Seasonal and spatial variations in methylmercury in the water column of sulfate-impacted lakes

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Final Project Data Report

with initial interpretations

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Summary

Two lakes in the mining-impacted St. Louis River Watershed, Lake Manganika and Lake McQuade, were studied extensively from May to October 2012 and again in June 2013, as part of a larger Mine Water Research Advisory Panel (MWRAP) study. Water samples were collected biweekly in inlet and outlet streams and lake surface and bottom waters, with more detailed water column depth profiles collected monthly. Samples were analyzed for various chemical constituents in order to understand net methylmercury (MeHg) production and export from sulfate-impacted lakes. The purpose of this report is to present and share data and provide preliminary interpretations to other MWRAP groups, with the intent of initiating a larger coordinated analysis which will produce final interpretations.

Preliminary analysis shows clear evidence of active sulfate reduction in the hypolimnion of both Lake McQuade and Lake Manganika, likely resulting in net MeHg production in the bottom waters. High concentrations of dissolved MeHg were observed during late summer in the bottom waters of both lakes (>3 ng/L in Manganika; >6 ng/L in McQuade), resulting from a combination of bottom water methylation and MeHg flux from sediment porewaters. Despite MeHg production throughout the summer months, a limited amount of MeHg transport out of the isolated hypolimnion when lakes are stably stratified appears to result in little net export of MeHg from the lakes.

Background

Mercury (Hg) is a trace metal with known adverse health effects and a pollutant of concern across the globe. Mercury pollution in soils and aquatic sediments of most ecosystems is predominantly a result of atmospheric deposition of anthropogenic sources (Morel et al. 1998). The form of mercury of greatest environmental concern is methylmercury (MeHg), as it is a highly potent neurotoxin which bioaccumulates in the food chain (Morel et al. 1998) and comprises nearly all of the accumulated mercury in fish tissue (Bloom 1992). Elevated mercury levels in fish are a serious concern to human health and have led to consumption advisories in most lakes in Minnesota. Fish with high levels of mercury have been shown to occur more regularly in lakes where dissolved mercury speciation is high in MeHg (Gill & Bruland 1990), thus the concentration of MeHg in the water column of a lake is of particular concern.

Atmospheric deposition of MeHg is very low, thus in situ methylation of inorganic mercury is the main source of MeHg to aquatic systems. Methylation of inorganic mercury in the environment is primarily a result of the activity of anaerobic sulfate-reducing bacteria (SRB) (Compeau & Bartha 1985, Gilmour et al. 1992), though methylation capability has also been observed in some species of iron reducers (Fleming et al. 2006; Kerin et al. 2006) and methanogens (Hamelin et al. 2011). Recent research has identified specific genes believed to be responsible for methylation and present in a wider variety of microorganisms than previously recognized (Parks et al. 2013). Even in light of the potential for other organisms to mediate mercury methylation, a plethora of empirical evidence suggests that sulfate reducing bacteria are the primary producers of MeHg in natural systems. As such, the study presented here had the goal of identifying (a) where and when sulfate reduction occurred in sulfate-impacted lake waters and sediments and (b) where and when MeHg produced as a result of sulfate reduction was transported within and out of lakes.

Net accumulation of MeHg in the water column is defined by a number of processes including: (1) flux of MeHg from anoxic sediments, (2) a balance between microbial methylation and demethylation in the water column, (3) photodegradation of MeHg, and (4) transport of MeHg into and out of the lake system.

MeHg production in most natural systems appears to be related to the activity of SRB, and thus is dependent on both the rate of sulfate reduction and the bioavailability of an inorganic mercury precursor to methylation (Hsu-Kim et al. 2013). Anoxic sediments are the primary environment in which production of MeHg occurs, and diffusive flux from sediment porewater can be an important pathway for MeHg into the water column (Hines et al. 2004; Hammerschmidt et al. 2004). Water column methylation has been shown to occur exclusively in the anoxic hypolimnia resulting from thermal stratification in productive lakes (Eckley & Hintelmann 2006), and where sulfate-reduction is an important pathway for organic matter decomposition (Matthews et al. 2008). In contrast, demethylation of mercury can occur throughout the water column, as it can result from the activity of both aerobic and anaerobic bacteria (Bridou et al. 2011). In addition, photodegradation of MeHg in lake surface water has been shown to be an important influence on lake mercury dynamics (Sellers et al. 1996; Hammerschmidt & Fitzgerald 2006; Hines & Brezonik 2007).

This study is part of a larger effort by the Minnesota Department of Natural Resources (MN DNR) to better understand the impact of sulfur from past, present, and future mining activity on MeHg production and transport. The specific purpose of the portion of the study described herein is to examine the effect of high sulfur-loading on MeHg production in freshwater lakes and to investigate the important processes and pathways influencing MeHg transport into the lake water column and out to the downstream water bodies.

Methods

Site Description

The two lakes investigated in this study are located in the upper reaches of the St. Louis River watershed in northeastern Minnesota, USA, an area influenced by historic and ongoing taconite-ore mining activity (Fig 1). Lake Manganika (N 47.49°, W 92.57°) is a hypereutrophic lake of maximum depth ~24 feet and surface area ~0.67 km^2, subjected to high sulfur and organic carbon loading from two inlets: dewatering activities from a taconite pit, and discharge from an approximately 4.2 MGD (175 L/s) local municipal wastewater plant (Berndt & Bavin 2011). Surface water sulfate concentrations range from 200-600 mg/L and excessive algal growth has historically been observed. Strong thermal stratification at 8-10 feet below the water surface was observed in Manganika from spring until mid-fall 2012 (Fig 2) although observations in summer 2004 suggest minimal thermal stratification (Berndt and Bavin 2011).

Lake McQuade (N 47.42°, W 92.77°) is a mesotrophic lake with maximum depth ~20 feet and surface area ~0.68 km^2, with comparably lower surface water sulfate concentrations (30-120 mg/L in 2012). However, consistent with increases in inlet river sulfate, observations of surface water sulfate were approximately 300 mg/L during spring 2013. Surface water observations at two locations were very similar, but lateral mixing of the lake may be incomplete at times due to the close proximity of the inlet and outlet streams on the northeastern edge of the lake and a narrow pinch point in the southern half of the lake. The deeper southern portion of Lake McQuade stratified in early summer 2012 (limnetic surface between 8-10 feet), with a hypolimnion persisting through mid-September.

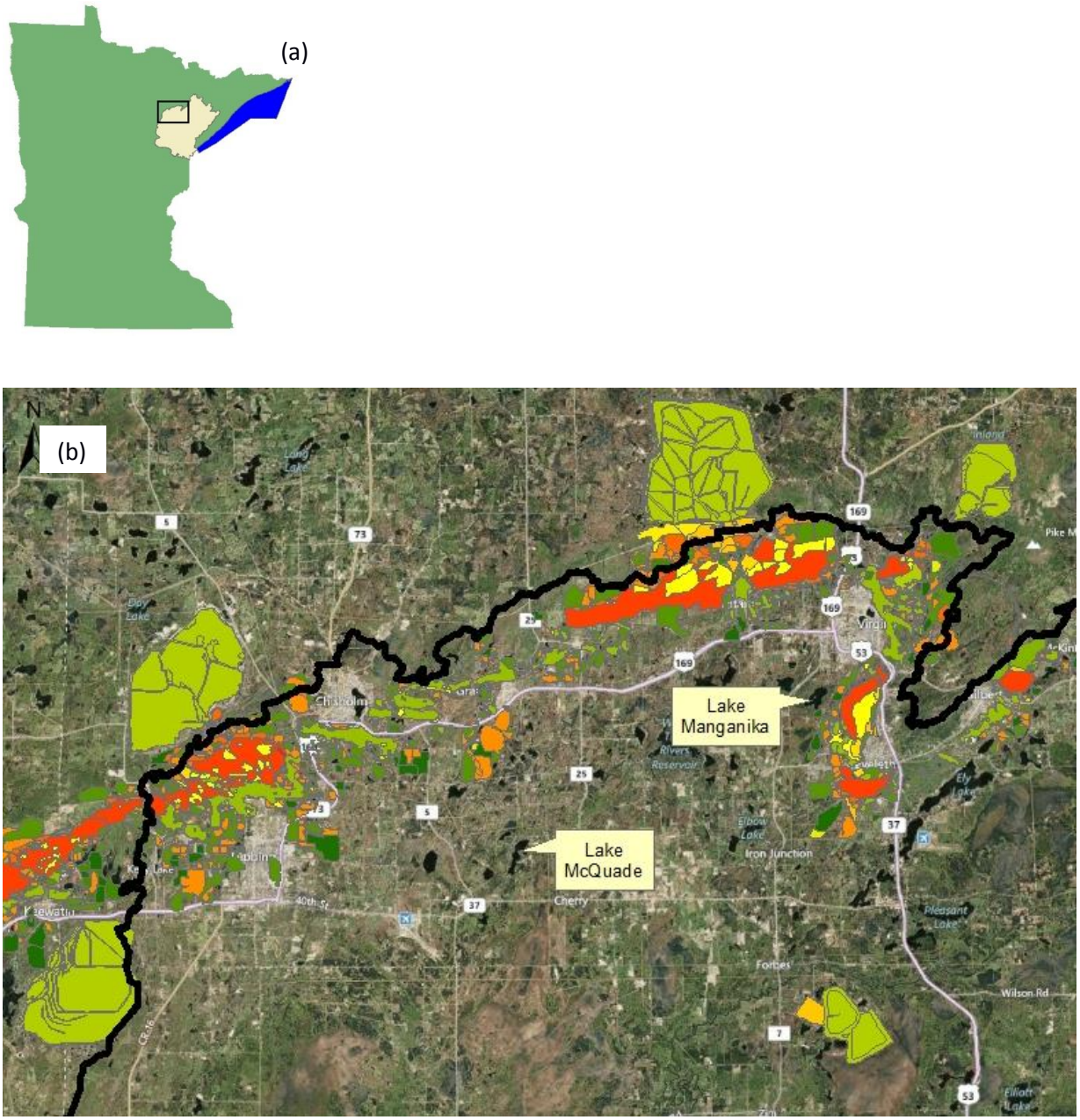

Fig. 1.(a) Location of the St. Louis River Watershed in Minnesota, USA. Black rectangle corresponds to location of inset (b) Location of lakes in the Mesabi Iron Range. Black line represents the northern boundary of the St. Louis River watershed; shaded regions represent mining influenced landscapes.

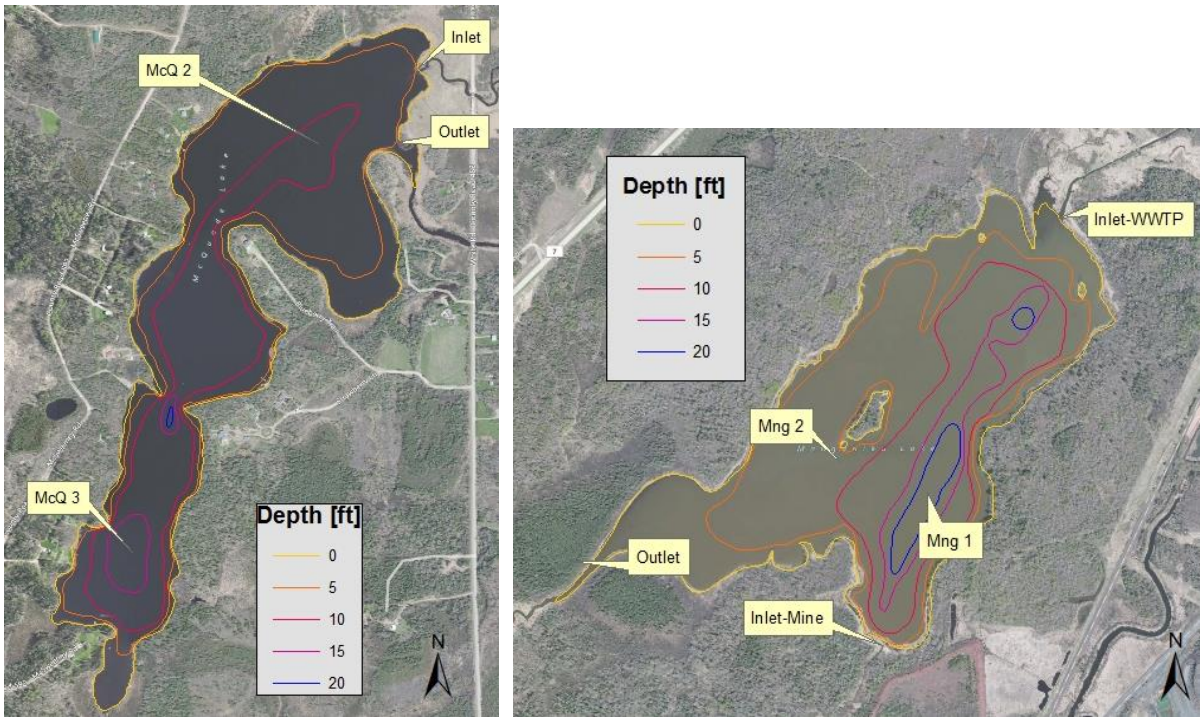

Fig. 2. Map of Lake McQuade (left) and Lake Manganika (right) sampling locations, with labeled inlet and outlet streams and bathymetry contours.

Sampling design

Water samples were collected from two locations within the lakes: a deeper basin location (depth of 15-18 feet in McQuade; 20-25 feet in Manganika) and a shallower basin location (8-10 feet in both lakes) and analyzed for total- and methyl- mercury as well as a host of geochemical parameters. The shallower locations corresponded with depths very near the limnetic surface through most of the summer. The deep sampling locations were labeled as 'Mng 1' and 'McQ 3'; the shallower sampling locations were labeled as 'Mng 2' and 'McQ 2'. Surface water and bottom water samples, in addition to depth profiles of general chemistry (hydrolab), were collected every 2-3 weeks from May to October 2012, and once in June 2013, totaling ten sampling trips.

A more intensive water column sampling scheme was employed at the deep sampling locations in June, July, August, and October 2012. Grab samples were collected at 4-6 depths spaced 2-5 feet apart in

order to construct a profile of mercury-related water chemistry from the surface, through the thermocline, into the hypolimnion, and to the lake bottom.

In order to evaluate net import and export of chemicals from the lakes, water samples from inlet and outlet streams of both lakes were collected approximately biweekly throughout the summer and fall of 2012 and analyzed for total- and methyl- mercury as well as a host of geochemical parameters. In addition, samples for isotopic analysis of sulfur and oxygen in sulfate and sulfide were collected at inlet and outlet streams, and within the water column, allowing for more complete understanding of sulfate transport and transformation processes.

Sampling methods

Raw (unfiltered) water samples were obtained using a peristaltic pump with teflon tubing and collected in new 1 liter PETG bottles free from mercury contamination. Samples were discharged into the collection bottle below the surface of the accumulating sample to prevent aeration, and bottles were completely filled (within 3 minutes) to minimize contact with the atmosphere and the loss of dissolved gases. Filtered samples for each specific analyte were obtained by placing 10 cm rhizon samplers (polyvinylpyrrolidine/polyethersulfone membrane, Seeberg-Elverfeld et al. 2005) with a nominal filter size of 0.2 microns into raw water in 1-liter PETG bottles. Sample was extracted while maintaining in-situ redox conditions by attaching the Rhizon sampler to teflon tubing and a stainless steel hypodermic needle and piercing a 1 cm thick butyl rubber stopper sealing an acid-washed, evacuated, borosilicate glass serum bottle. To limit exposure to oxygen, raw water samples were sealed with custom bottle caps that allowed nitrogen gas to continuously purge head space during filtration. Bottles collecting filtered samples ranged in size from 10 mL to 125 mL and filled within 1 – 10 hours.

Water Column Methylation and Demethylation Rate Potentials & Mercury Analyses

The potential for Hg methylation and MeHg demethylation were assessed via enriched stable isotope incubation techniques (Eckley & Hintelmann 2006; Mitchell & Gilmour 2008). Potential methylation and demethylation rate constants were measured by injecting raw unfiltered water samples with a mixture of stable isotope-enriched $^{200}Hg^{2+}$ & $Me^{201}Hg^{+}$ (94.3% $^{200}Hg^{2+}$ and 84.7% $Me^{201}Hg^{+}$) pre-equilibrated with filtered site water, incubating the samples in the dark at in-situ temperatures for approximately 24 hours, freezing to finish the assays, and then measuring the generation of enriched $Me^{200}Hg^{+}$ and loss of enriched $Me^{201}Hg^{+}$ via ICP-MS detection. Incubations took place in a mercury-free, 250 mL PETG bottle fitted with a 1 cm thick butyl rubber stopper through which isotopes were injected using a 100 µl gastight syringe.

For THg analysis (including detection of enriched isotopes), ~0.5% by volume of BrCl was added to the water samples to oxidize all Hg in the sample to Hg(II). After allowing to react overnight, THg was characterized following the USEPA method 1631 using a Tekran 2600 automated Hg analysis system that was hyphenated with an Agilent 7700x ICP-MS for detection of individual Hg isotopes. For MeHg analysis, water samples were distilled according to the methods of Horvat et al. (1993), but with the addition of a different enriched MeHg spike ($Me^{199}Hg$), for MeHg determination by isotope-dilution techniques (Hintelmann and Evans, 1997). All analyses used calculations from Hintelmann and Ogrinc (2003) to account for the <100% enrichment of isotopes in calculating enriched ^{200}Hg and ^{201}Hg concentration in THg and MeHg, as well as in calculating ambient THg and MeHg levels from the dominant naturally occurring ^{202}Hg isotope.

The methylation (kmeth) and demethylation (kdemeth) rate constants were calculated by:

$$k_{meth} = \frac{[Me^{200}Hg]/[T^{200}Hg]}{t_i}$$

$$k_{demeth} = \frac{([T^{201}Hg] - [Me^{201}Hg])/[T^{201}Hg]}{t_i}$$

$$t_i = incubationtime[hrs]$$

Clean hands protocols were utilized for mercury samples throughout sample handling, preservation, and analysis, and water samples were preserved by adding concentrated trace metal HCl to a concentration of 0.5%. Filtered water samples were analyzed for MeHg by isotope-dilution ICP-MS following distillation, as explained above (Hintelmann and Evans, 1997; Horvat et al., 1993), and THg according to USEPA method 1631, using a Tekran 2600 automated mercury analyzer. Inorganic mercury (iHg) concentrations were calculated by subtracting the MeHg concentration from the THg concentration, i.e. mercury was assumed to exist as either MeHg or iHg.

Chemical Analysis

A Hydrolab S5 sonde was used to take biweekly in-situ depth profiles with 3 foot depth increments at each sampling location. The sonde contained probes to measure for temperature, pH, dissolved oxygen (LDO), conductivity, and redox potential (ORP) and was calibrated immediately prior to use.

Filtered water samples for anion analysis were acidified to a pH<3 with HCl and bubbled with N_2 gas for 15 minutes to remove dissolved sulfide. A non-acidified duplicate sample was split from selected samples for chloride analysis. Sulfate (SO_4^{2-}), nitrate (NO_3^-), phosphate (PO_4^{3-}), and chloride (Cl^-) were quantified via ion chromatography (Method 300.1, USEPA 1997) on a Dionex ICS 1100 system. Water samples for dissolved sulfide ($H_2S + HS^-$) analysis were filtered into an evacuated serum bottle preloaded with ZnAc and NaOH preservative and quantified using automated methylene blue method (4500-S^{2-} E, Eaton 2005). Dissolved ferrous iron (Fe^{2+}) was quantified photometrically using the Phenanthroline Method (3500-FeB) (Eaton 2005). Ammonium was analyzed colorimetrically at the St. Croix Watershed Research Station (SCWRS) laboratory using the phenolate method (Lachat QuikChem method 10-107-

06-1-B). Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) were quantified on a Teledyne-Tekmar Torch Combustion TOC Analyzer. Dissolved carbon lability was assessed by analyzing samples for specific ultraviolet absorption at 254nm (SUVA, Weishaar et al. 2003) and spectral slope ratio (Helms et al. 2008) on a Varian Cary 50 scanning UV-Vis spectrophotometer to provide an indication of aromaticity and relative molecular weight, respectively.

Flux Equation

Estimates of methyl- and inorganic- mercury diffusive flux from lake sediment utilized filtered bottom water samples as well as filtered lake sediment porewater samples reported in earlier sections of this report (Bailey et al. 2013). Flux was estimated following a method employed by similar studies (Gill et al. 1999; Hammerschmidt et al. 2004), using an equation derived from Fick's first law and assuming no bulk water movement:

$$J = -\left(\frac{\varphi D_w}{\theta^2}\right)\frac{\partial C}{\partial z}$$

where diffusive flux (J) is a function of the change in concentration across the sediment-water interface (SWI), sediment porosity (φ), tortuosity (θ^2), and the diffusion coefficient of the chemical in water(D_w). Water-only diffusion was corrected for measured bottom water temperature (Li & Gregory 1974; Boudreau 1997). The concentration derivative was calculated using difference between filtered bottom water concentration and filtered porewater concentration of the composited 0-2 cm sediment sample, assuming 1 cm represented the change in depth between the concentrations. Sediment porosity was calculated using measured dry bulk density (ρ_b) and particle density (ρ_s):

$$\varphi = 1 - \left(\frac{\rho_b}{\rho_s}\right)$$

with ρ_s estimated using measured fractions of sediment composition:

$$\rho_s = 1.1 f_{organic} + 2.72 f_{calcite} + 2.65 f_{inorganic}$$

Tortuosity was calculated using sediment porosity, based on the relationship for unlithified fine-grained sediments proposed by Boudreau 1996.

$$\theta^2 = 1 - \ln(\varphi^2)$$

MeHg diffusion coefficient was estimated using the relationship with molar volume (V_m) for neutrally charged aqueous species (Hayduk & Laudie 1974; Schwarzenbach et al. 1993; Hammerschmidt et al. 2004):

$$D_w = \left(\frac{2.3 \text{ X } 10^{-4}}{V_m{}^{0.71}} \right)$$

with the molar volume calculated from molecular weight and the density of the species (ATSDR 1999).

For the purpose of estimating diffusion coefficients, MeHg was assumed to be present in the form CH_3HgSH^0 (Dyrssen & Wedborg 1991; Hammerschmidt et al. 2004)a form of mercury hypothesized to be present in Lake Manganika and other sulfide rich waters of the region by Berndt & Bavin (2011). The diffusion coefficient of inorganic mercury was assumed to be 5.5 X 10^{-6} cm^{-2} s^{-1} based on values used in previous studies (Bothner et al. 1980; Gobeil & Costa 1993; Covelli et al. 1999).

Results & Discussion

A. Investigation of Hg Analyses

Inter-lab Comparison

Water samples of inlet and outlet streams were filtered using a nominal filter size of 0.45 microns and were analyzed for Hg at the Gustavus Adolphus College laboratory, while water column samples were filtered through a 0.2 micron filter and were analyzed at the University of Toronto laboratory. To compare Hg analysis between the two labs, concurrent water column samples were collected and

filtered using both filter sizes and analyzed at the two labs (Table A). Measured concentrations between the two labs were correlated for both THg (R^2 = 0.66) and MeHg (R^2 = 0.66) (Fig 3a, 3c). This correlation was also present for THg and MeHg when analyzing the data in of each lake individually (Fig 3b, 3d). Comparisons of the data show that as a general trend, MeHg concentrations were generally 30 to 80 % higher in the measurements made by the Gustavus Adolphus lab, which was expected due to the use of a larger filter size. There were, however, several exceptions to this in which MeHg quantified at Gustavus Adolphus were 4 to 8 times larger than those quantified at Toronto. Additionally, in Manganika surface waters, Gustavus consistently quantified concentrations lower than Toronto (Table A). The reasons for these discrepancies are still being investigated at the time of this report. Total mercury comparisons were less variable between labs with values quantified at Gustavus typically falling between 50 and 150 % of those at Toronto, the surface waters of Lake Manganika again being an exception (Table A).

Filtered v. Unfiltered MeHg Samples

Dissolved MeHg and THg concentrations quantified most commonly in this study do not account for the total mass in the water column, because filtered samples were used to quantify MeHg and THg. In an effort to account for the entire Hg pool, several raw (unfiltered) water samples were quantified for MeHg and THg in addition to the filtered samples by the Gustavus Adolphus lab to determine the dissolved fraction of the THg and MeHg present in the water column (Table B). Due to the significant particle concentrations in the hypereutrophic surface waters of Lake Manganika, the pool of mercury in the unfiltered fraction represents the majority (56 – 88 %) of the total mercury pool at this location (Table B). Waters of the mesotrophic Lake McQuade contained on average 10 to 20 % of the total mercury pool and on the particulate (unfiltered minus filtered) phase. The particulate phase consistently comprised 24 to 65 % of the MeHg in the surface waters, but only 19 % of MeHg on average

in the bottom waters. These comparisons were used to help analyze and better understand mercury dynamics and export, as described in later sections.

B. Lake Manganika

Thermal stratification and anoxic conditions were observed in the deepest site at Lake Manganika from the onset of sampling in May 2012 until complete lake mixing occurred in mid-September (Fig 4a, 4b). The thermocline and redoxcline, consistently present between 7-13 feet, were strongest in July (Fig 7b) and, though temperature and pH profiles suggest the lake began to mix at intermediate depths in mid-August (Fig 7c, Fig 4c), reducing conditions persisted in the bottom waters through early to mid-September (Fig 4a,d). At the shallower site, Mng 2 (approximate depth: 9ft), the sediment surface remained below the thermocline until mid-August (Fig 5b), with anoxic conditions measured from early July to the end of August (Fig 5a).

Several geochemical observations provided evidence of active sulfate reduction in the bottom waters of the deepest portions of Lake Manganika. Sulfate concentrations decreased in Mng1 bottom waters between mid-June and early-August (Fig 4c, 7b) while depth profiles showed that sulfate concentrations remained homogenous in the epilimnion (Fig 7a & 7b). During this time, bottom waters experienced an increase in sulfide concentration, as well as thiosulfate (Fig 4e), a sulfur oxyanion which can disproportionate to sulfate and sulfide. The decrease in bottom water sulfate while surface water sulfate was rising (Fib 4c) suggests rapid consumption of sulfate in the hydrologically isolated hypolimnion. The speed of sulfate consumption (~50 μmol/L/day during July, Fig 4c), coupled with increases in reduced sulfur species in bottom waters and very low ORP measurements (Appendix B), suggest that active sulfate reduction was occurring above the sediment-water interface in the bottom waters of Lake Manganika.

Isotope data from Mng1 bottom water samples provides additional evidence for bottom water sulfate reduction. Because sulfate reduction preferentially targets molecules with lighter isotopes, the isotope fractionation of the remaining sulfate pool will be increasingly more positive (heavier) as sulfate reduction progresses. $\delta^{34}S_{SO4}$ in bottom waters was elevated (heavier) relative to sulfate in surface waters and $\delta^{34}S_{HS}$ in bottom waters was lower (lighter) relative to sulfate in surface waters (Fig 16). This observation provides strong evidence for active hypolimnetic reduction of sulfate supplied from surface waters. Consistent with the presence of thiosulfate in bottom waters, the trajectory of the $\delta^{18}O_{SO4}$ to $\delta^{34}S_{SO4}$ ratio in Lake Manganika's bottom waters further suggests that the sulfate reduction pathway is different from that observed in many other parts of the watershed (Kelly & Berndt 2013).

An increase in dissolved MeHg concentration to >3 ng/L occurred in the bottom waters of Mng1 in August (Fig 4g). The similar timing between the increase in MeHg and evidence of sulfate reduction in the hypolimnion, along with a corresponding increase in %MeHg (Fig 4f), resulting from relatively constant concentrations of inorganic mercury in bottom waters (Fig 4h), suggests bottom water methylation at Mng1 likely contributed to the increase in MeHg. The elevated BW dissolved MeHg observation in mid-May (>95 % MeHg, Fig 4f, g) could be a result of net methyl mercury production in the absence of high sulfide concentrations early in the year. This is supported by the measurement of methylation rates in Mng1 bottom water samples collected during late spring conditions (June 2013, Table C). However, it is also consistent with elevated MeHg observed in lake sediment pore fluids during spring and early summer, interpreted to be a result of lower biological activity and a greater influence of solid-liquid partitioning (Bailey et al. 2013). Though only a portion of the total- and methyl- mercury pool was present in the dissolved phase, the increases in hypolimnetic dissolved MeHg observed in a location supporting active sulfate reduction points towards in-situ production rather than changes due to partitioning from the solid phase.

In contrast to the deepest portion of the lake, MeHg concentrations in the bottom waters of Mng2 were uniformly below 0.2 ng/L throughout the year with %MeHg consistently lower than those at Mng1 (Fig 5f & 5g). This was likely due to nitrate, which was present in Mng 2 bottom waters (near the thermocline) in July (Fig 5d), but was absent below the thermocline (Fig 7b) and in the deep hypolimnion until early September (Fig 4d). Because nitrate is more energetically favorable than sulfate, sulfate reduction occurs only in environments where nitrate has been depleted (Matthews et al. 2008), thus the presence of nitrate will have an inhibitory effect on net methylation (Todorova et al. 2008). This effect is illustrated by the absence of methylation at the limnetic surface of Manganika (12.5 ft in June 2013, Table C), which had nitrate concentrations almost twice as high as in the bottom water, where methylation was quantified (Table C). The absence of sulfide at the bottom waters of Mng 2 (~9 ft water depth) throughout the summer (Fig 5e), further suggests that sulfate reduction was confined to the sediment in portions of the lake shallower than the thermocline (8-12 feet) and likely only extended into bottom waters in the deepest portion of the lake (Fig 3).

Dissolved MeHg and iHg were generally lower in the epilimnion relative to the hypolimnion throughout the year until lake turnover, with iHg concentrations ranging from 0.5 – 2 ng/L and MeHg concentrations < 1 ng/L in the surface water (Fig 4g-h, Fig 7a-c). However, the observed decrease in dissolved MeHg concentrations between the hypolimnion and epilimnion may not reflect the entire mercury pool. In the bottom waters of Lake Manganika, 24.0 % of the THg present was in the dissolved phase on average, with a similar dissolved fraction of THg seen in the surface waters (18.6 % average) (Table B). In contrast, the fraction of MeHg in the dissolved phase was very different between surface and bottom waters, representing a majority of the MeHg present in the bottom water (78.3 % average) but only a small fraction in the surface water (6.5 % average). Though several comparisons between filtered and unfiltered total- and methyl - mercury were made (Table B), at the time of this report an attempt has not been made to use an adjustment factor to quantitatively compare the total mercury pools in the

waters sampled. The results of additional data analysis and coordination with data sets from other groups may warrant a quantitative comparison in the future. High levels of algae and other organic matter in the surface waters of hypereutrophic lakes adsorb and otherwise incorporate much of the dissolved MeHg to particles larger than the nominal filter size, causing a large fraction of the MeHg present in the surface water to be excluded from the dissolved concentration (Pickhardt et al. 2002). The increase in surface water % MeHg (dissolved) in mid-summer could have been due to interactions with the solid phase or reduced photodemethylation as algal densities increased.

C. Lake McQuade

Lake McQuade thermally stratified in the early summer of 2012 (Fig 9b & 11), with low dissolved oxygen concentrations persisting in the hypolimnion until mid-September (Fig 9a). The limnetic surface was shllow enough to create anoxic conditions above the sediment surface of McQ2 (depth = 9 ft) until mid-August (Fig 10a).

Hypolimnetic sulfate concentrations at McQ3 declined by a total of ~0.3 mmol/L between late-June and mid-August during a time when sulfate was steadily increasing in the surface waters (Fig 9c). This suggests consumption of sulfate in the hydrologically isolated hypolimnion (Fig 9j), though sulfide concentrations in the hypolimnion remained relatively low throughout the year (<0.02 mmol/L) (Fig 9e & 10e). The presence of aqueous ferrous iron at 0.01 - 0.025 mmol/L in hypolimnetic waters during July and August (Fig 9i) suggests that sulfide-iron(II) precipitation reactions limited the dissolved sulfide able to accumulate in the bottom waters. Dissolved phosphorus in bottom waters averaged greater than 0.015 mM, suggesting release from dissolving iron oxide phases in sediments.

Bottom water sulfate increased sharply in mid-August (Fig 9a) due to mixing with the epilimnion (Fig 11d, Fig 9j), but anoxic conditions in bottom waters re-established quickly (Fig 12c). Hypolimnion sulfate again diverged from surface water sulfate from late August to early September (Fig 9c), suggesting that

sulfate consumption continued in the bottom waters following lake turnover. This observation is consistent with findings by Phelps & Zeikus 1985, which demonstrated active sulfate reduction in bottom waters and sediment porewaters directly following lake turnover. Though the surface waters also contained significant sulfate, the mixing of oxic surface waters with reduced bottom waters has been shown to result in the re-oxidation of reduced species in bottom waters and sediments. This can, in turn, supply favorable electron acceptors (oxidized iron and sulfate) for microbial metabolism if anoxic conditions are re-established in the bottom waters and/or sediment porewaters. Bottom water ammonia concentrations averaged nearly 0.1 mM in July and August and may explain the observed increase in bottom water nitrate following turnover (Fig 9d), as well as the increase of sulfate in McQuade sediment porewaters from July to October (Bailey et al. 2013).

Isotope analysis of sulfate molecules in the inlet and outlet of McQuade showed that both $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$ were increased in outlet samples compared to the inlet (Upstream McQuade and Downstream McQuade, Fig 17), indicating that sulfate reduction occurred within the lake. Isotope analysis of bottom water samples also suggested sulfate reduction in the bottom waters, particularly in late August and early September following lake turnover (McQuade surface and McQuade bottom, Figure 17; Kelly & Berndt 2013). The observed shifts in $\delta^{34}SO_4$ in bottom water sulfate further supports the hypothesis that sulfate reduction occurred in McQuade bottom waters both before and after lake turnover.

Bottom water MeHg concentrations at the deep site of Lake McQuade ranged between 1.0 – 2.5 ng/L for most of the summer, with the exception of a much higher concentration in early August (Fig 9g). This rise of up to more than 6 ng/L MeHg was also reflected in %MeHg (Fig 9f), and occurred while inorganic mercury concentrations were consistently between 1-2 ng/L (Fig 9i). Similar to Lake Manganika, elevated MeHg concentration and %MeHg occurred in bottom waters during late-July and early-August and corresponded with a period of decreasing sulfate in bottom waters. This time period

also coincided with a rise in bottom water DOC concentrations (Fig 9k). Fresh DOC supplied during a time when conditions were favorable for sulfate reduction may have facilitated more rapid sulfate reduction or increased the concentration or bioavailability of inorganic mercury, driving the production of MeHg at a faster rate. Additionally, since sulfide was present at low concentrations, DOC may have acted as the primary ligand for MeHg; thus, it is possible that the concentration of DOC influenced the capacity for bottom waters to hold dissolved MeHg.

Depth profiles at the deepest portion of McQuade Lake revealed higher %MeHg (25-50%) at depths below the redoxcline than at oxygenated shallower depths where no sulfate was being consumed (< 25%) (Fig 12a-c). This behavior was consistent in all three summer depth profiles, suggesting a connection with sulfate reduction in the hypolimnion. This implies that even though dissolved sulfide concentrations were near detection limits, sulfate reduction has an influence of mercury dynamics in the bottom waters – an influence that may be enhanced by increased DOC concentrations. Methylation rates were not detected in McQuade bottom water samples collected in June 2013 (Table C), though because the late spring season does not capture lake conditions favorable to sulfate reduction, it is expected that water column methylation will be negligible at that time.

D. Estimated sediment flux of Methyl- and inorganic- mercury

MeHg concentrations in the anoxic hypolimnion are a result of net methylation or demethylation as well as diffusive flux across the sediment-water interface. As the biogeochemical conditions influencing mercury dynamics can vary greatly between porewater and bottom water, diffusive flux can vary substantially over the course of the year. A caveat to these estimates is that diffusive flux may not be solely responsible for transport at the SWI. This is particularly relevant to Lake Manganika, where evidence of bubbles in the hypolimnon were observed during sample collection (Engstrom, Johnson, personal communication) and ebullition of methane has been previously hypothesized (Berndt & Bavin

2011). Additionally, methane was quantified in bottom waters of both lakes during summer 2012 (Berndt and Kelley, unpublished data).

Estimates of diffusive MeHg flux at Mng1 ranged from -18.0 to 70.8 pmol/m^2/d, with negative fluxes (*i.e.* into the sediment) estimated for the May and July 2012 data, while MeHg flux at Mng2 was always positive (*i.e.* towards the water column) and ranged from 1.3 to 186.8 pmol/m^2/d (Table D). Estimates of diffusive MeHg flux at Mng1 were highest in October 2012, possibly due to decreased bottom water MeHg concentrations resulting from lake mixing. A possible explanation for the negative flux values in May and July could be methylation in the bottom waters causing a build-up of MeHg in the spring and early summer, while MeHg concentrations stayed low in the sediment porewater due to high sulfide concentrations inhibiting production.

Diffusive flux estimates of inorganic mercury at Mng1 (range: -5.2 to 391.4 pmol/m^2/d) were also negative in July 2012 but positive at all other times, while inorganic mercury flux at Mng2 (range: -9.0 to 26.9 pmol/m^2/d) was positive in July 2012, but negative in October 2012 and June 2013 (Table D). It should be noted that fluxes of inorganic mercury were estimated assuming aqueous inorganic mercury existed as neutral complexes, while proposed mercury speciation models suggest that charged species dominate at sulfide concentrations equivalent to those present in Manganika sediment (Benoit et al. 1999). If this is the case, the inorganic mercury diffusion coefficient used to calculate flux estimates would then be overestimating the diffusive ability of the inorganic mercury species.

Diffusive flux of MeHg from Lake McQuade sediment was positive throughout the summer and ranged from 8.5 – 38.3 pmol/m^2/d at McQ3 and 5.0 – 11.6 pmol/m^2/d at McQ2 (Table D). Diffusive MeHg flux estimates at both sampling locations at Lake McQuade displayed similar seasonal trends, with the lowest flux occurring in July 2012, the median in October 2012, and the highest in June 2013 (Fig 15). During the late spring conditions in June 2013 MeHg production was likely occurring in the sediment but

because the lake had not yet stratified, methylation was not measured in the bottom waters (Table C). Conditions after lake stratification promote MeHg production, resulting in an increase in %MeHg and MeHg concentrations in the bottom waters and lower flux values in the summer months.

E. Net Export

Lake Manganika

Dissolved MeHg concentrations in the outlet from Lake Manganika remained uniformly low (<0.1 ng/L) throughout the year, despite (1) high MeHg concentrations in the bottom water (peaking at 3.3 ng/L), (2) evidence of MeHg production in the bottom waters under anoxic conditions, and (3) MeHg concentrations of 0.9 – 2.9 ng/L in the inlet from the municipal wastewater treatment plant. This may be due to net demethylation in the epilimnion resulting from demethylating aerobic bacteria and/or photo-degradation, or due to limited mixing between the epilimnion and the hypolimnion physically trapping the MeHg in the bottom waters. It is more likely, however, that due to the high levels of algal particles in the surface waters of Manganika much of the MeHg transported out of the epilimnion was adsorbed to particles too large to pass into the filtered samples, and thus were not accounted for in the outlet data. MeHg concentrations in unfiltered outlet water samples were around 10 times higher than MeHg concentrations in the filtered samples (TableB). This large portion of the total mercury pool (unfiltered fraction) was not consistently quantified and therefore presents a serious challenge for detailed accounting of MeHg in Lake Manganika.

Lake McQuade

Bottom water concentrations of MeHg were consistently elevated above surface water concentrations at McQ3, suggesting a spatial gradient to drive net transport of MeHg from bottom to surface waters (Fig 9g). However, the close similarity between inlet, surface, and outlet concentrations of total- and

methyl- mercury in May and June 2012 implies that the MeHg produced in the anoxic bottom water and sediment of Lake McQuade was contained in the hypolimnion, and therefore not transported out of the lake (Fig 13a). The capacity for transport out of the hypolimnion is limited by the mixing rate at the limnetic surface, which can be estimated with temperature profile data using the Flux-gradient method (Jassby & Powell 1975). The vertical diffusion coefficient calculated at the limnetic surface (11-12 ft) in early August was -1.33 X 10^{-3} cm^2/s, on the low end of values reported for other small inland water bodies (0.005 – 0.09 cm^2/s, Lake Onondaga; Matthews & Effler 2006)

Conductivity, magnesium, and sulfate steadily increased in the surface waters of Lake McQuade over the course of the summer (Fig 9c, 9j, 9l, 10c, 10j) in response to a rather abrupt increase in inlet concentrations in early July (Fig 13d, 13e, 13h). A simple mixing model based on observations of magnesium at the inlet and outlet of Lake McQuade in response to the relative step increase in early July was used to estimate an average hydraulic residence time of between 45 and 60 days (Appendix A). The lower sulfate observed in the outlet at the end of the summer, even when outlet magnesium was similar to inlet magnesium, can be described by an effective first order, areal mass transport coefficient of 0.0087 m/day. Appendix A provides an outline of preliminary calculations, including an estimate for the net methylmercury flux from hypolimnon to epilimnon and demethylation rate in the epilimnion. These calculations are preliminary at the time of this report and will be refined with input from other project partners.

Basic mixing calculations were performed to investigate if enough MeHg mass was present in hypolimnion waters to explain the observed increase in the outlet concentrations following lake turnover (Fig 13a). In lake samples taken on 8/21/2012 (immediately prior to the MeHg increase observed in the outlet) MeHg concentrations in surface and bottom waters were 0.08 and 1.99 ng/L respectively (Table E). Assuming conservative mixing (i.e. ignoring inputs, methylation and

demethylation reactions), complete mixing of the lake epilimnion and hypolimnion on 8/21/2012 would result in a MeHg concentration of 0.23 ng/L in the mixed, which equates to a 0.15 ng/L increase from the original surface water concentration on 8/21/2012.

Outlet MeHg concentrations were 0.15 – 0.2 in early August and rose to 0.35 ng/L on 8/27, suggesting that much of this increase can be explained by increased surface water MeHg related to lake mixing. In light of the estimated 1 to 2 month residence time of the lake (Appendix A) a rapid increase in outlet MeHg seems unlikely without an sudden change in a process or condition internal to the lake. The coincidence of an increase in outlet MeHg with evidence of lake turnover further supports the hypothesis that summer thermal stratification acts to contain most MeHg in the hypolimnion. Net export of MeHg from McQuade (outlet minus inlet concentration) was largest in the weeks following lake turnover when the stable limnetic surface was removed. Net export then decreased later in the fall, likely due to net demethylation in the aerobic water column.

At Lake McQuade, outlet DOC concentrations were consistently higher than inlet DOC throughout the year implying that Lake McQuade is a net source of DOC to the downstream system (Fig 14a). MeHg concentrations were positively correlated with DOC concentrations in both the inlet and outlet streams, and linear trendlines of the inlet and outlet have similar slopes with the outlet trendline shifted to the right (higher DOC concentrations) (Fig 14b). This means that for equivalent DOC concentrations, outlet MeHg concentrations are lower than inlet concentrations. A previous study of DOC and MeHg in the same watershed proposed that DOC pools composed of heavier molecules had a reduced capacity to carry MeHg (Berndt & Bavin 2012). Thus one explanation for the shift in the MeHg:DOC slope is that the DOC added in Lake McQuade was of higher molecular weight, causing the shift in MeHg binding capacity (Berndt & Bavin 2012).

Conclusions

Though significant differences exist among the two lakes presented here, both geochemical and isotopic evidence point towards significant sulfate reduction in the hypolimnion of Lake Manganika and Lake McQuade. Evidence suggests that water column methylation associated with the observed sulfate reduction has an impact on dissolved MeHg concentrations mostly in the hypolimnion. Flux of MeHg from sediment may also be impacting bottom water MeHg concentrations. A driving force for diffusive flux from porewaters to bottom waters existed for most of the summer at Lake McQuade, while resuspension of sediment-associated MeHg due to ebullition of methane bubbles could be a a source of MeHg at Lake Manganika. Quantitative accounting of MeHg is difficult at Lake Manganika due to a significant particle-associated component not quantified in filtered samples.

Despite production of MeHg in bottom waters and sediment porewaters, there is little evidence of MeHg export out of the lakes into the downstream water systems while lakes are stably stratified, likely due to limited exchange across the limnetic surface. At McQuade, export of MeHg appears to be highest during a brief period from after lake turnover, when mixing brought MeHg from the hypolimnion to the surface, until net demethylation has diminished MeHg concentrations in the water column. This process likely applies to both lakes, though quantitative accounting is difficult at Lake Manganika due to the export of MeHg bound to filterable particulate matter. Future mass balance modeling and quantitative data analysis will lead to a more robust and nuanced understanding of MeHg transport within and out of the lakes.

Upcoming Work

The preliminary interpretations included in this report will be shared with other project partners and refined in light of relevant observations and analysis. Future work is likely to include a mercury mass balance on the hypolimnion of both lakes to help quantify the relative influence of sediment flux, water column methylation and demethylation, and flux across the limnetic surface. This will require the calculation of the rate of vertical diffusion across the limnetic surface for each biweekly temperature profile at each sampling site, using the Flux-gradient method (Jassby & Powell 1975). Estimates will be made for typical conditions from spring to fall, using measured concentrations of redox species and flux estimates as boundary conditions. By quantifying different aspects of the mercury dynamics in the lakes, we will better understand the primary pathways for MeHg production and transport in these lakes.

In addition, refined estimates for lake residence time will be made at McQuade by further examining inlet, surface water, and outlet concentrations of conservative species, such as Magnesium (Mg). Calculation of a residence time will help to further understanding of the mass balance of sulfate and MeHg and the importance and magnitude of net export to the downstream water systems. A preliminary lake mixing model is included as Appendix A and will be expanded to more fully consider interactions with the hypolimnion and implications for transport across the limnetic surface.

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Table A. Comparison of Hg analysis between Gustavus Adolphus and U of Toronto laboratories

	MeHg [ng/L]			THg [ng/L]		
Site Location	Gustavus Adolphus	U of Toronto	Ratio	Gustavus Adolphus	U of Toronto	Ratio
Mng1 SW						
6/25/2012	0.03	0.08	0.37	1.42	1.29	1.10
7/10/2012	0.05	0.50	0.10	1.21	2.32	0.52
7/24/2012		1.11	n/a	1.00	2.10	0.48
8/7/2012	0.06	0.11	0.55		0.43	n/a
8/21/2012	0.13	0.25	0.52	0.97	0.78	1.24
9/5/2012	0.03	0.11	0.26	0.56	1.71	0.32
9/17/2012	0.19	0.24	0.78	0.50	1.31	0.38
10/6/2012	0.13	0.09	1.41	0.44	1.39	0.32
Mng1 **B**W						
6/25/2012	2.33	1.45	1.61	3.40	4.75	0.72
7/10/2012	3.13	0.62	5.06	6.27	3.76	1.67
7/24/2012	1.43	1.28	1.12		5.02	n/a
8/7/2012	4.26	3.30	1.29		6.68	n/a
9/5/2012	3.24	1.14	2.84		4.01	n/a
9/17/2012	0.76	0.09	8.23	1.74	1.20	1.45
10/6/2012	0.03	0.15	0.21	0.46	0.96	0.48
McQ3 SW						
6/25/2012	0.31	0.21	1.47	3.38	2.78	1.22
7/10/2012	0.29	0.43	0.68		2.87	n/a
7/25/2012	0.36	0.13	2.69	1.97	1.52	1.30
8/7/2012	0.18	0.10	1.74		0.84	n/a
8/21/2012	0.13	0.08	1.62	0.93	0.67	1.39
9/6/2012	0.08	0.06	1.29	0.67	1.24	0.54
9/17/2012	0.09	0.05	1.60	0.78	1.20	0.65
10/4/2012	0.01	0.11	0.09	0.57	0.91	0.63
McQ2 SW						
6/25/2012	0.28		n/a	3.79		n/a
7/10/2012	0.35	0.24	1.47	2.46	2.43	1.01
7/25/2012	0.23	0.18	1.27	1.48	1.89	0.78
McQ3 BW						
7/25/2012	4.36	1.52	2.88	6.45	3.29	1.96
8/7/2012	5.09	6.50	0.78		8.08	n/a
8/21/2012	3.74	1.99	1.88	3.41	2.68	1.27
9/6/2012	2.74	0.68	4.01	3.21	2.39	1.34
9/17/2012	0.18	0.08	2.41	0.76	1.48	0.51
10/4/2012	0.03	0.12	0.25	0.70	0.89	0.79
McQ2 BW						
7/10/2012		1.32	n/a	5.83	3.45	1.69
7/25/2012	0.67	0.39	1.73	2.21	1.74	1.27

Table B. Comparison of MeHg and THg concentrations in filtered water samples (0.45 microns) and unfiltered (raw) samples

Site Location	Date	MeHg (filtered) [ng/L]	MeHg (unfiltered) [ng/L]	%Filtered - MeHg []	THg (filtered) [ng/L]	THg (unfiltered) [ng/L]	%Filtered - THg []
Lake Manganika							
Mng1 SW	7/24/2012	n/a	n/a	n/a	1.00	3.71	27.0
	8/7/2012	0.06	0.89	6.5	n/a	n/a	n/a
	8/21/2012	n/a	n/a	n/a	0.97	4.25	22.8
	9/5/2012	n/a	n/a	n/a	0.56	3.14	17.7
	9/17/2012	n/a	n/a	n/a	0.50	3.93	12.8
	10/6/2012	n/a	n/a	n/a	0.44	3.44	12.9
Surface Water Average				*6.5 (n=1)*			*18.6 (n=5)*
Mng Outlet	7/17/2012	0.06	0.76	7.9	1.57	6.12	25.7
	8/1/2012	n/a	n/a	n/a	0.69	4.88	14.1
	10/16/2012	0.03	0.25	10.8	0.48	4.06	11.9
Outlet Average				*9.4 (n=2)*			*17.2 (n=3)*
Mng1 BW	7/24/2012	1.43	2.14	66.8	n/a	n/a	n/a
	8/7/2012	4.26	4.75	89.8	n/a	n/a	n/a
	9/17/2012	n/a	n/a	n/a	1.74	4.89	35.5
	10/6/2012	n/a	n/a	n/a	0.46	3.69	12.6
Bottom Water Average				*78.3 (n=2)*			*24.0 (n=2)*
Lake McQuade							
McQ2 SW McQ3 SW	7/25/2012	0.23	0.46	50.0	1.48	1.87	79.1
	7/25/2012	0.36	0.47	76.6	1.97	2.00	98.5
	8/7/2012	0.18	0.40	45.0	n/a	n/a	n/a
	8/21/2012	0.13	0.42	31.0	0.93	0.98	94.9
	9/6/2012	0.08	0.16	50.0	0.67	0.66	101.5
	9/17/2012	0.09	0.25	36.0	0.78	0.76	102.6
	10/4/2012	0.01	0.33	3.0	0.57	0.79	72.2
Surface Water Average				*41.7 (n=6)*			*91.5 (n=6)*
McQ2 BW McQ3 BW	7/25/2012	0.67	0.81	82.7	2.21	3.04	72.7
	7/25/2012	4.36	4.47	97.5	6.45	8.00	80.6
	8/7/2012	5.09	5.3	96.0	n/a	n/a	n/a
	8/21/2012	3.74	3.42	109.4	3.41	4.16	82.0
	9/6/2012	2.74	2.52	108.7	3.21	3.46	92.8
	9/17/2012	0.18	0.54	33.3	0.76	0.90	84.4
	10/4/2012	0.03	0.07	42.9	0.70	1.00	70.0
Bottom Water Average				*81.5 (n=7)*			*80.4 (n=7)*

Table C. Measured methylation and demethylation rates for June 2013 assays

Sample Location	k_{meth} [d^{-1}]	k_{demeth} [hr^{-1}]	MeHg [ng/L]	THg [ng/L]	%MeHg []	LDO [mM]	Sulfate [mM]	Sulfide [mM]	Nitrate [mM]	DOC [mg/L]
Mng 1 - 12.5 ft	< DL	< DL	0.46	2.14	21.66	0.002	6.18	0.001	0.028	5.14
Mng 1 - BW	0.009	0.014	0.94	1.07	87.98	0.000	6.75	0.176	0.017	8.45
McQ 3 - BW	< DL	0.031	0.21	2.58	8.26	0.000	3.28	0.001	0.009	7.63

Table D. Estimated sediment flux of MeHg (MeHg) and inorganic mercury (iHg)

Sample Location & Time	MeHg (BW) [ng/L]	MeHg (0-2) [ng/L]	**MeHg Flux [pmol/m^2/d]**	iHg (BW) [ng/L]	iHg (0-2) [ng/L]	**iHg Flux [pmol/m^2/d]**
Mng 1						
May '12	3.16	2.51	**-15.8**	0.12	2.86	**25.2**
July '12	1.28	0.69	**-18.0**	3.75	3.18	**-5.2**
October '12	0.15	2.91	**70.8**	0.81	5.92	**47.4**
June '13	0.94	1.32	**9.5**	0.13	41.85	**391.4**
Mng 2						
July '12	0.10	0.38	**10.3**	0.86	3.79	**26.9**
October '12	0.09	0.15	**1.3**	4.47	3.43	**-9.0**
June '13	0.20	6.59	**186.8**	3.87	3.59	**-2.4**
McQ 2						
July '12	0.39	0.54	**5.0**	1.35	2.81	**12.9**
October '12	0.07	0.33	**6.7**	0.92	1.80	**7.4**
June '13	0.21	0.65	**11.6**	4.02	8.51	**37.6**
McQ 3						
July '12	1.52	1.80	**8.5**	1.77	2.02	**2.3**
October '12	0.12	0.68	**15.9**	0.76	2.80	**18.7**
June '13	0.21	1.57	**38.3**	2.37	10.42	**72.9**

Table E. MeHg concentrations in Lake McQuade during August lake mixing

Date	Limnetic Surface Depth	Volume (Epilimnion)	Volume (Hypolimnion)	MeHg (McQ2 SW)	MeHg (McQ3 SW)	MeHg (McQ3BW)
	[ft]	[m3]	[m3]	[ng/L]	[ng/L]	[ng/L]
8/7/2012	10	1.73E+06	2.72E+05	0.02	0.10	6.50
8/21/2012	11 - 12	1.84E+06	1.60E+05	0.20	0.08	1.99

	MeHg (Inlet) [ng/L]	MeHg (Outlet) [ng/L]
7/31/2012	0.13	0.16
8/14/2012	0.10	0.20
8/27/2012	0.06	0.35

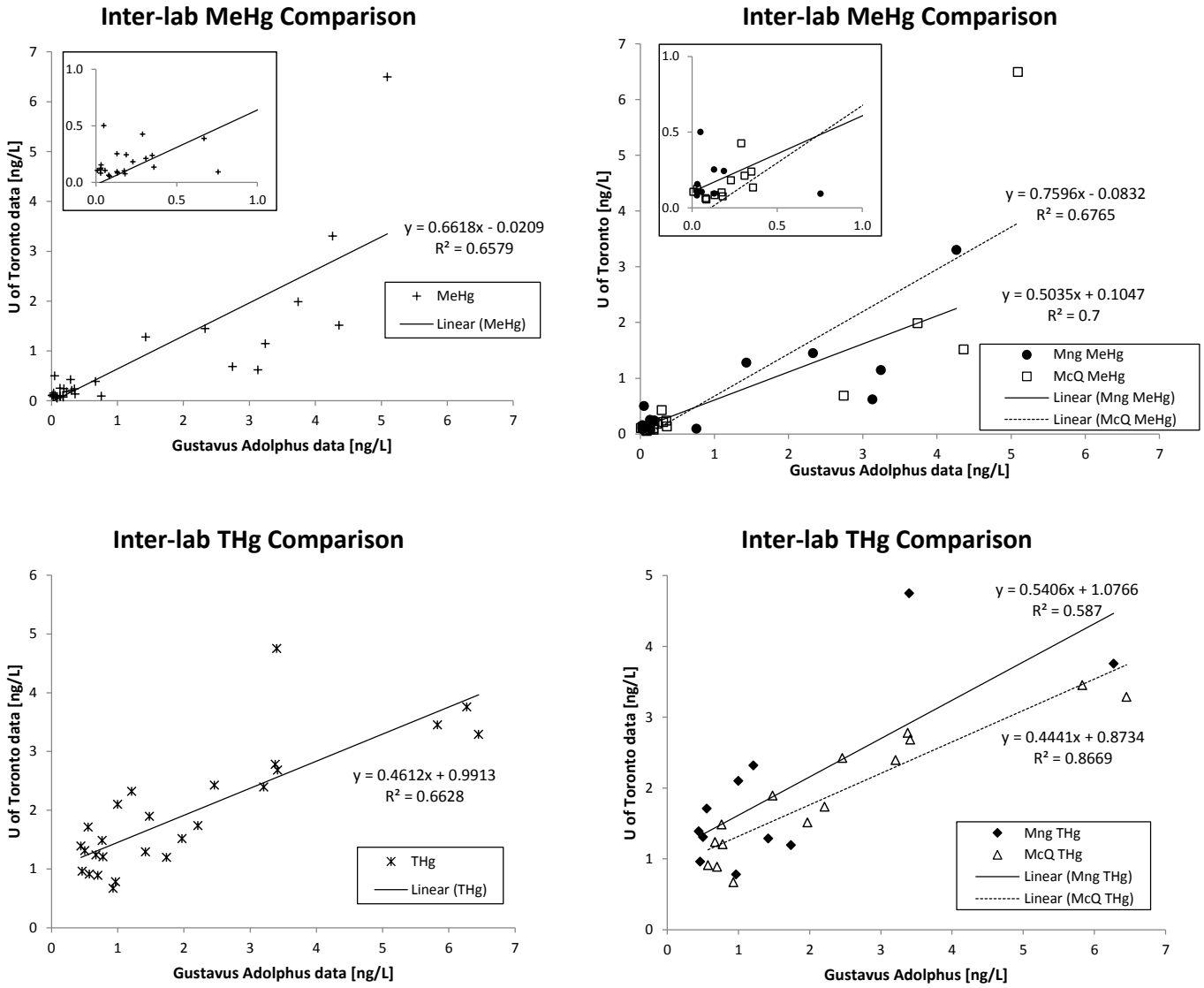

Fig. 3 . Comparisons of MeHg and THg measurments between Gustavus Adolphus lab (sample filter size of 0.45 microns) and U of Toronto lab (sample filter size of 0.2 microns

MNG 1 (Deeper site)

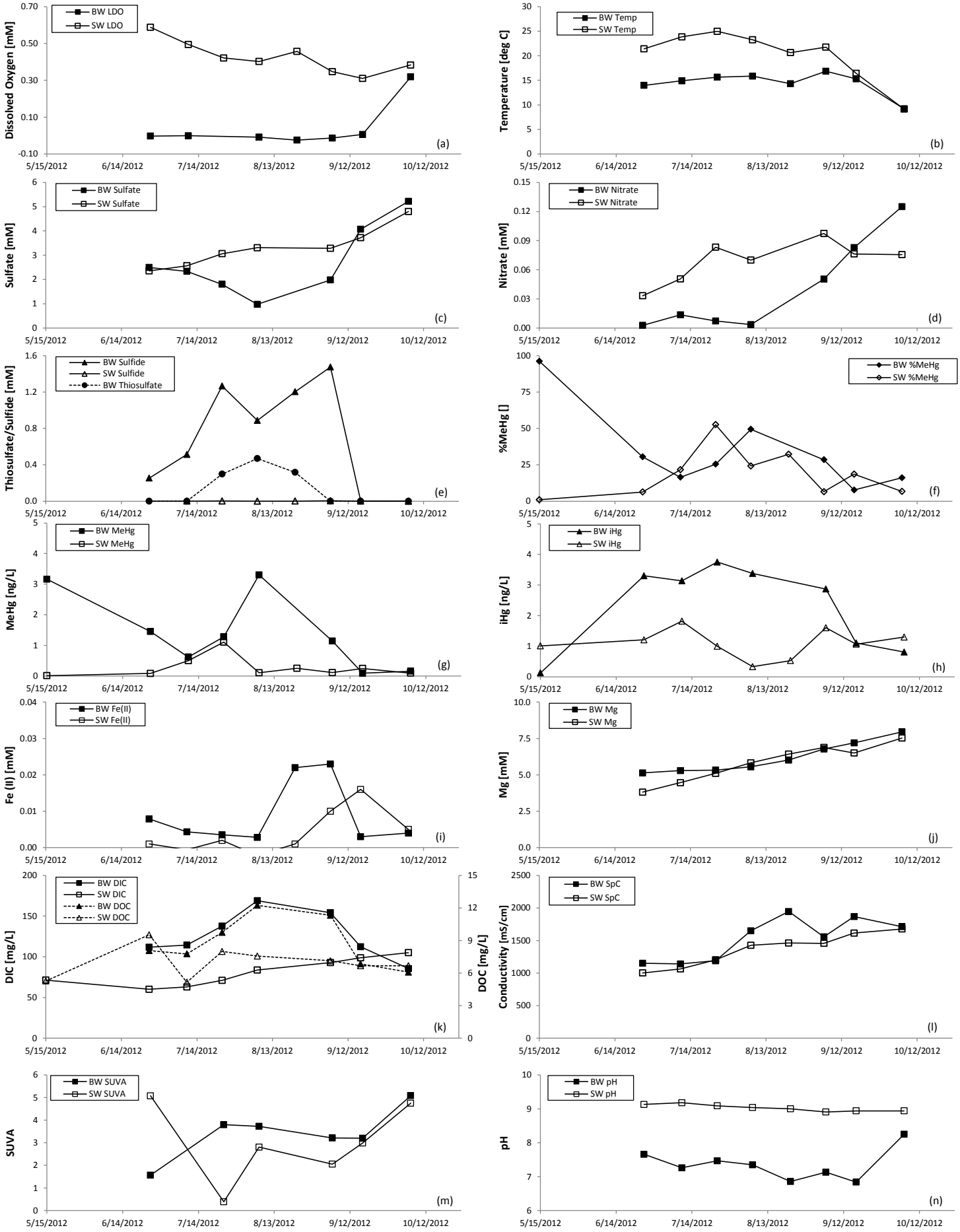

Fig. 4. Time-series of Mng1 surface and bottom water samples for: (a) dissolved O2, (b) temperature, (c) sulfate, (d) nitrate, (e) sulfide and thiosulfate, (f) %MeHg, (g) MeHg, (h) iHg, (i) ferrous iron, (j) Mg, (k) DOC & DIC, (l) conductivity, (m) SUVA, (n) pH

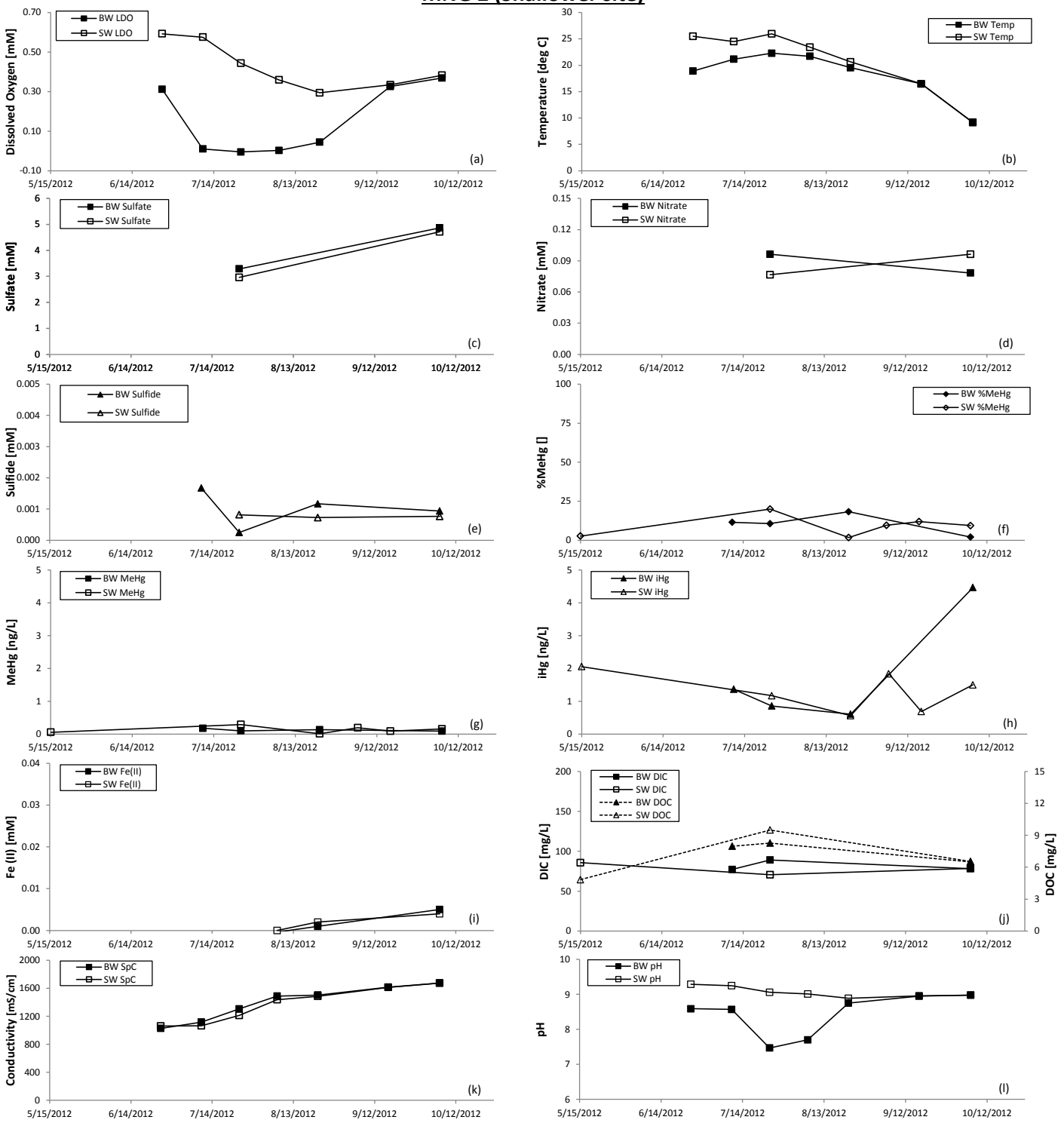

Fig. 5. Time-series of Mng2 surface and bottom water samples for: (a) dissolved O2, (b) temperature, (c) sulfate, (d) nitrate, (e) sulfide, (f) %MeHg, (g) MeHg, (h) inorganic-Hg, (i) ferrous iron, (j) DOC & DIC, (k) conductivity, (l) pH

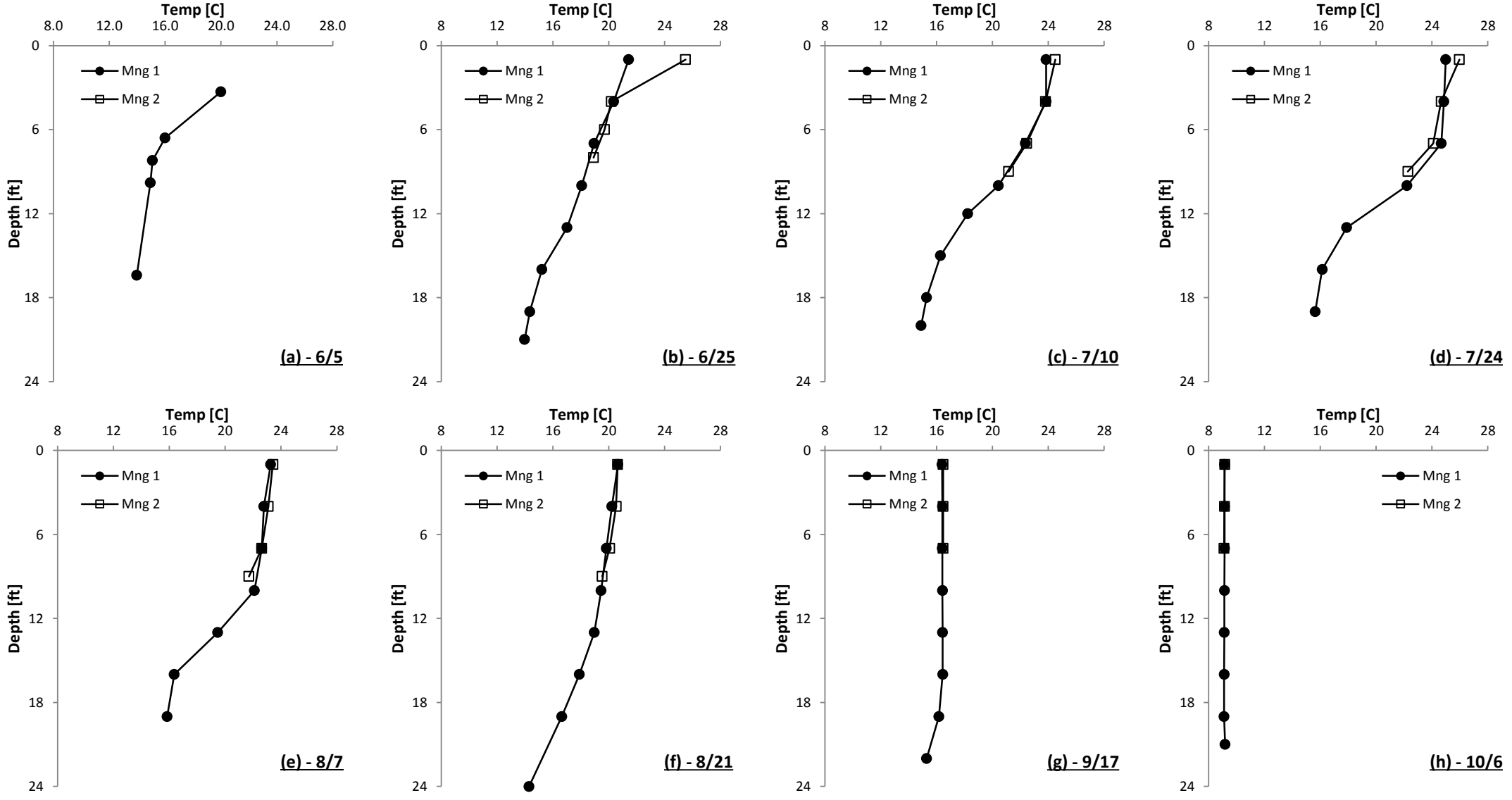

Fig. 6. Lake Manganika temperature profiles, taken biweekly at both sampling locations

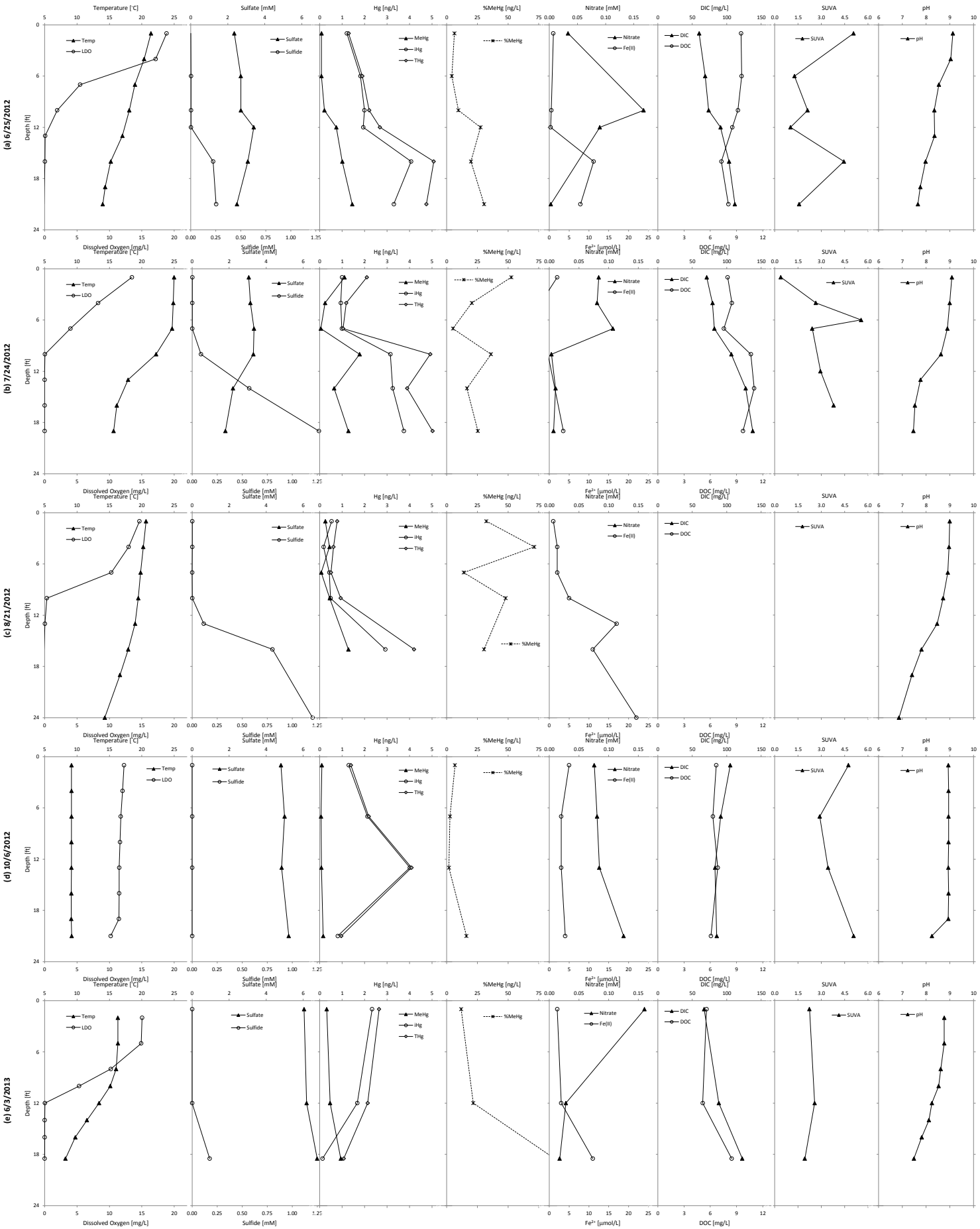

Fig. 7. Depth profiles at Mng 1

MNG Inlet & Outlet

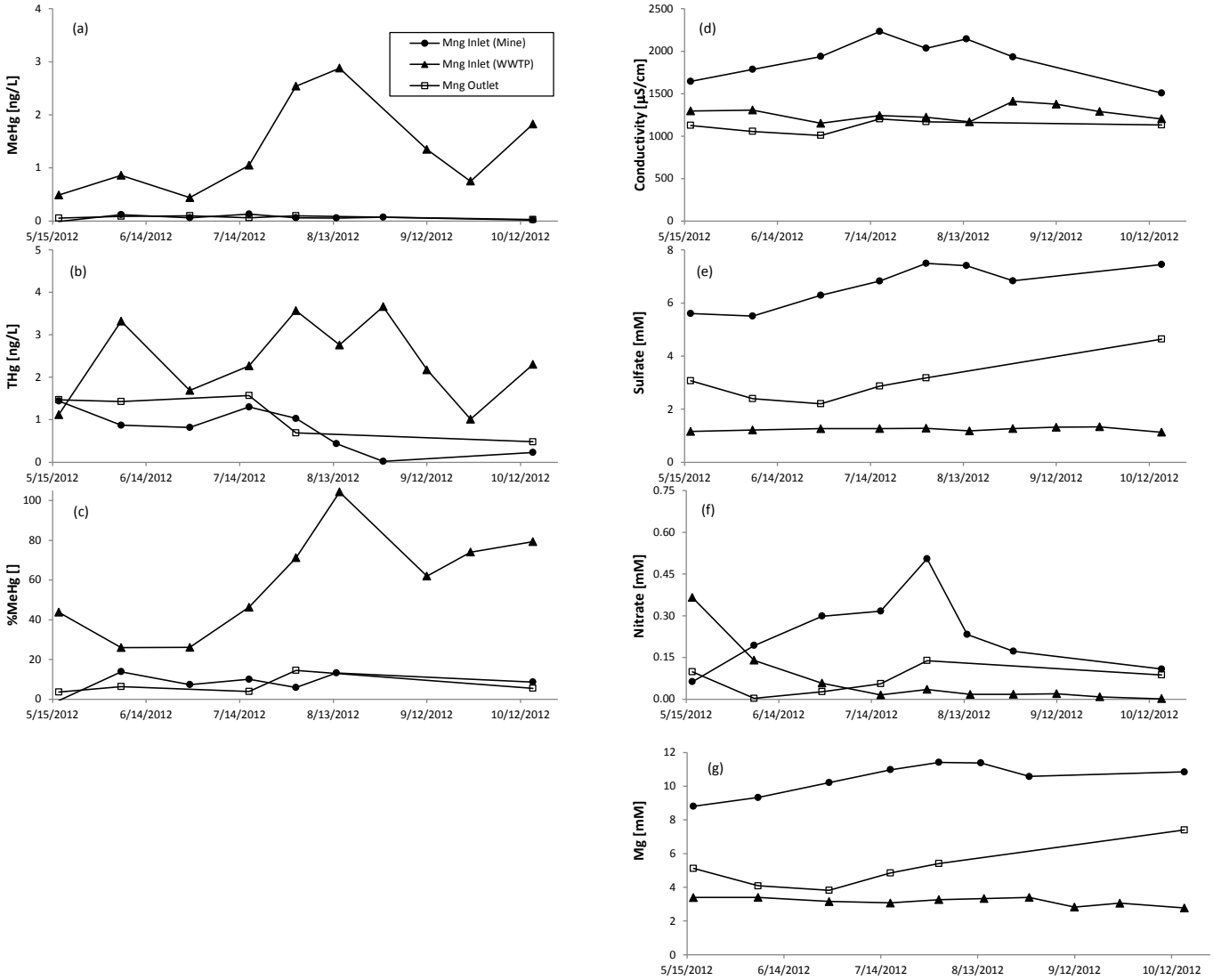

Fig. 8. Time-series of Lake Manganika inlet and outlet streams for: (a) MeHg, (b) THg, (c) %MeHg, (d) conductivity, (e) sulfate (f) nitrate, (g) Mg

McQ 3 (Deeper site)

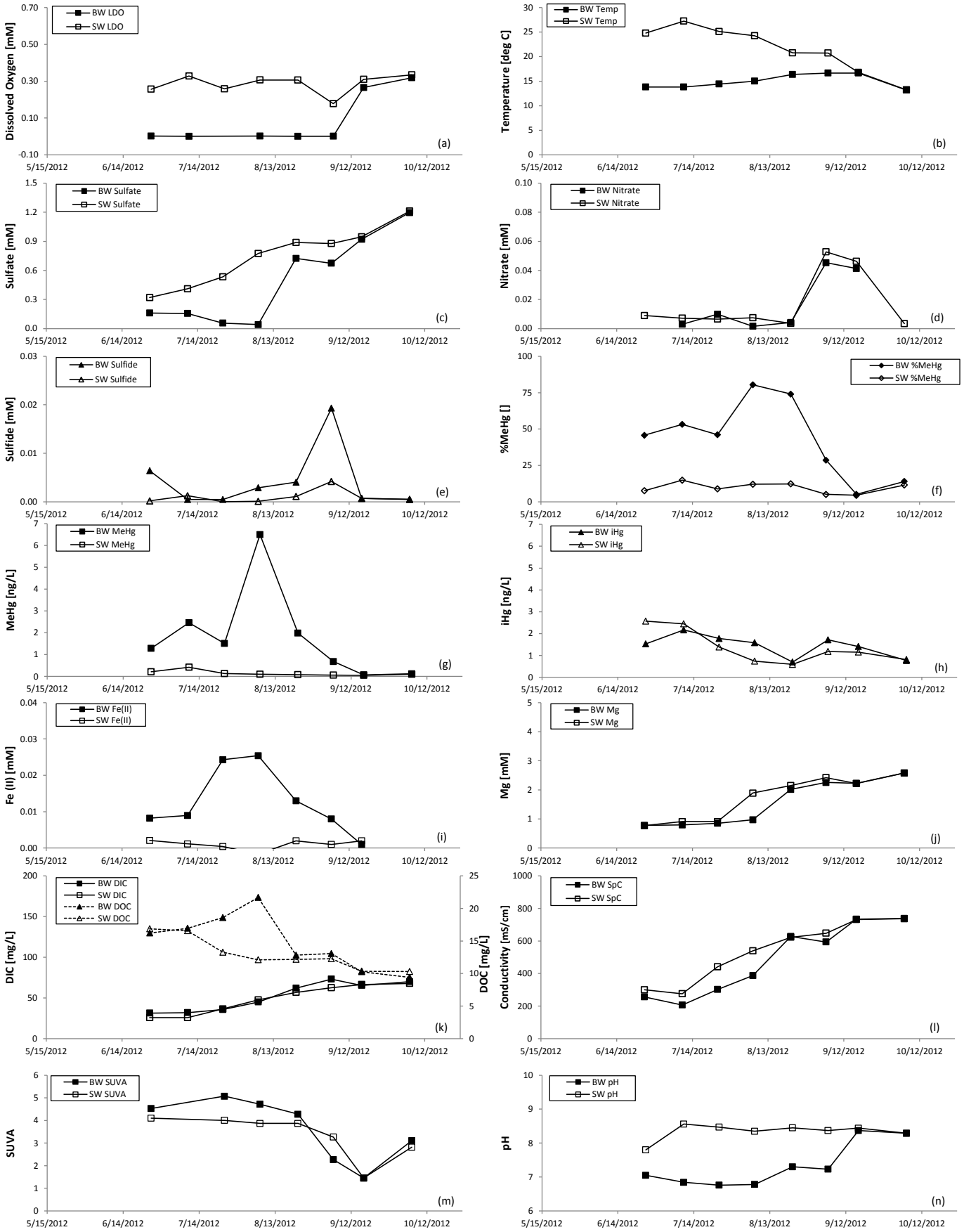

Fig. 9. Time-series of Mng3 surface and bottom water samples for: (a) dissolved O2, (b) temperature, (c) sulfate, (d) nitrate, (e) sulfide and thiosulfate, (f) %MeHg, (g) MeHg, (h) iHg, (i) ferrous iron, (j) Mg, (k) DOC & DIC, (l) conductivity, (m) SUVA, (n) pH

McQ 2 (Shallower site)

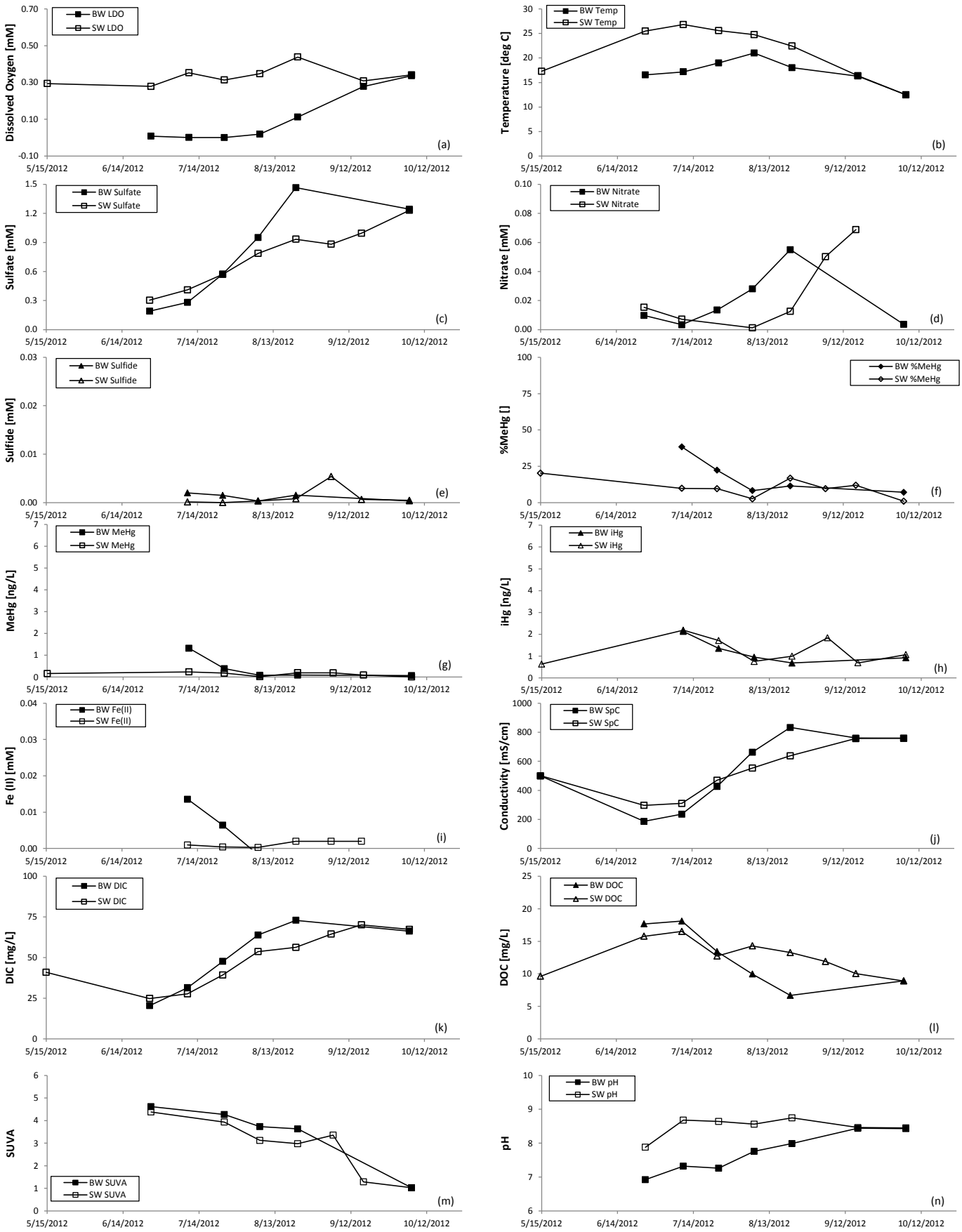

Fig. 10. Time-series of McQ2 surface and bottom water samples for: (a) dissolved O2, (b) temperature, (c) sulfate, (d) nitrate, (e) sulfide and thiosulfate, (f) %MeHg, (g) MeHg, (h) iHg, (i) ferrous iron, (j) Conductivity (k) DIC, (l) DOC, (m) SUVA, (n) pH

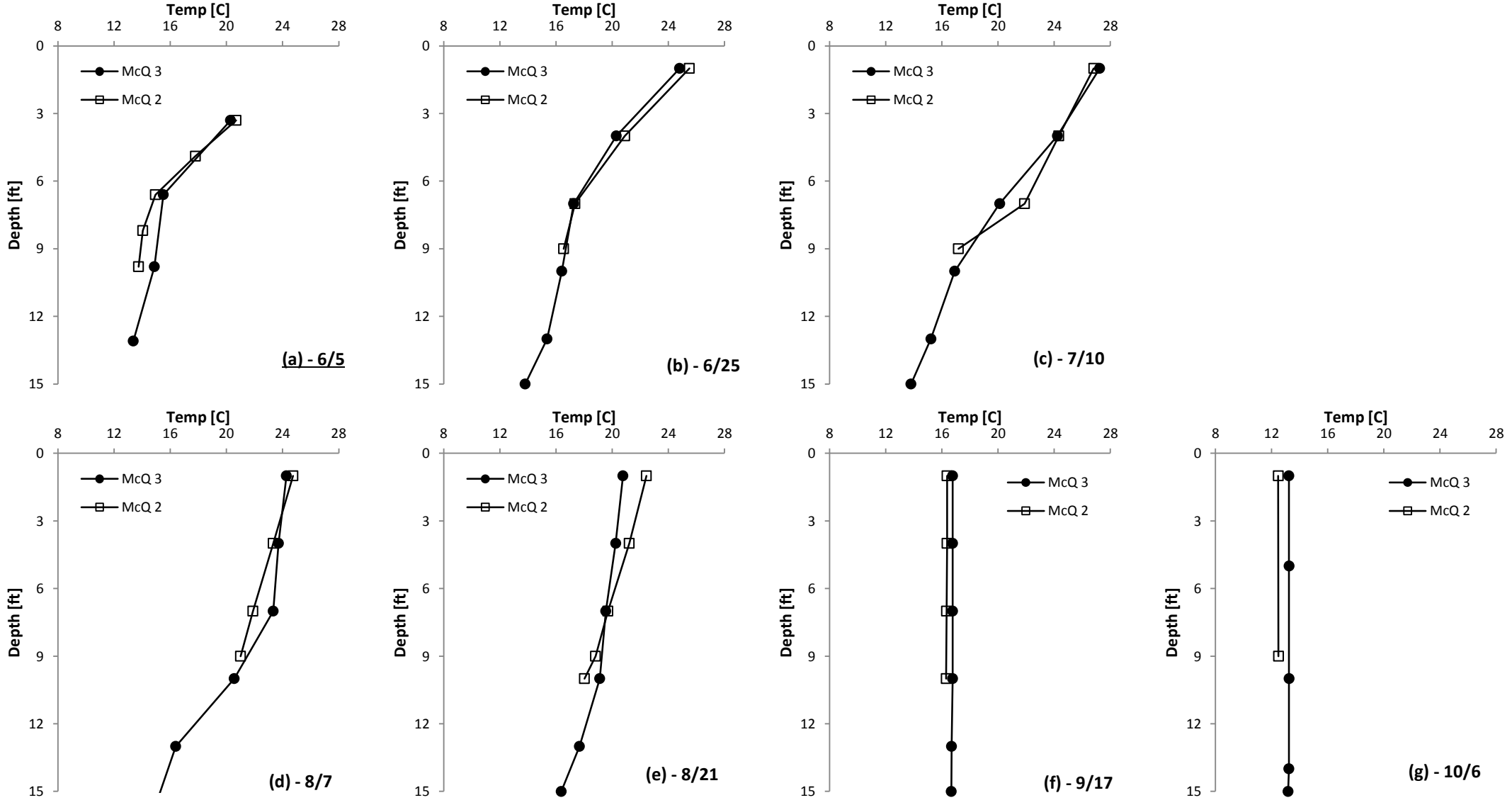

Fig. 11. Lake McQuade temperature profiles, taken biweekly at both sampling locations

McQ 3 Depth Profiles

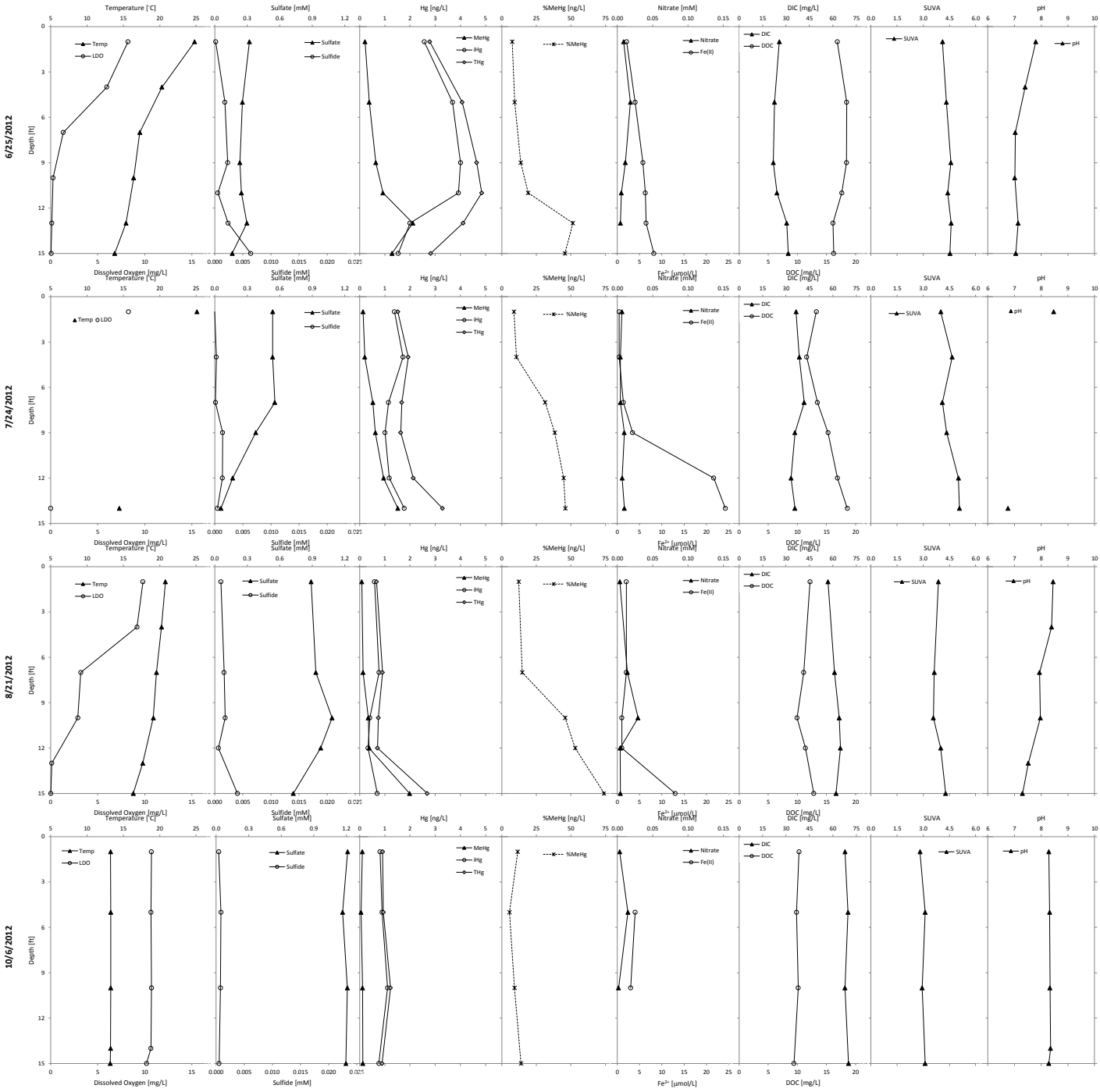

Fig. 12. Depth profiles at McQ 3

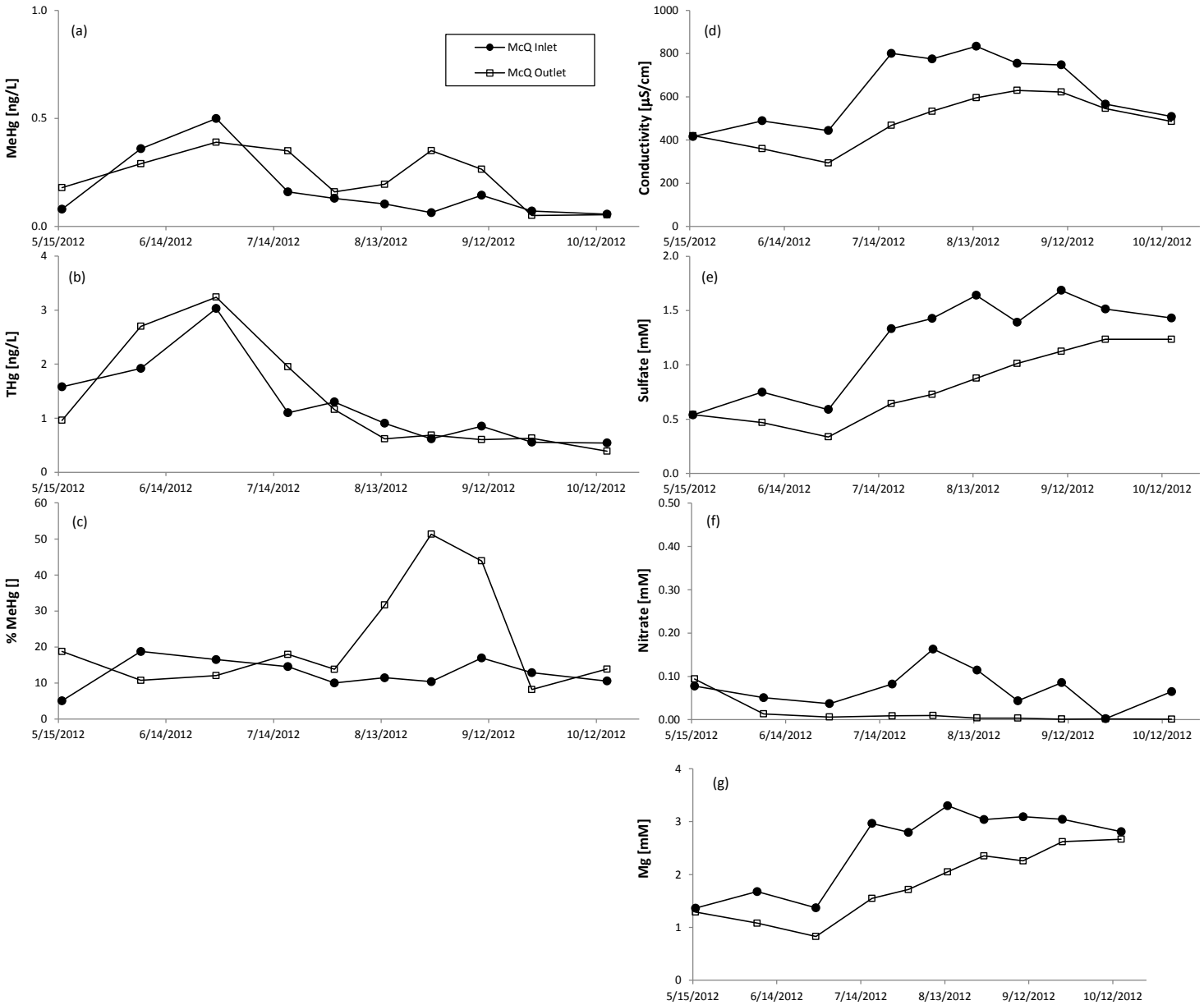

Fig. 13. Time-series of Lake McQuade inlet and outlet streams for: (a) MeHg, (b) THg, (c) %MeHg, (d) conductivity, (e) sulfate (f) nitrate, (g) Mg

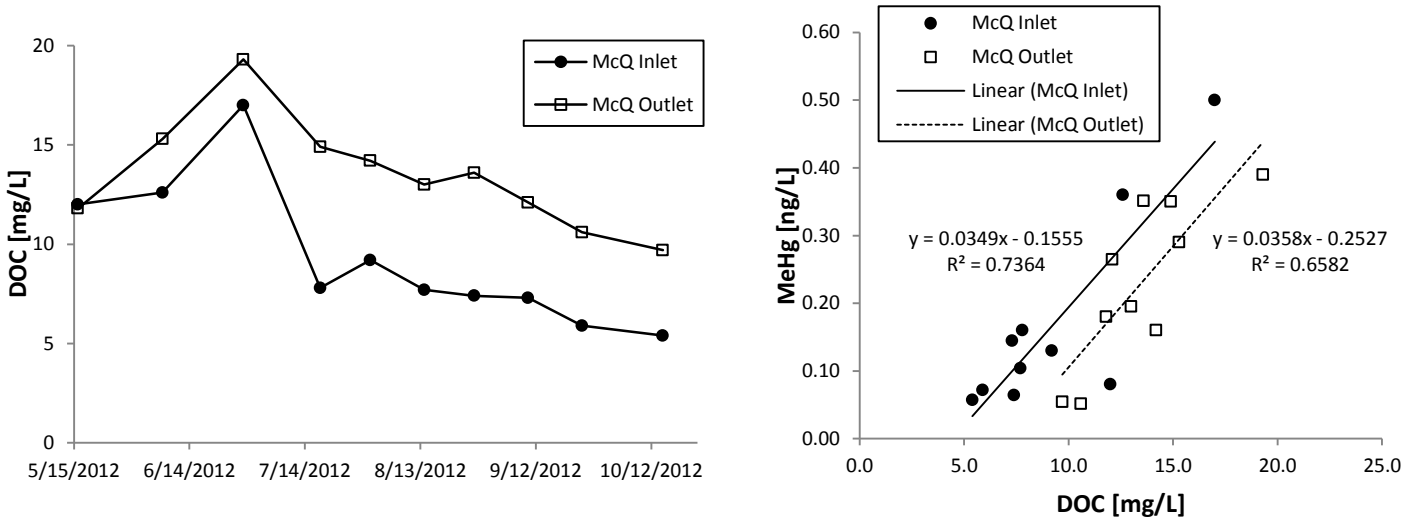

Fig. 14a. (left) DOC concntrations in inlet and outlet streams over summer and fall 2012

Fig. 14b. (right) MeHg and DOC concentrations of inlet and outlet water samples

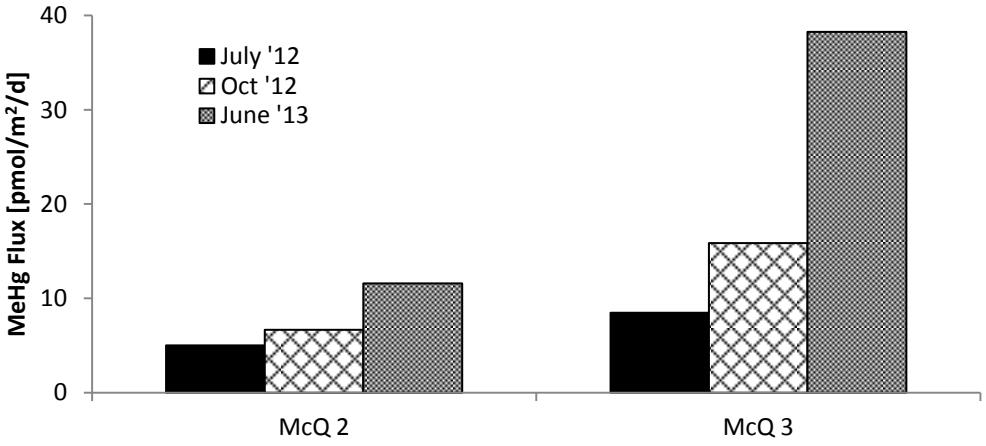

Fig. 15. Estimated flux of MeHg from Lake McQuade sediment

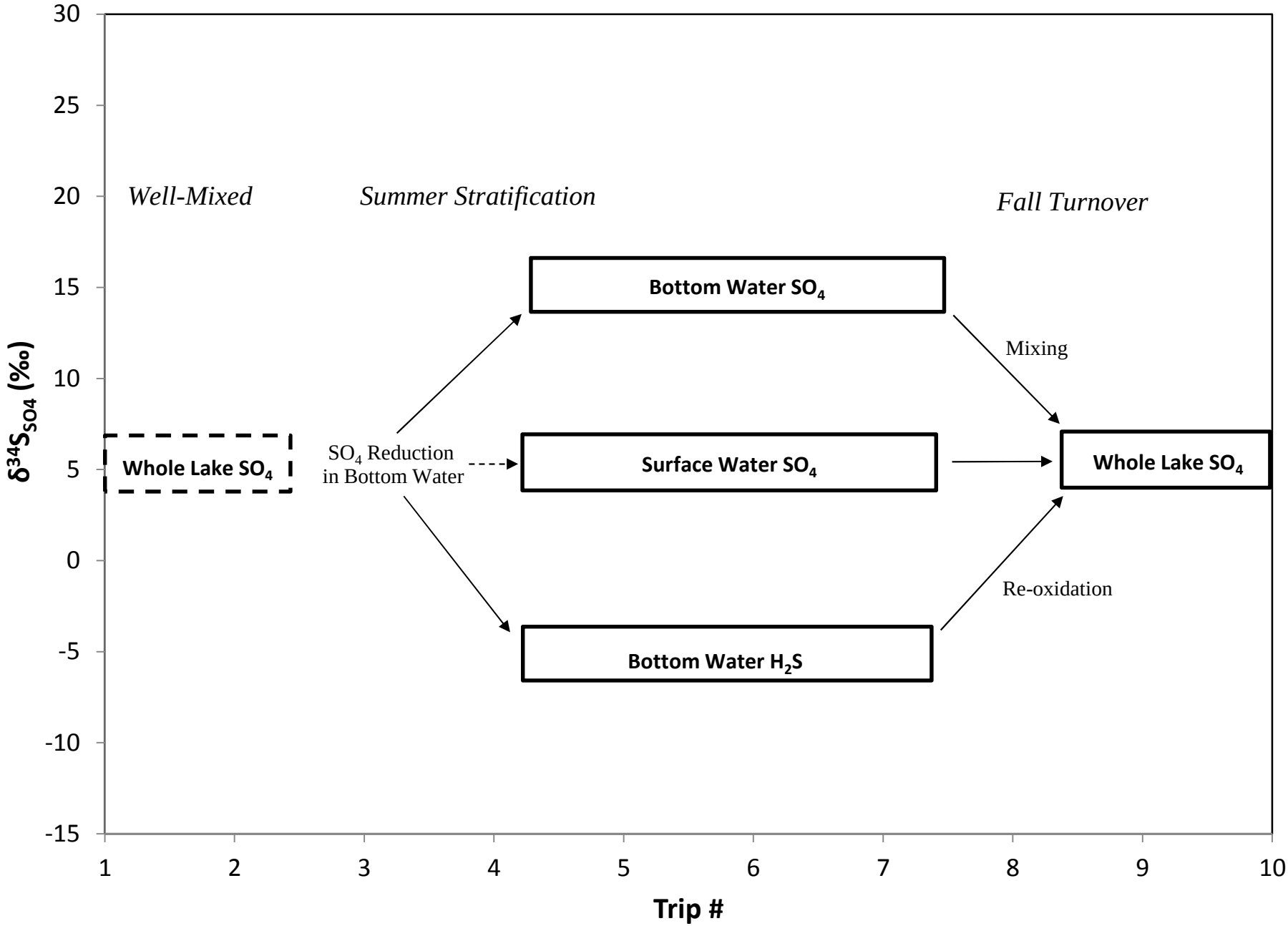

Fig 16 Schematic of sulfur sotopes in Lake Manganika bottom water.

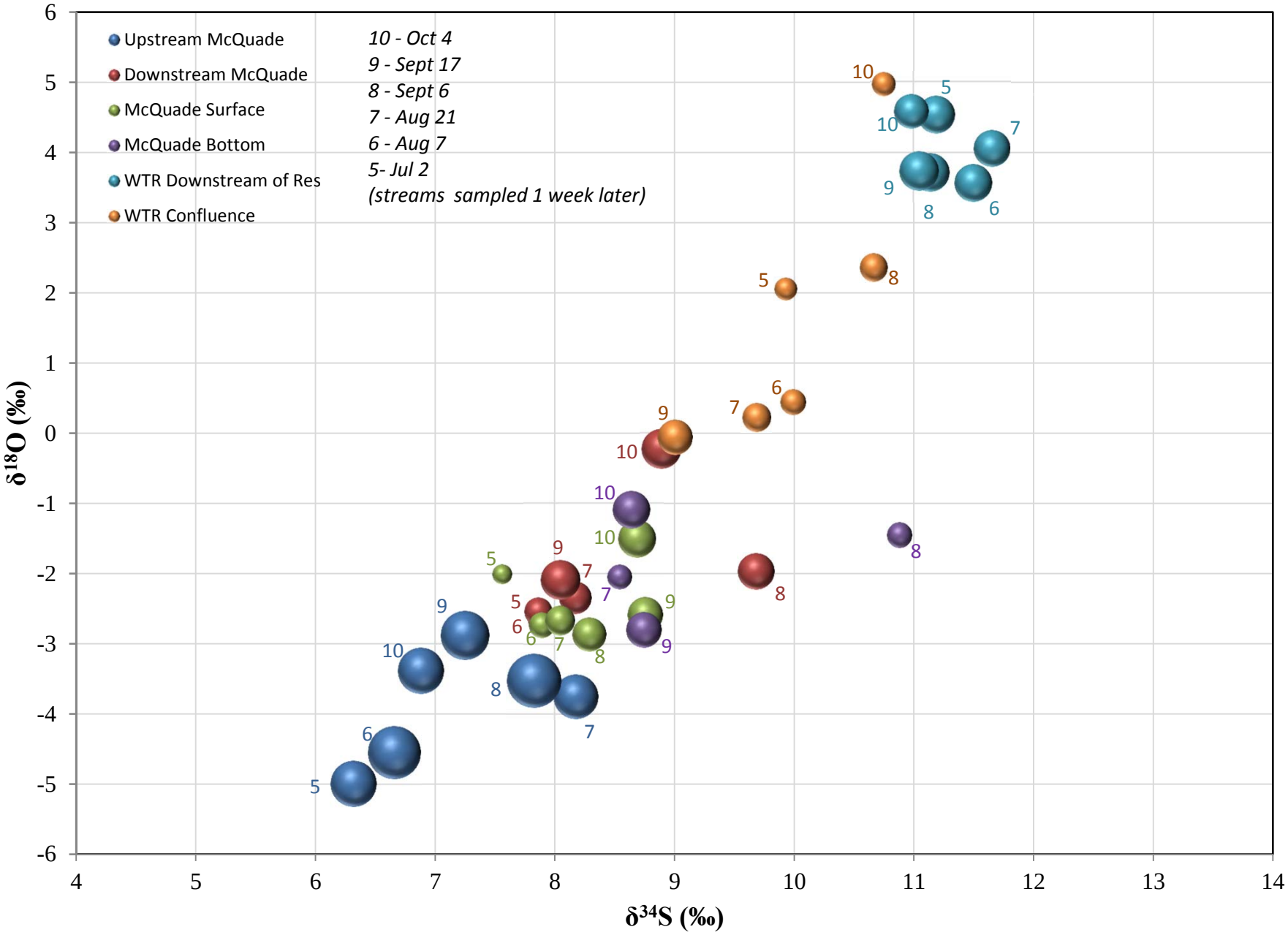

Fig 17 Isotopes in Lake McQuade and the West Two River. Samples from "WTR Downstream of Res" are from a different branch of the West Two River

Appendix A: Draft reactive transport model for sulfate and MeHg in McQuade Lake

Based on a mass balance on only the well-mixed epilimnion of a lake, the transient change in the concentration of a constituent can be described by:

$$V\frac{dC}{dt} = C_{in}Q - CQ - k_{mt}AC$$

Where

- k_{mt} is the mass transfer coefficient for a first-order, areal mass transport process out of the epilimnion
- C_{in} is the concentration in the inlet stream
- Q is the inlet and outlet flow
- V is the epilimnetic volume
- A is the area of the limnetic surface
- C is the concentration in the well-mixed epilimnion

The steady state solution to this equation is:

$$C_{ss} = \left(\frac{C_{in}}{\left(1 + \frac{k_{mt}A}{Q}\right)} \right)$$

And the transient response to a step up in concentration from C_0 to a new C_{in} is given by:

$$C(t) = C_{ss} + (C_0 - C_{ss})e^{-\left(1+\frac{k_{mt}A}{Q}\right)\frac{t}{\tau}}$$

Assuming negligible mass transport of magnesium across the limnetic surface (no consumption in bottom waters / sediment), the residence time (τ) can be adjusted to match concentrations at the outlet. A residence time of 45-60 days provided a reasonable estimate of the response in outlet Mg concentrations following the step up in inlet Mg in early July. (A MORE COMPLETE MODEL INCLUDING THE HYPOLIMNON LAKE VOLUME – AND MASS TRANSFER RESISTANCES ASSOCIATED WITH IT – IS UNDER DEVELOPMENT).

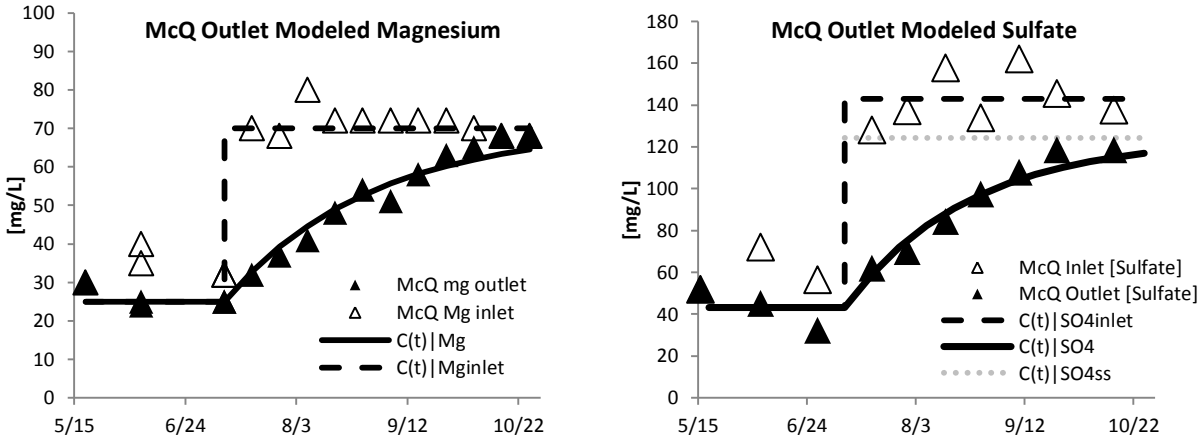

Figure A1 Observed and modeled epilimnetic concentrations of (a) magnesium, and (b) sulfate for Lake McQuade during summer 2012.

With an estimate for τ, an estimate for k_{mt} can be made to describe the mass transport of sulfate out of the epilimnion by fitting to outlet sulfate concentrations. The estimated mass transfer coefficient that matched observed outlet sulfate concentrations was 0.0087 m/day. This net mass transport coefficient, describes the flux of sulfate from the aerobic epilimnion to the anoxic areas of sulfate reduction (either in hypolimnion or sediments). Since sulfate reduction typically occurs concomitantly with mercury methylation, the same effective mass transfer coefficient could be used to estimate the rate of mass transport in the opposite direction, e.g. for MeHg from anoxic areas to the oxidized epilimnion.

When similarly applied to the difference between hypolimnion/porewater and epilimnion MeHg concentrations for the mid-summer, this effective mass transfer coefficient leads to an estimate of a flux of 14.5 mg/day to the epilimnion during the peak summer months.

$$\dot{m}_{hypo} = FA = k_{mt}\left(C_{h/s}^{\ MeHg} - C_{epi}^{\ MeHg}\right)A$$

$C_{h/s}$ = 2.75 ng/L
C_{epi} = 0.25 ng/L
A = 0.67 km^2
k_{mt} = 0.0087 / day

The flux out of the lake during mid-summer based on outlet concentrations and flow estimated from average residence time represents 9.7 mg/day, suggesting demethylation of MeHg in the lake epilimnion.

$$\dot{m}_{outlet} = QC_{epi}^{MeHg}$$

Q = 39,000 m3/day

C_{epi}^{MeHg} = 0.25 ng/L

Given the volume of the lake, the net demethylation rate can be estimated from the difference between hypolimnetic flux and outlet flux for the mid-summer months. This gives an estimated first order demethylation rate of 0.0095 / day, a value within the range of those reported for other small lakes in the Mercury Study report to congress (0.015 – 0.006 / day) (EPA 2006).

$$\dot{m}_{demeth} = k_{demeth}C_{epi}^{MeHg}V_{epi}$$

$m_{demeth} = m_{hypo} - m_{outlet}$

C_{epi}^{MeHg} = 0.25 ng/L

$V_{epi} = 2x10^6\ m^3$

Appendix B: Raw Data Tables

Lake Manganika Plot 1 - Surface Water

Parameter	Units	5/15/2012	6/25/2012	7/10/2012	7/24/2012	8/7/2012	8/22/2012	9/5/2012	9/17/2012	10/6/2012	6/3/2013
pH	[]		9.13	9.18	9.09	9.04	9.00	8.91	8.94	8.94	
Temp	[^{o}C]		21.42	23.84	24.99	23.26	20.65	21.76	16.4	9.15	
LDO	[mg/L]		18.82	15.82	13.47	12.88	14.63	11.1	9.92	12.26	
Conductivity	[μS/cm]		1002	1064	1204	1426	1461	1456	1614	1677	
ORP	[mV]		163.2	122.9	130.9	71.8	74	130	125	130.7	
Depth	[ft]		1	1	1	1	1	1	1	1	
Analytes											
Sulfate	[mM]		2.35	2.57	3.06	3.31		3.28	3.72	4.80	6.05
Nitrate	[mM]		0.03	0.05	0.08	0.07		0.10	0.08	0.08	0.16
Phosphate	[mM]		0.00	0.00	0.00	0.02		0.00		0.00	
Chloride	[mM]				1.51					1.79	2.36
Ferrous Iron	[mM]		0.001	-0.001	0.002	-0.002	0.001	0.010	0.016	0.005	0.002
Sulfide	[mM]		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Thiosulfate*	[mM]		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Ammonium	[mM]	0.000		0.001						0.060	0.005
Mg*	[mM]		3.81	4.47	5.10	5.83	6.42	6.88	6.51	7.53	
DIC	[mg/L]	71.3	60.1	62.9	71.1	83.7		92.8	98.7	105.1	67.2
DOC	[mg/L]	5.3	9.5	5.2	8.0	7.6		7.1	6.7	6.7	5.6
SUVA	[$Lm^{-1}mg^{-1}$]	9.0	5.1		0.4	2.8		2.1	3.0	4.7	2.2
Lactate*	[mg/L]		-0.01	-0.01	-0.01	-0.01					
Acetate*	[mg/L]		-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	
Formate*	[mg/L]		0.09	0.13	0.16	0.45	0.23	0.22	0.21	0.14	
Mercury Analysis											
MeHg	[ng/L]	0.01	0.08	0.50	1.11	0.11	0.25	0.11	0.24	0.09	0.31
THg	[ng/L]	1.02	1.29	2.32	2.10	0.43	0.78	1.71	1.31	1.39	2.64
iHg	[ng/L]	1.01	1.21	1.82	0.99	0.33	0.53	1.60	1.07	1.30	2.33
% MeHg	[]	1.0	6.3	21.6	52.7	24.2	32.3	6.5	18.6	6.7	11.8

*Analytes measured by DNR - Hibbing Lab, all others measured by UMD/SCWRS

Hg analysis by U of Toronto

Lake Manganika Plot 1 - Bottom Water

Parameter	Units	5/15/2012	6/25/2012	7/10/2012	7/24/2012	8/7/2012	8/22/2012	9/5/2012	9/17/2012	10/6/2012	6/3/2013
pH	[]		7.66	7.26	7.47	7.35	6.86	7.13	6.84	8.25	7.49
Temp	[^{o}C]		13.97	14.89	15.64	15.84	14.29	16.84	15.29	9.18	8.21
LDO	[mg/L]		-0.08	-0.02	0	-0.26	-0.78	-0.44	0.2	10.2	0
Conductivity	[µS/cm]		1150	1140	1189	1650	1945	1556	1868	1713	1982
ORP	[mV]		-315	-289.3	-329.7	-344.9	-343.4	-312	-27.4		-191
Depth	[ft]		21	20	19	19	24	22	22	21	
Analytes											
Sulfate	[mM]		2.50	2.33	1.80	0.97		1.98	4.07	5.22	6.75
Nitrate	[mM]		0.00	0.01	0.01	0.00		0.05	0.08	0.13	0.02
Phosphate	[mM]		0.02	0.00	0.04	0.05		0.03		0.00	
Chloride	[mM]				1.60					1.58	3.33
Ferrous Iron	[mM]		0.008	0.004	0.004	0.003	0.022	0.023	0.003	0.004	0.011
Sulfide	[mM]		0.25	0.51	1.27	0.89	1.20	1.48	0.00	0.00	0.18
Thiosulfate*	[mM]		0.00	0.00	0.30	0.47	0.32	0.00	0.00	0.00	
Ammonium	[mM]	0.000		0.516						0.056	
Mg*	[mM]										
DIC	[mg/L]	95.2	111.8	114.5	137.8	169.0		154.1	112.3	85.5	122.6
DOC	[mg/L]	4.8	8.1	7.8	9.7	12.2		11.3	6.9	6.1	8.5
SUVA	[$Lm^{-1}mg^{-1}$]		1.6		3.8	3.7		3.2	3.2	5.1	1.9
Lactate*	[mg/L]		-0.01	-0.01	-0.01	0.01					
Acetate*	[mg/L]		-0.01	-0.01	-0.01	6.24	13.38	0.62	-0.01	-0.01	
Formate*	[mg/L]		0.13	0.14	0.14	0.34	0.26	0.21	0.24	0.15	
Mercury Analysis											
MeHg	[ng/L]	3.16	1.45	0.62	1.28	3.30		1.14	0.09	0.15	0.94
THg	[ng/L]	3.29	4.75	3.76	5.02	6.68		4.01	1.20	0.96	1.07
iHg	[ng/L]	0.12	3.30	3.14	3.75	3.37	0.00	2.87	1.10	0.81	0.13
% MeHg	[]	96.2	30.5	16.5	25.4	49.5		28.5	7.7	16.1	88.0

Lake Manganika - Plot 1 Profiles (1 of 3)

Parameter	Units	6/25/2012									
Depth	[ft]	1	4	6	7	10	12	13	16	19	21
pH	[]	9.13	9.04		8.54	8.35		8.36	7.98	7.76	7.66
Temp	[^{o}C]	21.42	20.35		18.94	18.06		17.01	15.21	14.34	13.97
LDO	[mg/L]	18.82	17.14		5.48	1.94		0.08	0.04	-0.04	-0.08
Conductivity	[µS/cm]	1002	981		1017	1068		1191	1184	1158	1150
ORP	[mV]	163.2	157.7		160.8	147.4		-66	-270	-288	-315
Depth	[ft]										
Analytes											
Sulfate	[mM]	2.35		2.70		2.71	3.40		3.08		2.50
Nitrate	[mM]	0.03				0.17	0.09				0.00
Phosphate	[mM]	0.00				0.00	0.00		0.00		0.02
Chloride	[mM]										
Ferrous Iron	[mM]	0.001				0.001	0.000		0.011		0.008
Sulfide	[mM]	0.00		0.00		0.00	0.00		0.22		0.25
Thiosulfate*	[mM]										
Ammonium	[mM]										
Mg*	[mM]										
DIC	[mg/L]	60.1		68.8		73.8	91.1		103.5		111.8
DOC	[mg/L]	9.5		9.6		9.2	8.5		7.3		8.1
SUVA	[$Lm^{-1}mg^{-1}$]	5.1		1.3		2.1	1.0		4.5		1.6
Lactate*	[mg/L]										
Acetate*	[mg/L]										
Formate*	[mg/L]										
Mercury Analysis											
MeHg	[ng/L]	0.08		0.08		0.21	0.74		1.01		1.45
THg	[ng/L]	1.29		1.90		2.20	2.68		5.08		4.75
iHg	[ng/L]	1.21		1.82		1.99	1.94		4.07		3.30
%MeHg	[]	6.3		4.1		9.5	27.6		19.8		30.5

Lake Manganika - Plot 1 Profiles (2 of 3)

Parameter	Units	7/24/2012								8/21/2012							
Depth	[ft]	1	4	7	10	13	14	16	19	1	4	7	10	13	16	19	24
pH	[]	9.09	9	8.9	8.63	7.77		7.53	7.47	9	8.97	8.92	8.72	8.47	7.81	7.41	6.86
Temp	[^{o}C]	24.99	24.86	24.67	22.21	17.89		16.14	15.64	20.65	20.22	19.82	19.45	18.97	17.9	16.63	14.29
LDO	[mg/L]	13.47	8.25	3.99	0.04					14.63	12.97	10.28	0.34	0.04	-0.09	-0.47	-0.78
Conductivity	[µS/cm]	1204	1217	1245	1336	1232		1194	1189	1461	1464	1492	1527	1631	1668	1686	1945
ORP	[mV]	130.9	124.7	118.3	-160	-303		-321	-330	74	68.9	65.4	62.6	-310	-334	-350	-343
Depth	[ft]																
Analytes																	
Sulfate	[mM]	3.06	3.14	3.34	3.31		2.20		1.80								
Nitrate	[mM]	0.08	0.08	0.11	0.00		0.01		0.01								
Phosphate	[mM]	0.00	0.00	0.00	0.00		0.02		0.04								
Chloride	[mM]	1.51	1.52	1.50	1.43		1.54		1.60								
Ferrous Iron	[mM]	0.002	-0.002	-0.002					0.004	0.001	0.002	0.002	0.005	0.017	0.011		0.022
Sulfide	[mM]	0.00	0.00	0.00	0.09		0.57		1.27	0.00	0.00	0.00	0.00	0.12	0.80		1.20
Thiosulfate*	[mM]																
Ammonium	[mM]																
Mg*	[mM]																
DIC	[mg/L]	71.1	79.5	82.2	106.7		127.5		137.8								
DOC	[mg/L]	8.0	8.5	7.6	10.6		11.0		9.7								
SUVA	[$Lm^{-1}mg^{-1}$]	0.4	2.6	5.6	2.4		2.9		3.8								
Lactate*	[mg/L]																
Acetate*	[mg/L]																
Formate*	[mg/L]																
Mercury Analysis																	
MeHg	[ng/L]	1.11	0.24	0.05	1.78		0.64		1.28	0.25	0.44	0.07	0.45		1.28		
THg	[ng/L]	2.10	1.18	1.04	4.92		3.89		5.02	0.78	0.61	0.50	0.93		4.20		
iHg	[ng/L]	0.99	0.94	0.99	3.15		3.25		3.75	0.53	0.18	0.43	0.49		2.92		
%MeHg	[]	52.7	20.5	5.1	36.1		16.5		25.4	32.3	71.4	13.9	48.0		30.4		

Lake Manganika - Plot 1 Profiles (3 of 3)

Parameter	Units	10/6/2012								6/3/2013								
Depth	[ft]	1	4	7	10	13	16	19	21	1	2	5	8	10	12	14	16	18.5
pH	[]	8.94	8.95	8.95	8.95	8.94	8.95	8.94	8.25		8.77	8.77	8.62	8.53	8.25	8.12	7.82	7.49
Temp	[^{o}C]	9.15	9.15	9.15	9.14	9.13	9.12	9.11	9.18		16.3	16.32	16.04	15.13	13.4	11.52	9.74	8.21
LDO	[mg/L]	12.26	12.02	11.75	11.64	11.52	11.5	11.46	10.2		15.05	14.9	10.22	5.32	0.05	0.001	0.001	0.001
Conductivity	[µS/cm]	1677	1677	1677	1677	1678	1678	1678	1713		142	142	147	145	1568	1597	1750	1982
ORP	[mV]	130.7	121.2	119.9	118.5	116.6	114.3	114.4					391	390	387	-103	-176	-191
Depth	[ft]																	
Analytes																		
Sulfate	[mM]	4.80		4.99		4.83			5.22	6.05					6.18			6.75
Nitrate	[mM]	0.08		0.08		0.08			0.13	0.16					0.03			0.02
Phosphate	[mM]	0.00		0.00		0.00			0.00									
Chloride	[mM]	1.79							1.58	2.36					2.17			3.33
Ferrous Iron	[mM]	0.005		0.003		0.003			0.004	0.002					0.003			0.011
Sulfide	[mM]	0.00		0.00		0.00			0.00	0.00					0.00			0.18
Thiosulfate*	[mM]																	
Ammonium	[mM]	0.060		0.066		0.064			0.056	0.005					0.061			
Mg*	[mM]																	
DIC	[mg/L]	105.1		91.4		83.1			85.5	67.2					88.6			122.6
DOC	[mg/L]	6.7		6.3		6.9			6.1	5.6					5.1			8.5
SUVA	[$Lm^{-1}mg^{-1}$]	4.7		2.9		3.4			5.1	2.2					2.6			1.9
Lactate*	[mg/L]																	
Acetate*	[mg/L]																	
Formate*	[mg/L]																	
Mercury Analysis																		
MeHg	[ng/L]	0.09		0.06		0.08			0.15	0.31					0.46			0.94
THg	[ng/L]	1.39		2.19		4.09			0.96	2.64					2.14			1.07
iHg	[ng/L]	1.30		2.13		4.01			0.81	2.33					1.67			0.13
%MeHg	[]	6.7		2.7		1.9			16.1	11.8					21.7			88.0

Lake Manganika Plot 2 - Surface Water

Parameter	Units	5/15/2012	6/25/2012	7/10/2012	7/24/2012	8/7/2012	8/22/2012	9/5/2012	9/17/2012	10/6/2012	6/3/2013
pH	[]		9.29	9.25	9.06	9.01	8.89		8.96	8.98	
Temp	[^{o}C]		25.5	24.5	25.96	23.42	20.64		16.47	9.16	
LDO	[mg/L]		18.97	18.42	14.2	11.5	9.41		10.71	12.25	
Conductivity	[µS/cm]		1060	1064	1213	1438	1486		1613	1674	
ORP	[mV]		14.9	17.2			-21		7.3	21.5	
Depth	[ft]										
Analytes											
Sulfate	[mM]				2.96					4.71	
Nitrate	[mM]				0.08					0.10	
Phosphate	[mM]				0.00						
Chloride	[mM]				1.54					1.68	
Ferrous Iron	[mM]						0.002			0.004	
Sulfide	[mM]				0.00		0.00			0.00	
Thiosulfate*	[mM]										
Ammonium	[mM]	0.000								0.062	
Mg*	[mM]										
DIC	[mg/L]	85.6			70.6					78.4	
DOC	[mg/L]	4.8			9.5					6.5	
SUVA	[$Lm^{-1}mg^{-1}$]	9.9			3.1					4.8	
Lactate*	[mg/L]										
Acetate*	[mg/L]										
Formate*	[mg/L]										
Mercury Analysis											
MeHg	[ng/L]	0.06			0.29		0.01	0.19	0.09	0.16	
THg	[ng/L]	2.12			1.46		0.57	2.03	0.78	1.66	
iHg	[ng/L]	2.06			1.17		0.56	1.84	0.69	1.50	
% MeHg	[]	2.7			20.0		1.8	9.6	11.9	9.4	

Lake Manganika Plot 2 - Bottom Water

Parameter	Units	5/15/2012	6/25/2012	7/10/2012	7/24/2012	8/7/2012	8/22/2012	9/5/2012	9/17/2012	10/6/2012	6/3/2013
pH	[]		8.59	8.57	7.47	7.70	8.75		8.95	8.98	8.55
Temp	[^{o}C]		18.9	21.16	22.28	21.7	19.53		16.47	9.11	15.48
LDO	[mg/L]		9.97	0.32	-0.17	0.08	1.43		10.42	11.81	4.85
Conductivity	[µS/cm]		1026	1118	1306	1489	1503		1615	1675	1454
ORP	[mV]		9	-179	-361.4	-329	-123		11.9	31.4	
Depth	[ft]		8	9	9	9	9		7	7	
Analytes											
Sulfate	[mM]				3.29					4.87	3.00
Nitrate	[mM]				0.10					0.08	0.12
Phosphate	[mM]				0.00						
Chloride	[mM]				1.52						2.36
Ferrous Iron	[mM]			-0.001	-0.002		0.001			0.005	0.002
Sulfide	[mM]			0.00	0.00		0.00			0.00	0.00
Thiosulfate*	[mM]										
Ammonium	[mM]			0.092						0.065	0.002
Mg*	[mM]										
DIC	[mg/L]			77.2	89.2					78.2	70.7
DOC	[mg/L]			8.0	8.3					6.5	5.8
SUVA	[$Lm^{-1}mg^{-1}$]				3.4					3.1	2.3
Lactate*	[mg/L]										
Acetate*	[mg/L]										
Formate*	[mg/L]										
Mercury Analysis											
MeHg	[ng/L]			0.18	0.10		0.14			0.09	0.20
THg	[ng/L]			1.55	0.96		0.74			4.56	4.07
iHg	[ng/L]			1.37	0.86		0.61			4.47	3.87
% MeHg	[]			11.5	10.6		18.3			2.1	5.0

Lake McQuade Plot 2 - Surface Water

Parameter	Units	5/15/2012	6/25/2012	7/10/2012	7/25/2012	8/7/2012	8/22/2012	9/5/2012	9/17/2012	10/6/2012	6/3/2013
pH	[]	8.07	7.88	8.68	8.64	8.56	8.75		8.46	8.45	
Temp	[^{o}C]	17.28	25.5	26.82	25.59	24.75	22.44		16.37	12.48	
LDO	[mg/L]	9.41	8.92	11.3	10.04	11.13	14.04		9.87	10.92	
Conductivity	[µS/cm]	500.8	297	310	470	554	638		757	759	
ORP	[mV]	348	52.2		22		68		40.5	56.5	
Depth	[ft]										
Analytes											
Sulfate	[mM]		0.30	0.41	0.57	0.79	0.93	0.88	1.00	1.23	3.28
Nitrate	[mM]		0.02	0.01		0.00	0.01	0.05	0.07		0.01
Phosphate	[mM]		0.00			0.00	0.02	0.01			
Chloride	[mM]				1.54					0.21	
Ferrous Iron	[mM]			0.001	0.000	0.000	0.002	0.002	0.002		0.006
Sulfide	[mM]			0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Thiosulfate*	[mM]		0.00	0.00	0.00						
Ammonium	[mM]	0.001		0.002						0.000	
Mg*	[mM]		0.75	1.05	1.55						
DIC	[mg/L]	40.9	24.9	27.7	39.2	53.6	56.3	64.5	70.1	67.3	32.6
DOC	[mg/L]	9.6	15.8	16.5	12.7	14.3	13.3	11.9	10.0	8.9	9.6
SUVA	[$Lm^{-1}mg^{-1}$]	6.9	4.4		3.9	3.1	3.0	3.4	1.3	1.0	3.9
Lactate*	[mg/L]		-0.01	-0.01	-0.01						
Acetate*	[mg/L]		-0.01	-0.01	-0.01						
Formate*	[mg/L]		0.01	0.02	0.02						
Mercury Analysis											
MeHg	[ng/L]	0.16		0.24	0.18	0.02	0.20	0.19	0.09	0.01	0.41
THg	[ng/L]	0.79		2.43	1.89	0.77	1.19	2.03	0.78	1.07	1.98
iHg	[ng/L]	0.63		2.19	1.71	0.75	0.99	1.84	0.69	1.06	1.57
% MeHg	[]	20.2		9.8	9.6	2.6	16.8	9.6	11.9	0.9	20.6

Lake McQuade Plot 2 - Bottom Water

Parameter	Units	5/15/2012	6/25/2012	7/10/2012	7/25/2012	8/7/2012	8/22/2012	9/5/2012	9/17/2012	10/6/2012	6/3/2013
pH	[]	7.98	6.92	7.32	7.26	7.76	7.99		8.44	8.43	7.40
Temp	[^{o}C]	15.3	16.55	17.18	18.99	21	18.02		16.31	12.5	13.86
LDO	[mg/L]	7.17	0.27	0.04	0.02	0.6	3.59		8.91	10.78	6.19
Conductivity	[µS/cm]	499.4	187	236	427	663	833		760	759	461
ORP	[mV]	333	71.2	-70.5	-120	-60	-70.4		41.2	67.1	
Depth	[ft]		9	9	8.5	9	10		10	9	
Analytes											
Sulfate	[mM]		0.19	0.28	0.57	0.95	1.47			1.24	
Nitrate	[mM]		0.01	0.00	0.01	0.03	0.06			0.00	
Phosphate	[mM]					0.01	0.01			0.01	
Chloride	[mM]				1.49					0.22	
Ferrous Iron	[mM]			0.014	0.006	-0.002					0.004
Sulfide	[mM]			0.00	0.00	0.00	0.00			0.00	0.00
Thiosulfate*	[mM]		0.00	0.00	0.00						
Ammonium	[mM]			0.036						0.002	
Mg*	[mM]		0.55	1.64	1.64						
DIC	[mg/L]		20.4	31.4	47.6	63.9	72.9			66.2	
DOC	[mg/L]		17.7	18.1	13.4	10.0	6.7			8.9	
SUVA	[$Lm^{-1}mg^{-1}$]		4.6		4.3	3.7	3.6			1.0	
Lactate*	[mg/L]		-0.01	-0.01	-0.01						
Acetate*	[mg/L]		-0.01	-0.01	-0.01						
Formate*	[mg/L]		-0.01	0.01	0.02						
Mercury Analysis											
MeHg	[ng/L]			1.32	0.39	0.09	0.09			0.07	0.21
THg	[ng/L]			3.45	1.74	1.03	0.77			0.99	4.23
iHg	[ng/L]			2.13	1.35	0.95	0.68			0.92	4.02
% MeHg	[]			38.3	22.3	8.2	11.4			7.1	5.0

Lake McQuade Plot 3 - Surface Water

Parameter	Units	5/15/2012	6/25/2012	7/10/2012	7/25/2012	8/7/2012	8/22/2012	9/5/2012	9/17/2012	10/6/2012	6/3/2013
pH	[]		7.80	8.56	8.47	8.35	8.45	8.37	8.44	8.29	
Temp	[^{o}C]		24.8	27.24	25.11	24.27	20.77	20.73	16.77	13.24	
LDO	[mg/L]		8.21	10.5	8.26	9.81	9.8	5.7	9.92	10.7	
Conductivity	[µS/cm]		300	276	441	539	623	648	732	737	
ORP	[mV]		72.2	32.9	117		139.6	115	43.5	132.9	
Depth	[ft]										
Analytes											
Sulfate	[mM]		0.32	0.41	0.53	0.77	0.89	0.88	0.95	1.21	3.27
Nitrate	[mM]		0.01	0.01	0.01	0.01	0.00	0.05	0.05	0.00	0.01
Phosphate	[mM]									0.00	
Chloride	[mM]									0.21	0.31
Ferrous Iron	[mM]		0.002	0.001	0.000	-0.002	0.002	0.001	0.002		0.003
Sulfide	[mM]		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Thiosulfate*	[mM]										
Ammonium	[mM]			0.001						0.002	0.001
Mg*	[mM]		0.77	0.91	0.91	1.89	2.15	2.42	2.22	2.58	
DIC	[mg/L]		25.7	25.8	36.5	47.6	56.9	62.6	66.5	67.8	34.2
DOC	[mg/L]		16.9	16.6	13.3	12.1	12.2	12.3	10.4	10.3	8.3
SUVA	[$Lm^{-1}mg^{-1}$]		4.1		4.0	3.9	3.9	3.3	1.5	2.8	3.5
Lactate*	[mg/L]		-0.01	-0.01	-0.01	-0.01					
Acetate*	[mg/L]		-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	
Formate*	[mg/L]		0.01	0.01	0.02	0.07	0.04	0.04	0.04	0.01	
Mercury Analysis											
MeHg	[ng/L]		0.21	0.43	0.13	0.10	0.08	0.06	0.05	0.11	0.14
THg	[ng/L]		2.78	2.87	1.52	0.84	0.67	1.24	1.20	0.91	2.74
iHg	[ng/L]		2.57	2.45	1.38	0.74	0.59	1.18	1.15	0.81	2.60
% MeHg	[]		7.6	14.8	8.8	12.0	12.3	5.0	4.4	11.5	5.1

Lake McQuade Plot 3 - Bottom Water

Parameter	Units	5/15/2012	6/25/2012	7/10/2012	7/25/2012	8/7/2012	8/22/2012	9/5/2012	9/17/2012	10/6/2012	6/3/2013
pH	[]		7.05	6.84	6.76	6.78	7.30	7.23	8.37	8.29	
Temp	[^{o}C]		13.81	13.81	14.43	15.02	16.37	16.66	16.67	13.19	
LDO	[mg/L]		0.05	0.01		0.06	0.01	0.04	8.49	10.19	
Conductivity	[µS/cm]		256	207	302	387	628	594	734	738	
ORP	[mV]		-183.7	-173	-221	-205.6	-241.7	-277			
Depth	[ft]		15	15	14	15.5	15		15	15	
Analytes											
Sulfate	[mM]		0.16	0.16	0.06	0.04	0.72	0.67	0.92	1.20	3.28
Nitrate	[mM]			0.00	0.01	0.00	0.00	0.05	0.04		0.01
Phosphate	[mM]		0.01	0.00	0.03	0.04	0.02	0.02	0.00	0.00	
Chloride	[mM]									0.21	0.29
Ferrous Iron	[mM]		0.008	0.009	0.024	0.025	0.013	0.008	0.001		0.004
Sulfide	[mM]		0.01	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
Thiosulfate*	[mM]										
Ammonium	[mM]									0.002	0.006
Mg*	[mM]		0.78	0.79	0.85	0.97	2.01	2.25	2.23	2.58	
DIC	[mg/L]		31.5	31.9	35.7	45.0	62.0	73.1	65.4	70.1	35.4
DOC	[mg/L]		16.2	17.0	18.6	21.7	12.8	13.1	10.3	9.4	7.6
SUVA	[$Lm^{-1}mg^{-1}$]		4.5		5.1	4.7	4.3	2.3	1.4	3.1	3.5
Lactate*	[mg/L]		-0.01	-0.01	0.01	0.01					
Acetate*	[mg/L]		-0.01	-0.01	0.01	0.01	-0.01	-0.01	-0.01	-0.01	
Formate*	[mg/L]		-0.01	-0.01	0.01	0.02	0.03	0.07	0.04	-0.01	
Mercury Analysis											
MeHg	[ng/L]		1.29	2.46	1.52	6.50	1.99	0.68	0.08	0.12	0.21
THg	[ng/L]		2.82	4.63	3.29	8.08	2.68	2.39	1.48	0.89	2.58
iHg	[ng/L]		1.53	2.17	1.77	1.58	0.70	1.71	1.41	0.76	2.37
% MeHg	[]		45.7	53.2	46.1	80.4	74.0	28.6	5.1	14.0	8.3

Lake McQuade - Plot 3 Profiles (1 of 2)

Parameter	Units	6/25/2012									7/25/2012					
Depth	[ft]	1	4	5	7	9	10	11	13	15	1	4	7	9	12	14
pH	[]	7.8	7.4		7.03		7.01		7.14	7.05	8.47					6.76
Temp	[^{o}C]	24.8	20.29		17.26		16.41		15.36	13.81	25.11					14.43
LDO	[mg/L]	8.21	5.95		1.33		0.25		0.11	0.05	8.26					
Conductivity	[µS/cm]	300	266		199		213		268	256	441					302
ORP	[mV]	72.2	84.5		89.9		83.7		-102.6	-183.7	117					-221
Depth	[ft]															
Analytes																
Sulfate	[mM]	0.32		0.26		0.23		0.25	0.30	0.16	0.53	0.53	0.55	0.38	0.17	0.06
Nitrate	[mM]	0.01		0.02		0.01		0.01	0.00		0.01	0.00	0.00	0.01	0.01	0.01
Phosphate	[mM]								0.00	0.01					0.02	0.03
Chloride	[mM]															
Ferrous Iron	[mM]	0.002		0.004		0.006		0.006	0.006	0.008	0.000	0.000	0.001	0.003	0.022	0.024
Sulfide	[mM]	0.000		0.002		0.002		0.001	0.002	0.006	0.000	0.000	0.000	0.001	0.001	0.000
Thiosulfate*	[mM]															
Ammonium	[mM]															
Mg*	[mM]															
DIC	[mg/L]	25.7		22.6		21.9		24.2	30.5	31.5	36.5	38.6	41.6	35.7	33.2	35.7
DOC	[mg/L]	16.9		18.5		18.4		17.6	16.1	16.2	13.3	11.6	13.4	15.3	16.9	18.6
SUVA	[$Lm^{-1}mg^{-1}$]	4.1		4.3		4.6		4.4	4.6	4.5	4.0	4.7	4.1	4.3	5.0	5.1
Lactate*	[mg/L]															
Acetate*	[mg/L]															
Formate*	[mg/L]															
Mercury Analysis																
MeHg	[ng/L]	0.21		0.38		0.64		0.92	2.11	1.29	0.13	0.20	0.52	0.63	0.95	1.52
THg	[ng/L]	2.78		4.07		4.65		4.85	4.11	2.82	1.52	1.93	1.67	1.63	2.13	3.29
iHg	[ng/L]	2.57		3.69		4.01		3.93	2.00	1.53	1.38	1.72	1.15	1.00	1.18	1.77
%MeHg	[]	7.6		9.3		13.8		19.1	51.4	45.7	8.8	10.6	31.4	38.4	44.8	46.1

Lake McQuade - Plot 3 Profiles (2 of 2)

Parameter	Units	8/21/2012							10/6/2012				
Depth	[ft]	1	4	7	10	12	13	15	1	5	10	14	15
pH	[]	8.45	8.39	7.94	7.97		7.52	7.3	8.29	8.32	8.33	8.35	8.29
Temp	[^{o}C]	20.77	20.25	19.55	19.12		17.67	16.37	13.24	13.25	13.25	13.24	13.19
LDO	[mg/L]	9.8	9.17	3.2	2.89		0.11	0.01	10.7	10.66	10.72	10.65	10.19
Conductivity	[µS/cm]	623	634	666	706		671	628	737	737	737	738	738
ORP	[mV]	139.6	129.1	139	136.1		-200.8	-241.7	132.9	133.6	131.6		
Depth	[ft]												
Analytes													
Sulfate	[mM]	0.89		0.93	1.08	0.98		0.72	1.21	1.16	1.21		1.20
Nitrate	[mM]	0.00		0.01	0.03	0.00		0.00	0.00	0.01	0.00		
Phosphate	[mM]					0.01		0.02	0.00	0.00			0.00
Chloride	[mM]					0.24			0.21	0.21	0.21		0.21
Ferrous Iron	[mM]	0.002		0.002	0.001	0.001		0.013		0.004	0.003		
Sulfide	[mM]	0.001		0.002	0.002	0.001		0.004	0.000	0.001	0.001		0.001
Thiosulfate*	[mM]												
Ammonium	[mM]								0.002	0.003	0.003		0.002
Mg*	[mM]												
DIC	[mg/L]	56.9		61.1	64.1	64.8		62.0	67.8	69.7	67.7		70.1
DOC	[mg/L]	12.2		11.1	9.9	11.4		12.8	10.3	9.8	10.1		9.4
SUVA	[$Lm^{-1}mg^{-1}$]	3.9		3.6	3.6	4.0		4.3	2.8	3.1	2.9		3.1
Lactate*	[mg/L]												
Acetate*	[mg/L]												
Formate*	[mg/L]												
Mercury Analysis													
MeHg	[ng/L]	0.08		0.13	0.34	0.38		1.99	0.11	0.05	0.11		0.12
THg	[ng/L]	0.67		0.90	0.74	0.71		2.68	0.91	0.94	1.22		0.89
iHg	[ng/L]	0.59		0.77	0.40	0.33		0.70	0.81	0.89	1.11		0.76
%MeHg	[]	12.3		14.9	46.0	53.2		74.0	11.5	5.6	9.3		14.0