## Geochemical factors influencing methylmercury production and partitioning in sulfate-impacted lake sediments

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Final Project Data Report with initial interpretations

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#### **Summary**

Sediment samples from several lakes and wetlands within the mining-impacted St. Louis River

Watershed were studied extensively as part of a larger Mine Water Research Advisory Panel (MWRAP)

study of methylmercury (MeHg) production and transport in sulfur-impacted ecosystems. Sediment

from sulfur-impacted and non sulfur-impacted lake and wetland sites was collected during four major

sampling trips between May 2012 and June 2013. Trends in MeHg and the associated sulfur

geochemistry were investigated both spatially and seasonally among the sites to understand the effect

of high sulfur loads on MeHg production and transport. 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.

Mercury dynamics in sulfur-impacted sediments (>60  $\mu$ mol/L sulfide in porewater) appeared to be governed by different mechanisms than in sediments unimpacted by high sulfur loading (<20  $\mu$ mol/L sulfide in porewater). Net MeHg production appeared to be the dominant mechanism governing the quantity of MeHg in both the solid and dissolved phase in low sulfur sediments. However, sulfur impacted sediments had uniformly low net MeHg production, likely due to high sulfide concentrations inhibiting MeHg formation. High sulfide concentrations also appeared to increase MeHg partitioning into the aqueous phase, often leading to porewater MeHg in sulfur impacted sediments higher than what would be expected based on the solid-phase MeHg present.

#### Background

globe. Mercury pollution in soils and aquatic sediments is predominantly a result of atmospheric deposition of anthropogenic sources (Morel 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 1998). Methylation of inorganic mercury in the environment is primarily a result of the activity of sulfate-reducing bacteria (SRB) (Compeau & Bartha 1985, Gilmour et al. 1992), which are active in anoxic sediment and the anoxic bottom waters of lakes. In addition to the activity of SRB, the bioavailability of inorganic mercury also influences MeHg production, as bacterial uptake of inorganic mercury is required for methylation to occur. Evidence suggests bacteria predominantly uptake dissolved Hg(II) complexes whereas particle-bound mercury is biologically unavailable (Benoit et al. 2001; Skyllberg et al. 2003), though nanoparticulate HgS may also be available for uptake (Zhang et al. 2012). Demethylation (the transformation of MeHg back to inorganic mercury) also occurs under a variety of conditions, as a result of biotic and abiotic processes in both aerobic and anaerobic environments (Bridou et al. 2011). Thus, net MeHg production is expected to be most dependent on the activity of SRB, the bioavailability of inorganic mercury, and the activity of demethylating bacteria. MeHg concentrations in porewater are of particular concern due to the potential for transport into surface waters, which is the primary mechanism for MeHg accumulation in biota (Mason et al. 2005). Sulfur can influence porewater MeHg concentrations in at least three ways: (1) the presence of sulfate promotes metabolic activity of methylating sulfate-reducing bacteria, (2) sulfide-Hg bonds may reduce the bioavailability of inorganic mercury (Benoit et al. 2001, Hsu-Kim et al. 2013), and (3) reduced organic or inorganic sulfur ligands can increase the partitioning of MeHg in the porewater (Dyrssen & Wedborg 1991; Jay et al. 2000; Jonsson et al. 2010).

Mercury (Hg) is a trace metal with known adverse health effects and a pollutant of concern across the

Northern Minnesota has been home to iron mining for more than a century and a legacy of these activities is a landscape of large open pits, tailings basins, and waste rock piles with sulfur concentrations in excess of the regional background. Sulfate in these landscapes, which forms from the oxidation of sulfide minerals in the waste rock, eventually makes its way into the downstream wetlands and lakes, In the area south of the Laurentian divide, this water eventually drains to the St. Louis River. The purpose of this study is to examine the effect of high sulfur-loading on MeHg dynamics in fresh water sediment, and 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. This report will present the data collected and provide preliminary interpretations which will be considered and refined in light of the work performed by other project partners.

#### **Methods**

Site Description

Two lakes and three wetlands with varying sulfur loads were investigated in this study. All sites were 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. Lake Manganika (N 47.49°, W 92.57°) is a hypereutrophic lake of maximum depth ~25 feet and surface area ~0.67 km², 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 (16,000 m³/day) local municipal wastewater plant (Berndt & Bavin 2011). Surface water sulfate concentrations range from 200-600 mg/L and an extremely high amount of algal growth has historically been observed. Inlet and outlet MeHg concentrations reported by Berndt & Bavin (2011) indicated that the lake was a net exporter of MeHg and hypothesized that MeHg was being produced in and released from sediments. Lake McQuade (N 47.42°, W 92.77°) is a mesotrophic lake with a maximum depth ~20 feet and surface area ~0.68 km², with comparably lower

surface water sulfate concentrations (30-120 mg/L in 2012); however, consistent with inlet river sulfate, observations of surface waters were approximately 300 mg/L during summer 2013. Lake McQuade also stratified in early summer (limnetic surface between 8-10 feet), with a hypolimnion persisting through mid-September.

The Long Lake Creek wetland (N 47.42°, W 92.56°) is a ~0.14 km² sulfate-impacted boreal peatland located downstream from mining activities with typical upstream sulfate concentrations between 200-300 mg/L. However, fall season pumping of mine-pit water increased the inlet sulfate concentrations to above 500 mg/L in both 2011 and 2012 between the months of September and November. The periphery of the LLC wetland is dominated by typical fen/bog vegetation (sedges, woody shrubs, and mosses) that grades to a cattail (*Typha*) margin fringing an open-water pool through which Long Lake Creek flows. Observations of inlet and outlet stream concentrations at LLC by Berndt & Bavin (2011) showed that significant sulfate reduction occurs in the wetland. MeHg in the wetland outlet was elevated above MeHg in inlet waters, particularly during high flows. The West Two River wetland (N 47.465°, W 92.77°) is a large sedge peatland fringing the northern margins of a small pond. It is subjected to low sulfur loading and comprised of organic-rich sediment and peat with open water sulfate concentrations <5 mg/L. The West Swan River wetland (N 47.24°, W 92.80°) is a riparian wetland with intermediate sulfate-loading comprised of a thin peat layer overlying inorganic sediment.

#### Sample Collection

Field samples were collected on four sampling trips, occurring in the months of May, July, and October 2012 and June 2013. Due to a persistence of winter conditions in spring 2013, the June 2013 sampling date also reflected late spring conditions (similar to May 2012). West Swan River was replaced with West Two River after May 2012, in an effort to include a low-sulfur wetland with similar geomorphology and vegetation to the high-sulfur Long Lake Creek.

Sediment was collected from lake sites at two locations: a deeper basin location (>15 feet) and a shallower basin location (8-10 feet). The shallower locations at lake sites 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'. At wetland sites, sediment from a single location in the near shore open water area was targeted (2-3 feet water depth at Long Lake Creek, 4-6 feet at West Two River). As a part of the larger project, samples were also collected from within the peat and peat pore fluids, but due to the significantly different geochemistry and hydrology of the peatland, results are summarized in a separate report (Johnson et al. 2013).

At each sample location, multiple cores were collected using a HTH Teknik gravity corer (70-mm polycarbonate core tube) and composited to obtain sufficient sediment volume for both solid-phase analysis and pore-water extraction. One set of replicate cores from each location was sub-sectioned into 0-2, 2-4, & 4-8 cm depth intervals and composited to concurrently investigate depth trends. Two additional samples at each location were comprised of only the top 4 cm of sediment from replicate, composited cores.

In an effort to minimize oxidation of anoxic sediments during sample collection, handling, and allocation, nitrogen gas was used to purge the head space in collection jars while the samples were being extracted and composited, and jars were immediately placed in an oxygen-free environment upon completion of core sectioning. Porewater was extracted from the sediment samples using a 5 cm rhizon sampler (tension lysimeter with polyvinylpyrrolidine/polyethersulfone membrane, Seeberg-Elverfeld et al. 2005) with a nominal filter size of 0.2 microns attached to an evacuated borosilicate glass serum bottle. Samples for analysis of solid-phase constituents were homogenized, allocated, and preserved in oxygen free conditions independently of porewater samples. All solid-phase samples were immediately

frozen and, with the exception of AVS, freeze-dried and homogenized prior to chemical analysis. All solid-phase measurements were adjusted to a dry-weight basis.

Methylation and Demethylation Rate Potentials and Mercury Analyses

The potential for inorganic mercury methylation and MeHg demethylation were assessed via enriched stable isotope incubation techniques (Hintelmann et al., 2000; Mitchell and Gilmour, 2008). Potential methylation and demethylation rate constants were measured by injecting sediment cores with a mixture of stable isotope-enriched  $^{200}$ Hg $^{2+}$  & Me $^{201}$ Hg $^{+}$  (94.3%  $^{200}$ Hg $^{2+}$  and 84.7% Me $^{201}$ Hg $^{+}$ ) equilibrated with anoxic, filtered pore water, incubating the cores at in-situ temperatures for approximately 5 hours, freezing to finish the assays, and measuring the generation of enriched Me $^{200}$ Hg $^{+}$  and loss of enriched Me $^{201}$ Hg $^{+}$  via ICP-MS detection. Soil cores were spiked through injection septa spaced at 1 cm intervals on the core tubes using a 100  $\mu$ l gastight syringe.

Prior to mercury analysis, freeze-dried and homogenized sediment samples were microwave digested in concentrated nitric acid for THg determination. For total mercury (THg) analysis (including detection of enriched isotopes), sample digestates were diluted with deionized water and ~0.5% by volume of BrCl was added 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, with the final detection of Hg by ICP-MS. The Tekran 2600 system automates Hg reduction by addition of SnCl<sub>2</sub> and dual gold trap amalgamation of vapour. Rather than standard detection via fluorescence spectroscopy, the Tekran is hyphenated to the ICP-MS and the amalgamated Hg vapour is released into the ICP-MS for isotope detection. Samples for MeHg analysis were distilled according to the methods of Horvat et al. (1993), but with the addition of a different enriched MeHg isotope (Me<sup>199</sup>Hg) and quantified 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 <sup>200</sup>Hg and <sup>201</sup>Hg concentration in THg and MeHg, as well as in calculating ambient THg and MeHg levels from the dominant naturally occurring <sup>202</sup>Hg isotope.

Final concentrations of mercury isotopes were using to calculate methylation and demethylation rates. The ratio of  $k_{meth}/k_{demeth}$  was used as a metric for in-situ net MeHg production rate.

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

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

$$t_i = incubation time[hrs]$$

Clean hands protocols were utilized for mercury samples throughout sample handling, preservation, and analysis, and pore water samples were preserved by adding 0.5% HCl. Pore waters were analyzed for MeHg by isotope-dilution ICP-MS following distillation, as explained above for sediment samples (Hintelmann and Evans, 1997; Horvat et al., 1993). Pore waters were analyzed for THg according to USEPA method 1631, using a Tekran 2600 automated mercury analyzer. Where reported, 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**

Sediment samples were analyzed for acid-volatile sulfide at the St. Croix Watershed Research Station (SCWRS), using the SCWRS laboratory standard operating procedure adopted from standard method 4500-S<sup>2-</sup> (Eaton 2005). Weakly extractable metals were quantified in a subset (July only) of sediment samples for Fe, Al, Mn, Zn, Ca, K, Mg, & Na. Following an acid extraction (0.5N HCl), metal concentrations measured on a PE SCIEX ELAN 6000 ICP-Mass Spectrometer. Though redox-active sulfur

may change form rapidly (seasonally) in sediment-solid phases, the total quantity of metals in sediment is not expected to vary significantly over the course of the study. Sediment total carbon (TC) and total nitrogen (TN) was measured using a CHNS elemental analyzer. Sediment bulk density and water content were calculated (ASTM D2216-10). Ignition tests were used to quantify sediment organic and mineral composition (ASTM D7348).

Porewater samples for anion analysis were acidified to a pH<3 with HCl and bubbled with N<sub>2</sub> gas to remove dissolved sulfide, with a non-acidified duplicate sample used for chloride analysis.

Concentrations of sulfate (SO<sub>4</sub><sup>2</sup>), nitrate (NO<sub>3</sub>), phosphate (PO<sub>4</sub><sup>2</sup>), and chloride (Cl) were measured via ion chromatography (Method 300.1, USEPA 1997) on a Dionex ICS 1100 system. Porewater samples for dissolved sulfide (H<sub>2</sub>S + HS') analysis were filtered into an evacuated serum bottle preloaded with ZnAc and NaOH preservative and quantified using automated methylene blue method (4500-S<sup>2-</sup> E.) (Eaton 2005). Porewater ferrous iron (Fe<sup>2+</sup>) concentrations were measure photometrically using the Phenanthroline Method (3500-FeB) (Eaton 2005). Porewater ammonium was analyzed colorimetrically (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. Carbon lability in porewater was assessed by analyzing samples for specific ultraviolet absorption at 254nm (SUVA) and spectral slope ratio on a Varian Cary 50 scanning UV-Vis spectrophotometer to provide an indication of aromaticity and relative molecular weight, respectively. Additionally, in-situ porewater measurements included temperature, pH, and ORP using electrodes.

#### Data Analysis

For each sampling location a weighted average of measurements from three independent core samples (each comprised of several composited cores) between 0-4 cm depth was primarily used to characterize physical and chemical conditions in surficial sediment  $\frac{1}{2}(A_{0-2}+A_{2-4})+B_{0-4}+C_{0-4}}{3}$ . This approach applies to

all reported values in both solid phase and porewater samples except for those related to the direct analysis of depth dependent trends.

Because the timescales for MeHg production, degradation, and partitioning are not known with certainty, equilibrium conditions in the sediment cannot be assumed. Observed ratios of porewater to solid phase concentrations cannot be properly thought of as representing equilibrium conditions if active methylation or demethylation processes are maintaining higher or lower concentrations in sediment pore water than would be present at equilibrium with the solid phase. In place of equilibrium constants, therefore, an apparent partitioning coefficient  $(K_D^*)$  is reported for inorganic and methylmercury, defined by the ratio of solid-phase concentration to filtered porewater concentration. Inorganic mercury, in both solid and dissolved phases, is defined as the difference between the quantity of total mercury and MeHg.

$$K_D^*(A) = \left(\frac{[C]_{solid} \left[\frac{ng}{kg}\right]}{[C]_{pw} \left[\frac{ng}{L}\right]}\right)$$

#### **Results & Discussion**

#### A. Geochemical Context of Sites

The overwhelming majority of mercury mass in the sediment upon which methylation, demethylation, and partitioning processes act exists on the solid phase as inorganic mercury. Concentrations were between 50 and 300 ng/g at all sampling locations except Manganika's shallow site (Mng2) which had by far the highest mercury levels, averaging 773 ng/g (Fig 1a). Solid phase MeHg concentrations typically comprised less than 2% of the total mercury present in the sediments (Fig 1c). Porewater total- and methyl- mercury concentrations were typically less than 0.1% of the total mercury pool (Fig 1b & d).

Concentrations of porewater sulfide reflect a combination of the degree of sulfate loading and sulfate reducing activity, and often exceeded 1200  $\mu$ M in the sulfur impacted lake sediments and 200  $\mu$ M in the sulfur-impacted open water wetland sediment. Dissolved sulfide was typically below 10  $\mu$ M in non-sulfur impacted sediments (Fig 2). Fe<sub>WEM</sub>:AVS ratios were greater than 2 at the non-sulfur impacted sites and near 1.0 at sulfur-impacted sites, a pattern which reflects the long term sulfur accumulation from historic sulfur-loading relative to the available iron pool (Fig 3) . The likely mechanism producing solid phase sulfur compounds is precipitation reactions between aqueous sulfide and iron species. Thus, continual loads of sulfur to sediment appear to reduce the pool of labile ferrous iron available for precipitating sulfide out of the aqueous phase. Diminished porewater ferrous iron concentrations (< 10  $\mu$ mol/L) at sulfur-impacted sites reflect this process, and are consistent with the high observed dissolved sulfide concentrations (Fig 3).

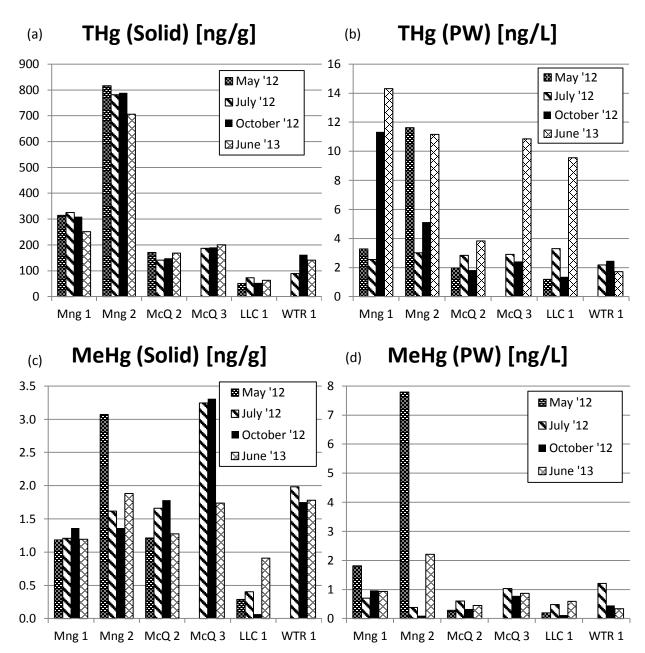
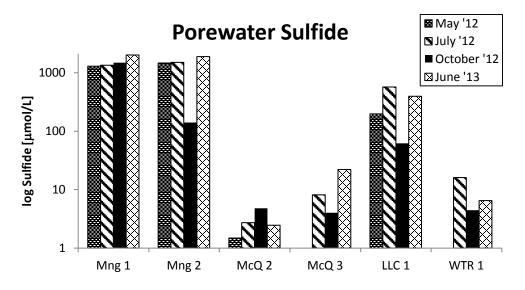


Fig. 1 Mercury concentrations at each site: (a) total mercury in the solid phase, (b) total mercury in porewater, (c) MeHg in the solid phase, (d) MeHg in porewater.



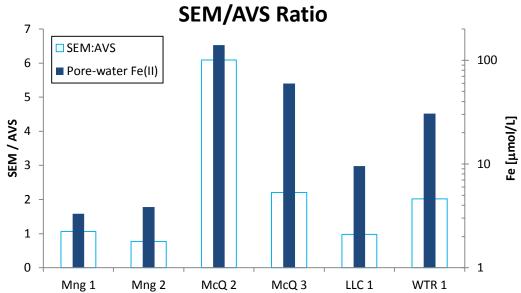


Fig. 2. (top) Average porewater sulfide concentrations (log scale) at each sampling location.

Fig. 3. (bottom) Ratio of extracted Iron to AVS, overlaid with porewater iron (II) concentrations. From July 2012 data.

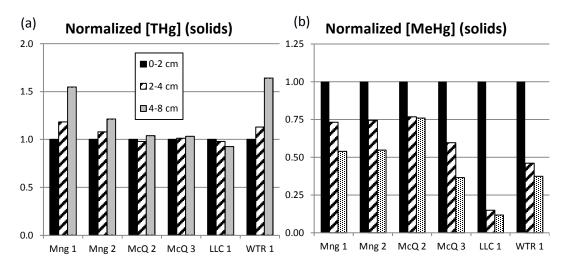
#### B. Sediment Depth Profiles

To characterize the distribution of total- and methyl- mercury with depth in sediments, discrete depth-interval concentrations were normalized to the 0-2 cm increment for each sub-sectioned core set.

Though seasonal variability existed, the average concentrations for each sample location illustrate that solid phase total mercury concentrations were relatively uniform with depth at a majority of sampling locations (Fig 4a). In contrast, solid phase and porewater MeHg concentrations displayed a progressive decline with increasing depth at nearly all sampling locations (Fig 4b & 4c). Similar vertical distribution of mercury was observed in another northern Minnesota lake sediments by Hines et al. (2004). On average, 72.5% of all porewater MeHg and 66.4% of all solid phase MeHg in an 8 cm sediment core exists in the top 4 cm (Table A & Fig 5).

Because sediment total mercury was constant or increasing with depth, processes related to net MeHg production and/or partitioning must be exerting a greater influence in the top 4 cm in order to produce the decreasing depth trend of MeHg concentrations. Previous studies have shown methylation to follow this pattern, with rates greatest immediately below the oxic-anoxic transition (Benoit et al. 2003; Merritt et al. 2008) then declining as sediment depth increases (Gilmour et al. 1998; King et al. 1999). Net methylation rates in this study also showed a consistent downward trend with depth at each location (Fig 6), although the trend was less clear at the shallow water sites (Mng2 and McQ2) and the deep site in lake McQuade (McQ3), where the sediment water interface was near the limnetic surface and the role of the sediment in defining the sulfate-sulfide redox boundary may have been less important.

These depth profile trends establish that the bulk of activity affecting MeHg production and transport occurred in the top 4 cm, and that important process influencing MeHg will not be overlooked if sampling locations are characterized by the 0-4 cm interval.



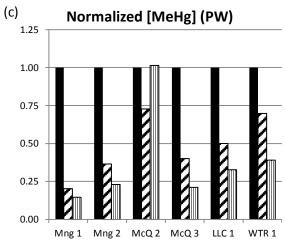


Fig. 4 Average mercury depth profiles for each sampling location, normalized to 0-2 depth interval concentration. (a) solid phase total mercury, (b) solid phase MeHg, (c) porewater MeHg.

	Cumulati	ive % of [I	MeHg] by	Cumulat	ive % of [I	MeHg] by		Cum
	dept	h (solid pl	hase)	dept	h (pore-w	ater)	100 7	
Site Avr	0-2 cm	2-4 cm	4-8 cm	0-2 cm	2-4 cm	4-8 cm		
Mng 1	36.1	62.0	100.0	68.9	82.3	100.0	75 -	
Mng 2	36.3	62.7	100.0	60.7	79.3	100.0	50 -	
McQ 2	31.4	54.8	100.0	31.8	51.4	100.0		
McQ 3	43.6	69.0	100.0	58.3	80.1	100.0	25 -	/,
LLC 1	74.2	84.5	100.0	51.6	73.7	100.0		
WTR 1	45.3	66.2	100.0	41.4	69.2	100.0	0 +	<i></i>
All	44.5	66.4	100.0	52.3	72.5	100.0	0	

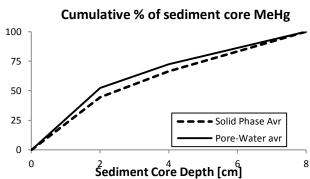


Table A & Fig 5. Cumulative percent of MeHg with depth in an 8 cm sample core

#### **Normalized Net Methylation Potential**

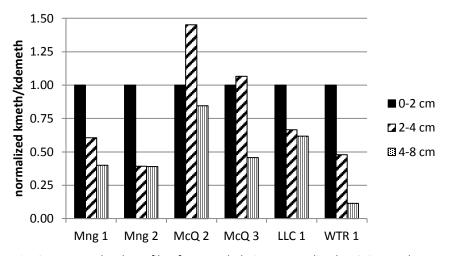


Fig. 6. Average depth profile of net methylation, normalized to 0-2 cm value.

#### C. Methylation potential and solid phase MeHg

Previous research has proposed that %MeHg in sediments ( [MeHg]/[THg] ) is a good estimator for long term methylation potential (Drott 2007b). This long-term proxy of methylation potential was strongly correlated with the instantaneous measures of net methylation potential determined experimentally with stable isotopes. This implies that the instantaneous measures of net methylation potential quantified during this study are consistent with historic net methylation rates as reflected in the accumulation of solid phase MeHg (Fig 7). This trend was consistent for individual samples as well, though the values depicted in Fig 7 represent the average (0-4 cm) of replicate cores for each site during different seasons. The low-sulfur wetland, WTR, had consistently high net methylation potentials relative to %MeHg in the solid phase, largely owing to low rates of demethylation. The shallow site at McQuade had a high methylation potential and low demethylation potential in July 2012 (Fig 7), leading to a large net methylation potential that was not reflected in solid phase %MeHg.. Sulfate consumption was observed in the bottom waters of Lake McQuade during this time (Bailey et al. 2014). A depletion of oxygen and nitrate near the limnetic surface may have caused active sulfate reduction in surficial sediments and/or overlying water and contributed to higher methylation rates at this time. The only

high-sulfate sample having solid-phase %MeHg greater than 0.6 % was the Long Lake Creek site in June 2013, following the large inundation of the wetland with high sulfate water in Fall 2012 (Johnson et al. 2014).

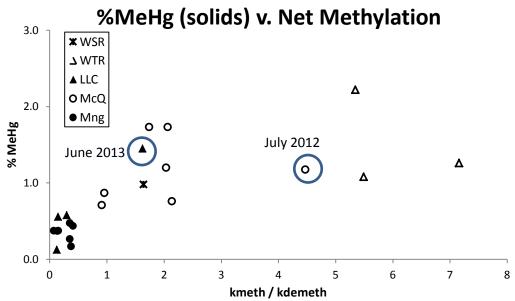


Fig. 7. Comparison of solid phase %MeHg, which represents long-term methylation potential, with experimentally measured net methylation rates. Triangles denote wetland sediment, circles denote lake sediment. Shaded symbols correspond to sulfur-impacted sites, while open symbols correspond to sites with low sulfur loading.

#### D. Influence of Sulfide on MeHg Production

Figure 8 shows two distinct regions in a plot of coincident measurements of %MeHg in the solid phase and dissolved sulfide in porewater (log scale). At lower sulfide concentrations ( $<25 \mu mol/L$ ) there is a positive relationship between solid-phase %MeHg (0.7% - 2.2%) and sulfide. At high sulfide concentrations ( $>60 \mu mol/L$ ) %MeHg is consistently low (<0.6%), aside from one exception (June 2013 LLC), with neither a positive or negative trend. The only observation of greater than 1 % MeHg in sediments of the high sulfate sites also came during June 2013 at Long Lake Creek. The highest sulfide observed in sediment from the low sulfate sites was from Lake McQuade's deep site during June 2013, and this had a relatively lower % MeHg (Fig 8).

## %MeHg (solids) v. Sulfide (PW)

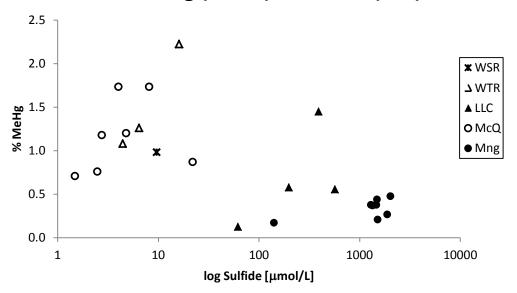


Fig. 8. Solid phase %MeHg, which represents long-term methylation potential, across a range of porewater sulfide concentrations.

Since sulfate was present in all of these surficial sediments at levels sufficient to drive sulfate reduction (see raw data tables in Appendix A), one possible cause of lower net methylation in the presence of high dissolved sulfide is the nature of the dissolved, inorganic mercury pool available for methyl mercury production. Mercury speciation calculations with varying sulfide concentrations, performed by Benoit et al. (1999), show that between 10 and 100 µmol/L sulfide, the predominant mercury species shifts from neutral to charged. It has been proposed that this shift in speciation to charged complexes reduces the bioavailability of inorganic mercury, suppressing methylmercury production at higher sulfide concentrations. This dependence of methylation efficiency on neutral Hg-species has been used to interpret data from several field studies (Drott 2007a), and is consistent with the results from this study. Recent research, however, has questioned the use of the HgS<sup>0</sup>(aq) species in the speciation model (Skyllberg 2008). Alternative hypotheses have highlighted the influence of DOM- stabilized colloidal HgS and nanoparticulate HgS as precursors to mercury methylation, which was not accounted for in the

Benoit (1999) model (Zhang et al 2012; Hsu-Kim et al 2013). Regardless of the specific mechanism, observations show that among the sulfate-impacted freshwater sediments sampled in this study, conditions changed between approximately 20 and 60  $\mu$ mol/L dissolved sulfide in a manner that appears to inhibit net methyl mercury production.

Although %MeHg in the solid phase is often considered a proxy for net methylation potential, instantaneous in-situ measurements of %MeHg in the porewater are a result of not only the production of MeHg in the sediment, but also transport processes and differences between inorganic Hg and MeHg partitioning. At low sulfide concentrations (<25  $\mu$ mol/L), porewater the trend of %MeHg in the pore water resembles that of %MeHg in the solid phase, generally increasing with increased sulfide concentrations (Fig 9). At higher sulfide concentrations (> 60  $\mu$ mol/L) however, porewater %MeHg, was not consistently low. Porewater %MeHg in excess of 55% was observed in Lake Manganika sediments in May 2012 at a time when net methylation potentials were some of the lowest observed in the study.

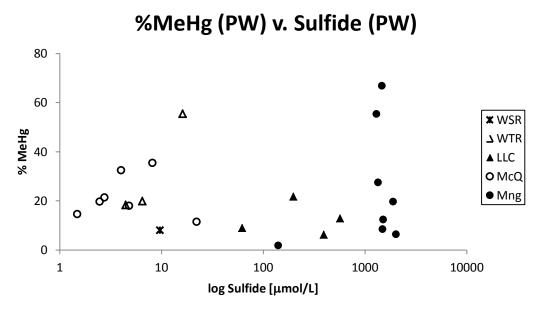


Fig. 9. Porewater %MeHg values across a range of porewater sulfide concentrations.

The variation in *porewater %MeHg* observed in sediments having high dissolved sulfide, combined with the uniformly low *solid phase % MeHg* in sediments having high dissolved sulfide, illustrates a clear difference in the processes influencing porewater %MeHg between low and high sulfide conditions (Fig 10). Low sulfide sites display a strong correlation ( $R^2 = 0.91$ ) between porewater and solid phase %MeHg. Conversely, high sulfide sites display no correlation ( $R^2 = 0.04$ ) between porewater and solid phase %MeHg. These distinct differences imply that in environments with high sulfide concentrations, porewater %MeHg does not mirror net methylation potential (as reflected in the accumulation of MeHg on the solid phase), but rather may be governed by partitioning and/or transport processes.

#### %MeHg (PW) v. %MeHg (solid) 80 60 % MeHg (PW) 40 8 ■ Low Sulfide (<25 umol) Mud + High-Sulfide (>60 umol) Mud 20 0 0.00 0.50 2.50 1.00 1.50 2.00 % MeHg (solid)

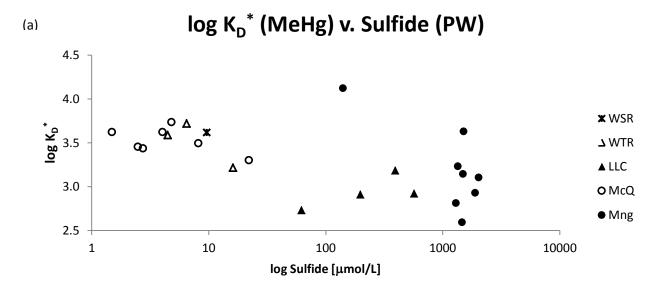
Fig. 10. Comparison of solid phase and porewater %MeHg values, with data points separated into two groups based on porewater sulfide concentration

#### E. Mercury Partitioning

At low sulfide concentrations, apparent MeHg partitioning coefficients display little variability (ranging from log values of 3.2 to 3.7) (Fig 11a). At high sulfide conditions, apparent MeHg partitioning coefficients are more variable and generally lower (average log  $K_D$ \*=3.11 at >60  $\mu$ mol/L sulfide, average

log  $K_D^*=3.53$  at <25  $\mu$ mol/L sulfide), signifying an increase in the relative proportion of MeHg in the pore waters versus the solid phase. Since net methylation potentials were substantially lower at the high sulfide sites (Fig 7), the higher proportion of MeHg in the liquid phase is not likely to be a result of rapid MeHg production and release to sediment pore fluids.

This trend of lower apparent partitioning coefficients across a wide range of increasing pore water sulfide concentrations is stronger in the late spring months, but less apparent in the summer and fall (Fig 11b). A possible explanation for this behavior is more active methylation and demethylation conditions in sediments during the mid-summer months. Warmer temperatures during summer months correspond with increased biological activity and likely rapid rates of biologically-driven methylation/demethylation in sediment pore fluids, potentially making porewater MeHg dependent on these reaction rates. By contrast spring conditions, following months of relatively less biological activity under cold temperatures, may more closely reflect equilibrium conditions between the solid and porewater phases. Under these conditions, the presence of elevated sulfide, a strong ligand for MeHg, could act to pull additional MeHg into the pore fluids from the pool on the solid phase. Unopposed by active methylation/demethylation in sediment pore fluids, the release of MeHg from the sediment solid phase could act to elevate concentrations in sediment pore fluids relative to times when biological demethylation is more active. It has been hypothesized that kinetics may be an important factor in understanding mercury partitioning (Hsu-Kim et al. 2013) as the kinetics of mercury-ligand binding is on the order of days (Miller et al. 2004).



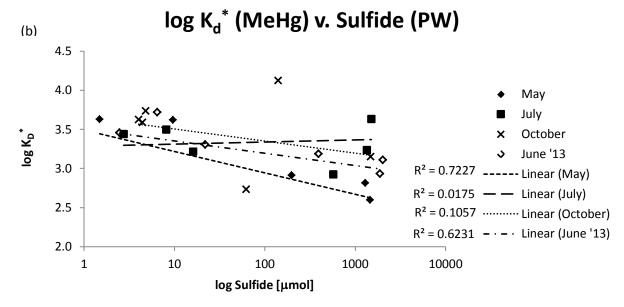


Fig. 11 Measured MeHg partitioning coefficient across a range of porewater sulfide concentrations, with data points grouped (a) by sampling location (top) and (b) seasonally (bottom).

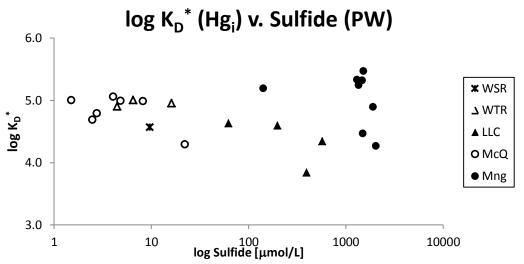


Fig. 12. Measured partitioning coefficient of inorganic mercury across a range of porewater sulfide concentrations.

Since a vast majority of the MeHg in sediments resides on the solid phase, porewater %MeHg depends strongly on the partitioning of both MeHg partitioning and inorganic mercury partitioning. Though some variability was present at sulfide concentrations above 100 µM, this study found no clear trend in inorganic mercury partitioning across a wide range of pore water sulfide concentrations. This suggests that the influence of sulfide on pore water % MeHg is due to changes in MeHg production (at low sulfide concentrations) or partitioning (at high sulfide concentrations) rather than due to solid-liquid partitioning of inorganic mercury (Fig 12). Previous studies in freshwater systems at low sulfur conditions have often used porewater %MeHg as an estimation of net methylation (Jeremiason et al. 2006, Mitchell et al. 2008, Coleman-Wasik et al. 2012), but in environments with high porewater sulfide concentrations this assumption may not be appropriate.

Organic carbon often plays an important role in mercury partitioning in sediments because it can bind dissolved mercury (Berndt and Bavin 2012) and also stabilize nanocolloidal HgS crystals (Gerbig et al., 2011, Zhang et al., 2011). While no apparent trend existed between log  $K_D^*$  for MeHg and DOC in this study (Fig 13 a), the absolute concentration of MeHg generally increased with increasing DOC except in sediments of Lake Manganika (Fig 13b). It should also be noted that the sampling locations had a

relatively narrow range of DOC relative to the observed range in sulfide (Figs 8-12). This lack of correlation remained when  $\log K_D^*$  was compared to SUVA and slope ratio (appendix) indicating that SUVA and slope ratio may not adequately predict mercury-ligand strength in sites from similar geochemical settings. Overall, pore water sulfide was the only analyte that displayed a correlation with varying MeHg partition coefficients.

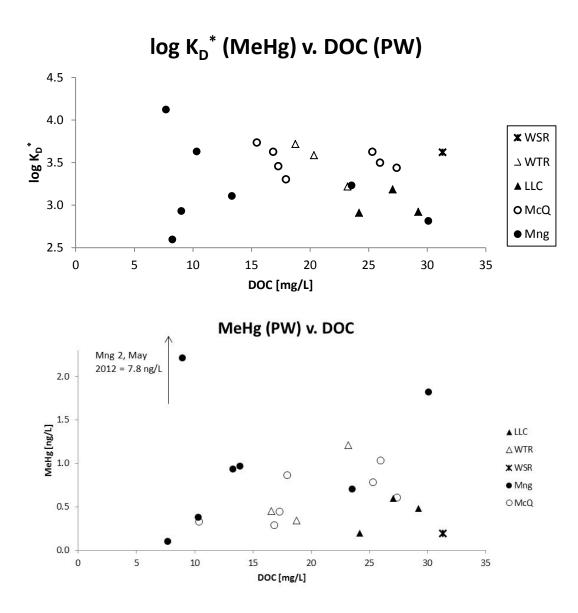


Fig. 13. (a) Measured MeHg partitioning coefficient as a function of DOC concentration (b) MeHg concentration vs. DOC concentration.

The two notable exceptions to the trend of increasing MeHg with increasing DOC were the shallow sites at Lake Manganika in May 2012 and June 2013 which both had very high porewater MeHg despite quite low DOC. This departure of Lake Manganika from typical MeHg-DOC relationships is consistent with trends observed by Berndt and Bavin (2011) at the outlet of Lake Manganika in 2010 and may indicate the presence of a transport mechanism not associated with DOC. Studies aimed at extracting methyl mercury bisulfide (MeHgHS<sup>0</sup>) from Lake Manganika bottom waters and sediments were performed during summer 2012 (Berndt and Kelley, unpublished data). These studies found no difference between samples treated to encourage the formation of the assumedly gaseous MeHgHS<sup>0</sup> (according to thermodynamic calculations) and purged with nitrogen and those samples which were not purged.

#### **Conclusions**

Consistent with previous research, MeHg dynamics in sulfur-impacted freshwater sediments having sulfide concentrations in excess of 60  $\mu$ mol/L appear to be governed by different mechanisms than sediments with lower porewater sulfide concentrations (<20  $\mu$ mol/L) (Gilmour et al. 1998; Benoit et al. 2001; Ravichandran 2004). At low sulfide concentrations, net MeHg production appears to be the dominant process influencing %MeHg in the porewater and solid phase. In contrast, high sulfide concentrations appear to inhibit net MeHg production but may increase MeHg partitioning into the porewater. As a result, our preliminary interpretation of the observations is that porewater %MeHg in these high sulfide freshwater sediments may be largely governed by partitioning processes, particularly in spring conditions.

An explanation that encompasses the MeHg dynamics observed in this study may relate to the dual role of dissolved sulfide in defining porewater MeHg by acting as a ligand for both inorganic- and methylmercury. As a ligand for MeHg, dissolved sulfide can increase partitioning from the solid phase, while in its capacity as a ligand for inorganic mercury, it can inhibit MeHg production. At low sulfur sites,

porewater sulfide may not be present in large enough concentrations to have an important impact on either inorganic- or methyl- mercury. Sulfide itself, therefore may have little influence over MeHg production or partitioning but simply be indicative of active sulfate reduction. At high sulfur sites, dissolved sulfide likely exists at concentrations sufficient (100 µmol/L) for it to act as an important ligand for both inorganic- and methyl- mercury. Sulfide's role as a methylation inhibitor will have the greatest influence under active biological conditions (summer/fall) with robust methylation and demethylation activity in pore waters, while its role as a ligand for binding MeHg may be more important under less active biological conditions (early spring).

These findings may have implications in efforts to reduce MeHg concentrations within and export from freshwater systems with large sulfur loads, such as those impacted by mining activity in Northeastern Minnesota. This study suggests that high sulfur loading can influence porewater MeHg concentrations in a number of ways, and that the influence may not be confined to biotic processes during summer months. Thus, the potential influence of dissolved, inorganic sulfide on MeHg should also be accounted for during seasons with low biological activity and in areas with sulfide concentrations high enough to inhibit methylation.

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<u>Appendix A: Raw Data Tables</u>
Lake Manganika - Plot 1 Sediment Porewater (1 of 2)

		5/15/2012						-	7/24/2012	2			-	10/6/2012	2	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)
Analy	/tes															
Sulfate	[mg/L]	2.5	3.7	10.9	8.3	2.5	2.6	2.3	3.6	2.8	6.4	52.7	25.1	10.8	48.8	51.3
Nitrate	[mg/L]						0.1	0.2	1.1	0.7	0.5	0.7	0.3	1.4		2.6
Phosphate	[mg/L]	5.9	12.6	22.1	8.8	8.8	13.6	3.0	32.9	16.4	12.6	12.2	18.2	26.9	15.2	16.0
Chloride	[mg/L]			116.2					692.4							
Ferrous Iron	[mmol/L]	0.011	0.005	0.004	0.004	0.007	0.004	0.002	0.006	0.003	0.004	0.004	0.005	0.006	0.007	0.007
Sulfide	[µmol/L]	1152	1720	1648	898	1542	1631	1301	882	906	1656	1678	1661	716	829	1954
Ammonium	[mg/L]			42.5										57.7		
DIC	[mg/L]	202.0	226.9	231.7	220.9	207.1	211.3	234.4	273.0	216.8	206.7	191.8				
DOC	[mg/L]	78.1	10.5	10.3	19.9	26.1	42.5	15.4	17.2	18.3	23.3	13.9				
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]	1.0	6.4	7.8	3.7	3.8	1.1	2.6		2.3		3.1				
Mercury .	Analysis															
MeHg	[ng/L]	2.51	0.52	0.01	2.78	1.16	0.69	0.19	0.19	0.80	0.87	2.91	0.32	0.23	0.73	0.56
THg	[ng/L]	5.38	2.31	1.22	2.86	3.14	3.88	1.72	1.63	2.28	2.57	8.83	3.06	1.78	24.18	3.88
iHg	[ng/L]	2.9	1.78	1.21	0.08	1.98	3.18	1.53	1.44	1.48	1.70	5.92	2.73	1.56	23.45	3.32
% MeHg	[]	46.8	22.6	0.8	97.2	36.9	17.9	10.9	11.9	35.1	33.9	32.9	10.5	12.7	3.0	14.4

## Lake Manganika - Plot 1 Sediment Porewater (2 of 2)

#### **SUMMARY STATISTICS**

				6/3/2013				Top 4cm	Average	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	5/15/2012	7/24/2012	10/6/2012	6/3/2013
Analytes		_					_			
Sulfate	[mg/L]	25.2	13.2	16.7	32.5	124.5	4.6	3.9	46.3	58.7
Nitrate	[mg/L]	1.6	0.3	2.7	2.6	2.2		0.4	1.5	1.9
Phosphate	[mg/L]	11.7	26.3	29.6	10.8	10.7	9.0	12.4	15.5	13.5
Chloride	[mg/L]		149.1	149.6		135.7				135.7
Ferrous Iron	[mM]	0.008	0.006	0.009	0.004	0.007	0.006	0.003	0.006	0.006
Sulfide	[μmol]	2112	1815	1503	2442	1644	1292	1342	1484	2017
Ammonium	[mg/L]		38.0	47.6						
DIC	[mg/L]	220.2	236.4	250.2	223.0	234.0	214.2	215.5		228.4
DOC	[mg/L]	14.1	12.5	14.2	13.4	13.3	30.1	23.5		13.3
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]		3.6	3.3	2.5	2.9	3.7	2.1		2.7
Mercury A	Analysis									
MeHg	[ng/L]	1.32	0.29	0.30	1.48	0.51	1.82	0.71	0.97	0.93
THg	[ng/L]	43.16	1.95	51.36	17.47	2.93	3.28	2.55	11.33	14.32
iHg	[ng/L]	41.85	1.66	51.06	15.99	2.42	1.46	1.85	10.37	13.39
% MeHg	[]	3.1	15.0	0.6	8.5	17.3	55.5	27.6	8.5	6.5

## Lake Manganika - Plot 1 Solid Phase (1 of 3)

		5/15/2012												7	7/24/201	2			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	139.3	166.0	252.8		161.6			191.6		307.9	284.9	383.5		248.3			358.7	
%C-Organic	[]	23.4	22.3	21.9		22.5			22.0		24.9	21.0	21.1		24.0			23.1	
%C-Calcite	[]	37.0	31.6	29.9		35.8			37.6		31.7	32.8	32.2		32.6			30.4	
%C-Inorganic	[]	39.6	46.1	48.2		41.6			40.5		43.5	46.1	46.7		43.4			46.5	
Dry density	[g/cc]	0.06	0.07	0.07		0.08			0.08		0.06	0.07	0.07		0.05			0.06	
dry/wet	[]	0.06	0.07	0.07		0.07			0.07		0.05	0.07	0.07		0.05			0.06	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	1.15	1.14	1.05	1.23	0.95	0.94	1.43	1.20	0.78	1.34	0.93	0.69	1.15	1.12	0.69	1.56	1.15	0.75
THg	[ng/g]	355.3	260.5	397.8	246.2	402.3	412.3	302.7	323.2	392.8	320.9	361.8	386.9	286.0	373.3	474.4	256.6	355.5	451.2
iHg	[ng/g]	354.2	259.4	396.7	245.0	401.4	411.4	301.3	322.0	392.0	319.5	360.8	386.2	284.9	372.2	473.7	255.0	354.3	450.5
% MeHg	[]	0.32	0.44	0.26	0.50	0.24	0.23	0.47	0.37	0.20	0.42	0.26	0.18	0.40	0.30	0.15	0.61	0.32	0.17
log K <sub>D</sub> (THg)	[]	4.82	5.05	5.51							4.92	5.32	5.38						
log K <sub>D</sub> (MeHg)	[]	2.66	3.34	5.02							3.29	3.69	3.55						
$K_{\text{meth}}$	[d <sup>-1</sup> ]	0.006	0.010	0.003	0.007	0.004	0.002	0.006	0.003	0.002	0.024	0.012	0.011	0.013	0.008	0.006	0.010	0.006	0.005
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.088	0.071	0.073	0.086	0.077	0.105	0.104	0.105	0.104	0.084	0.086	0.065	0.087	0.096	0.097	0.110	0.110	0.126
$K_m/K_d$	[]	0.07	0.14	0.04	0.08	0.05	0.02	0.05	0.02	0.02	0.28	0.14	0.17	0.15	0.08	0.07	0.09	0.06	0.04
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]										17.4	16.8	18.3		16.8			19.9	
Al	[g/kg]										22.9	21.8	21.1		4.6			5.3	
Mn	[g/kg]										1.1	0.9	0.9		1.2			1.3	
Zn	[g/kg]										0.2	0.1	0.1		0.1			0.1	
Ca	[g/kg]										105.4	93.7	93.5		106.8			100.4	
K	[g/kg]										9.1	5.6	4.3		0.8			0.5	
Mg	[g/kg]										8.2	7.1	6.5		7.3			7.3	
Na	[g/kg]										-27.4	-32.0	-33.2		4.5			1.8	

## Lake Manganika - Plot 1 Solid Phase (2 of 3)

		10/6/2012													6/3/2013	}			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	366.6	308.9	349.8		136.2			287.8		293.0	243.7	356.6		269.6			396.8	
%C-Organic	[]	22.6	21.1	21.1		21.4			21.9		26.7	19.7	19.3		20.7			22.5	
%C-Calcite	[]	36.7	31.8	30.3		35.2			35.7		36.1	41.1	35.4		41.7			37.6	
%C-Inorganic	[]	40.7	47.1	48.6		43.4			42.4		37.2	39.2	45.2		37.5			39.9	
Dry density	[g/cc]	0.05	0.07	0.08		0.08			0.07		0.04	0.08	0.08		0.06			0.05	
dry/wet	[]	0.05	0.07	0.07		0.07			0.07		0.04	0.07	0.08		0.06			0.05	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	1.77	1.03	0.96	1.81	0.96	0.79	1.77	0.82	0.60	1.36	0.97	0.59	1.21	0.95	0.61	1.54	1.12	0.70
THg	[ng/g]	276.3	326.2	447.1	277.8	355.1	455.1	273.9	345.0	393.1	226.9	278.6	433.1	229.8	256.2	394.6	246.9	266.4	419.4
iHg	[ng/g]	274.5	325.2	446.2	276.0	354.1	454.4	272.1	344.2	392.5	225.6	277.7	432.5	228.6	255.2	394.0	245.4	265.2	418.7
% MeHg	[]	0.64	0.32	0.21	0.65	0.27	0.17	0.65	0.24	0.15	0.60	0.35	0.14	0.53	0.37	0.15	0.62	0.42	0.17
log K <sub>D</sub> (THg)	[]	4.50	5.03	5.40							3.72	5.16	3.93						
log K <sub>D</sub> (MeHg)	[]	2.78	3.51	3.63							3.01	3.52	3.29						
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.045	0.017	0.013	0.042	0.014	0.011	0.026	0.010	0.010	0.028	0.014	0.003	0.022	0.010	0.004	0.023	0.018	0.004
$K_{demeth}$	[hr <sup>-1</sup> ]	0.054	0.074	0.063	0.071	0.047	0.063	0.081	0.072	0.085	0.059	0.052	0.019	0.042	0.050	0.023	0.056	0.080	0.030
$K_m/K_d$	[]	0.84	0.23	0.21	0.59	0.31	0.18	0.32	0.14	0.12	0.47	0.26	0.16	0.53	0.20	0.19	0.41	0.23	0.15
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]																		
Al	[g/kg]																		
Mn	[g/kg]																		
Zn	[g/kg]																		
Ca	[g/kg]																		
K	[g/kg]																		
Mg	[g/kg]																		
Na	[g/kg]																		

# Lake Manganika - Plot 1 Solid Phase (3 of 3) SUMMARY STATISTICS

			Top 4cm	Average	
Parameter	Units	5/15/2012	7/24/2012	10/6/2012	6/3/2013
AVS	[µmol/g]	168.6	301.1	253.9	311.6
%C-Organic	[]	22.5	23.4	21.7	22.1
%C-Calcite	[]	35.9	31.7	35.0	39.3
%C-Inorganic	[]	41.7	44.9	43.2	38.5
Dry density	[g/cc]	0.07	0.06	0.07	0.06
dry/wet	[]	0.07	0.06	0.07	0.05
Mercury A	nalysis				
MeHg	[ng/g]	1.18	1.21	1.36	1.19
THg	[ng/g]	315.0	325.7	309.0	250.8
iHg	[ng/g]	313.9	324.5	307.7	249.6
% MeHg	[]	0.38	0.37	0.44	0.48
log K <sub>D</sub> (THg)	[]	4.98	5.11	4.44	4.24
log K <sub>D</sub> (MeHg)	[]	2.81	3.23	3.15	3.11
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.006	0.012	0.026	0.019
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.089	0.095	0.066	0.057
K <sub>m</sub> /K <sub>d</sub>	[]	0.07	0.13	0.41	0.35
Metals Ex	ract				
Fe	[g/kg]		17.9		
Al	[g/kg]		10.7		
Mn	[g/kg]		1.2		
Zn	[g/kg]		0.1		
Ca [g/kg			102.3		
K [g/kg]			2.9		
Mg [g/kg]			7.4		
Na	[g/kg]		0.0*		

<sup>\*</sup>measured value negative

## Lake Manganika - Plot 2 Sediment Porewater (1 of 2)

			5	5/15/2012	2			-	7/24/2012	2			1	10/6/2012	2	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)
Analy	tes															
Sulfate	[mg/L]	68.3	80.3	200.3	92.6	51.3	42.3	10.7	14.9	31.6	34.8	168.2	83.4	50.5	208.4	167.3
Nitrate	[mg/L]	0.0	0.9	0.0	0.0	0.7	0.0	0.2	0.0	0.5	0.3	0.0	0.0	0.3	0.0	0.0
Phosphate	[mg/L]	0.0	2.1	0.0	0.0	0.0	3.8	5.6	6.1	6.6	8.0	4.4	6.0	7.1	4.1	3.9
Chloride	[mg/L]										1043					
Ferrous Iron	[mmol/L]	0.009	0.011	0.007	0.007	0.007	0.013	0.005	0.004	0.002	0.001	0.003	0.002	0.009	0.003	0.004
Sulfide	[µmol/L]	1405	1563	1453	1340	1555	2292	981	1519	1379	1504	35	524	288	109	32
Ammonium	[mg/L]		6.6	3.7												
DIC	[mg/L]	140.5	150.3	109.0	155.2	154.2	171.8	190.5	169.0	174.6	171.8		184.1	191.4	157.7	169.4
DOC	[mg/L]	10.9	6.6	5.9	6.9	9.0	11.2	9.2	10.0	10.0	10.7		11.4	11.1	9.8	5.6
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]	6.6	10.1	9.9	9.5	7.7		4.0	3.9	3.4	3.2		4.4	4.9	4.5	8.4
Mercury A	Analysis															
MeHg	[ng/L]	9.42	5.69	0.42	8.21	7.61	0.38	0.08	0.18	0.27	0.63	0.15	0.09	0.06	0.08	0.11
THg	[ng/L]	14.61	9.96	2.39	10.86	11.75	4.17	2.06	2.37	2.87	3.06	3.58	4.88	1.53	9.09	2.09
iHg	[ng/L]	5.2	4.27	1.96	2.65	4.15	3.79	1.98	2.19	2.60	2.43	3.43	4.80	1.47	9.02	1.97
% MeHg	[]	64.5	57.2	17.6	75.6	64.7	9.1	3.9	7.7	9.5	20.7	4.2	1.8	3.9	0.8	5.4

## Lake Manganika - Plot 2 Sediment Porewater (2 of 2)

				6/3/2013				Top 4cm	Average	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	5/15/2012	7/24/2012	10/6/2012	6/3/2013
Analy	tes									
Sulfate	[mg/L]	69.1	77.1		24.5	38.2	72.7	31.0	167.2	45.3
Nitrate	[mg/L]	1.1	0.2		0.4	2.3	0.4	0.3	0.0	1.1
Phosphate	[mg/L]	6.4	6.7		6.9	5.9	0.4	6.5	4.4	6.5
Chloride	[mg/L]		84.6	81.4	82.7	84.8				83.8
Ferrous Iron	[mM]	0.005	0.002	0.003	0.004	0.003	0.008	0.004	0.003	0.004
Sulfide	[μmol]	2321	939	1154	2121	1902	1460	1507	140	1884
Ammonium	[mg/L]			11.2						
DIC	[mg/L]	139.8	147.0	158.7	163.2	157.3	151.6	175.8	163.5	154.6
DOC	[mg/L]	9.9	6.4	7.4	9.4	9.4	8.2	10.3	7.7	9.0
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]	3.6	5.2	5.4	4.5	3.5	8.5	3.3	6.4	4.0
Mercury A	Analysis									
MeHg	[ng/L]	6.59	0.27		2.09	1.10	7.79	0.38	0.10	2.21
THg	[ng/L]	10.18	35.21	43.65	6.40	4.42	11.63	3.02	5.14	11.17
iHg	[ng/L]	3.59	34.95		4.30	3.32	3.84	2.64	5.04	8.96
% MeHg	[]	64.8	0.8		32.7	24.9	67.0	12.6	2.0	19.8

## Lake Manganika - Plot 2 Solid Phase (1 of 3)

					5	5/15/201	2							7	7/24/201	2			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	182.2	160.8	159.6		242.8			227.6		488.7	441.2	515.8		627.7			470.8	
%C-Organic	[]	19.9	20.0	19.2		19.9			20.0		24.9	21.0	21.1		24.0			23.1	
%C-Calcite	[]	31.8	30.7	27.3		28.8			31.0		31.7	32.8	32.2		32.6			30.4	
%C-Inorganic	[]	48.3	49.3	53.5		51.3			49.0		43.5	46.1	46.7		43.4			46.5	
Dry density	[g/cc]	0.10	0.11	0.14		0.11			0.11		0.06	0.07	0.07		0.048			0.059	
dry/wet	[]	0.09	0.11	0.13		0.11			0.10		0.05	0.07	0.07		0.047			0.057	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	3.55	3.13	1.10	3.69	2.30	1.17	3.00	2.75	1.02	1.75	1.22	1.30	1.78	1.67	1.14	1.89	1.40	1.08
THg	[ng/g]	824.9	831.0	964.1	772.2	840.9	971.9	802.3	823.4	1022.1	706.2	805.9	842.9	772.0	830.6	859.5	764.5	809.5	877.0
iHg	[ng/g]	821.4	827.9	963.0	768.5	838.6	970.7	799.3	820.7	1021.1	704.4	804.7	841.6	770.3	828.9	858.4	762.6	808.1	875.9
% MeHg	[]	0.43	0.38	0.11	0.48	0.27	0.12	0.37	0.33	0.10	0.25	0.15	0.15	0.23	0.20	0.13	0.25	0.17	0.12
log K <sub>D</sub> (THg)	[]	4.75	4.92	5.61							5.23	5.59	5.55						
log K <sub>D</sub> (MeHg)	[]	2.58	2.74	3.42							3.67	4.18	3.85						
$K_{\text{meth}}$	[d <sup>-1</sup> ]	0.017	0.014	0.010	0.016	0.011	0.009	0.015	0.014	0.010	0.037	0.012	0.021	0.026	0.013	0.007	0.025	0.007	0.013
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.103	0.072	0.124	0.100	0.118	0.120	0.118	0.101	0.067	0.006		0.038	0.056		0.022	0.060	0.123	0.067
$K_m/K_d$	[]	0.16	0.19	0.08	0.16	0.09	0.08	0.13	0.14	0.15	6.01		0.54	0.47		0.32	0.42	0.05	0.19
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]										22.0	22.4	26.9		23.0			22.7	
Al	[g/kg]										56.9	56.9	14.5		58.1			58.5	
Mn	[g/kg]										3.1	3.1	3.6		3.2			3.1	
Zn	[g/kg]										0.4	0.4	0.7		0.4			0.4	
Ca	[g/kg]										164.2	166.7	158.3		159.4			155.7	
K	[g/kg]										12.7	11.7	2.1		12.0			11.7	
Mg	[g/kg]										19.4	19.6	19.0		19.4			19.6	
Na	[g/kg]										-69.3	-72.3	41.0		-71.4			-67.8	

## Lake Manganika - Plot 2 Solid Phase (2 of 3)

					1	.0/6/201	2								6/3/2013	}			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	216.7	287.7	164.5		276.2					258.7	249.3	324.9		259.2			299.1	
%C-Organic	[]	20.2	19.4	19.3		19.3					19.9	19.5	18.8		19.4			19.1	
%C-Calcite	[]	29.4	30.4	28.8		31.2					31.9	29.9	25.9		32.8			33.0	
%C-Inorganic	[]	50.4	50.1	52.0		49.5					48.2	50.6	55.3		47.8			48.0	
Dry density	[g/cc]	0.10	0.09	0.11		0.095					0.10	0.11	0.13		0.110			0.108	
dry/wet	[]	0.10	0.09	0.11		0.090					0.09	0.10	0.12		0.104			0.102	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	1.52	1.46	1.13	1.44	1.22	1.50	1.38	1.14	0.95	2.21	1.10	0.91	2.70	1.49	1.04	2.58	1.23	1.01
THg	[ng/g]	809.1	810.0	871.2	789.4	717.1	848.1	772.8	834.0	880.1	680.5	709.8	885.1	670.2	840.0	874.5	585.2	750.3	889.7
iHg	[ng/g]	807.6	808.6	870.0	788.0	715.9	846.6	771.4	832.8	879.2	678.3	708.7	884.2	667.5	838.5	873.5	582.6	749.0	888.7
% MeHg	[]	0.19	0.18	0.13	0.18	0.17	0.18	0.18	0.14	0.11	0.33	0.15	0.10	0.40	0.18	0.12	0.44	0.16	0.11
log K <sub>D</sub> (THg)	[]	5.35	5.22	5.76							5.19	4.79	5.47						
log K <sub>D</sub> (MeHg)	[]	4.01	4.21	4.28							3.30	2.15	3.38						
$K_{\text{meth}}$	[d <sup>-1</sup> ]	0.018	0.016	0.012	0.022	0.014	0.015	0.020	0.015	0.014	0.085	0.012	0.005	0.084	0.013	0.006	0.116	0.012	0.008
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.050	0.047	0.086	0.040	0.053	0.020	0.036	0.104	0.124	0.146	0.160	0.165	0.156	0.176	0.172	0.154	0.185	0.195
$K_m/K_d$	[]	0.37	0.34	0.13	0.55	0.27	0.73	0.55	0.14	0.12	0.58	0.07	0.03	0.54	0.08	0.04	0.75	0.07	0.04
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]																		
Al	[g/kg]																		
Mn	[g/kg]																		
Zn	[g/kg]																		
Ca	[g/kg]																		
K	[g/kg]																		
Mg	[g/kg]																		
Na	[g/kg]																		

# Lake Manganika - Plot 2 Solid Phase (3 of 3) SUMMARY STATISTICS

			Top 4cm	Average	
Parameter	Units	5/15/2012	7/24/2012	10/6/2012	6/3/2013
AVS	[µmol/g]	214.0	521.1	264.2	270.8
%C-Organic	[]	19.9	23.4	19.5	19.4
%C-Calcite	[]	30.4	31.7	30.6	32.2
%C-Inorganic	[]	49.7	44.9	49.9	48.4
Dry density	[g/cc]	0.11	0.06	0.10	0.11
dry/wet	[]	0.10	0.06	0.09	0.10
Mercury A	nalysis				
MeHg	[ng/g]	3.07	1.62	1.36	1.88
THg	[ng/g]	815.8	781.5	788.7	706.0
iHg	[ng/g]	812.7	779.8	787.4	704.1
% MeHg	[]	0.38	0.21	0.17	0.27
log K <sub>D</sub> (THg)	[]	4.85	5.41	5.19	4.80
log K <sub>D</sub> (MeHg)	[]	2.60	3.63	4.12	2.93
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.014	0.020	0.018	0.054
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.102	0.061	0.055	0.163
K <sub>m</sub> /K <sub>d</sub>	[]	0.15	1.74	0.37	0.35
Metals Ex	tract				
Fe	[g/kg]		22.6		
Al	[g/kg]		57.8		
Mn	[g/kg]		3.1		
Zn	[g/kg]		0.4		
Ca	[g/kg]		160.2		
K	[g/kg]		11.9		
Mg	[g/kg]		19.5		
Na	[g/kg]		0.0*		

<sup>\*</sup>measured value negative

## Lake McQuade - Plot 2 Sediment Porewater (1 of 2)

			Į	5/15/2012	2			-	7/24/2012	2			-	10/6/2012	2	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)
Analy	rtes															
Sulfate	[mg/L]	13.0	8.8	24.5	20.4	22.1	1.6	0.3	0.2	0.4	0.4	62.4	44.3	67.0	58.6	
Nitrate	[mg/L]	0.0	0.4	0.4	0.3	0.3	20.0	0.9	0.3	0.3	0.4	0.9	0.3	0.2	0.0	
Phosphate	[mg/L]	1.1	2.1	1.9	1.2	1.2	8.6	8.0	10.5	9.2	9.0	1.8	4.2	2.8	0.7	
Chloride	[mg/L]							9.1	9.8			7.4	7.2	7.4		7.2
Ferrous Iron	[mmol/L]	0.245	0.043	0.073	0.041	0.043	0.141	0.121	0.077	0.106	0.183	0.025	0.024	0.035	0.029	0.032
Sulfide	[µmol/L]	1.4	1.3	1.4	1.6	1.5	5.2				2.7	5.3	5.3	1.6	3.4	5.7
Ammonium	[mg/L]			0.9	0.8	0.9		3.7	3.5			1.8		2.6		0.0
DIC	[mg/L]	55.6	57.0	57.4	56.3	56.0		63.7	72.7	59.8	63.2	91.0	79.8	79.0	83.7	85.4
DOC	[mg/L]	21.7	17.1	12.2	15.0	16.1		27.4	23.4	27.7	27.0	16.6	15.5	13.1		14.9
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]	8.0	8.5	8.9	2.4	8.5				5.0	7.3	5.0	5.8	6.2		6.7
Mercury /	Analysis															
MeHg	[ng/L]	0.21	0.06	0.14	0.56	0.17	0.54	0.51	0.47	0.71	0.58	0.33	0.39	0.72	0.40	0.22
THg	[ng/L]	2.08	1.52	1.13	1.99	2.08	3.35	2.11	1.91	2.82	2.94	2.12	1.34	1.84	1.94	1.77
iHg	[ng/L]	1.9	1.47	0.99	1.43	1.92	2.81	1.60	1.44	2.11	2.36	1.80	0.95	1.12	1.54	1.55
% MeHg	[]	10.1	3.8	12.7	28.3	7.9	16.1	24.2	24.6	25.2	19.9	15.4	28.9	39.2	20.7	12.6

## Lake McQuade - Plot 2 Sediment Porewater (2 of 2)

				6/3/2013				Top 4cm	Average	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	5/15/2012	7/24/2012	10/6/2012	6/3/2013
Analy	tes									
Sulfate	[mg/L]	11.3	20.5	25.3	20.2	27.3	17.8	0.6	56.0	21.1
Nitrate	[mg/L]	3.7	0.5	0.3	0.7	0.1	0.3	3.7	0.3	1.0
Phosphate	[mg/L]	4.4	3.8	2.8	3.1	2.9	1.3	8.8	1.9	3.4
Chloride	[mg/L]	10.5	10.6	11.8		12.2		1.5	7.2	11.4
Ferrous Iron	[mM]	0.032	0.024	0.030	0.023	0.045	0.076	0.140	0.029	0.032
Sulfide	[μmol]	2.8	3.1	3.0	3.7	0.8	1.5	2.7	4.8	2.5
Ammonium	[mg/L]	0.8	0.8	0.8		0.7	0.85			0.73
DIC	[mg/L]	53.3	43.7	45.5	41.1	41.8	56.2	61.5	84.8	43.8
DOC	[mg/L]	22.6	15.9	12.6	17.3	15.3	16.8	27.4	15.5	17.3
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]	6.8	5.6	5.3	5.8	5.5	6.4	6.2	6.0	5.8
Mercury A	Analysis									
MeHg	[ng/L]	0.65	0.33	0.19	0.54	0.31	0.29	0.61	0.33	0.45
THg	[ng/L]	9.15	6.03	4.45	1.87	2.04	1.96	2.83	1.81	3.83
iHg	[ng/L]	8.51	5.70	4.26	1.33	1.73	1.67	2.23	1.49	3.39
% MeHg	[]	7.0	5.5	4.3	28.9	15.2	14.7	21.4	18.0	11.6

# Lake McQuade - Plot 2 Solid Phase (1 of 3)

					5/15/2012					7	7/24/201	2			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	4.7	42.1	121.4	95.8	29.0	141.5	98.9	93.3		63.5			112.1	
%C-Organic	[]	18.5	17.5	16.6	17.8	17.8	18.0	16.3	16.1		17.3			16.3	
%C-Calcite	[]	4.2	4.7	5.3	4.3	4.2	5.0	6.5	4.7		4.3			4.7	
%C-Inorganic	[]	77.4	77.9	78.1	78.0	78.1	77.0	77.3	79.2		78.3			79.0	
Dry density	[g/cc]	0.11	0.13	0.13	0.113	0.116	0.09	0.16	0.15		0.129			0.154	
dry/wet	[]	0.10	0.12	0.12	0.107	0.109	0.09	0.14	0.14		0.121			0.142	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	1.09	0.98	1.22	1.64	0.97	2.85	1.12	1.02	1.91	1.01	1.28	1.81	1.27	1.82
THg	[ng/g]	160.8	154.3	168.4	180.8	175.4	132.2	141.4	147.1	141.9	144.1	145.1	143.2	143.4	152.7
iHg	[ng/g]	159.7	153.3	167.2	179.2	174.4	129.3	140.3	146.1	140.0	143.1	143.8	141.4	142.1	150.9
% MeHg	[]	0.68	0.63	0.72	0.91	0.55	2.16	0.79	0.70	1.35	0.70	0.88	1.26	0.89	1.19
log K <sub>D</sub> (THg)	[]	4.89	5.01	5.17			4.60	4.83	4.89						
log K <sub>D</sub> (MeHg)	[]	3.72	4.23	3.93			3.72	3.34	3.34						
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.071	0.101	0.081	0.047	0.058	0.177	0.121	0.091	0.160	0.114	0.072	0.149	0.080	0.063
$K_{demeth}$	[hr <sup>-1</sup> ]	0.058	0.052	0.079	0.080	0.103	0.029	0.025	0.040	0.027		0.047	0.038	0.047	0.039
$K_m/K_d$	[]	1.23	1.95	1.02	0.58	0.56	6.13	4.78	2.28	5.82		1.54	3.91	1.71	1.60
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]						22.5	22.1	23.4		21.9			24.0	
Al	[g/kg]						15.2	26.8	37.3		14.7			38.2	
Mn	[g/kg]						3.0	1.7	1.3		3.0			1.8	
Zn	[g/kg]						0.2	-0.8	-0.8		0.1			-0.8	
Ca	[g/kg]						4.4	3.3	3.9		4.3			4.7	
K	[g/kg]						1.6	-25.1	-22.5		1.5			-23.9	
Mg	[g/kg]						9.2	8.7	9.9		8.9			9.7	
Na	[g/kg]						-1.0	-52.7	-52.4		5.3			-44.7	

## Lake McQuade - Plot 2 Solid Phase (2 of 3)

					1	.0/6/201	2								6/3/2013	}			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	59.6	151.0	176.1		149.8			132.0		71.3	102.8	153.2		74.6			110.3	
%C-Organic	[]	17.1	17.0	15.8		16.5			16.9		16.5	16.4	15.7		16.5			16.4	
%C-Calcite	[]	5.3	5.9	5.6		5.4			5.2		7.0	6.9	6.9		6.7			7.0	
%C-Inorganic	[]	77.6	77.1	78.6		78.1			77.9		76.6	76.7	77.4		76.9			76.7	
Dry density	[g/cc]	0.13	0.13	0.13		0.126			0.113		0.13	0.15	0.16		0.114			0.120	
dry/wet	[]	0.12	0.12	0.12		0.118			0.106		0.12	0.14	0.15		0.107			0.113	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	2.84	1.72	1.06	1.69	1.39	0.97	1.56	1.48	0.94	1.25	1.34	1.21	1.34	1.06	1.04	1.44	1.24	1.00
THg	[ng/g]	161.5	144.0	150.5	143.5	148.4	152.6	148.0	142.6	164.0	173.2	163.4	170.1	166.5	168.4	176.0	171.9	166.2	174.5
iHg	[ng/g]	158.6	142.3	149.4	141.8	147.0	151.6	146.5	141.1	163.1	172.0	162.1	168.9	165.1	167.3	174.9	170.4	164.9	173.5
% MeHg	[]	1.76	1.20	0.70	1.18	0.94	0.63	1.05	1.04	0.57	0.72	0.82	0.71	0.81	0.63	0.59	0.84	0.75	0.57
log K <sub>D</sub> (THg)	[]	4.88	5.03	4.91							4.28	4.43	4.58						
log K <sub>D</sub> (MeHg)	[]	3.94	3.65	3.17							3.29	3.61	3.80						
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.082	0.085	0.096	0.082	0.080	0.063	0.103	0.087	0.070	0.088	0.076	0.045	0.074	0.084	0.038	0.085	0.077	0.048
$K_{demeth}$	[hr <sup>-1</sup> ]	0.040	0.045	0.013	0.046	0.053	0.030	0.046	0.032	0.050	0.028	0.068	0.078	0.062	0.071	0.043	0.067	0.016	0.074
$K_m/K_d$	[]	2.04	1.89	7.58	1.79	1.52	2.10	2.22	2.75	1.39	3.14	1.12	0.58	1.18	1.19	0.87	1.28	4.89	0.65
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]																		
Al	[g/kg]																		
Mn	[g/kg]																		
Zn	[g/kg]																		
Ca	[g/kg]																		
K	[g/kg]																		
Mg	[g/kg]																		
Na	[g/kg]																		

# Lake McQuade - Plot 2 Solid Phase (3 of 3) SUMMARY STATISTICS

			Top 4cm	Average	
Parameter	Units	5/15/2012	7/24/2012	10/6/2012	6/3/2013
AVS	[µmol/g]	49.4	98.6	129.1	90.6
%C-Organic	[]	17.8	16.9	16.8	16.4
%C-Calcite	[]	4.3	4.9	5.4	6.8
%C-Inorganic	[]	77.9	78.2	77.8	76.7
Dry density	[g/cc]	0.12	0.14	0.12	0.13
dry/wet	[]	0.11	0.13	0.11	0.12
Mercury A	nalysis				
MeHg	[ng/g]	1.22	1.66	1.78	1.28
THg	[ng/g]	171.3	141.0	148.0	168.3
iHg	[ng/g]	170.0	139.4	146.2	167.0
% MeHg	[]	0.71	1.18	1.20	0.76
log K <sub>D</sub> (THg)	[]	4.94	4.70	4.91	4.64
log K <sub>D</sub> (MeHg)	[]	3.63	3.44	3.74	3.46
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.063	0.134	0.087	0.081
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.079	0.033	0.044	0.052
$K_m/K_d$	[]	0.91	4.47	2.04	2.13
Metals Ex	tract				
Fe	[g/kg]		22.7		
Al	[g/kg]		24.7		
Mn	[g/kg]		2.4		
Zn	[g/kg]		0.0*		
Ca	[g/kg]		4.3		
K	[g/kg]		0.0*		
Mg	[g/kg]		9.2		
Na	[g/kg]		0.0*		

<sup>\*</sup>measured value negative

## Lake McQuade - Plot 2 Solid Phase (1 of 3)

					5/15/2012					7	7/24/201	2			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	4.7	42.1	121.4	95.8	29.0	141.5	98.9	93.3		63.5			112.1	
%C-Organic	[]	18.5	17.5	16.6	17.8	17.8	18.0	16.3	16.1		17.3			16.3	
%C-Calcite	[]	4.2	4.7	5.3	4.3	4.2	5.0	6.5	4.7		4.3			4.7	
%C-Inorganic	[]	77.4	77.9	78.1	78.0	78.1	77.0	77.3	79.2		78.3			79.0	
Dry density	[g/cc]	0.11	0.13	0.13	0.113	0.116	0.09	0.16	0.15		0.129			0.154	
dry/wet	[]	0.10	0.12	0.12	0.107	0.109	0.09	0.14	0.14		0.121			0.142	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	1.09	0.98	1.22	1.64	0.97	2.85	1.12	1.02	1.91	1.01	1.28	1.81	1.27	1.82
THg	[ng/g]	160.8	154.3	168.4	180.8	175.4	132.2	141.4	147.1	141.9	144.1	145.1	143.2	143.4	152.7
iHg	[ng/g]	159.7	153.3	167.2	179.2	174.4	129.3	140.3	146.1	140.0	143.1	143.8	141.4	142.1	150.9
% MeHg	[]	0.68	0.63	0.72	0.91	0.55	2.16	0.79	0.70	1.35	0.70	0.88	1.26	0.89	1.19
log K <sub>D</sub> (THg)	[]	4.89	5.01	5.17			4.60	4.83	4.89						
log K <sub>D</sub> (MeHg)	[]	3.72	4.23	3.93			3.72	3.34	3.34						
$K_{meth}$	[d <sup>-1</sup> ]	0.071	0.101	0.081	0.047	0.058	0.177	0.121	0.091	0.160	0.114	0.072	0.149	0.080	0.063
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.058	0.052	0.079	0.080	0.103	0.029	0.025	0.040	0.027		0.047	0.038	0.047	0.039
$K_m/K_d$	[]	1.23	1.95	1.02	0.58	0.56	6.13	4.78	2.28	5.82		1.54	3.91	1.71	1.60
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]						22.5	22.1	23.4		21.9			24.0	
Al	[g/kg]						15.2	26.8	37.3		14.7			38.2	
Mn	[g/kg]						3.0	1.7	1.3		3.0			1.8	
Zn	[g/kg]						0.2	-0.8	-0.8		0.1			-0.8	
Ca	[g/kg]						4.4	3.3	3.9		4.3			4.7	
K	[g/kg]						1.6	-25.1	-22.5		1.5			-23.9	
Mg	[g/kg]						9.2	8.7	9.9		8.9			9.7	
Na	[g/kg]						-1.0	-52.7	-52.4		5.3			-44.7	

# Lake McQuade - Plot 2 Solid Phase (2 of 3)

					1	.0/6/201	2								6/3/2013	}			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	59.6	151.0	176.1		149.8			132.0		71.3	102.8	153.2		74.6			110.3	
%C-Organic	[]	17.1	17.0	15.8		16.5			16.9		16.5	16.4	15.7		16.5			16.4	
%C-Calcite	[]	5.3	5.9	5.6		5.4			5.2		7.0	6.9	6.9		6.7			7.0	
%C-Inorganic	[]	77.6	77.1	78.6		78.1			77.9		76.6	76.7	77.4		76.9			76.7	
Dry density	[g/cc]	0.13	0.13	0.13		0.126			0.113		0.13	0.15	0.16		0.114			0.120	
dry/wet	[]	0.12	0.12	0.12		0.118			0.106		0.12	0.14	0.15		0.107			0.113	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	2.84	1.72	1.06	1.69	1.39	0.97	1.56	1.48	0.94	1.25	1.34	1.21	1.34	1.06	1.04	1.44	1.24	1.00
THg	[ng/g]	161.5	144.0	150.5	143.5	148.4	152.6	148.0	142.6	164.0	173.2	163.4	170.1	166.5	168.4	176.0	171.9	166.2	174.5
iHg	[ng/g]	158.6	142.3	149.4	141.8	147.0	151.6	146.5	141.1	163.1	172.0	162.1	168.9	165.1	167.3	174.9	170.4	164.9	173.5
% MeHg	[]	1.76	1.20	0.70	1.18	0.94	0.63	1.05	1.04	0.57	0.72	0.82	0.71	0.81	0.63	0.59	0.84	0.75	0.57
log K <sub>D</sub> (THg)	[]	4.88	5.03	4.91							4.28	4.43	4.58						
log K <sub>D</sub> (MeHg)	[]	3.94	3.65	3.17							3.29	3.61	3.80						
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.082	0.085	0.096	0.082	0.080	0.063	0.103	0.087	0.070	0.088	0.076	0.045	0.074	0.084	0.038	0.085	0.077	0.048
$K_{demeth}$	[hr <sup>-1</sup> ]	0.040	0.045	0.013	0.046	0.053	0.030	0.046	0.032	0.050	0.028	0.068	0.078	0.062	0.071	0.043	0.067	0.016	0.074
$K_m/K_d$	[]	2.04	1.89	7.58	1.79	1.52	2.10	2.22	2.75	1.39	3.14	1.12	0.58	1.18	1.19	0.87	1.28	4.89	0.65
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]																		
Al	[g/kg]																		
Mn	[g/kg]																		
Zn	[g/kg]																		
Ca	[g/kg]																		
K	[g/kg]																		
Mg	[g/kg]																		
Na	[g/kg]																		

# Lake McQuade - Plot 2 Solid Phase (3 of 3) SUMMARY STATISTICS

			Top 4cm	Average	
Parameter	Units	5/15/2012	7/24/2012	10/6/2012	6/3/2013
AVS	[µmol/g]	49.4	98.6	129.1	90.6
%C-Organic	[]	17.8	16.9	16.8	16.4
%C-Calcite	[]	4.3	4.9	5.4	6.8
%C-Inorganic	[]	77.9	78.2	77.8	76.7
Dry density	[g/cc]	0.12	0.14	0.12	0.13
dry/wet	[]	0.11	0.13	0.11	0.12
Mercury A	nalysis				
MeHg	[ng/g]	1.22	1.66	1.78	1.28
THg	[ng/g]	171.3	141.0	148.0	168.3
iHg	[ng/g]	170.0	139.4	146.2	167.0
% MeHg	[]	0.71	1.18	1.20	0.76
log K <sub>D</sub> (THg)	[]	4.94	4.70	4.91	4.64
log K <sub>D</sub> (MeHg)	[]	3.63	3.44	3.74	3.46
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.063	0.134	0.087	0.081
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.079	0.033	0.044	0.052
K <sub>m</sub> /K <sub>d</sub>	[]	0.91	4.47	2.04	2.13
Metals Ex	tract				
Fe	[g/kg]		22.7		
Al	[g/kg]		24.7		
Mn	[g/kg]		2.4		
Zn	[g/kg]		0.0*		
Ca	[g/kg]		4.3		
K	[g/kg]		0.0*		
Mg	[g/kg]		9.2		
Na	[g/kg]		0.0*		

<sup>\*</sup>measured value negative

## Lake McQuade - Plot 3 Sediment Porewater (1 of 2)

			Į	5/15/2012	2			-	7/24/2012	2				10/6/201	2	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)
Analy	rtes .															
Sulfate	[mg/L]						0.3	0.2	0.2	0.3	0.5	2.5	4.1	3.3	5.6	7.4
Nitrate	[mg/L]						0.4	0.4	0.3	0.2	0.4	0.7	0.2	1.0	0.2	0.3
Phosphate	[mg/L]						10.3	13.0	14.0	10.2	11.2	8.7	8.4	9.2	7.0	5.8
Chloride	[mg/L]							11.3	11.7	10.8		7.4			7.5	7.2
Ferrous Iron	[mmol/L]						0.069	0.093	0.118	0.036	0.062	0.055	0.054	0.083	0.031	0.046
Sulfide	[µmol/L]						6.5	10.9		8.1	7.6	5.2	7.4	3.4	3.4	2.4
Ammonium	[mg/L]											8.5	5.5	11.4	7.1	5.6
DIC	[mg/L]						50.5	61.9	81.5	49.9	48.5	89.5	102.7	88.7	87.0	97.4
DOC	[mg/L]						27.6	25.8	24.4	25.1	26.1	25.8	28.0	25.5	25.6	23.4
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]						6.2	5.8	4.5	5.0	5.6	5.6	5.8	7.4	5.2	6.0
Mercury	Analysis												-			
MeHg	[ng/L]						1.80	0.67	0.33	1.22	0.64	0.68	0.39	0.29	1.20	0.62
THg	[ng/L]						3.82	2.21	1.91	3.38	2.31	3.48	1.88	1.84	2.39	2.16
iHg	[ng/L]		_	_	_		2.02	1.55	1.58	2.17	1.67	2.80	1.49	1.55	1.19	1.55
% MeHg	[]						47.1	30.1	17.2	36.0	27.7	19.5	20.5	15.7	50.4	28.5

## Lake McQuade - Plot 3 Sediment Porewater (2 of 2)

				6/3/2013				Top 4cm	Average	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	5/15/2012	7/24/2012	10/6/2012	6/3/2013
Analy	tes									
Sulfate	[mg/L]	2.2	2.0	1.5	4.1	2.6		0.4	5.5	2.9
Nitrate	[mg/L]	0.4	0.3	0.2	0.2	0.3		0.3	0.3	0.3
Phosphate	[mg/L]	5.8	6.7	12.4	7.8	7.3		11.0	7.2	7.1
Chloride	[mg/L]	10.2	10.2	10.0	9.2			10.8	7.3	9.7
Ferrous Iron	[mM]	0.010	0.058	0.083	0.065	0.020		0.060	0.044	0.040
Sulfide	[μmol]	31.8	26.2	5.3	13.9	23.1		8.1	4.0	22.0
Ammonium	[mg/L]	4.5	5.6	7.0	5.4				6.5	5.2
DIC	[mg/L]	34.2	68.7	76.9	79.8	70.6		51.5	93.5	67.3
DOC	[mg/L]	8.3	20.0	21.8	19.4	20.2		26.0	25.3	17.9
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]	13.0	5.9	5.9	5.7	5.1		5.5	5.6	6.8
Mercury A	Analysis	_								
MeHg	[ng/L]	1.57	0.42	0.04	0.84	0.76		1.03	0.78	0.86
THg	[ng/L]	12.00	2.32	1.51	11.26	14.15		2.90	2.41	10.86
iHg	[ng/L]	10.42	1.91	1.47	10.42	13.39		1.87	1.63	9.99
% MeHg	[]	13.1	18.0	2.4	7.4	5.4		35.5	32.5	8.0

# Lake McQuade - Plot 3 Solid Phase (1 of 2)

\*Not sampled in May 2012

					7	//24/201	2							1	10/6/201	2			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	350.0	379.2	224.2		135.6			173.1		324.9	326.5	296.4		293.3			417.0	
%C-Organic	[]	25.4	24.8	23.5		24.1			24.4		25.9	24.5	24.4		24.8			25.4	
%C-Calcite	[]	7.1	7.9	7.9		8.1			7.6		8.8	8.6	8.3		7.9			8.0	
%C-Inorganic	[]	67.6	67.3	68.6		67.8			68.0		65.3	66.9	67.3		67.3			66.6	
Dry density	[g/cc]	0.05	0.07	0.08		0.150			0.087		0.06	0.08	0.08		0.076			0.065	
dry/wet	[]	0.05	0.07	0.08		0.139			0.083		0.05	0.08	0.07		0.073			0.062	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	3.37	1.96	1.12	4.90	2.22	1.35	5.10	1.92	1.40	4.94	3.36	1.50	3.38	1.84	1.11	3.87	2.45	1.23
THg	[ng/g]	191.6	191.8	185.6	177.9	190.8	196.1	183.9	185.7	195.4	187.7	187.5	197.1	189.2	197.1	196.1	191.9	189.8	199.1
iHg	[ng/g]	188.3	189.9	184.5	173.0	188.5	194.8	178.8	183.8	194.0	182.8	184.2	195.6	185.8	195.2	195.0	188.0	187.4	197.8
% MeHg	[]	1.76	1.02	0.60	2.76	1.16	0.69	2.77	1.03	0.72	2.63	1.79	0.76	1.79	0.93	0.57	2.02	1.29	0.62
log K <sub>D</sub> (THg)	[]	4.70	4.94	4.99							4.73	5.00	5.03						
log K <sub>D</sub> (MeHg)	[]	3.27	3.47	3.53							3.86	3.94	3.72						
$K_{meth}$	[d <sup>-1</sup> ]	0.067	0.059	0.028	0.089	0.061	0.040	0.095	0.060	0.031	0.108	0.061	0.039	0.100	0.059	0.031	0.114	0.049	0.035
$K_{demeth}$	[hr <sup>-1</sup> ]	0.043	0.059	0.060	0.029	0.042	0.038	0.044	0.050	0.057	0.038	0.043	0.039	0.049	0.041	0.056	0.037	0.030	0.033
$K_m/K_d$	[]	1.54	1.00	0.46	3.10	1.43	1.06	2.18	1.20	0.55	2.80	1.42	1.02	2.02	1.43	0.56	3.06	1.64	1.07
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]	28.1	29.6	24.8		27.7			26.7										
Al	[g/kg]	40.8	39.5	15.7		38.7			41.7										
Mn	[g/kg]	2.3	2.1	2.6		1.9			2.0										
Zn	[g/kg]	-0.7	-0.8	0.1		-0.8			-0.8										
Ca	[g/kg]	5.7	5.1	5.1		4.5			6.6										
K	[g/kg]	-23.3	-28.9	1.2		-31.8			-28.6										
Mg	[g/kg]	10.0	9.8	8.9		8.8			11.1										
Na	[g/kg]	-50.3	-51.8	3.5		-53.7			-49.2										

# Lake McQuade - Plot 3 Solid Phase (2 of 2)

						6/3/2013						Top 4cm	Average	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		5/15/2012	7/24/2012	10/6/2012	6/3/2013
AVS	[µmol/g]	533.7	438.1	361.4		402.2			367.3			224.4	345.3	418.5
%C-Organic	[]	24.5	23.6	23.0		23.4			22.6			24.5	25.1	23.3
%C-Calcite	[]	12.8	12.2	11.0		11.1			11.4			7.7	8.2	11.7
%C-Inorganic	[]	62.7	64.2	66.0		65.5			66.0			67.7	66.7	65.0
Dry density	[g/cc]	0.07	0.09	0.09		0.070			0.075			0.10	0.07	0.07
dry/wet	[]	0.06	0.09	0.08		0.067			0.072			0.09	0.07	0.07
Mercury Ar	alysis	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)				
MeHg	[ng/g]	2.09	1.63	1.07	2.62	1.46	1.00	1.42	1.22	0.92		3.24	3.31	1.74
THg	[ng/g]	209.7	207.0	210.0	198.5	201.4	198.6	191.5	191.8	200.8		187.0	190.5	200.0
iHg	[ng/g]	207.6	205.3	208.9	195.9	199.9	197.6	190.1	190.6	199.9		183.7	187.2	198.2
% MeHg	[]	1.00	0.79	0.51	1.32	0.73	0.51	0.74	0.63	0.46		1.74	1.74	0.87
log K <sub>D</sub> (THg)	[]	4.24	4.95	5.14								4.81	4.90	4.27
log K <sub>D</sub> (MeHg)	[]	2.80	3.27	4.15								3.50	3.63	3.30
$K_{meth}$	[d <sup>-1</sup> ]	0.045	0.044	0.024	0.040	0.034	0.023	0.041	0.026	0.024		0.072	0.082	0.039
$K_{demeth}$	[hr <sup>-1</sup> ]	0.074	0.057	0.044	0.062	0.055	0.052	0.070	0.011	0.067		0.044	0.040	0.055
$K_m/K_d$	[]	0.61	0.76	0.54	0.65	0.62	0.45	0.59	2.49	0.35		1.74	2.06	0.95
Metals Ext	tract	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		_			
Fe	[g/kg]											27.8		
Al	[g/kg]											40.2		
Mn	[g/kg]											2.0		
Zn	[g/kg]											0.0*		
Ca	[g/kg]											5.5		
K	[g/kg]											0.0*		
Mg	[g/kg]											9.9		
Na	[g/kg]											0.0*		

<sup>\*</sup>measured value negative

## Long Lake Creek Wetland - Plot 1 Sediment Porewater (1 of 2)

				5/15/2012	2			-	7/24/2012	2			1	10/6/2012	2	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)
Analy	tes															
Sulfate	[mg/L]	50.2	9.2	5.0	9.2	26.5	22.0	10.6	7.6	22.9	22.4	521.5		397.5		482.3
Nitrate	[mg/L]	0.7	0.2	0.3	0.0	0.0	0.3	0.2	0.2	0.3	0.1	0.9		1.2		1.2
Phosphate	[mg/L]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.3	0.0		0.0		0.0
Chloride	[mg/L]												33.7		32.4	
Ferrous Iron	[mmol/L]	0.007	0.005	0.011	0.023	0.040	0.009	0.007	0.012	0.008	0.013	0.005	0.004	0.005	0.004	0.003
Sulfide	[µmol/L]	7.6	362.4	425.4	70.4	339.1	753.9	806.2	779.0	505.5	422.1	10.9	103.5	700.8	113.3	15.6
Ammonium	[mg/L]															
DIC	[mg/L]	97.9	112.1	124.7	117.7	103.2	120.8	117.8	124.7	112.7	124.1		114.5			
DOC	[mg/L]	27.9	22.7	17.7	25.3	21.9	30.9	26.6	26.6	29.7	29.3		8.1			
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]	5.0	5.3	6.1	5.6	5.9	4.4	4.2	3.6	4.2			3.2			
Mercury A	Analysis															
MeHg	[ng/L]	0.28	0.12	0.02	0.67	0.19	1.64	0.23	0.19	0.13	0.37	0.22	0.16	0.11	0.06	0.11
THg	[ng/L]	1.56	1.41	1.28	1.95	1.47		4.05	2.82	3.77	3.75	1.59	1.30	1.22	1.31	1.34
iHg	[ng/L]	1.3	1.28	1.26	1.28	1.27		3.81	2.63	3.64	3.38	1.37	1.14	1.11	1.25	1.23
% MeHg	[]	17.7	8.8	1.5	34.5	13.3	n/a	5.8	6.8	3.6	10.0	14.0	12.6	9.1	4.7	8.5

# Long Lake Creek Wetland - Plot 1 Sediment Porewater (2 of 2)

				6/3/2013				Top 4cm	Average	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	5/15/2012	7/24/2012	10/6/2012	6/3/2013
Analy	rtes									
Sulfate	[mg/L]	15.8	14.7	36.9	22.0	25.8	21.8	20.5	482.3	21.0
Nitrate	[mg/L]	4.3	0.7	2.2	0.9	0.5	0.1	0.2	1.2	1.3
Phosphate	[mg/L]	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0
Chloride	[mg/L]		10.7	12.7	10.9	8.8			32.4	9.9
Ferrous Iron	[mM]	0.000	0.000	0.021	0.000	0.000	0.023	0.010	0.004	0.000
Sulfide	[μmol]			1197.5	421.6	364.6	198.2	569.2	62.0	393.1
Ammonium	[mg/L]	2.0	2.7	3.2		1.1				1.70
DIC	[mg/L]	82.1	94.8	111.4	66.7	68.8	108.6	118.7		74.7
DOC	[mg/L]	27.9	20.2	15.1	29.2	27.9	24.2	29.2		27.1
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]	3.1	3.2	4.0	3.3	3.1	5.5	4.3		3.2
Mercury A	Analysis									
MeHg	[ng/L]	0.22	0.14	0.14	1.06	0.55	0.36	0.48	0.12	0.60
THg	[ng/L]	6.27	3.00	9.95	7.19	16.82	1.63	3.76	1.36	9.55
iHg	[ng/L]	6.05	2.86	9.81	6.13	16.27	1.28	3.51	1.24	8.95
% MeHg	[]	3.4	4.8	1.4	14.7	3.3	21.8	12.8	9.0	6.2

# Long Lake Creek Wetland - Plot 1 Solid Phase (1 of 3)

					5/15/2012					7	7/24/201	2			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	76.4	65.7	107.1	100.0	100.5	208.3	197.2	120.6		202.5			207.4	
%C-Organic	[]	38.8	30.6	34.2	37.6	39.3	55.3	47.0	27.1		37.7			41.8	
%C-Calcite	[]	33.3	42.3	39.8	36.3	33.7	13.0	22.1	47.0		36.3			30.3	
%C-Inorganic	[]	27.9	27.0	26.1	26.1	27.0	31.7	30.8	25.9		26.0			27.8	
Dry density	[g/cc]	0.06	0.09	0.08	0.066	0.063	0.06	0.06	0.11		0.055			0.053	
dry/wet	[]	0.06	0.09	0.08	0.064	0.061	0.06	0.06	0.10		0.054			0.051	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	0.35	0.05	0.08	0.61	0.06	1.56	0.13	0.01	0.32	0.18	0.07	0.12	0.11	0.22
THg	[ng/g]	50.4	53.5	30.9	61.7	37.0	65.8	54.2	53.3	96.8	87.6	87.9	67.1	64.9	65.3
iHg	[ng/g]	50.1	53.5	30.8	61.1	37.0	64.3	54.1	53.3	96.4	87.4	87.8	66.9	64.8	65.1
% MeHg	[]	0.69	0.09	0.26	0.99	0.16	2.36	0.23	0.01	0.33	0.21	0.08	0.18	0.17	0.34
log K <sub>D</sub> (THg)	[]	4.51	4.58	4.38				4.13	4.28						
log K <sub>D</sub> (MeHg)	[]	3.10	2.58	3.60			2.98	2.73	1.46						
$K_{\text{meth}}$	[d <sup>-1</sup> ]	0.014	0.007	0.007	0.010	0.016	0.008	0.006	0.006	0.011	0.006	0.003	0.007	0.003	0.004
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.032	0.037	0.033	0.051	0.044	0.038	0.036	0.045	0.057	0.042	0.042	0.072	0.050	0.044
$K_m/K_d$	[]	0.43	0.20	0.21	0.21	0.37	0.21	0.18	0.13	0.19	0.14	0.08	0.09	0.07	0.10
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]						13.4	10.5	8.9		9.9			11.6	
Al	[g/kg]						3.4	3.1	-5.7		-5.3			-1.3	
Mn	[g/kg]						5.5	6.6	14.6		10.1			9.9	
Zn	[g/kg]						-0.2	0.1	-0.2		-0.2			-0.2	
Ca	[g/kg]						52.4	60.9	167.2		123.4			112.2	
K	[g/kg]						2.7	0.9	-5.1		1.2			3.5	
Mg	[g/kg]						9.0	6.4	6.6		6.7			8.3	
Na	[g/kg]						-8.3	66.1	-10.3		-9.0			-8.5	

# Long Lake Creek Wetland - Plot 1 Solid Phase (2 of 3)

					1	10/6/201	2								6/3/2013	}			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	136.2	129.6	125.6		70.0			53.1		132.5	103.9	88.3		64.1			140.5	
%C-Organic	[]	48.9	46.0	35.5		30.7			25.5		39.9	33.9	29.6		28.6			34.9	
%C-Calcite	[]	21.3	23.7	35.0		40.5			51.6		32.1	39.6	46.9		47.7			41.8	
%C-Inorganic	[]	29.8	30.3	29.5		28.7			22.9		28.0	26.5	23.5		23.7			23.3	
Dry density	[g/cc]	0.05	0.06	0.07		0.104			0.123		0.05	0.09	0.11		0.11			0.07	
dry/wet	[]	0.05	0.06	0.07		0.099			0.115		0.05	0.08	0.10		0.11			0.07	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	0.04	0.04	0.03		0.20	0.10	0.02	0.03	0.00		0.33	0.14	1.44	0.24	0.11	1.52	0.45	0.12
THg	[ng/g]	61.4	61.0	59.7	49.0	57.8	104.0	52.4	36.7	23.0		70.7	55.9	69.9	59.3	60.3	55.7	59.5	81.1
iHg	[ng/g]	61.4	61.0	59.7		57.6	103.9	52.4	36.7	23.0		70.3	55.8	68.4	59.1	60.2	54.1	59.0	80.9
% MeHg	[]	0.06	0.07	0.05		0.35	0.09	0.03	0.08	0.01		0.47	0.25	2.06	0.41	0.18	2.73	0.76	0.15
log K <sub>D</sub> (THg)	[]	4.59	4.67	4.69								4.37	3.75						
log K <sub>D</sub> (MeHg)	[]	2.25	2.42	2.40								3.36	3.01						
$K_{\text{meth}}$	[d <sup>-1</sup> ]	0.016	0.011	0.012	0.011	0.012	0.010	0.015	0.010	0.011		0.021	0.013	0.079	0.026	0.012	0.118	0.051	0.017
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.093	0.105	0.098	0.098	0.104	0.099	0.095	0.113	0.104		0.023		0.034					0.051
$K_m/K_d$	[]	0.17	0.11	0.12	0.11	0.12	0.10	0.16	0.09	0.10		0.91		2.34					0.33
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]																		
Al	[g/kg]																		
Mn	[g/kg]																		
Zn	[g/kg]																		
Ca	[g/kg]																		
K	[g/kg]																		
Mg	[g/kg]																		
Na	[g/kg]																		

# Long Lake Creek Wetland - Plot 1 Solid Phase (3 of 3) SUMMARY STATISTICS

			Top 4cm	Average	
Parameter	Units	5/15/2012	7/24/2012	10/6/2012	6/3/2013
AVS	[µmol/g]	90.5	204.2	85.4	107.6
%C-Organic	[]	37.2	43.6	34.6	33.5
%C-Calcite	[]	35.9	28.1	38.2	41.8
%C-Inorganic	[]	26.9	28.4	27.2	24.7
Dry density	[g/cc]	0.07	0.06	0.09	0.08
dry/wet	[]	0.07	0.05	0.09	0.08
Mercury A	nalysis				
MeHg	[ng/g]	0.29	0.40	0.07	0.91
THg	[ng/g]	50.2	72.7	53.0	63.0
iHg	[ng/g]	49.9	72.3	53.8	62.2
% MeHg	[]	0.58	0.55	0.12	1.45
log K <sub>D</sub> (THg)	[]	4.49	4.29	4.59	3.82
log K <sub>D</sub> (MeHg)	[]	2.91	2.92	2.73	3.18
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.012	0.007	0.013	0.066
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.043	0.049	0.101	0.028
K <sub>m</sub> /K <sub>d</sub>	[]	0.30	0.15	0.13	1.63
Metals Ex	ktract				
Fe	[g/kg]		11.2		
Al	[g/kg]		0.0*		
Mn	[g/kg]		8.7		
Zn	[g/kg]		0.0*		
Ca	[g/kg]		97.4		
K	[g/kg]		2.1		
Mg	[g/kg]		7.6		
Na	[g/kg]		3.8		

<sup>\*</sup>measured value negative

## West Two River Wetland - Plot 1 Sediment Porewater (1 of 2)

			Ĺ	5/15/2012	2			-	7/24/2012	2			-	10/6/2012	2	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)
Analy	tes															
Sulfate	[mg/L]						0.8	0.5	0.5	5.5	0.8	2.1	1.0	0.9	0.5	
Nitrate	[mg/L]						2.1	1.0	0.4	3.5	2.1	0.7	0.1	0.4	0.4	
Phosphate	[mg/L]						1.3	2.7	2.5	2.0	0.4	0.0	0.8	0.2	0.0	
Chloride	[mg/L]												1.9	1.7	1.8	
Ferrous Iron	[mmol/L]						0.033	0.030	0.045	0.027	0.034	0.011	0.013	0.043	0.010	0.009
Sulfide	[µmol/L]						3.5	13.8	10.1	20.0	19.8	4.2	5.6	3.4	3.8	4.6
Ammonium	[mg/L]								6.3		3.9		2.7	2.5		1.7
DIC	[mg/L]						42.4	41.3	52.0	37.6	39.6		35.0	32.7	37.7	41.1
DOC	[mg/L]						22.8	23.5	21.7	22.0	24.4		18.2	17.5	18.9	21.7
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]						3.6	3.2	3.6	4.9			4.8	4.9	4.6	5.0
Mercury A	Analysis															
MeHg	[ng/L]						1.37	0.86	0.36	1.06	1.45	0.75	0.38	0.26	0.38	0.41
THg	[ng/L]		·	·			1.95	1.77	1.08	2.11	2.55	2.83	1.70	1.88	3.15	1.99
iHg	[ng/L]			·			0.58	0.91	0.72	1.06	1.10	2.08	1.32	1.62	2.76	1.58
% MeHg	[]			·			70.3	48.6	33.0	50.1	56.8	26.5	22.1	14.1	12.2	20.8

# West Two River Wetland - Plot 1 Sediment Porewater (2 of 2)

				6/3/2013				Top 4cm	Average	
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)	5/15/2012	7/24/2012	10/6/2012	6/3/2013
Analy	tes									
Sulfate	[mg/L]	2.1	1.5	1.3	1.5	1.6		2.3	1.0	1.6
Nitrate	[mg/L]	6.5	2.3	2.2	7.2	0.2		2.4	0.4	3.9
Phosphate	[mg/L]	0.0	0.0	0.1	0.3	0.1		1.5	0.2	0.1
Chloride	[mg/L]	2.0	1.8	1.6	2.3	1.7			1.8	2.0
Ferrous Iron	[mM]	0.027	0.053	0.056	0.060	0.122		0.031	0.010	0.074
Sulfide	[μmol]	4.0	11.3	11.0	7.4	4.4		16.1	4.5	6.5
Ammonium	[mg/L]	0.9	1.0	1.0	1.8	1.2		3.9	1.7	1.3
DIC	[mg/L]	42.0	30.1	33.5	40.6	28.8		39.7	39.4	35.2
DOC	[mg/L]	21.2	17.2	14.6	20.1	17.0		23.2	20.3	18.8
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]	4.3	4.4	4.4	4.8	4.6		4.2	4.8	4.6
Mercury A	Analysis									
MeHg	[ng/L]	0.52	0.50	0.29	0.34	0.18		1.21	0.45	0.34
THg	[ng/L]	2.14	1.85	1.82	1.72	1.44		2.17	2.47	1.72
iHg	[ng/L]	1.63	1.35	1.53	1.38	1.26		0.97	2.01	1.38
% MeHg	[]	24.2	27.1	15.8	19.8	12.2		55.5	18.4	19.9

## West Two River Wetland - Plot 1 Solid Phase (1 of 2)

\*Not sampled in May 2012

					7	//24/201	2							1	10/6/201	2			
Parameter	Units	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
AVS	[µmol/g]	137.6	87.7	43.2		101.5			55.9		57.8	130.6	38.9		177.7			37.7	
%C-Organic	[]	49.6	50.1	49.9		51.0			50.3		50.6	50.5	50.0		49.0			49.9	
%C-Calcite	[]	9.1	8.1	9.8		8.6			10.2		11.2	10.8	11.0		11.1			10.7	
%C-Inorganic	[]	41.3	41.8	40.3		40.3			39.5		38.3	38.7	38.9		39.9			39.3	
Dry density	[g/cc]	0.03	0.05	0.06		0.050			0.044		0.03	0.03	0.04		0.034			0.041	
dry/wet	[]	0.03	0.05	0.05		0.049			0.043		0.03	0.03	0.04		0.034			0.040	
Mercury Ar	nalysis	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)	A(0-2)	A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)
MeHg	[ng/g]	0.81	0.71	0.80	3.66	1.90	0.78	3.76	1.07	1.13	2.78	1.04	0.92	1.86	1.07	0.83	2.50	1.26	0.92
THg	[ng/g]	80.2	91.6	143.4	79.1	84.4	149.0	83.1	117.5	188.7	172.5	198.6	195.7	141.9	160.4	197.1	147.4	153.3	216.9
iHg	[ng/g]	79.4	90.9	142.6	75.5	82.5	148.2	79.3	116.5	187.6	169.7	197.6	194.8	140.1	159.4	196.3	144.9	152.1	216.0
% MeHg	[]	1.01	0.78	0.56	4.62	2.25	0.53	4.53	0.91	0.60	1.61	0.52	0.47	1.31	0.67	0.42	1.70	0.82	0.43
log K <sub>D</sub> (THg)	[]	4.62	4.71	5.12							4.79	5.07	5.02						
log K <sub>D</sub> (MeHg)	[]	2.77	2.92	3.35							3.57	3.44	3.54						
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.094	0.045	0.026	0.266	0.132	0.037	0.309	0.108	0.062	0.061	0.033	0.016	0.066	0.045	0.027	0.059	0.047	0.022
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.022	0.016	0.038	0.038	0.035	0.030	0.028	0.032	0.095	0.023	0.016	0.014	0.008	0.010	0.032	0.006	0.010	0.044
$K_m/K_d$	[]	4.24	2.76	0.69	7.00	3.77	1.23	10.88	3.44	0.65	2.65	2.09	1.10	8.56	4.38	0.84	10.70	4.58	0.50
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)	
Fe	[g/kg]	10.7	9.0	7.7		12.5			8.2										
Al	[g/kg]	20.4	23.0	6.7		20.5			29.0										
Mn	[g/kg]	0.3	0.6	0.8		0.4			0.7										
Zn	[g/kg]	0.1	0.1	0.1		0.1			0.1										
Ca	[g/kg]	7.6	16.5	7.9		7.1			8.7										_
К	[g/kg]	9.3	5.9	-0.2		8.3			4.8										
Mg	[g/kg]	3.9	3.8	3.4		3.8			3.6										
Na	[g/kg]	16.8	15.8	-0.5		-19.8			-15.7										

# West Two River Wetland - Plot 1 Solid Phase (2 of 2)

		6/3/2013						Top 4cm Average						
Parameter	Units	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		5/15/2012	7/24/2012	10/6/2012	6/3/2013
AVS	[µmol/g]	77.9	81.5	33.6		50.0			152.7			90.0	103.2	94.1
%C-Organic	[]	49.6	50.0	47.7		50.5			46.7			50.4	49.8	49.0
%C-Calcite	[]	14.0	14.4	12.5		12.7			14.6			9.2	10.9	13.8
%C-Inorganic	[]	36.4	35.5	39.7		36.8			38.8			40.5	39.2	37.1
Dry density	[g/cc]	0.04	0.05	0.06		0.04			0.04			0.04	0.04	0.04
dry/wet	[]	0.04	0.05	0.06		0.04			0.04			0.04	0.04	0.04
Mercury Ar	Mercury Analysis		A(2-4)	A(4-8)	B(0-2)	B(2-4)	B(4-8)	C(0-2)	C(2-4)	C(4-8)	_			
MeHg	[ng/g]	1.44	0.75	0.75	2.70	1.10	1.10	3.17	1.54	1.20		1.98	1.75	1.78
THg	[ng/g]	153.4	183.3	251.8	116.5	109.0	203.4	139.8	146.1	210.0		89.3	162.4	141.3
iHg	[ng/g]	152.0	182.5	251.0	113.8	107.9	202.3	136.7	144.5	208.8		87.4	160.6	139.6
% MeHg	[]	0.94	0.41	0.30	2.31	1.01	0.54	2.27	1.05	0.57		2.22	1.08	1.26
log K <sub>D</sub> (THg)	[]	4.85	5.00	5.14								4.61	4.82	4.92
log K <sub>D</sub> (MeHg)	[]	3.44	3.17	3.42								3.22	3.59	3.72
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.049	0.026	0.014	0.104	0.075	0.040	0.107	0.065	0.033		0.159	0.052	0.071
K <sub>demeth</sub>	[hr <sup>-1</sup> ]		0.017	0.027	0.006	0.028	0.059	0.013	0.042	0.037		0.029	0.012	0.019
$K_m/K_d$	[]		1.53	0.53	16.57	2.65	0.68	8.27	1.52	0.90		5.35	5.49	7.16
Metals Ex	tract	A(0-2)	A(2-4)	A(4-8)		B(0-4)			C(0-4)		_			
Fe	[g/kg]											10.2		
Al	[g/kg]											23.8		
Mn	[g/kg]											0.5		
Zn	[g/kg]											0.1		
Ca	[g/kg]											9.3		
K	[g/kg]											6.9		
Mg	[g/kg]											3.7		
Na	[g/kg]											0.0*		

<sup>\*</sup>measured value negative

#### West Swan River Wetland - Plot 1 Sediment Porewater

		Į	5/15/2012	Top 4cm Average					
Parameter	er Units		A(2-4)	A(4-8)	B(0-4)	C(0-4)	5/15/2012		
Analy	/tes								
Sulfate	[mg/L]								
Nitrate	[mg/L]								
Phosphate	Phosphate [mg/L]								
Chloride	[mg/L]								
Ferrous Iron	[mmol/L]								
Sulfide	[µmol/L]	12.5	9.7	7.4	6.8	10.9	9.6		
Ammonium	[mg/L]								
DIC	[mg/L]	49.9	37.5	36.4	54.8	54.5	51.0		
DOC	[mg/L]	29.2	23.0	31.7	33.9	33.9	31.3		
SUVA	[Lm <sup>-1</sup> mg <sup>-1</sup> ]	11.1	12.7	7.6	7.4	6.7	8.7		
Mercury Analysis									
MeHg	[ng/L]	0.41	0.38	0.24	0.08	0.10	0.19		
THg	[ng/L]	2.39	2.86	1.20	2.34	2.16	2.37		
iHg	[ng/L]	2.0	2.48	0.96	2.25	2.06	2.18		
% MeHg	[]	17.0	13.4	20.0	3.6	4.6	8.1		

#### West Swan River Wetland - Plot 1 Solid Phase

						Top 4cm Average		
Parameter	Units	A(0-2)	A(2-4)	A(4-8)	5/15/2012 B(0-4)	C(0-4)	5/15/2012	
AVS	[µmol/g]	8.3	3.9	4.7	4.8	6.4	5.8	
%C-Organic	[]	15.7	13.1	7.6	14.1	12.1	13.5	
%C-Calcite	[]	3.0	2.7	1.7	2.5	2.6	2.6	
%C-Inorganic	[]	81.3	84.2	90.7	83.4	85.4	83.8	
Dry density	[g/cc]	0.24	0.35	0.63	0.30	0.35	0.31	
dry/wet	[]	0.21	0.29	0.46	0.26	0.29	0.27	
Mercury Analysis		A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)		
MeHg	[ng/g]	1.14	0.59	0.96	0.75	0.79	0.80	
THg	[ng/g]	75.4	72.0	57.7	87.6	84.0	81.8	
iHg	[ng/g]	74.3	71.4	56.8	86.8	83.2	81.0	
% MeHg	[]	1.51	0.81	1.66	0.85	0.94	0.98	
log K <sub>D</sub> (THg)	[]						4.54	
log K <sub>D</sub> (MeHg)	[]						3.62	
K <sub>meth</sub>	[d <sup>-1</sup> ]	0.114	0.047	0.041	0.109	0.124	0.104	
K <sub>demeth</sub>	[hr <sup>-1</sup> ]	0.042	0.108	0.000	0.076	0.064	0.072	
K <sub>m</sub> /K <sub>d</sub>	[]	2.69	0.44		1.42	1.94	1.64	
Metals Extract		A(0-2)	A(2-4)	A(4-8)	B(0-4)	C(0-4)		
Fe	[g/kg]							
Al	[g/kg]							
Mn	[g/kg]							
Zn	[g/kg]							
Ca	[g/kg]							
K	[g/kg]							
Mg	[g/kg]							
Na	[g/kg]							