycle in the summer months with DO data and visual observations of algal blooms indicating a microbial influence in redox conditions, particularly in the hypolimnion (Torgersen and Bronco, 2007).

Ancillary chemical parameters (Cl^- , NO_3^{2-} , SO_4^{2-}) were measured for all outlet samples and all stratification events in 2009 and 2010 (Supplemental Information, Figure S4) with pH values ranging from 6-8 with a similar stratification pattern to temperature (data not shown).

Anion concentrations increased during dry periods and decreased following rain events, likely due to evaporation and/or groundwater contributions. SO_4^{-2} is significantly negatively correlated with MeHg concentrations in 2009 at the 15-cm level (-0.92 , $\alpha = 0.05$, $n = 11$), indicating as expected that sulfate reduction to reduced sulfur species is connected with MeHg production (Gilmour and Henry, 1991; Benoit et al., 1999; Ullrich et al., 2001). TSS values ranged from non-detect to 14 mg L^{-1} for stratified and outlet samples (Supplemental Information Figure S1, S2, S3). These values are low relative to other eutrophic lakes (Zhu et al., 2008), reflecting the high visibility present in Mirror Lake in 2009 and 2010. Lake sediments generally were visible on the majority of sampling days. The low TSS and high visibility likely is due to the lake management strategies conducted during the 2008, 2009 and 2010 summer seasons to improve the aesthetical value of the lake, including suction harvesting (20 August 2008, 17-21 August 2009), which reduced a large portion of decayed biotic surficial sediments.

Stratified sampling

MeHg concentrations measured at the 15-cm, 55-cm and surface levels in 2009 and 2010 remained relatively constant throughout the stratified sampling events at $0.023\text{-}0.062 \text{ ng L}^{-1}$, $0.020\text{-}0.061 \text{ ng L}^{-1}$, and $0.027\text{-}0.062 \text{ ng L}^{-1}$, respectively, and did not vary with level (Figure 2). Values are near the detection limit (DL) of 0.02 ng L^{-1} , lower than those reported for stratified samples collected from Mirror Lake in 2008 (Segal et al. 2011). THg concentrations in the stratified samples also remained relatively constant, with a maximum concentration of 1.49 ng L^{-1} (Figure 2). These values are similar to those reported for stratified samples in 2008 which were generally less than 5 ng L^{-1} except for two 15-cm samples that measured 17 and 48 ng L^{-1} THg due to high solids. THg, THgD and MeHg concentrations in 2009 generally are lower than

concentrations in other small lakes. Watras et al. (1995) reported concentrations ranging from 0.15–4.79 ng L⁻¹ THg, 0.23–4.5 ng L⁻¹ THgD and 0.02–2.2 ng L⁻¹ MeHg in a set of small lakes in Wisconsin. Weekly water chemical samples collected in Mirror Lake in 2008 had higher THg, THgD and MeHg concentrations than in the current study (Segal et al., 2011). While the MeHg concentration range was similar in 2008 for the 55-cm and surface levels between 0–0.5 ng L⁻¹, 15-cm level concentrations were lower than those reported for 2008 (1 – 3 ng L⁻¹). Unlike the prior stratified sampling in 2008, MeHg results for 2009 and 2010 level sampling (Figures 2, 3) suggest that polymixis and extended stratification events did not impact Hg species concentration in the water column.

While sampling events were intended to be conducted over hot, dry days when strong stratification could develop, the sampling event in 2010 experienced small rain events due to changing summer convective weather patterns. DO and temperature profiles from stratified sampling in 2009 demonstrate diel stratification and mixing cycles with continuous stratification in the 20-cm level during the sampling event (Figure 2). Unfortunately, due to difficulties with BORIS, DO and temperature data is only available from 4 - 5 August 2009 17:00. Given the weather conditions, the diel stratification pattern with possible extended stratification in the 20-cm level is assumed to hold until 7 August 2009 (Figure 2). In 2010, a diel stratification pattern developed in the 2010 sampling with a full mixing event every night (Figure 3).

The difference in THg, THgD and MeHg concentrations between 2008 and 2009/2010 may be due the lake management strategies that occurred in late 2008 and 2009. Two suction harvest treatments significantly decreased the amount of decaying biotic material present in Mirror Lake, removing nutrients with the SAV and surficial sediment material. After the suction

harvest in 2009, visibility in Mirror Lake increased and such conditions continued through the 2010 sampling period. The excessive amount of SAV and algal growth in 2008 may have inhibited horizontal and vertical mixing increasing the ability for anoxic conditions to develop over prolonged periods in the 15-cm hypolimnetic layer. Additionally, the penetration of light would have increased with treatment, increasing the amount of demethylation in the water column (Sellers et al., 1996) as well as increasing algal photosynthetic activity in the bottom waters. The resulting generation of oxygen would decrease the sulfate-reducing conditions under which methylation has been shown to occur. These results are supported by the relatively constant DOC concentrations ($3.2 - 4.3 \text{ mg L}^{-1}$) with no apparent difference with depth (Supplemental information, Figure S3) and the relatively constant and low TSS.

Outlet sampling

Long-term sampling from the outlet of Mirror Lake was conducted to monitor the long term effects of polymixis on Hg species concentrations. Outlet samples provide a representation of Mirror Lake water chemistry over a temporal scale not possible for water level sampling. Due to the consistency of sampling in 2010 the majority of the data analysis and discussion will be of 2010 outlet sampling. Temperature data in 2010 generally experiences diel stratification and mixing; though during 24 -25 July, 4-6 Aug and 8-10 Aug extended stratification develops in the 20-cm layer (Figure 3). These extended stratification events do not appear to contribute to MeHg accumulation in the hypolimnion even though the DO concentration at the sediment water interface are most likely very low.. Yet, even during extended stratification, MeHg concentration in the outlet samples remained low (ND - 0.08 ng L^{-1} ; Figure 1). The lack of a response during short-term extended stratification is consistent with the slow production

reported for many dimictic lakes (Regnell et al., 1997). However, MeHg concentrations were elevated in Mirror Lake during 2008 sampling (Segal et al., 2011), suggestive that factors other than the rate of MeHg production are influencing MeHg accumulation in these shallow, eutrophic ponds.

Outlet samples were analyzed for THg and THgD for a daily representation of Hg cycling with values ranging from ND - 2.79 ng L⁻¹ and ND -0.98 ng L⁻¹, respectively (Figure 1). THg concentrations increased during and after storm events due to an influx of particulates and sediment resuspension (Segal et al., 2011), yet, remained relatively low for surface waters (Scherbatoskoy et al., 1998), only increasing to 1.44 ng L⁻¹ following a 2.31 cm storm event (21 August). Small increases in THg also occurred during non-storm events (8 July 2010, 0.49 ng L⁻¹; 14 August, 0.42 ng L⁻¹) but, in general, concentrations were near the detection limit (0.02 ng L⁻¹). THgD concentrations increased slightly after storm events on 23 June, 28 July and 22 August due to the influx of THgD present in precipitation (Figure 1; Amyot et al., 2000). THgD increases during dry periods may be due to an atmospheric deposition of Hg⁰ and oxidation to Hg(II) (Amyot et al., 2000; Schroeder et al., 1992).

DOC outlet concentrations range from 1.9 to 4.2 mg L⁻¹ and slowly increase from 18 June to 23 July which may be from increased microbial activity due to the summer season (Supplemental Information, Figure S1; Selvendiran et al., 2008). However, after 23 July DOC concentrations level off for the rest of the sampling event. TSS concentrations remain low, with the majority of samples under 5 mg L⁻¹, consistent with low-flow conditions from a lake. TSS increases after rain events due to sediment resuspension (Mason and Sullivan, 1998) as on 10 – 24 July. However, occasionally there was not an increase in TSS after a rain event (e.g., 23 June, 2.5 cm total precipitation) (Supplemental Information, Figure S3).

Flux of THg and MeHg from Mirror Lake during dry periods in June and July 2010 averaged $0.04 \text{ ng m}^{-2} \text{ d}^{-1}$ for THg and THgD and $0.001 \text{ ng m}^{-2} \text{ d}^{-1}$ for MeHg. Due to the lack of flow data from June to July, dry periods were assumed to be sampling periods where a precipitation event did not occur 48 hrs beforehand with an outflow of $0.0166 \text{ m}^3 \text{ s}^{-1}$ (Branco and Torgersen, 2009; Torgersen, 2008). Hg species flux from Mirror Lake is much lower than reported for wetlands ($6.03 \text{ ng m}^{-2} \text{ d}^{-1}$ THg; Driscoll et al., 1998) and for forested catchments containing mineral soil and peatland ($2.5 - 4.9 \text{ ng m}^{-2} \text{ d}^{-1}$ THg, $0.082 - 0.90 \text{ ng m}^{-2} \text{ d}^{-1}$ MeHg; Porvari and Verta, 2003). Low fluxes from Mirror Lake indicate the influence of the urban watershed on Hg species contributions to the lake as well as the low DOC content and lack of sediment mobilization. These relatively low values also do not account for the elevated flux which occurs during high discharge events and is likely to dominate the mass flux from the lake.

MeHg accumulation experiments

Net MeHg accumulation rates were measured using laboratory mesocosms with sediment and filtered lake water. Mesocosms spiked with Hg averaged an accumulation of $0.004 \text{ ng L}^{-1} \text{ hr}^{-1}$ from 0-120 hrs (Figure 4). Control samples ranged from $0.041-0.076 \text{ ng L}^{-1}$ over 336 hours which indicates that existing MeHg in the lake sediment did not contribute significantly to MeHg accumulation in the mesocosms. Mesocosms not spiked with Hg demonstrated similar net accumulation rates, suggesting that the mesocosm system was not limited by the amount of THg. A slight increase in net accumulation occurs from 12 to 24 hrs followed by an increase between 24 to 48 hrs from $0.44 \text{ ng hr}^{-1} \text{ m}^{-2}$ to $0.52 \text{ ng hr}^{-1} \text{ m}^{-2}$ (Figure 4). After 48 hrs, the net accumulation decreases which is consistent to previous investigations

(Mason et al., 2006). The decrease in accumulation with time may be due to the changing nature of the redox conditions of the sediment (Mason et al., 2006) or the accumulation of sulfide species which can inhibit Hg methylation by forming charged Hg-S complexes (Gilmour and Henry, 1991). A decrease in MeHg concentration from 120 (0.54 ng L⁻¹) to 336 (0.35 ng L⁻¹) hrs indicates that demethylation processes were greater than the methylation during that time period (Mason et al., 2006). However, microbial demethylation processes are not expected to be the dominant removal process in freshwater systems (Branfireun et al., 1998; Sellers et al., 1996). The prevention of light in the mesocosms may have allowed microbial process to govern the removal of MeHg rather than the photolytic processes expected to control demethylation in the lake (Sellers et al., 1996).

While water samples do not indicate that polymixis has contributed to MeHg accumulation in Mirror Lake, the mesocosm experiments demonstrate that the potential exists for accumulation to occur given the right chemical and hydrologic conditions. The accumulation of MeHg appears to undergo an initial lag period of approximately 0 - 12 hrs during which net accumulation is lower relative to later values. While the mesocosms were purged with N_{2(g)}, sufficient O_{2(g)} may have persisted to delay the onset of sulfate-reducing conditions. Similarly, the NO₃⁻ present in the sediments and lake water may have had a similar effect, as redox chemistry has been demonstrated to control the release of MeHg from sediments (Regnell and Tunlid, 1991). Alternatively, the differences in the net accumulation rate may signify an acclimation period for the microbial population in adjusting to the shifting redox conditions. Understanding the influence and drivers on accumulation is critical in assessing the potential conditions which may be conducive to MeHg accumulation.

Model

Results from the 2-layer stratified lake model support the water chemical data (Figure 5). The base case scenario of MeHg in the epilimnion represents the actual conditions measured for the lake over a 5-day period and accurately reflects daytime MeHg trends in the 2009 and 2010 data. A method of least squares analysis was used to fit model results to the measured data by varying J_I , with a resulting input rate to the lake of $7.57 \text{ E}^{-5} \text{ ng m}^{-3} \text{ s}^{-1}$ (Figure 5). Model fit concentrations at 8:00 DST in the outlet (31 July – 04 August 2010) agreed with measured concentrations (0.04 ng L^{-1}). Model output concentrations exhibiting an overall daily range from $0.03 - 0.06 \text{ ng L}^{-1}$. Generally, concentrations decrease with demethylation during the day and increase with input to the lake during the night. This result is expected given the input conditions to the model (Table 1). DO concentrations in Mirror Lake in 2010 were high in the hypolimnion during the day due to light penetration and photosynthesis but remained elevated at night when the lake mixed and prevented the development of anoxic conditions in the hypolimnion. As such, methylation was not expected to occur. To promote MeHg accumulation, the lake would need to remain stratified overnight, allowing for a decrease in DO near the sediments.

Assuming a net methylation generation rate of $4.3\text{E}^{-4} \text{ ng m}^{-3} \text{ s}^{-1}$, which was adjusted from the rate measured in laboratory mesocosm experiments to the hypolimnion volume relative to that in the mesocosms and a J_I input rate of $7.57 \text{ E}^{-5} \text{ ng m}^{-3} \text{ s}^{-1}$, we assessed the influence of the length of stratification across 1, 4 and 29 nights on MeHg accumulation in the hypolimnion (4 night; Figure 6). All three cases reached equilibrium after 200 hrs and had maximum concentrations of 0.23 ng L^{-1} occurring at approximately 2:00 DST, due to the nighttime increase in MeHg accumulation and decrease in demethylation. Stratification across 1, 4 and 29

nights did not result in long-term accumulation of MeHg and concentrations drop to 0.03 ng L^{-1} from 9:00-17:00. During nighttime mixing events the peak concentration for all three scenarios was 0.06 ng L^{-1} MeHg, offset only by the difference in stratification period in between turnover. Maximum MeHg concentrations from 20:00 – 5:00 are within the range of concentrations measured in the epilimnion of Mirror Lake in 2008 (Segal et al., 2011). However, samples in 2008 were collected during the late morning/afternoon, a period of low MeHg concentrations in the model. Additionally, hypolimnion concentrations in the model are lower than those reported for the sampling event on Mirror Lake in 2008. The difference in model predictions relative to prior lake MeHg data suggests that factors other than short-term MeHg generation are influencing MeHg trends, due to the fact that there is little accumulation of MeHg due to continued demethylation during the day removing any MeHg produced during the nighttime.

An analysis was performed to determine the controlling variables in the lake system and to replicate potential environmental conditions that may occur in Mirror Lake. We assessed the impact of three scenarios: (1) decreased eddy diffusion (from 4.88E^{-5} to $2.0\text{E}^{-6} \text{ m}^2 \text{ s}^{-1}$), (2) methylation during nighttime mixing (from 0 to $4.3\text{E}^{-4} \text{ ng m}^{-3} \text{ s}^{-1}$), and (3) decreased demethylation ($k_{\text{DE}} = 2.8\text{E}^{-7}$, $k_{\text{DH}} = 2.0\text{E}^{-8}$) accompanied by daytime methylation (from 0 to $4.3\text{E}^{-4} \text{ ng m}^{-3} \text{ s}^{-1}$ and decreased eddy diffusion (from 4.88E^{-5} to $2.0\text{E}^{-6} \text{ m}^2 \text{ s}^{-1}$; Table 1). Demethylation rates for scenario (3) were decreased to 25% of the base and 10% of the base for the epilimnion and hypolimnion, respectively. The three scenarios were assessed independently and were selected to (1) assess lower reported literature values for thermal eddy diffusion coefficients, (2) methylation at night due to the prevalence of anoxic conditions prior to turnover, and (3) increased algal/SAV biomass growth in the water column preventing mixing and light penetration. High SAV decreases the eddy diffusion coefficient in shallow, eutrophic

lakes (Imboden and Emerson, 1978) as well as decreases light penetration, which leads to a decreased demethylation and enhances the development of anoxic conditions (i.e., increased methylation). Initial Scenario (3) simulations included the accumulation of MeHg in phytoplankton, adding a MeHg biotic uptake process that was not included in previous simulations. To account for the addition of phytoplankton, a f_w relation was calculated to scale the fraction of the total aqueous concentration of MeHg, f_w , that is available for demethylation (Equation 8; Schwarzenbach et al., 2003). As phytoplankton move with the water column, flushing and exchange were not affected by uptake.

$$f_w = \frac{1}{1+r_{sw}K_D} \quad (8)$$

where:

$$\begin{aligned} f_w &= \text{fraction of MeHg in the water column} \\ K_D &= \text{partition coefficient [m}^3 \text{ kg}^{-1}\text{]} \\ r_{sw} &= \text{phytoplankton / volume of water [kg m}^{-3}\text{]} \end{aligned}$$

Estimation of r_{sw} assumed that partitioning between the water column and phytoplankton is rapid in comparison to MeHg accumulation. Phytoplankton mass was estimated from TSS values measured in 2008 with f_w calculated to be 0.9, which indicates that demethylation rates will be reduced by 10% due to decreased availability on top of the decrease due to decreased light penetration.

The first two scenarios did not result in an accumulation of MeHg in the hypolimnion of the model. Reducing the eddy diffusion coefficient had no effect on the hypolimnion concentration of MeHg, while increasing nighttime generation of MeHg increased the maximum concentration of MeHg during stratification events but did not result in an accumulation over a multi-day period. Only the third simulation that represented increased SAV resulted in an increase of MeHg (Figure 6). MeHg concentrations were 0.21-0.25 ng L⁻¹ while

stratification persisted and the minimum concentration during stratification increase from 0.03 ng L⁻¹ (base simulation) to 0.05 ng L⁻¹ (3). This indicates that the decreased E_{th} and k_{DE}/k_{DH} decrease the removal of the accumulated MeHg from the hypolimnion.

Scenario (3) incorporated phytoplankton uptake on MeHg accumulation. However, f_w did not account for the accumulation of MeHg in SAV. SAV MeHg accumulation was included using a f_w relation, as with the phytoplankton except for in the case of SAV the f_w affects the aqueous concentration for flushing and exchange in addition to demethylation. Assumptions include 90% SAV water content, equilibrium partitioning within the water column is rapid in comparison to MeHg accumulation, and that rate processes do not affect MeHg accumulated in SAV. Model results were subsequently fit to 2008 hypolimnion and epilimnion water column MeHg concentration data by adjusting E_{th} and the SAV f_w . The initial value for SAV f_w of 0.29 was estimated with 2.46 kg m⁻³ of SAV from eutrophic lake data (Havens, 2003). The best fit model adjusted E_{th} from 2.0E⁻⁶ m² s⁻¹ to 1.7 E⁻⁸ m² s⁻¹ and f_w from 0.29 to 0.08 (Figure 7). The high measured MeHg on 3 July 2008 followed a Cu algaecide application with some subsequent algal degradation, a process not included in the model. The estimated E_{th} of 1.7 E⁻⁸ m² s⁻¹ is lower than values typically measured in dimictic lakes (Jassby and Powell, 1978), but has been measured in a small, thermally-stratified, artificial eutrophic lake in Canada that experienced very low light penetration (Hesslein and Quay, 1973). The estimated SAV f_w of 0.08 is equivalent to 11500 g wet vegetation m⁻³, a value not uncommon in eutrophic areas with similar SAV values, as reported in a eutrophic Swedish lake (16500 g m⁻³; Blindow et al., 2002). Similarities between our model predictions and measured data from eutrophic lakes indicates that our predicted values for E_{th} and f_w are realistic and in agreement with visual observations cited for the 2008 sampling period (Segal et al., 2011). The model fit suggests that the

combination of high SAV and very low mixing could be responsible for the high hypolimnetic accumulation of MeHg in 2008.

Increasing the time of MeHg generation, decreasing demethylation rates, and increasing the input of MeHg result in MeHg accumulation. However, accumulation was most sensitive to the growth of SAV and the impacts on E_{th} and demethylation. A relatively low f_w similar to that predicted for the SAV inclusion, and not the phytoplankton, was required to account for the sustained accumulation of MeHg in the hypolimnion. Additionally, E_{th} must be decreased below $10E^{-8}$ to account for the elevated concentration in the hypolimnion relative to the epilimnion. Increasing J_2 alone does not result in an accumulation of MeHg, though the maximum concentration increases/decreases with J_2 . Increasing J_1 does result in accumulation, as the minimum concentration during stratification increases, an expected result as J_1 represents a continuous input source. Yet, the maximum concentration of MeHg was more sensitive to J_2 than J_1 . Regarding k_{DE}/k_{DH} , decreasing the rate constants below $10E^{-7}$ was necessary to effect an increase in the minimum concentration.

Increases in generation can occur from increased anoxia in the hypolimnion due to increases in biomass production and decreased light penetration, while increases in input can occur from changes in landscape and the addition of areas such as wetlands and peatlands (Porvari and Verta, 2003). Watershed modifications did not occur over the period of study (2008-2010). Therefore, the most likely scenario for differences in MeHg concentrations and the accumulation of MeHg in the hypolimnion during the summer of 2008 is an increase in algal and SAV biomass which decreased mixing and light penetration. As demonstrated by the model, the increased anoxia, enhanced methylation and decreased demethylation resulting from these changes would account for the differences between the previous lake MeHg results (Segal

et al., 2011) and those for the current study. The model analysis suggests that the accumulation of MeHg in the hypolimnion of Mirror Lake is most likely due to a combination of prolonged anoxic conditions in the hypolimnion, high production rates of MeHg and decreased demethylation rates. These results suggest that MeHg accumulation is possible in similar retention systems to Mirror Lake under eutrophic conditions, supporting the significance of characterizing the potential contributions from such systems to MeHg flux. As these ponds become more dominated with plant growth, photolytic demethylation decreases while methylating conditions persist and the accumulation of MeHg in the hypolimnion can occur.

Conclusions

Field sampling and sediment methylation analysis were performed on a suburban retention pond to determine if polymictic conditions could increase MeHg accumulation and the potential for MeHg accumulation. MeHg water column and lake outlet concentrations in 2009 and 2010 were low compared to a previous study on Mirror Lake in 2008 and other lake studies, ranging from ND – 0.095 ng L⁻¹ (outlet samples) and ND – 0.104 ng L⁻¹ (stratified sampling). MeHg accumulation experiments determined that sediments from Mirror Lake have the capacity for methylation with an average accumulation rate of 0.00155 ng L⁻¹ hr⁻¹ (12- 120 hrs). A model was developed to investigate the difference in water chemistry between the study years and to determine critical lake characteristics and rate processes for MeHg accumulation. Model analyses determined that extended stratification events with MeHg generation occurring only during nighttime stratification do not result in MeHg accumulation within the hypolimnion due to daytime removal processes (flushing and demethylation). Model simulations representing

lake characteristics that would occur with high SAV conditions were able to predict MeHg accumulation in the hypolimnion previously observed in Mirror Lake with majority of accumulation due to increased length of time for MeHg accumulation. Analysis of rate process sensitivity demonstrated that while decreased demethylation, increased length of MeHg generation and increased MeHg inputs result in hypolimnetic accumulation, the biotic uptake and decreased mixing resulting from SAV growth had the greatest impact..

Changes in lake characteristics such as increased algal/SAV biomass, low light penetration and long term anoxic events can increase the probability for MeHg accumulation in small, shallow lake systems. These results demonstrate that such shallow, engineered systems are important considerations in quantifying watershed MeHg flux in developed systems. When shallow lake systems become more eutrophic light penetration decreases allowing for decreased photolytic demethylation rates and longer periods of anoxia, and thus, higher concentration of MeHg. MeHg concentration in the hypolimnion of 2008 and in Scenario (3) are similar to concentrations measured in wetlands in the summer months. areas of the landscape generally associated with high MeHg production. Such similarities in MeHg concentrations indicates that small, shallow eutrophic systems can behave and accumulate MeHg similar to wetlands under certain circumstances. As development pressures increase, the number of such small, shallow systems will increase. Therefore, understanding the BGC cycles and the impact on system design and management will be particularly important in limiting contaminant transport downstream and understanding the potential for methylation.

Highlights

- MeHg does not accumulate in polymictic lakes with low SAV and high light penetration.
- Demethylation processes effectively remove MeHg.
- Lake characteristics may alter MeHg biogeochemistry and hypolimnetic accumulation.
- Increasing MeHg generation length critical parameter for increasing MeHg accumulation.

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Table 1. Model input variables for all scenarios. Base conditions reflect initial model simulation. Variables are assumed to be constant for the additional simulations except for those noted. Time periods reflect the daily time variation in parameter values. Stratified refers to time periods when the lake is stratified, while mix refers 00:00 – 6:00 during mixing time periods. Variables for Scenario 3 represent the base case including bio-partitioning to phytoplankton ($f_w = 0.9$) and the model fit for bio-partitioning to SAV.

Variable	Units	Stratified					Mix
		0:00-5:00	5:00-6:00	6:00-18:00	18:00-19:00	19:00-24:00	00:00-6:00
<u>Base Conditions</u>							
J_1	$\text{ng m}^{-3} \text{ s}^{-1}$	7.6E-05	7.6E-05	7.6E-05	7.6E-05	7.6E-05	-
J_2	$\text{ng m}^{-3} \text{ s}^{-1}$	4.3E-04	4.3E-04	0.0E+00	0.0E+00	4.3E-04	0.0E+00
E_{th}	$\text{m}^{-2} \text{ s}^{-1}$	4.9E-05	4.9E-05	4.9E-05	4.9E-05	4.9E-05	1.0E+00
k_{DE}	s^{-1}	0.0E+00	0.0E+00	1.1E-06	1.1E-06	0.0E+00	
k_{DH}	s^{-1}	0.0E+00	0.0E+00	2.0E-07	2.0E-07	0.0E+00	
<u>Scenario 1</u>							
E_{th}	$\text{m}^{-2} \text{ s}^{-1}$	2.0E-06	2.0E-06	2.0E-06	2.0E-06	2.0E-06	-
<u>Scenario 2</u>							
J_2	$\text{ng m}^{-3} \text{ s}^{-1}$	4.3E-04	4.3E-04	0.0E+00	0.0E+00	4.3E-04	4.3E-04
<u>Scenario 3</u>							
k_{DE}	s^{-1}	0.0E+00	0.0E+00	2.8E-07	2.0E-08	0.0E+00	-
k_{DH}	s^{-1}	0.0E+00	0.0E+00	2.8E-07	2.0E-08	0.0E+00	
E_{th}	$\text{m}^{-2} \text{ s}^{-1}$	2.0E-06	2.0E-06	2.0E-06	2.0E-06	2.0E-06	

Figure Captions

Figure 1. Temperature (T), long-term precipitation, total mercury (THg), dissolved mercury (THgD) and methyl mercury (MeHg) during summer 2010. Major tick marks with date represent 00:00. T data collected using BORIS at 20, 45, 80 and 110 cm above sediments listed every 6 min. The shorter length of temperature data is due to sampler difficulties. Daily precipitation data from the weather station at the University of Connecticut Plant Farm. MeHg, THg and THgD data collected below the weir at the lake outlet. Detection limit for THg and MeHg is 0.2 ng L^{-1} and 0.02 ng L^{-1} , respectively. Lines for interpretive purposes only and do not reflect trends. Vertical lines represent extended periods of stratification in the hypolimnion: (1) July 24-26, (2) Aug 4-6 and (3) Aug 8-10.

Figure 2. Temperature (T), dissolved oxygen (DO), total mercury (THg), dissolved mercury (THgD) and methyl mercury (MeHg) data during stratified sampling for the period 4 Aug – 8 Aug 2009. Major tick marks with date represent 00:00. T and DO data collected using BORIS at 20, 45, 80 and 110 cm above sediments listed every 6 min. THg, THgD and MeHg data collected at 15, 55 and water surface above sediments using a water column profiler. Lack of T and DO data after Aug 6 due to malfunction in probes. Detection limit for THg and MeHg is 0.2 ng L^{-1} and 0.02 ng L^{-1} , respectively. Lines for interpretive purposes only and do not reflect trends.

Figure 3. Temperature (T), 6-hr precipitation, total mercury (THg), dissolved mercury (THgD) and methyl mercury (MeHg) during stratified sampling for the period 18 Jul – 23 Jul 2010. Major tick marks with date represent 00:00. T data collected using BORIS at 20, 45, 80 and 110 cm above sediments listed every 6 min. Total 6-hr precipitation data from the weather station at the University of Connecticut Plant Farm. THg, THgD and MeHg data collected at 15, 55 and water surface above sediments using a water column profiler. Dissolved oxygen probes not functional for 2010. Detection limit for THg and MeHg is 0.2 ng L^{-1} and 0.02 ng L^{-1} , respectively. Lines for interpretive purposes only and do not reflect trends.

Figure 4. Methyl mercury (MeHg) accumulation in laboratory mesocosm over 336 hours. Sediment collected from Mirror Lake 17 May 2011, sieved to remove particles larger than 2.0 μm , and allowed to settle prior to use. Mesocosms prepared with 50 ml wet sediment and 220 mL lake water and purged with $\text{N}_{2(\text{g})}$ to remove oxygen and promote anaerobic conditions. Samples spiked with 5 ng L^{-1} total mercury (Hg) as HgCl_2 . NS represents control samples without an Hg spike. Control represents an abiotic control spiked with sodium azide.

Figure 5. Methyl mercury (MeHg) concentrations in the epilimnion for the base model run (---) using temperature data collected from Mirror Lake representing the period July 31 – Aug 4 2010. Major tick marks with date represent 00:00 of the respective date. Watershed input rate was adjusted to $7.57 \text{ E}^{-5} \text{ ng m}^{-3} \text{ s}^{-1}$ using sum of least squares to mimic outlet concentrations. Only input is from the watershed as oxygenated conditions limit methylation with demethylation and flushing as the removal processes. Initial concentration of MeHg is assumed to be 0.04 ng L^{-1} . Data (•) represent MeHg concentrations measured in the outlet of Mirror Lake.

Figure 6. Model prediction for the hypolimnion concentration of MeHg during a representative 5-day stratification event without (---) and with (—) low-light penetration conditions due to SAV/algae growth. Assume stratification persist through four nighttime periods with methylation occurring during stratification at night during anoxic conditions. For the condition with low-light penetration, daytime methyl mercury (MeHg) generation occurs and photolytic demethylation was set to 25% (epilimnion) and 10% (hypolimnion) of the base demethylation rate value, E_{th} was adjusted to $2.0 \text{ E}^{-6} \text{ m}^2 \text{ s}^{-1}$ and $f_w = 0.9$ was included for phytoplankton uptake. The MeHg pattern repeats after 350 hours.

Figure 7. Model prediction for the epilimnion (- - -) and hypolimnion (—) concentration of MeHg from 28 June – 12 July 2008 with low-light penetration conditions due to SAV/algae growth. Tick marks represent 00:00 of respective date. Data (•) represent measured concentrations on 28 June, 30 June, 3 July and 12 July. Predicted aqueous concentrations of MeHg fit measured data using method of least squares assuming stratification persists with MeHg accumulation occurring during day and nighttime periods. Photolytic demethylation was set to 25% (epilimnion) and 10% (hypolimnion) of the base demethylation rate value. Resulting best fit parameters were an E_{th} of $1.65.0 \text{ E}^{-8} \text{ m}^2 \text{ s}^{-1}$ and f_w of 0.08.

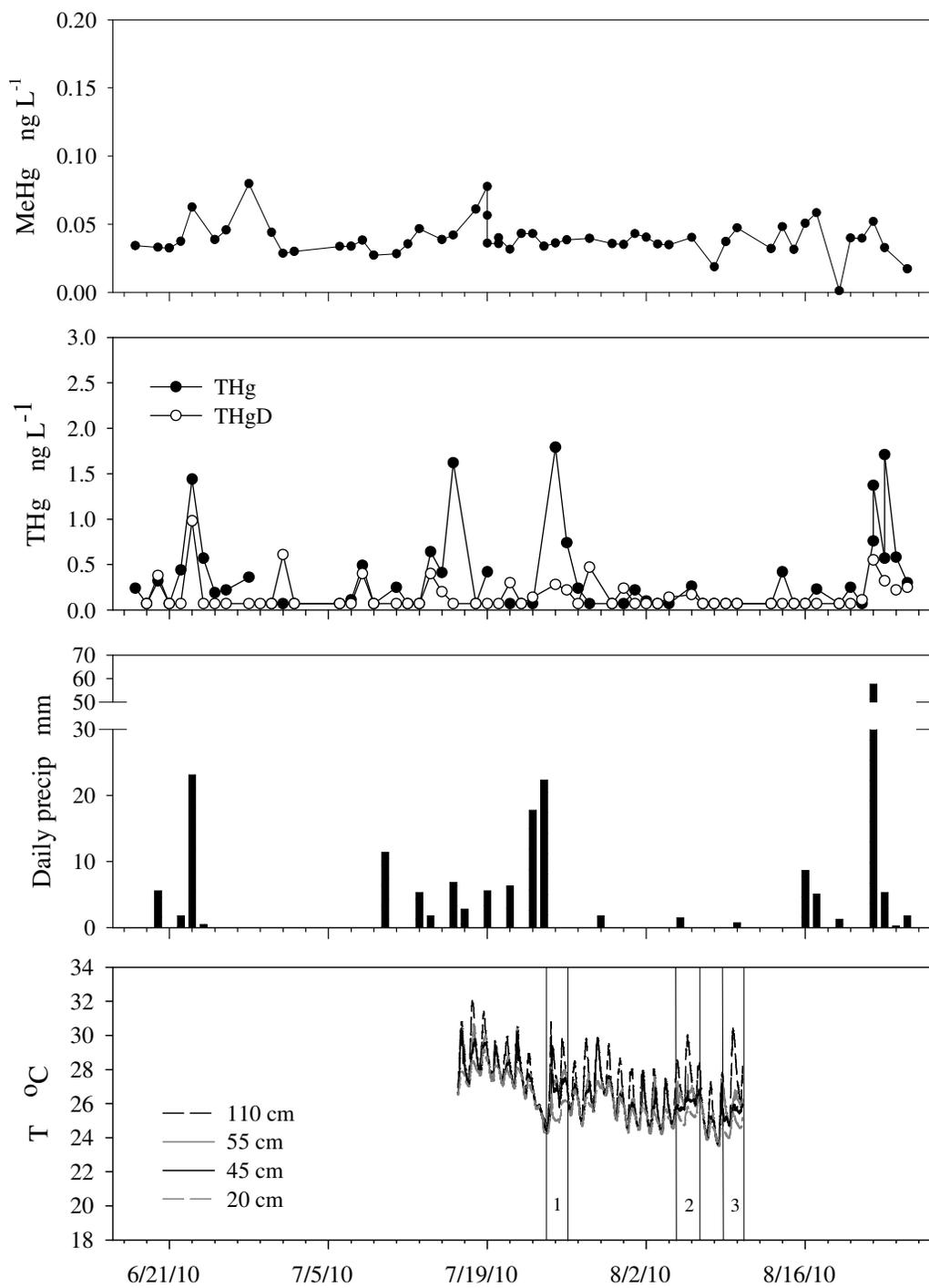


Figure 1

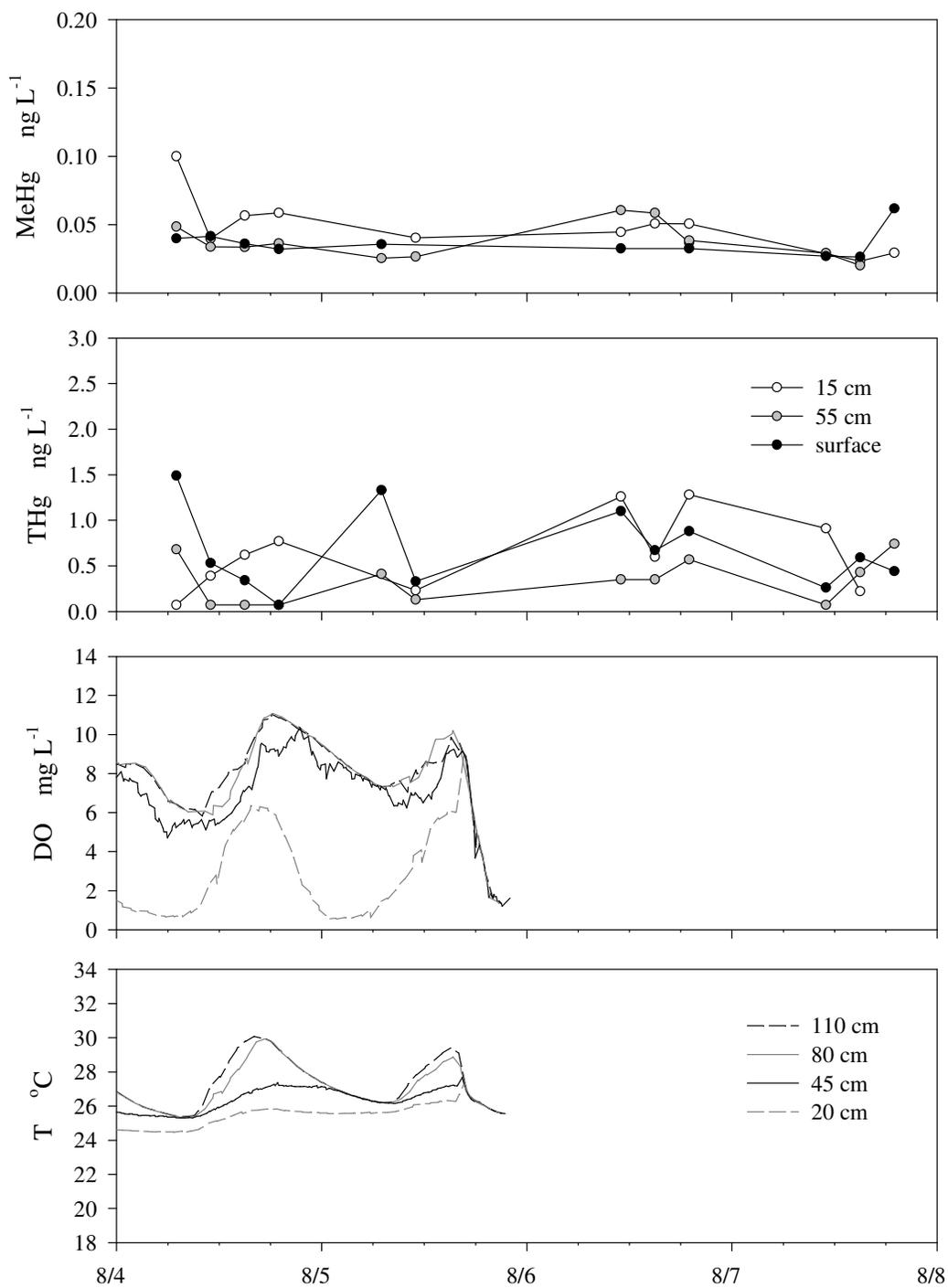


Figure 2

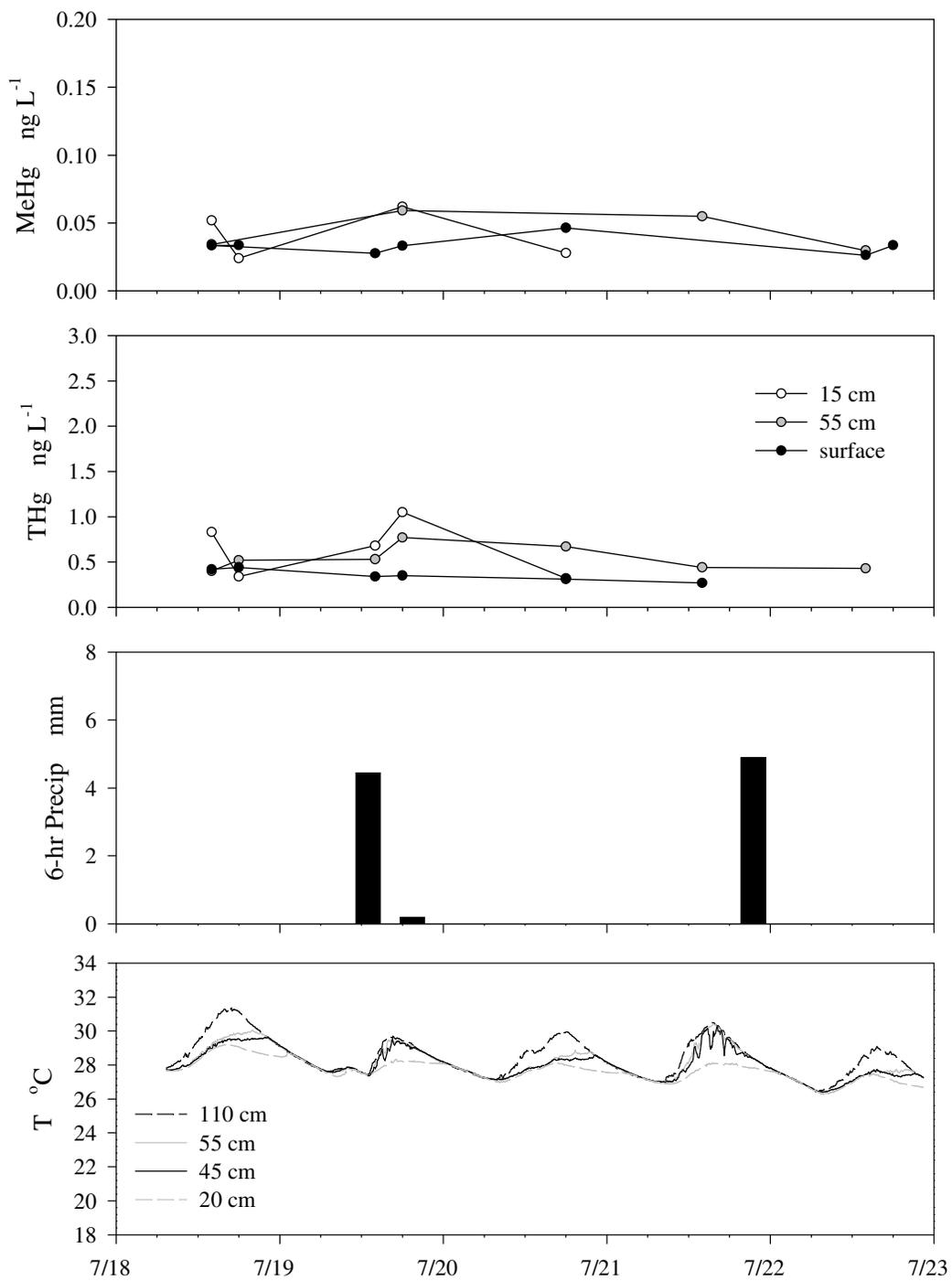


Figure 3

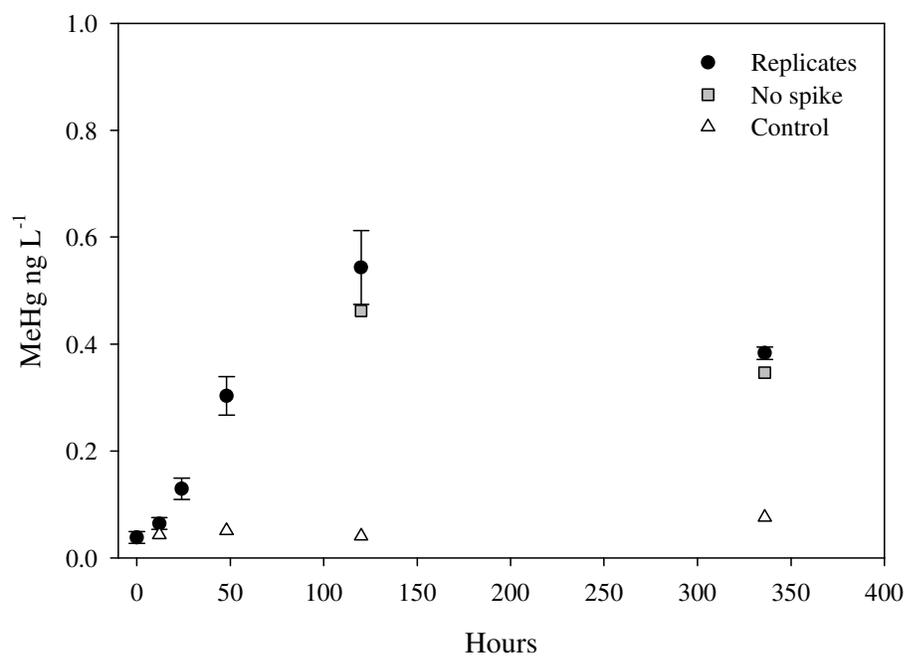


Figure 4

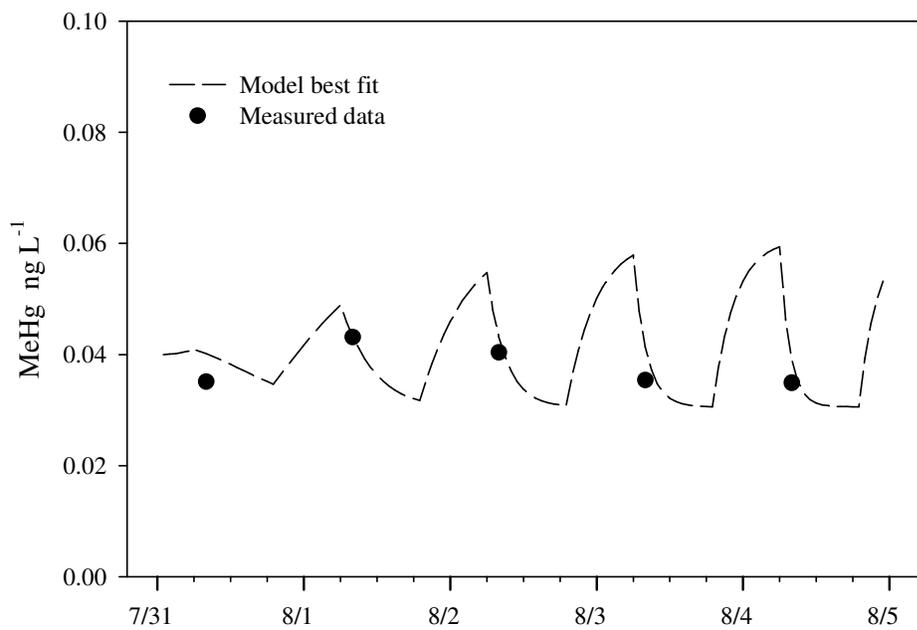


Figure 5

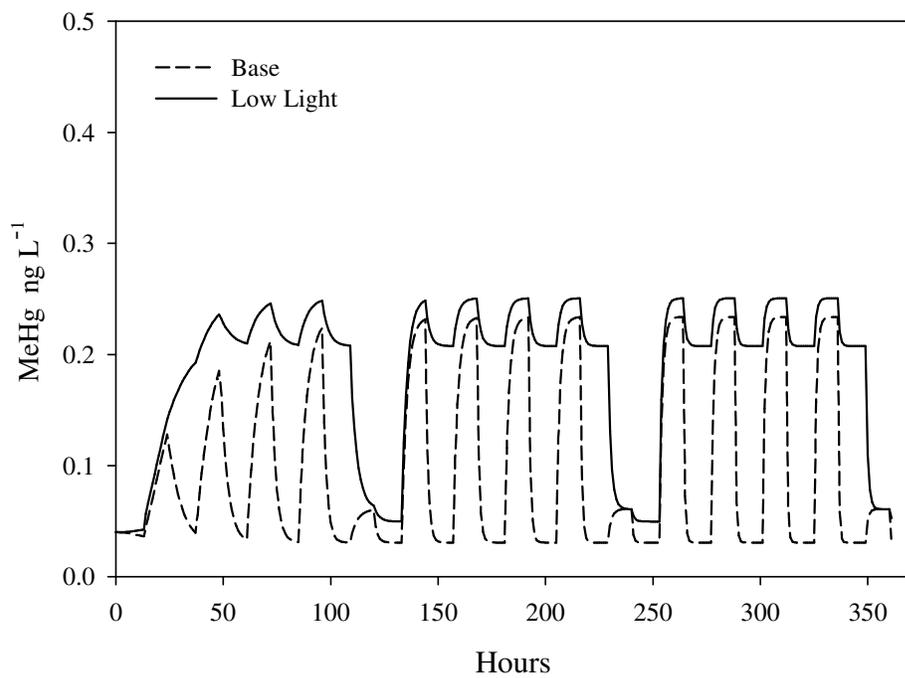


Figure 6

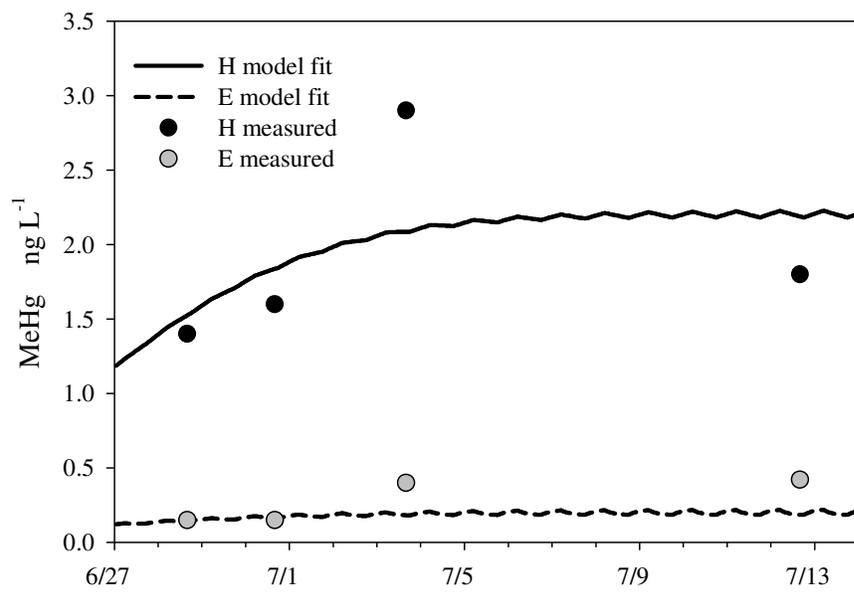


Figure 7

Supplemental Information

Equation 1: Calculation of eddy diffusivity coefficient (Hondzo et al., 1991)

$$E_{th} = \frac{\frac{1}{\Delta t} \sum_{i=1}^N (\Delta T_t \Delta Z)_i - \left(\frac{H_{sol(z)}}{\rho c_p} + \frac{H_{sed}}{\rho c_p} \right)}{\frac{1}{2 \Delta Z} \Delta T_z} \quad (S1)$$

where:

- E_{th} = eddy diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]
- t = time [s^{-1}]
- i = bottom layer of the lake
- N = top layer of the lake
- ΔT_t = water temperature difference over time Δt at a depth z [C]
- z = depth in question [m]
- $H_{sol(z)}$ = estimated in equation (3) [$\text{cal s}^{-1} \text{m}^{-2}$]
- ρ = density [kg m^{-3}]
- c_p = heat capacity [$\text{cal kg}^{-1} \text{C}^{-1}$]
- H_{sed} = water – sediment interface heat flux [$\text{cal s}^{-1} \text{m}^{-2}$]
- ΔT_z = temperature difference over Δz averaged over Δt [C]

Temperature and radiation data collected during the sampling events were used to estimate $H_{sol(z)}$, ΔT_t , and ΔT_z .

Figure S1. Total suspended solids (TSS) and dissolved organic carbon (DOC) data from summer 2010. Tick marks represent 00:00. TSS and DOC data collected below the weir at the lake outlet. Lines for interpretive purposes only and do not reflect trends.

Figure S2. Total suspended solids (TSS) data from 4 Aug – 8 Aug 2009. Major tick marks with date represent 00:00 of the respective date. TSS data collected from 15, 55 and surface water above sediments using a water column profiler. Lines for interpretive purposes only and do not reflect trends

Figure S3. Total suspended solids (TSS) and dissolved organic carbon (DOC) data from 18 -23 July 2010. Tick marks represent 00:00. TSS and DOC data collected from 15, 55 and surface water above sediments using a water column profiler. Lines for interpretive purposes only and do not reflect trends.

Figure S4. Anion (NO_3^- , Cl^- , SO_4^{2-}) data from summer 2010. Tick marks represent 00:00. Data collected below the weir at the lake outlet. Lines for interpretive purposes only and do not reflect trends.

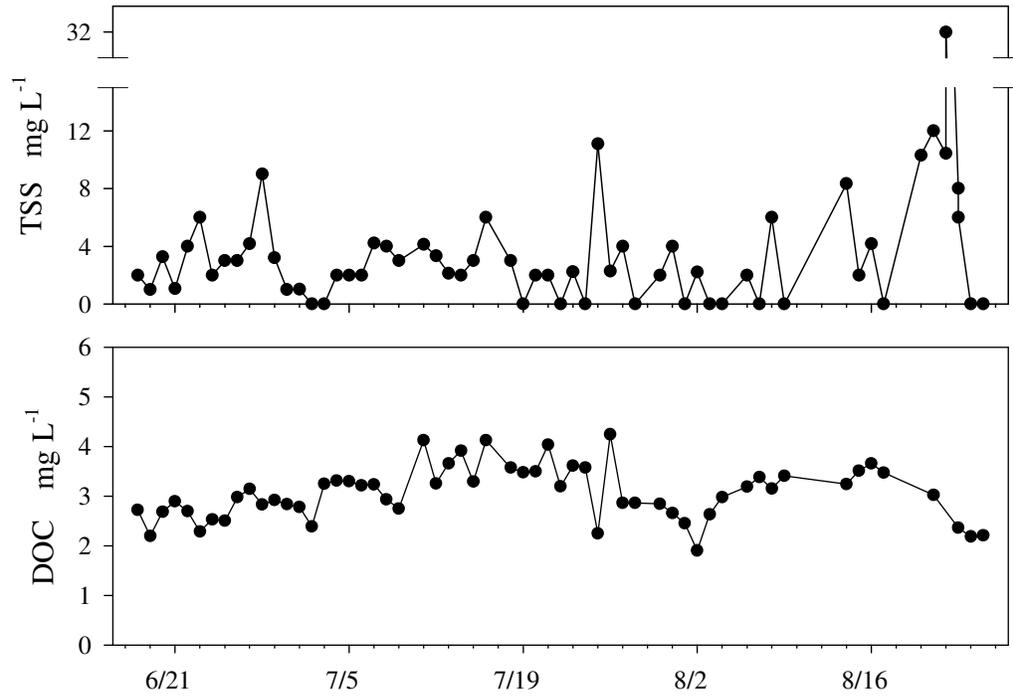


Figure S1

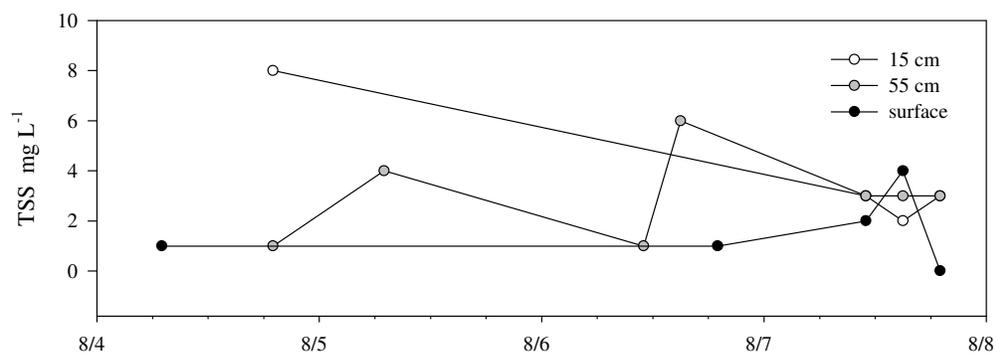


Figure S2

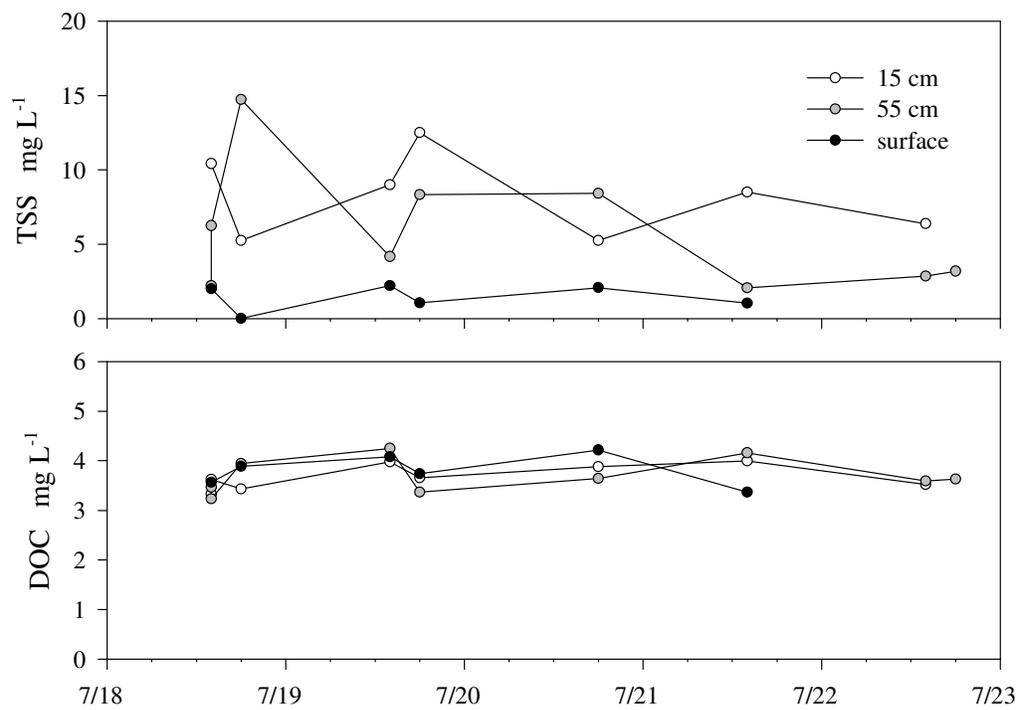


Figure S3

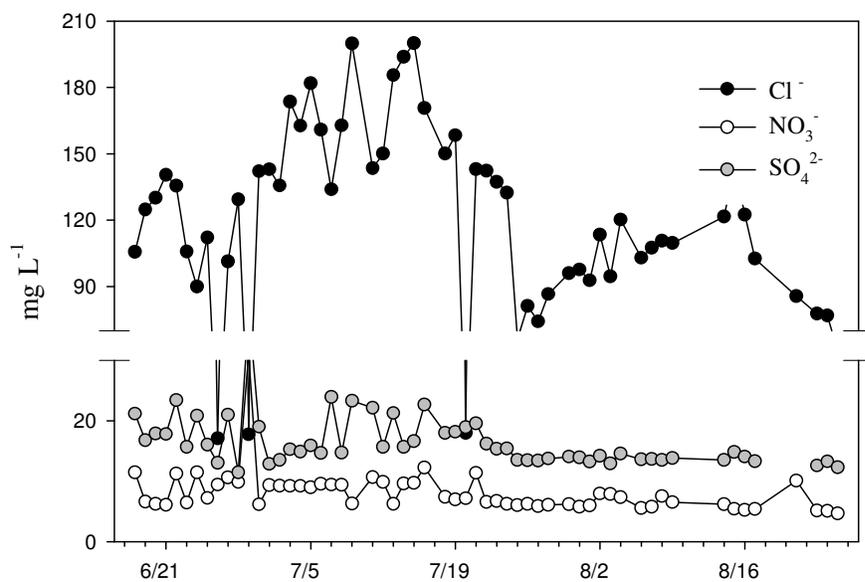


Figure S4