Methyl mercury production and transport in a sulfate-impacted sub-boreal wetland

Nathan Johnson[‡], Carl Mitchell[⊢], Daniel Engstrom[+], Logan Bailey[†], Megan Kelly[⊣], Jill Coleman-Wasik[+], Michael Berndt[⊣]

[‡]Department of Civil Engineering, University of Minnesota Duluth; [⊢]Department of Physical and Environmental Sciences, University of Toronto – Scarborough; [†]Water Resources Science Program, University of Minnesota; [+]St. Croix Watershed Research Station, Science Museum of Minnesota, [⊣]Minnesota Department of Natural Resources, Division of Lands and Minerals

*Corresponding author, email: nwjohnso@d.umn.edu, phone: 218-726-6435, fax: 218-726-6445

Final Project Data Report

with preliminary interpretations

Minnesota DNR MWRAP 2012-2013 Study

6/30/2014

Table of Contents

List of Tables

List of Figures

Summary

As a part of a larger effort by the MN DNR to understand the role of sulfate in methyl mercury production and transport in the St. Louis River watershed, a wetland complex (Long Lake Creek) downstream from a mine pit discharge on the Mesabi Iron range was studied intensively during the summer of 2012. The ~1.25 km long wetland complex typically receives a relatively small upstream discharge of mining-influenced water (elevated sulfate and magnesium) which flows mostly through the open-water portion of the wetland and is diluted by additions of water along its length. During 2012, the peat surface was inundated in response to large spring (June) rainfall events. During the fall of 2011 and 2012, the peat surface was also inundated with water elevated in sulfate as a result of active discharging from a mine pit to supplement flow in the St. Louis River main stem. Water samples were collected at the inlet and outlets of the wetland complex and analyzed for total- and methyl- mercury as well as a host of geochemically related parameters. Additionally, solid phase and pore water samples were collected throughout the summer of 2012 at two locations in the wetland peat (near shore and upland) with the goal of ascertaining the mechanisms leading to methyl mercury production and release in the wetland complex. Samples were also collected from the pore water and solid phase of a wetland with similar vegetation that receives far lower sulfate loads. 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.

Data from both wetlands showed that the net methylation potential was highest in July compared to May and October. However, the instantaneous rate of MeHg production quantified with isotope tracers was not always closely mirrored by the fraction of the total mercury pool present as MeHg in either the pore water or solid phase. At lower sulfide concentrations, the fraction of mercury present as MeHg in the solid phase appeared to be positively related to sulfide in both the pore water and solid phase. At higher sulfide concentrations, MeHg was unrelated or even inversely related to sulfide. Though some seasonal variability was observed, solid phase sulfides in surficial peat were generally higher in locations nearer to

the open water where peat retained more moisture. Despite having sulfur concentrations 10-100x lower than Long Lake Creek wetland (and comparable total mercury concentrations), the West Two River peat had MeHg concentrations in both the dissolved and solid phases similar to those observed at Long Lake Creek.

Inlet and outlet samples showed considerable additions of MeHg and dissolved organic carbon (DOC) to the stream as it passed through the Long Lake Creek wetland immediately following the Spring 2012 (natural) flooding event. This was consistent with elevated concentrations of MeHg and DOC in the peat pore fluids during this time. Dissolved concentrations of MeHg were strongly correlated with DOC at the wetland outlet and generally related in locations farther from the open water (upland), which suggests that DOC is playing an important role in transporting MeHg in these locations. At locations near the open water of both wetlands DOC and MeHg were not obviously related, and active methylation and demethylation processes may have been more important to defining dissolved MeHg than DOC-facilitated transport. During the pumping event which inundated the peat at Long Lake Creek in fall 2012, concentrations of DOC and MeHg in peat pore fluids were uniformly low and in-stream DOC and MeHg concentrations at the wetland outlet mirrored those at the inlet.

The seasonal sampling suggests that a vast majority of the MeHg and DOC export from the Long Lake Creek wetland occurred in the month following the large, natural hydrologic event in June 2012 an that relatively little MeHg was exported from the wetland during the flooding event as a result of fall pumping of mine water. A distinct difference in chemical signatures of the water entering the wetland during the fall pumping event and the normal summertime discharge allows for an evaluation of the fate of the water that flooded the wetland in the fall. Evidence suggests that some of the fall-flooding water (from 2011) was still making its way out of the wetland up to a year later (late summer, 2012), highlighting the fact that the residence time of the peat portions of the wetland complex can be hugely different from the residence time of the open-water portions.

1. Introduction

The accumulation of methylmercury (MeHg) in edible fish tissue has led to fish consumption advisories for thousands of lakes in Minnesota and across the US (US EPA 1997, Fitzgerald et al. 1998). The quantity of MeHg present in an aquatic ecosystem is a result of chemical and biological processes that produce, break down, and transport MeHg (Morel et al. 1998). The production of MeHg from the more prevalent inorganic mercury is primarily a biologically-driven process, while both biotic and abiotic processes can break down MeHg. Though other bacteria have shown capabilities to produce MeHg (Kerin et al. 2006, Parks et al. 2013), sulfate reducing bacteria (SRB) have been consistently shown to be the most efficient producers of MeHg (Compeau and Bartha 1985, Gilmour et al. 1992, Harmon et al. 2004). A wide variety of bacteria, including aerobic and SRB, have shown the capacity to breakdown, or demethylate, MeHg (Compeau and Bartha 1984).

Due to their dynamic hydrologic and geochemical nature, wetlands have been identified as net producers of MeHg and exporters to downstream ecosystems (St. Louis et al. 1994, Branfireun et al. 1996). Recent research has sought to ascertain the specific factors limiting MeHg production and export from wetlands. Experimental additions of sulfate from the atmosphere and of labile carbon to low-sulfur wetlands have shown a relatively quick response in stimulating MeHg production (Jeremiasson et al. 2006, Coleman-Wasik et al. 2012, Mitchell et al. 2008a). Other research has identified both micro- and local- scale topography (Branfireun 2004, Mitchell et al. 2009, Mitchell and Branfireun 2005, Mitchell et al. 2007, Mitchell et al. 2008b), as an important factor for defining the mercury-related nutrient loads and redox conditions in peatlands. The study described herein was designed to investigate MeHg production and transport in a wetland downstream from an active mining operation discharging seasonally varying quantities of circumneutral pH water with elevated sulfate, calcium, and magnesium.

While sulfate clearly stimulates the activity of SRB in low sulfate aquatic ecosystems, leading to greater net MeHg production, its role in systems with higher amounts of sulfate is more difficult to ascertain. In the Florida Everglades, samples collected from sediments exposed to a range of sulfate and nutrient loads showed lower net MeHg production in sites with high sulfate and nutrient loads (Gilmour et al. 1998). The buildup of sulfide in porewaters of anoxic sediments exposed to high sulfur loads is thought to change the form of dissolved inorganic mercury in ways that alter its availability to methylating microbes due either to thermodynamic or kinetic limitations (Benoit et al. 1999, Hsu-Kim et al. 2013).

Beyond the production of MeHg, transport from the anoxic environments where it is produced may be largely controlled by binding to dissolved organic matter. Observations on many spatial scales have suggested that mercury binding to dissolved organic matter is important for defining the form of both inorganic- and methyl- mercury in environmental systems (Khwaia et al. 2006, Miller et al. 2007, Hurley et al. 1995, Berndt and Bavin 2012). Thiol groups on organic matter have shown strong interactions with mercury (Skyllberg et al. 2006) and evidence in the region of the present study has suggested that high and low- molecular weight DOC may transport mercury with different capacities (Berndt and Bavin 2012), especially in the context of high ionic strength mine water. Previous studies in the region of the present study have showed strong relationships between both inorganic- and methyl- mercury and DOC (Berndt and Bavin 2011) but deviations from the trend were observed from some systems immediately following large hydrologic events and possibly in presence of dissolved H_2S in anoxic waters.

Despite receiving far larger loads of sulfate, tributary streams impacted by mining in the St. Louis River watershed carry similar concentrations of MeHg as their non-sulfate impacted counterparts (Berndt and Bavin 2012) and showed no relation to stream sulfate concentration. The present study took place in the context of a larger study conducted by the Minnesota Department of Natural Resources (MN DNR) to help understand the role of sulfate in the production and transport of MeHg from aquatic systems downstream from mines in Northeastern Minnesota. The purpose of this report is to provide preliminary interpretations of the data collected in wetlands and share them with project partners. A more holistic assessment of the data will follow once reports from all project partners have been reviewed and incorporated with one another.

2. Methods

Site Description

Two wetland sites having a contrast in upstream mining impacts were selected for the study. The Long Lake Creek (LLC) wetland (N 47.42°, W 92.56°) is a boreal peatland of ~1.25 km length which receives sulfur loads from an upstream discharge from a mining pit and typically has surface water sulfate concentrations in excess of 200 mg/L (Berndt and Bavin 2011). The LLC periphery contains typical fen/bog vegetation and grades into a margin dominated by cattails up to an approximately 0.14 km^2 open-water pool. The West Two River (WTR) wetland (N 47.465°, W 92.77°) lies in the small subwatershed of a tributary to the west branch of the West Two River. WTR is a large sedge peatland comprised of organic-rich sediment and peat on the north side of a small pond with surface water sulfate concentrations typically less than 5 mg/L. Samples were collected in May 2012 from the West Swan River (WSR), a riparian wetland with a thin peat layer over inorganic sediment that receives moderate sulfate loads. After the first sapling event, WTR was substituted for WSR in an attempt to find a wetland with similar geomorphology and vegetation similar to LLC without large upstream sulfate loads or the periodic mine-induced flooding events.

The summer of 2012 was characterized by very large hydrologic events in June that inundated both wetlands which slowly dried out over the rest of the mostly dry summer. The water table ranged from 10-20 cm above the peat surface in late June and early July to approximately 5-10 cm below the peat surface later in the summer. In mid-September 2012, the LLC wetland was subject to a flooding event in response to pumping from upstream mine water. The company reported that the flow in the Long Lake Creek watershed increased from near zero to 4000-6000 GPM during the week following September 15, 2013 (Cliffs Natural Resources Inc., 2013). The pumping lasted through November and resulted in an inundation of the entire wetland area with 30 – 50 cm of water. This same type of pumping occurred during the year of 2011 and possibly in years prior as well, meaning the LLC wetland complex was inundated by high sulfate water during the fall prior to the results reported here for summer 2012.

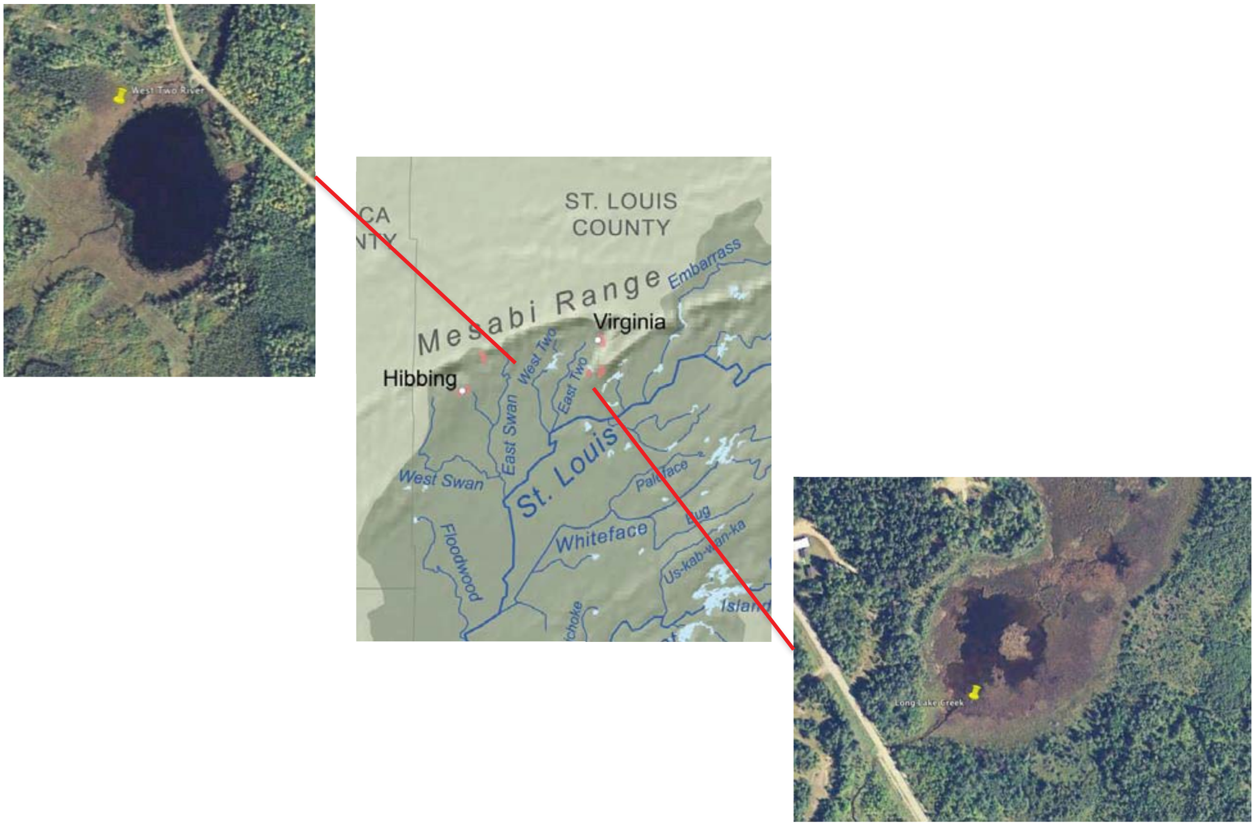

Fig 1 Study site locations downstream from mining features on the Mesabi Iron Ragne in Northeastern MN, USA.

Sampling methods

Samples were collected from two sampling plots at each site along a transect from the open water area upland. Plot 2 represented the near shore (5-10 m from open water) sampling location and plot 3 represents the upland sampling location (20-25 m from open water) in each wetland. The sediment at the bottom of the open water area (plot 1) was also characterized and results are included in a separate report (Bailey et al. 2013a). Solid phase samples were collected from wetland peat material in May, July, and October 2012 at Long Lake Creek and in July and October 2012 at West Two River. Triplicate peat blocks from each sampling plot were cut in the field, wrapped in plastic wrap to preserve moisture, and transported to a local lab for sample sectioning and preservation. Peat blocks were sliced into 0-2, 2-4, and 4-8 cm sections and immediately placed into an oxygen-free atmosphere where individual samples were homogenized and allocated for different analyses. Peat material for methylation and demethylation assays was collected in the field using 3cm diameter polycarbonate tubing with silicone-sealed injection ports drilled spaced at 1 cm intervals. Triplicate cores were collected at each sampling location in the peatlands, capped on the bottom and top with rubber stoppers, and stored upright in coolers during transport to the lab for injection of enriched mercury isotopes.

Fig 2 Sampling plots in wetlands along a transect form open water to upland. One set of replicate samples was collected from each plot at wetland sites seasonally over the summer of 2012.

Filtered porewater samples were collected in triplicate from each sampling plot in May 2012 and then approximately biweekly during July, August, and September using three replicate 10 cm Rhizon filters installed *in situ* and connected to acid-washed, evacuated serum bottles with PTFE tubing and a stainless steel hypodermic needles. In the case of a water table at or above the peat surface, porewater was collected from the surficial 10 cm of peat pore fluids. When the water table was below the peat surface, porewater was collected from the first 10 cm of saturated peat material. Rhizons were typically installed in the afternoon and retrieved the following morning, allowing time for the in-situ filtration of four bottles totaling approximately 325 mL. One bottle was pre-loaded with ZnAc for the preservation of sulfide while other bottles containing no preservative were opened in the lab, allocated, and preserved for redox-sensitive analyses.

In an effort to avoid sampling of disturbed areas, an approximately 15 meter diameter area was staked out at each plot at the beginning of the season and samples were collected from different areas within the plot during each sampling event. Since previous research has shown that microtopographic characteristics of peatlands can have significant influence on mercury and related geochemistry (Branfireun 2004), an effort was made to consistently collect both solid and porewater samples from representative hollows between hummocks that appeared similarly moist or inundated compared to other hollows in the immediate area.

Analytical methods

Solid phase and pore water samples were analyzed using methods identical to those described in Bailey et al. 2013a. Briefly, solid phase methyl mercury was analyzed via isotope dilution ICP-MS, solid phase total mercury was quantified via CVAFS, AVS was analyzed with the automated methylene blue method, and solid phase carbon and nitrogen were analyzed on an elemental analyzer. All solid phase samples were accompanied by a measurement of water content and are reported on a dry mass basis. In peat porewaters, methyl mercury was analyzed on an ICP-MS and total mercury via CVAFS. Rates of mercury methylation and methyl mercury demethylation were assessed using enriched stable isotope techniques as outlined in Hintelmann et al. (2000) and Mitchel and Gilmour (2008). Methylation potentials are reported in units of per day, while demethylation potentials are reported in per hour. Net methylation potentials are the ratio of these two (methylation divided by demethylation) and do not have dimensionally consistent units. As such, net methylation potential should not be thought of as an absolute rate, but a net capacity that is characteristic of a system's ability to produce MeHg under the present conditions. While the absolute value of this ratio is not objectively meaningful, qualitative comparisons among sites and seasons are possible.

Dissolved sulfide was measured using the automated methylene blue method, ferrous iron was measured using the phenanthroline method, anions were quantified using ion chromatography, and total nitrogen, phosphorus, and ammonia were quantified on a Lachat Autoanalyzer. Dissolved organic carbon was quantified using a carbon analyzer and also by ultraviolet absorbance at 254 and 440 nm for SUVA and slope ratio (S_R) characterization (Helms et al. 2008). pH and ORP were measured in-situ using a field pH electrode with automated temperature correction and a platinum electrode with Ag/AgCl reference calibrated in the field against quinhydrone-pH buffer standards.

3. Results & Discussion

MeHg production in peat

Measurements of instantaneous net methylation potential (Fig 3, ratio of methylation to demethylation) made with stable isotopes in the top 4 cm of peat samples were not highly correlated with % MeHg in the wetland solid phase or pore water. Since the accumulation of MeHg on the solid phase is believed to be a good indicator of a medium- or long- term methylation potential of a site, the lack of correlation between kmeth and % MeHg in the peat suggests that the instantaneous methylation rate does not accurately reflect the long term accumulation in the solid phase in these systems. The transient hydrologic setting of wetlands create varying redox conditions in surficial sediment and could explain why instantaneous rates do not reflect longer-term rates of accumulation. Methylation potentials and MeHg in the solid phase were closely related in lake sediments which experience much slower redox changes and are subject to little advective water movement (Bailey et al. 2014b).

At all sites, net methylation potentials were highest in July and substantially lower in October (Fig 4a). It is important to note that the May samples in the unimpacted wetland took place in a different system (West Swan River) than the July and October sampling (West Two River). The methylation (and net methylation potential) was particularly low for the LLC sites in October at a time when the pore fluids had been inundated with cold, well oxygenated, high-sulfate water pumped from a mine. Temperatures were warmest during July, likely leading to the most active time for biological processes which drive MeHg production. Additionally, the water table was lowest during July at LLC and, though not apparent from the pore water sulfate measurements, the oxidation of sulfides in surficial peat could have led to increased availability of sulfate to drive methylation by sulfate reducing bacteria.

At LLC, a strong depth dependence was evident in both kmeth and % MeHg at the nearshore site (Fig 4c,e) with the highest % MeHg in the 0-2 cm interval. At the upland site, kmeth did not consistently decrease with depth (Fig 4d) though % MeHg was still elevated near the surface (Fig 4f) during all seasons. Observations at the near-shore unimpacted wetlands (WTR/WSR) were similar, although neither kmeth nor % MeHg showed any consistent depth dependence at the upland site (Appendix A).

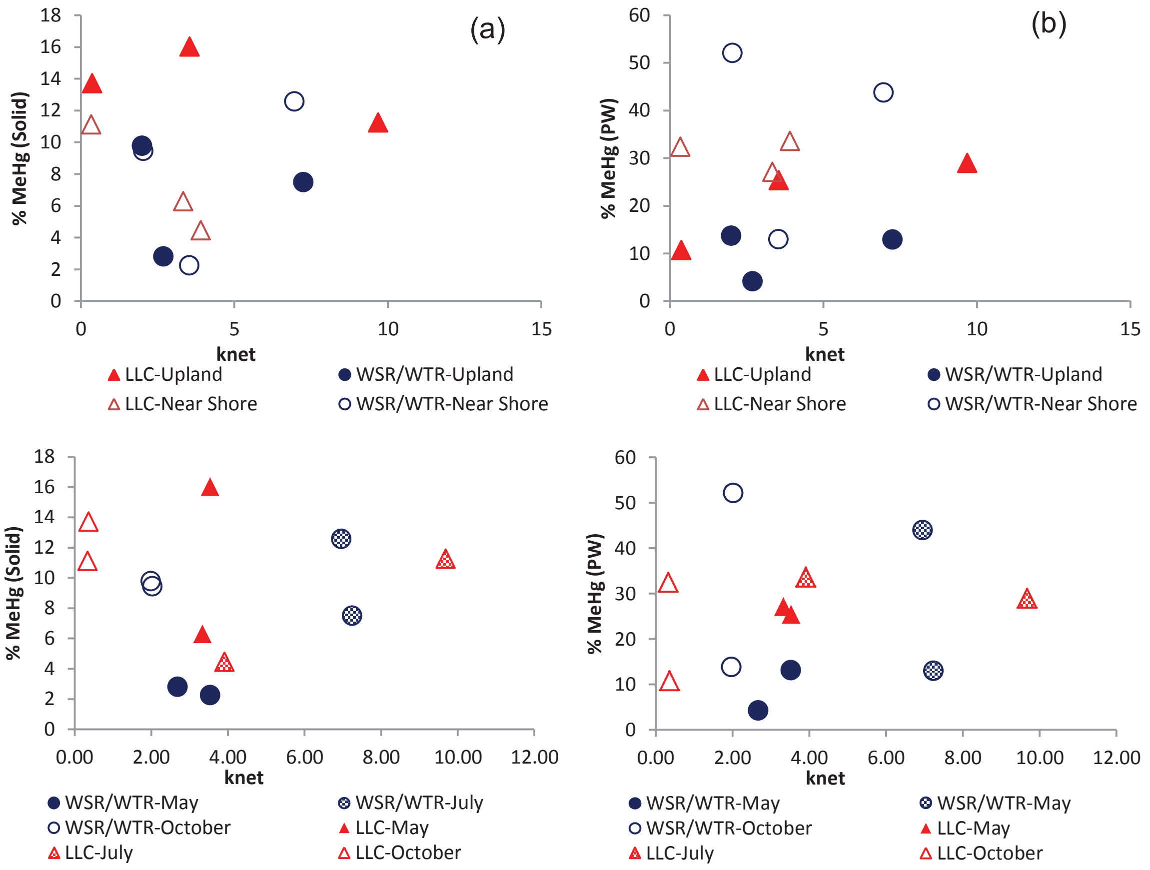

Fig 3 Fraction methyl mercury vs. instantaneous methylation potential measurements in peat solid phase and pore fluids. (a) % MeHg in solid phase vs. net methylation potential (kmeth/kdemeth), (b) % MeHg in porewater vs. net methylation potential (kmeth/kdemeth)

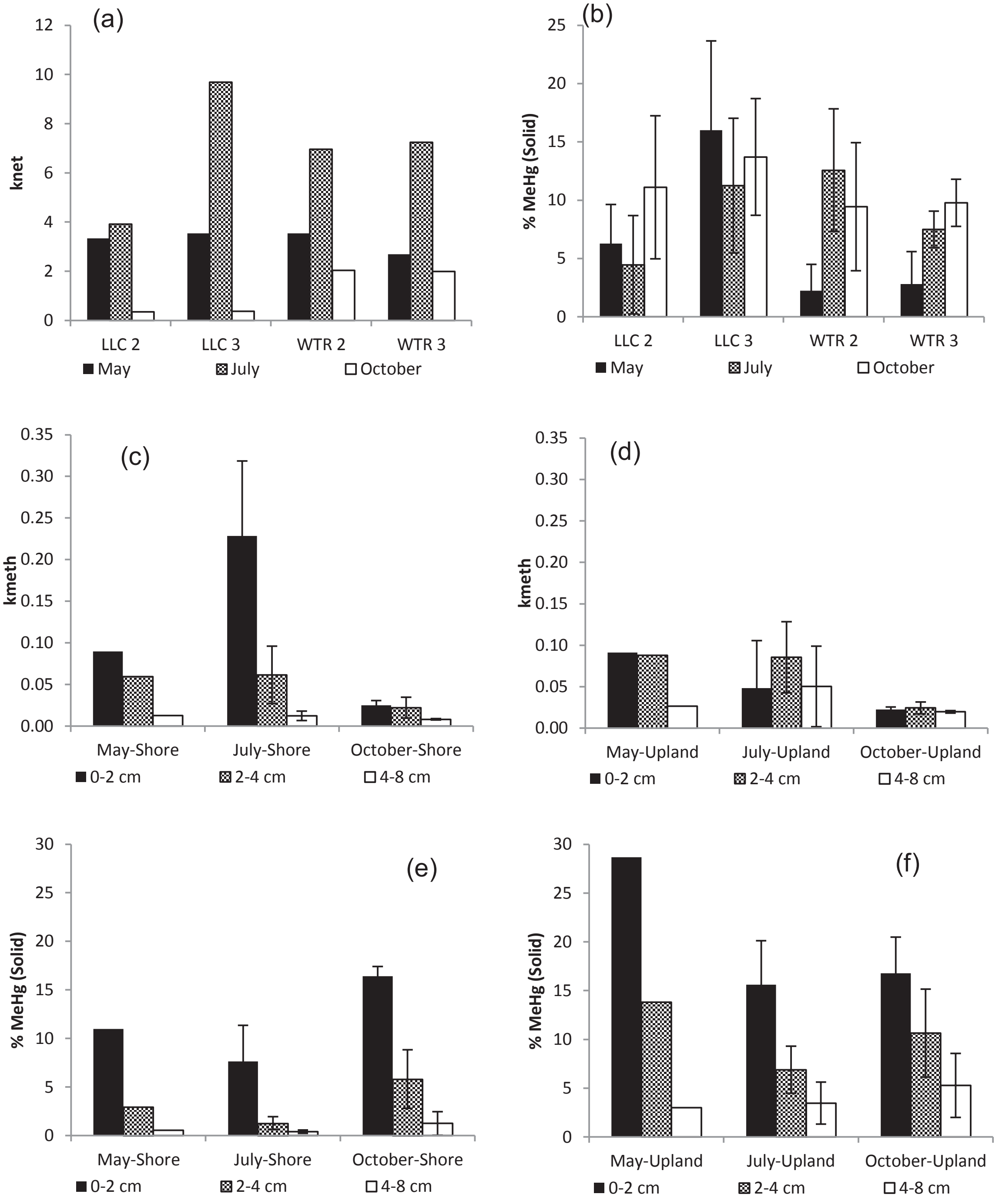

Fig 4 Spatial and temporal distribution of net methylation potential and fraction MeHg in peat samples. Seasonal differences in 0-4 cm average (a) kmeth, and (b) % MeHg (solids). Vertical heterogeneity in knet at LLC (c) nearshore, and (d) upland sites. Vertical heterogeneity in % MeHg (solids) at (e) nearshore, and (f) upland sites.

Solid phase sulfides and MeHg

Samples collected from the unimpacted West Swan River wetland in May showed % MeHg in the solid phase substantially lower than all other samples. Visual observations during sample collection suggested that both the near-shore and upland areas were very dissimilar to typical peat, and carbon concentrations (< 40 % for WSR) were approximately half of that observed at the other two wetlands (75-85 % at LLC, and 85-90 % at WTR). For these reasons, it is expected that the May observations at WSR do not represent those typical of sub-boreal peat.

Dissolved sulfide concentrations were higher in the sulfate impacted wetland pore fluids (LLC), but were not consistently higher in the near shore site and never exceeded 100 uM (Fig 5). When the WSR samples are excluded from the data, a trend between % MeHg in the solid phase and sulfide in the pore waters for peat samples is similar to that observed in the sediment underlying open water sites in the region (Fig5 a,c, Bailey et al. 2014a). At dissolved sulfide concentrations below ~20 uM in porewater, there is an increase in % MeHg in the solid with increasing dissolved sulfide (from ~8 % to 12 %). At higher dissolved sulfide concentrations (LLC), no trend is apparent (range from 4 % to 16 %). A similar trend in % MeHg in pore fluids is not present (Fig 5 b,d).

Solid phase sulfides (AVS) were consistently higher in the nearshore peat at both impacted and unimpacted wetlands (Fib 6a). At LLC, % MeHg in the solids showed an inverse relationship with AVS, while at WTR, a positive correlation was present between % MeHg in solids and AVS (Fig 6a,c). AVS showed no apparent relation with % MeHg in peat pore waters (Fig 6b,d). While solid-phase sulfides increased consistently throughout the summer in sediment samples from open water locations (Bailey et al. 2014a), no consistent seasonal trend was apparent in AVS in peat samples (Fig 7). This could be due to the relative inhomogeneity of the peat material or due to the variable redox conditions observed in surficial peat over the summer season.

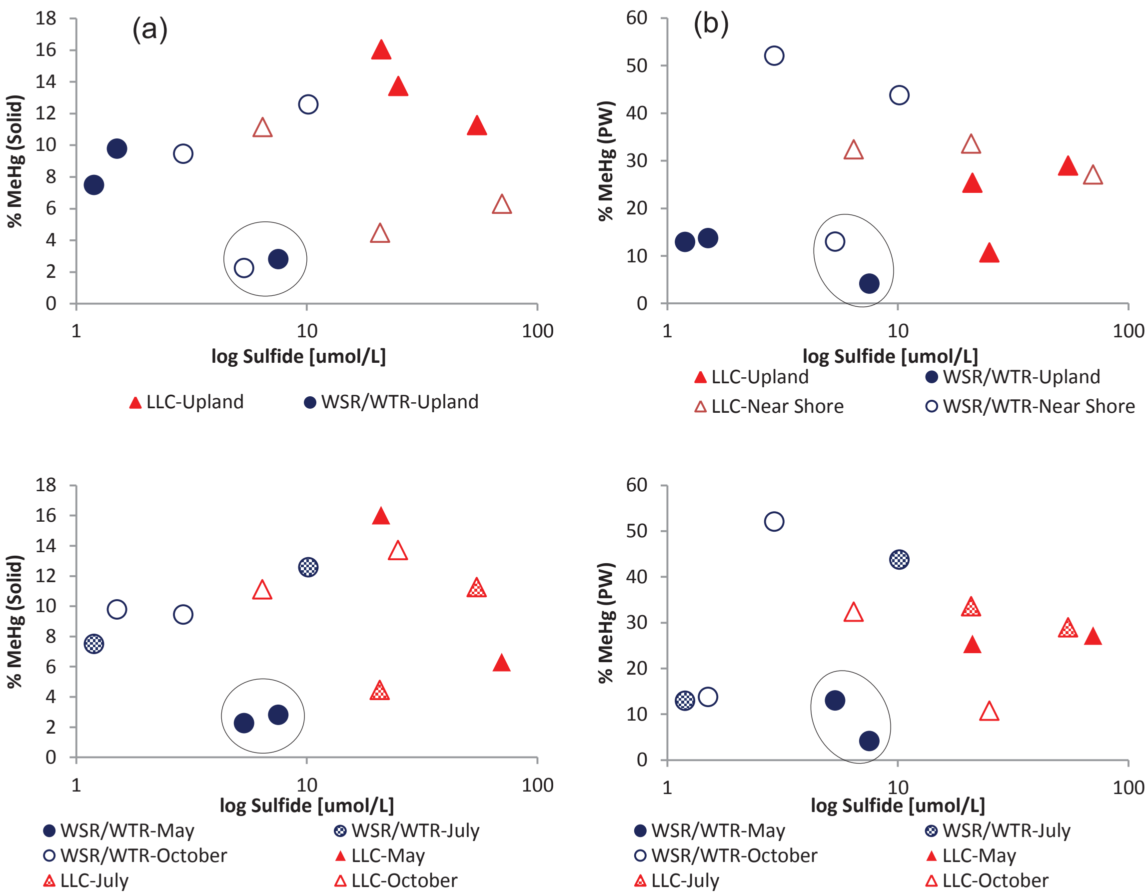

Fig 5 MeHg vs. dissolved sulfide in peat samples. Spatial (top) and seasonal (bottom) distribution (upland vs. nearshore) in % MeHg in (a) solid phase, and (b) pore water.

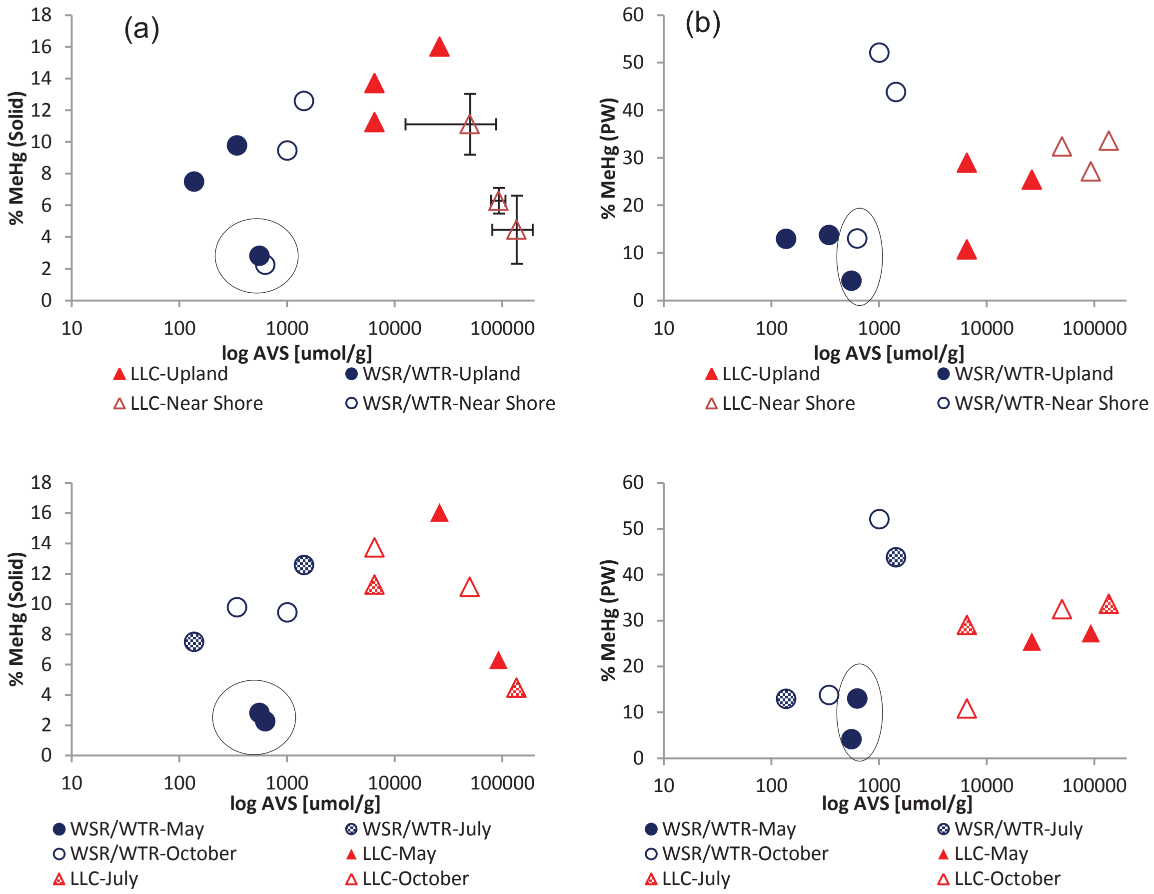

Fig 6 MeHg vs. solid phase sulfide (AVS) in peat samples. Spatial (top) and seasonal (bottom) distribution in % MeHg in (a) solid phase, and (b) pore water.

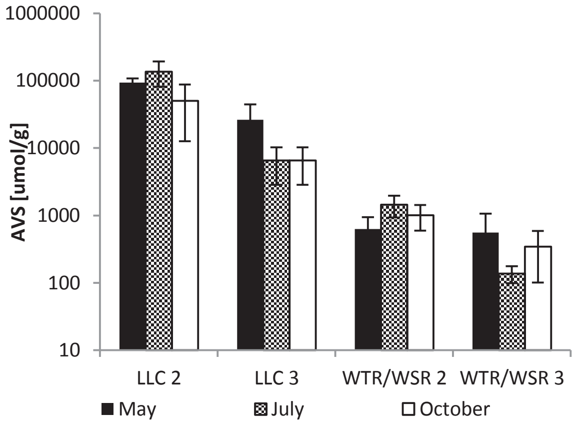

Fig 7 Seasonal and spatial distribution in solid phase sulfide (AVS) in peat samples, 0-4cm average.

At the sulfate-impacted lake (Lake Manganika) presented in Bailey et al. (2014), the location of sulfate reduction was far removed in space from the oxic-anoxic transition zone for most of the summer. The low MeHg observed in this high sulfate system was interpreted to be a result of the inhibition of methylation due to shifts in inorganic mercury bioavailability related to dissolved sulfide concentrations (Bailey et al. 2014a). In the sulfate-impacted wetland site, dissolved sulfide remained below 100 uM, because the location of the transition zone between oxic and anoxic conditions is much more transient and closer to the location of active sulfate reduction. Sulfur is most likely cycling seasonally between sulfide and sulfate in surficial peat material. Therefore, the inverse relationship observed in sulfate-impacted peat between solid phase MeHg and solid phase sulfides (Fig 6 a, c) is not likely a result of sulfide inhibition of methylation, but could be a result of transient changes in the redox environment providing sulfate to drive sulfate reduction following oxidation events (Gustin et al. 2006, Jeremiason et al. 2006, Coleman-Wasik et al. 2012). When peat dries out (a more frequent phenomena at the upland location), AVS is oxidized, providing sulfate to stimulate the activity of sulfate reducers after anoxic conditions are restored.

DOC and MeHg in pore fluids

MeHg in peat pore fluids appeared to be related to DOC at the upland location at both LLC and WTR (not including WSR); however, no clear relationship was observed in the near shore sites (Fig 8). The pore fluids at LLC were significantly influenced by the overlying water after flooding began in September, and the pore water samples collected during pumping-induced flooding event are indicated in Fig. 8a. All samples during this time were characterized by low DOC and MeHg and were excluded from the regression.

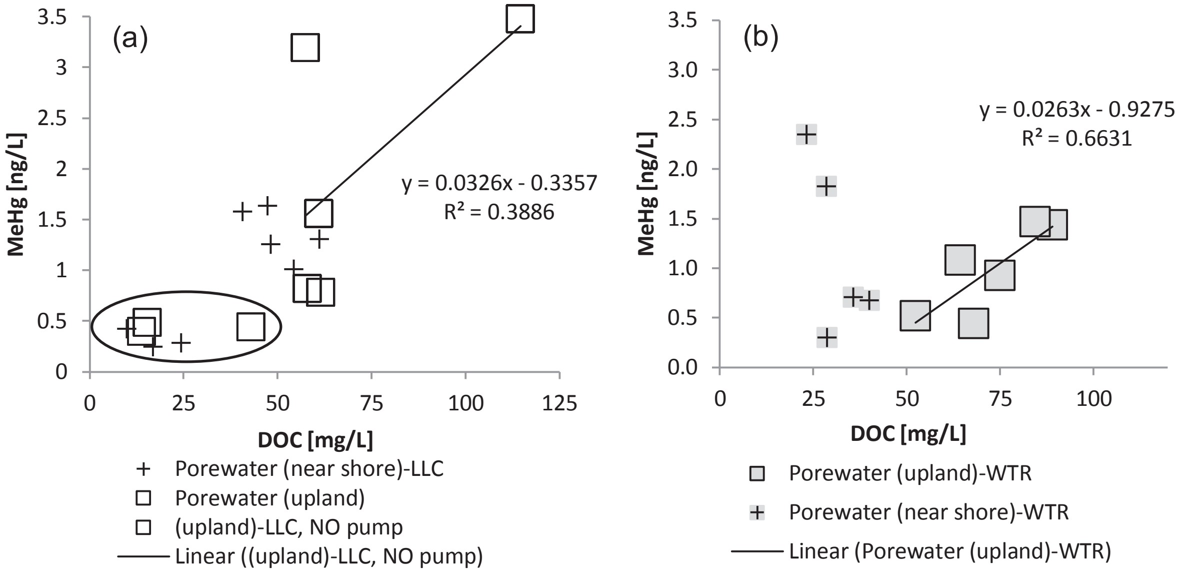

Fig 8 Porewater MeHg and DOC in wetland pore fluids. Samples during September/October pumping at LLC are excluded from the trend analysis.

At the outlet of the LLC wetland, consistent with observations made by Berndt and Bavin (2011), a trend was observed between MeHg and DOC that appeared similar to that of the upland porewaters (Fig 9a). This relationship is presumably due to the capacity for DOC to bind MeHg and transport it in open streams (Berndt and Bavin 2012) but may be affected by the type of DOC present in high-ionic strength waters. Inorganic mercury at the outlet of the wetland was closely related to DOC and had a slope considerably steeper than that for MeHg. Inorganic mercury at the inlet of the wetland showed considerable variability but was unrelated to DOC (Fig 9b).

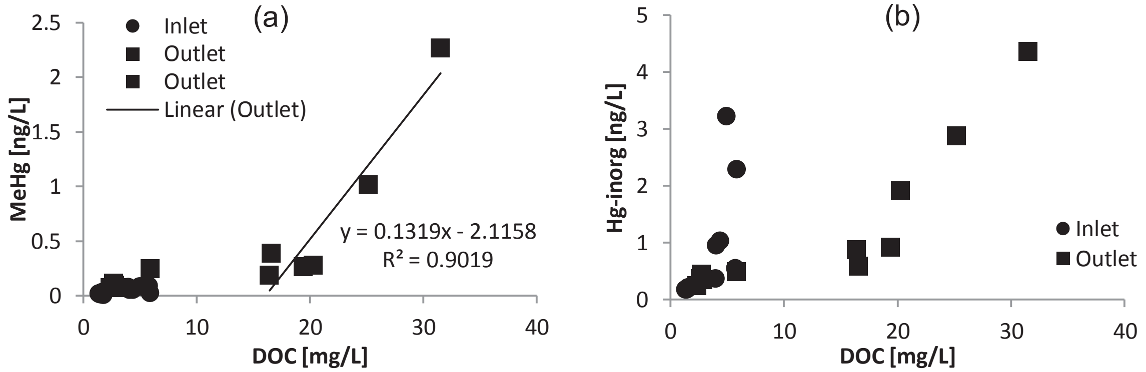

Fig 9 (a) MeHg and (b) Hg-inorg at the inlets and outlets of LLC wetland. Samples during September/October pumping at LLC are excluded from the trend analysis.

Mitchell et al. (2009) suggested that labile DOC transported from upland mineral soils drives MeHg production at the upland-peatland interface, but observed no significant correlation between MeHg and DOC. The upland sampling location in this study was not immediately adjacent to the upland-peatland interface and, contrary to the dilution of high DOC waters observed by Mitchell et al. (2009), typically had higher DOC than the nearshore location. The similarity between the MeHg-DOC trends observed in upland porewater and wetland outlets (Fig 9) suggests that MeHg transport via DOC is an important mechanism for mobilizing and moving MeHg from the wetland's upland margins. Active methylation and demethylation processes in the typically saturated and reduced pore fluids of the near shore peat may be more important to defining porewater concentrations than DOC-dominated transport and therefore mute the relationship between MeHg and DOC.

Seasonal trends in Hg & geochemistry of peat pore fluids

A large increase (4-8 times) in both dissolved total- and dissolved methyl- mercury concentrations in peat pore fluids was observed at LLC, the sulfate-impacted wetland, between late May and early July after which a relatively steady decrease was observed for the remainder of the summer. Peak total- and methyl-mercury concentrations occurred at both sites in early July and were both higher at the upland sampling location. This seasonal distribution of total- and methyl- mercury in the peat pore fluids appeared related to the major hydrologic event in late June 2012. DOC in pore fluids also increased during late May through early July from 20-40 mg/L to 50-100 mg/L. The increase in porewater DOC was less exaggerated than the increase in MeHg, but the observed peaks in DOC occurred at the same sampling times as peaks in total- and methyl- mercury at each wetland plot.

Porewater concentrations of mercury-related redox-active constituents also changed over the course of the summer. Both sites contained some evidence of the prior year's sulfate loading during the first sampling in May as porewater sulfate concentrations in surficial (0-10 cm) peat were in excess of 130 mg/L. By late June, porewater sulfate had fallen to <20 mg/L suggesting that sulfate was either flushed out of the surficial peat during the deluge or reduced to sulfide. AVS concentrations in the 0-2 and 2-4 cm depth interval of the upland peat were significantly elevated in May compared to July and October (Fig 7), suggesting reduction of sulfate from the prior year's inundation was occurring in surficial peat during the winter and spring. Iron concentrations at both the nearshore and upland plots rose quickly on the receding limb of the hydrograph, peaked in mid-late July, and then fell to less than 30 umol/L by mid-August. Sulfide remained very low compared to sulfate-impacted lake sediments (Bailey et al. 2014), rising to a maximum of 60 umol/L and 35 umol/L in the upland and nearshore sites, respectively, in early August. pH of the pore fluids ranged from between 6.4 and 7.1 until the October inundation when it rose to over 7.5 to match that of the stream water.

Though porewater total mercury concentrations were very similar between the upland and near shore sites from late July through August, MeHg concentrations rose in porewater of the nearshore site but continued to fall in porewater of the upland site. DOC remained constant or even decreased slightly during this time. Sulfate concentration in surficial peat was between 3 and 10 mg/L, and a rise in sulfide suggests that active sulfate reduction could have been occurring and may explain the slight rise in MeHg at the nearshore site where the water table remained near the peat surface during August.

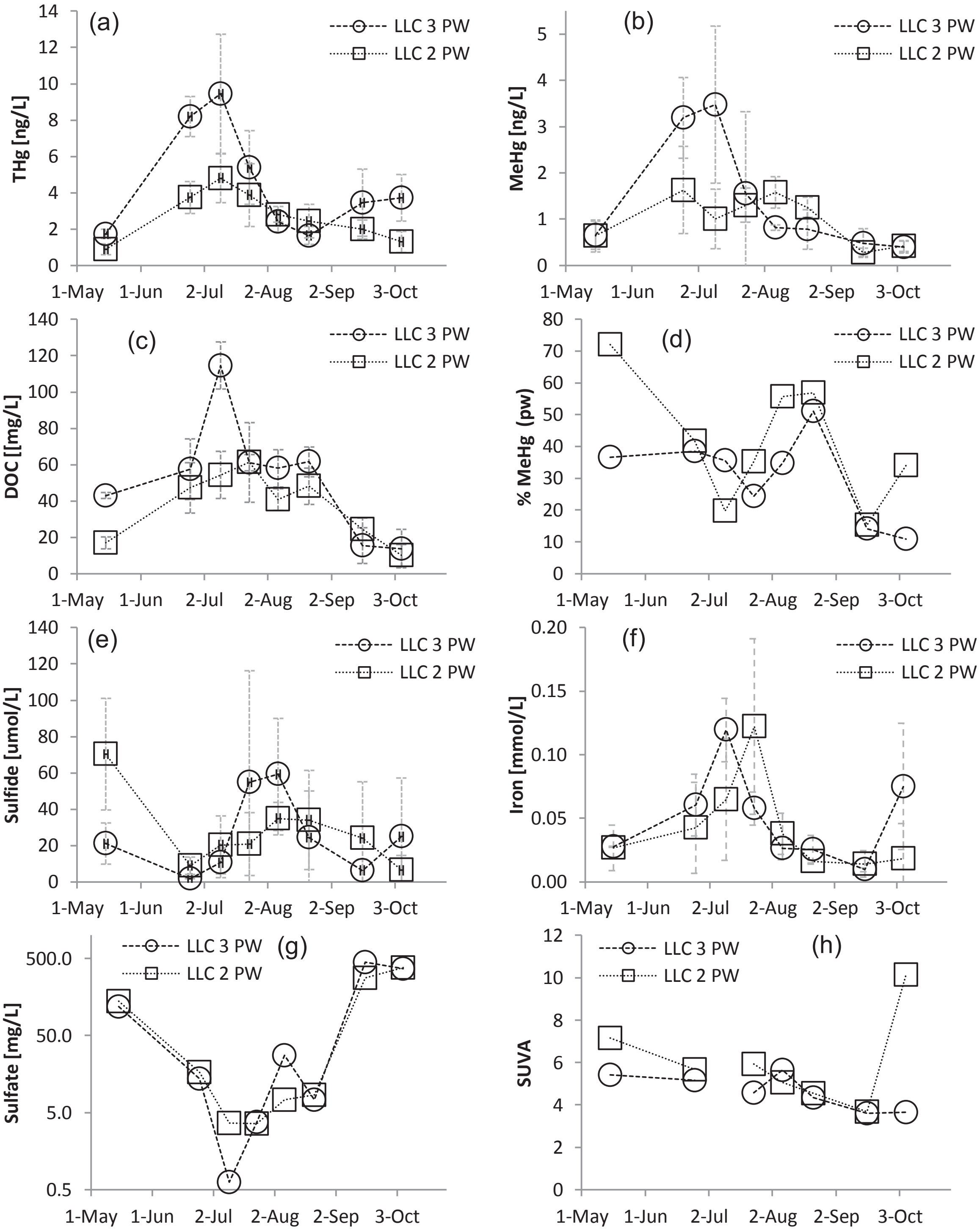

Fig 10 Pore water concentrations at upland (LLC3) and nearshore (LLC2) wetland sampling locations during summer 2012. (a) dissolved total mercury, (b) dissolved methylmercury, (c) dissolved organic carbon, (d) % MeHg-PW (MeHg / THg) (e) dissolved sulfide, (f) dissolved iron, (g) sulfate, (h) SUVA.

At WTR, the unimpacted wetland which had similar total mercury concentrations on the solid phase, porewater concentrations were not collected in May or June. However, the observed range of porewater total- and methyl- mercury was remarkably similar to that of LLC, despite having 1-2 orders of magnitude less sulfur in the solid phase (Fig 11). DOC and total mercury in porewater at the upland site remained high (>60 mg/L, >4 ng/L, respectively) through August which was similar to observations at LLC prior to the fall flooding. MeHg at both WTR plots fell to below 2 ng/L in late July and remained mostly below 1.5 ng/L for the remainder of the fall.

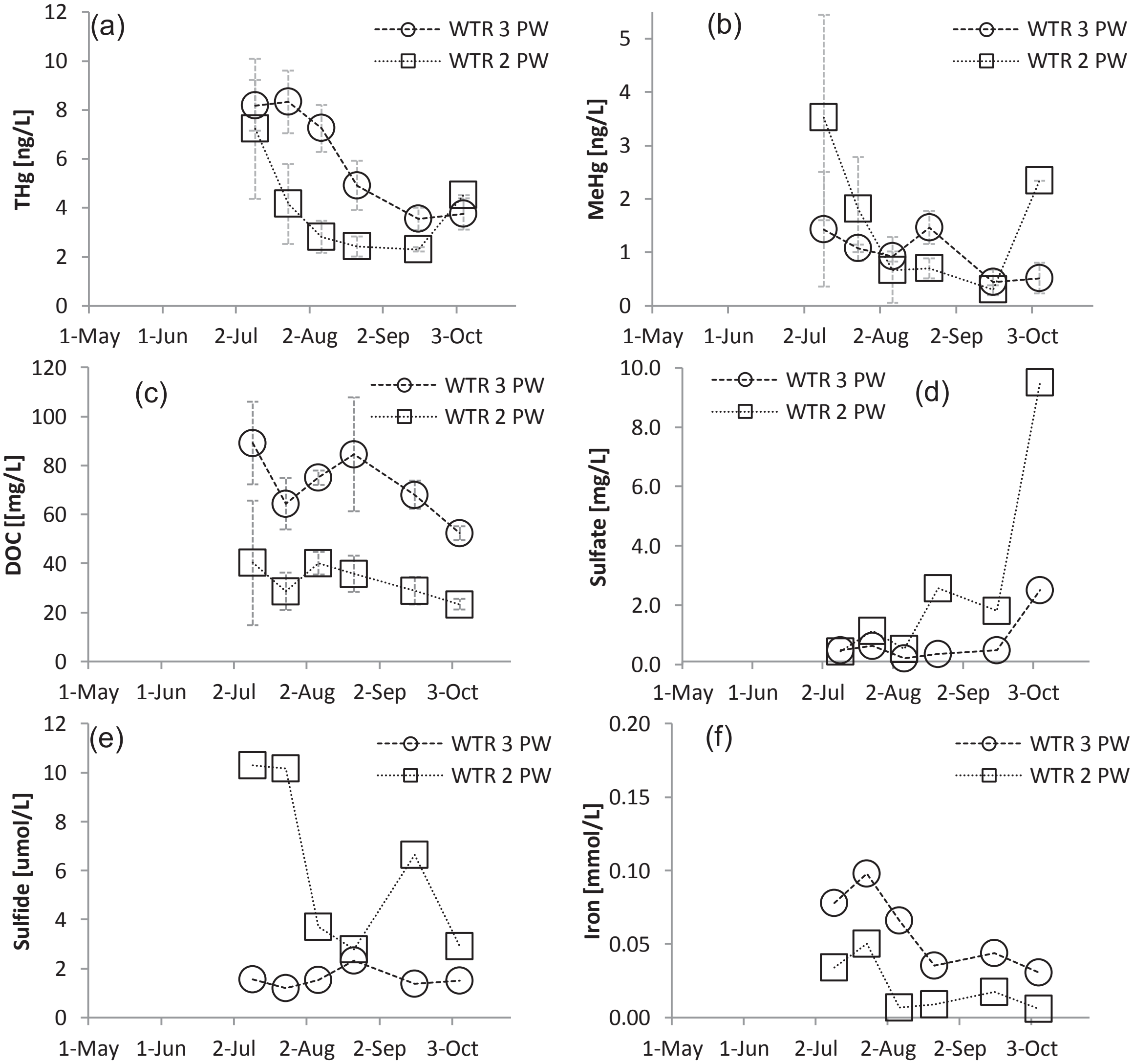

Fig 11 Pore water concentrations at upland (WTR3) and nearshore (WTR2) wetland sampling locations during summer 2012. (a) dissolved total mercury, (b) dissolved methylmercury, (c) dissolved organic carbon, (d) sulfate, (e) dissolved sulfide, (f) dissolved iron

pH and dissolved sulfide were significantly lower in porewaters of WTR relative to LLC, while dissolved iron concentration were similar. The ion activity product for iron sulfide in porewaters at WTR averaged

-4.9 and -6.4 for the nearshore and upland plots, respectively, while at LLC (-2.5 and -2.9 for nearshore and upland, respectively) it was much closer to the solubility of amorphous iron sulfide (-2.7 to -3.0, Stumm and Morgan, 1996). This suggests that porewater sulfide concentrations at LLC were controlled by iron, but that iron was not limiting the solubility of sulfide at the WTR wetland.

The coincidence of the regional hydrograph and peat porewater DOC and total- and methyl- mercury (Fig 10) and the relationship between porewater DOC and MeHg (Fig 8) suggests that DOC-facilitated transport plays a major role in defining the amount of mercury in peat pore fluids at these wetlands.

Net export from Long Lake Creek

Observations from the inlets and outlets of the LLC wetland clearly showed that DOC and MeHg were added to the stream as it passed through the wetland complex (Fig 12b,f). Conversely, Mg and SO4 were lower in the outlet than the inlet (Fig 12c,e). Since porewater was elevated in DOC and MeHg and depleted in SO4 (Mg was not measured), the diffuse input of water lower in Mg and SO4 from the wetland to the stream over the course of the summer is a likely explanation for the sustained differences between inlet and outlet stream chemistry. The inlet and outlet concentrations measured in 2012 are consistent with those observed by Berndt and Bavin (2011) at LLC during the summer of 2010.

During the pumping event beginning in mid-September, sulfate concentrations in pore fluids (Fig 10g) rose dramatically and DOC and MeHg in pore fluids dropped considerably (Fig 10c,d). This suggests a reversal of the hydrologic gradient from the overlying water to the pore fluids and, consequently, a relatively lower proportion of outlet flow from diffuse wetland contributions.

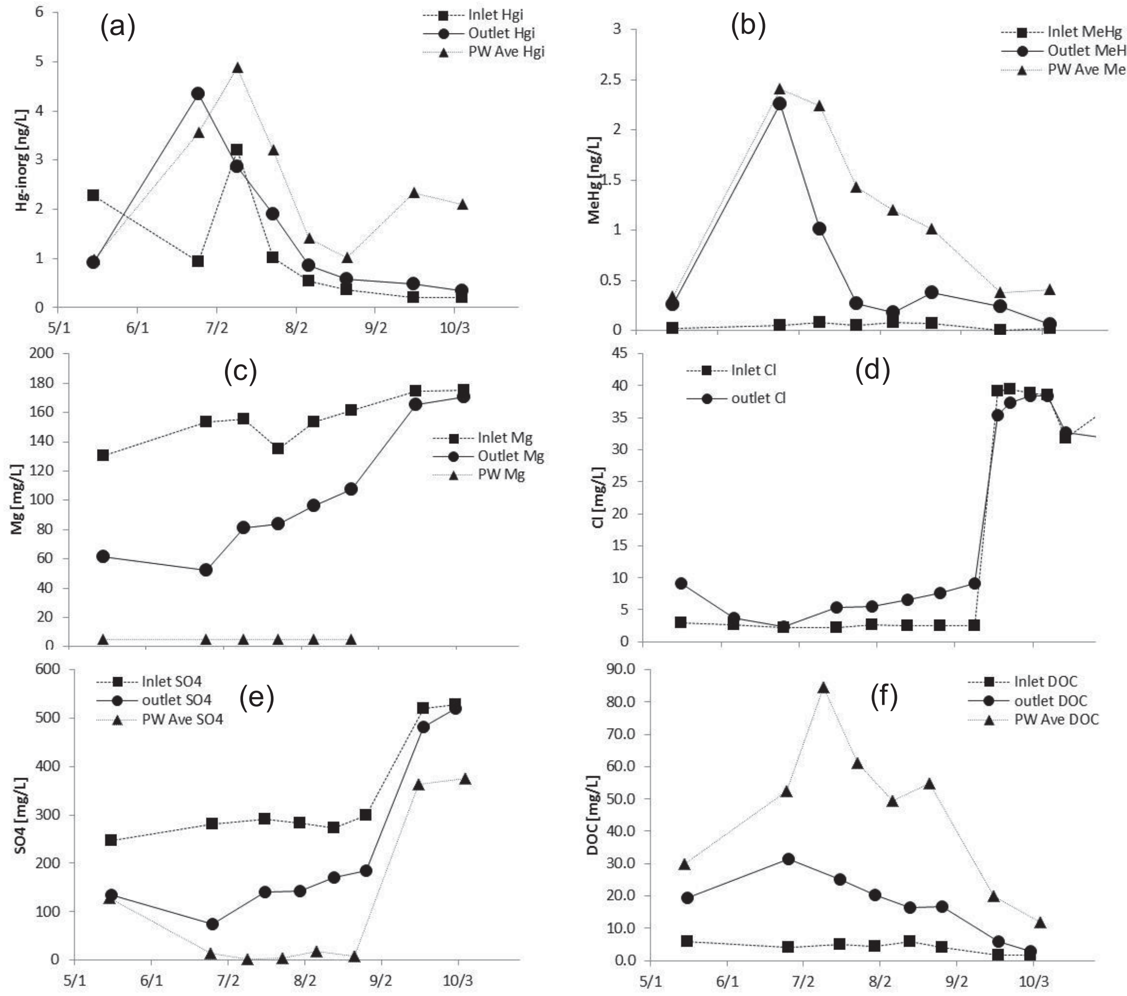

Fig 12 Inlet, outlet, and average pore water concentrations of (a) Mg, (c) DOC, (e) SO4, (g) MeHg, and (i) Hg-inorg. Outlet concentrations and those predicted by mixing according to Mg dilution for (b) Mg, (d) DOC, (f) SO4, (h) MeHg, and (j) Hg-inorg.

If a bulk of the water entering the wetland between the inlet and outlet sampling locations is a result of rainwater inputs low in sulfate and magnesium that pick up wetland-derived DOC similar in concentration to that measured in pore fluids, a simple two component dilution model can be used to explain the differences between upstream and downstream concentrations. Consistent with expectation of flow fed by shallow groundwater driven by precipitation, the estimated fraction of water contributed to the stream from the wetland (high DOC, low Mg water) was relatively high (50-70 %) in June and July following major hydrologic events, but only 30-40 % during August prior to the flooding due pumped mine water in

September. This dilution is consistent with that estimated by Berndt and Bavin (2011) based on observed sulfate decreases and shifts in sulfate stable isotopes.

If diffuse inputs have concentrations similar to that of the wetland pore fluids and little in-stream reaction is assumed, the simple two component mixing model suggests that 85 – 97 % of DOC and 88 – 99 % of MeHg exiting the wetland was transported to the stream via diffuse flow other than the upstream inputs. Although in-stream reactions may influence DOC and MeHg between the wetland inlet and outlet – especially later in summer under more stagnant conditions with longer residence times – the data clearly point to the wetland as a major source of both MeHg and DOC to the stream, particularly following the major late June hydrologic event.

Fate of flood water at Long Lake Creek

While the simple two component mixing model is useful for considering how water carrying MeHg and DOC may enter the open-water portion of the stream from the wetland, it cannot, by itself, help to elucidate the fate of the high sulfate/magnesium/chloride water that flooded the wetland the previous fall. Additionally, it does not explain the slowly increasing outlet chloride concentrations over July and August, nor the significant shift in $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ observed in stream water between the wetland inlet and outlet (Kelley and Berndt, 2013). A slow rinsing out of high chloride water originating from the pumping-associated flooding in fall 2011 provides a plausible explanation for the increasing chloride concentrations at the wetland outlet. Though inlet magnesium shifted only marginally during the fall pumping, sulfate concentrations doubled and chloride concentrations increased by an order of magnitude. This stark difference in geochemistry allows for the introduction of a third component to the mixing model incorporating the fall pumping and focused on the origin of water rather than the most recent flow path to the stream outlet (Table 1).

Table 1 Components of water exiting the wetland by upstream origin.

Component	Magnesium [mg/L]	Sulfate [mg/L]	Chloride [mg/L]
Drain (inlet-no flood)	176	280	2.6
Flood (inlet-during flood)	150	530	39.5
Runoff (rainwater inputs)	0	0	0

This three component mixing model (Table 1, Fig 13) attributes a similar or even greater fraction of the outlet flow to diffuse inputs during June and July (55-80 %) and August (45-55 %) than the two component model since some of the diffuse input has high magnesium water leftover from the previous year's fall pumping flood. It is somewhat surprising that the water from the previous year's fall pumping flood remained in the wetland complex after the extremely large hydrologic event of June 2012, but the slow increase in chloride and the distinct shift in $\delta^{34}SO_4$ provide compelling evidence. The $\delta^{34}SO_4$ predicted by the 3 component mixing model is consistent with observations at the inlet and outlet reported by Kelly and Berndt (2013) and a net reduction of approximately 20 % of the sulfate during transport through the wetland.

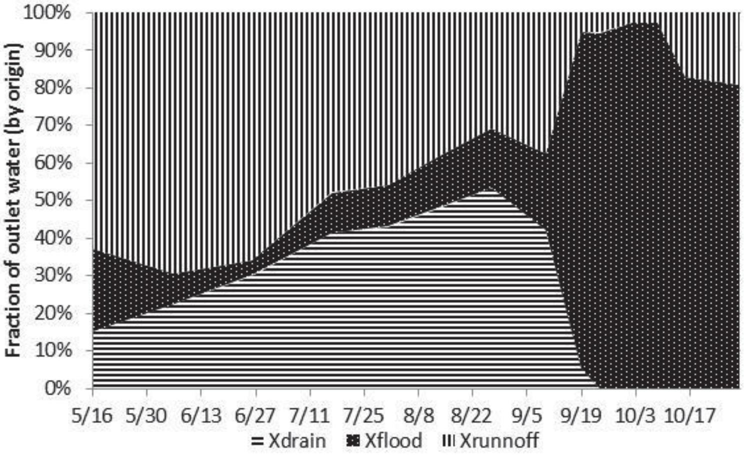

Fig 13 Predicted origin of water exiting the LLC wetland during summer 2012. Components are defined in Table 1.

The implications of the evidence for pumped flood waters from the previous fall continuing to make their way out of the wetland up to a year later have not been fully incorporated into interpretations at LLC. While it is not clear whether this framework will prove useful for quantifying the transport and transformation of sulfate and mercury within the wetland, it does suggest that the residence time of the entire wetland complex needs to be considered separately from the residence time of the open channel portion of the wetland.

4. Conclusions

MeHg concentrations in peatland solid phase and pore fluids at the unimpacted WTR wetland were similar to those observed in the heavily sulfate-impacted LLC wetland. Sulfur concentrations in peat were positively correlated with % MeHg in the solid phase at the unimpacted site, but negatively correlated at the sulfate-impacted site. The wetting and drying of peat, especially at the upland site, appeared to play a role in cycling sulfur between AVS and sulfate and may have affected MeHg concentrations even in the sulfate-impacted wetland. The seasonal trends in porewater MeHg appeared to be closely related to the major early-summer hydrologic event and were similar to those observed at the outlet of the sulfate-impacted LLC wetland. Strong correlations between MeHg and DOC were observed in the upland wetland pore fluids and the wetland stream outlet. However, the nearshore site showed little correlation between DOC and MeHg. This suggests that DOC-facilitated transport is important at the upland margin of the wetlands, but that the balance between methylation and demethylation may be important in defining porewater MeHg in the near-shore pore fluids.

Despite an unprecedented precipitation events in the region during early summer 2012, some of the high-sulfate water pumped into LLC wetland in Fall 2011 appeared to remain in the wetland complex through the following summer. Although the sulfate added directly to the peatland at LLC during the Fall 2011 inundation was reduced to sulfide or flushed out of the system by early summer, MeHg concentrations in the solid phase and pore fluids was in the range of that observed in a nearby, geomorphically similar peatland. A vast majority of the MeHg and DOC exiting the wetland complex appeared to originate within the complex and be released primary in the 2-3 weeks following the very large hydrologic event.

5. References

Bailey LT, Johnson NW, Mitchell CPJ, Engstrom DR, Brendt ME, Coleman-Wasik, JK (2014a) Geochemical factors influencing methylmercury production and partitioning in sulfate-impacted lake sediments. Project Report. Minnesota Department of Natural Resources, Division of Lands and Minerals, St. Paul, MN.

Bailey LT, Johnson NW, Mitchell CPJ, Engstrom DR, Berndt ME, Coleman-Wasik, JK (2014b) Seasonal and spatial variations in methylmercury in the water column of sulfate-impacted lakes. Project Report. Minnesota Department of Natural Resources, Division of Lands and Minerals, St. Paul, MN.

Benoit JM, Gilmour CC, Mason RP, Heyes A (1999) Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Environmental Science & Technology (33)951-957.

Berndt ME, Jeremiason J, Bavin T, Von Korff B. (2013) Hydrologic and Geochemical Controls on St. Louis River Chemistry with Implications for Regulating Sulfate to Control Methylmercury Concentrations. A report to the ENRTF. Minnesota Department of Natural Resources, Division of Lands and Minerals, St. Paul, MN, pp. 27.

Berndt ME, Bavin TK (2012) Methylmercury and dissolved organic carbon relationships in a wetland-rich watershed impacted by elevated sulfate from mining. Environ. Pollut. (161) 321-327.

Berndt ME, Bavin TK (2011) Sulfur and Mercury Cycling in Five Wetlands and a Lake Receiving Sulfate from Taconite Mines in Northeastern Minnesota: A Report to Iron Ore Cooperative Research Program, Minnesota Department of Natural Resources, Division of Lands and Minerals, St. Paul, MN, pp. 77.

Branfireun B (2004) Does microtopography influence subsurface pore-water chemistry? Implications for the study of methylmercury in peatlands. Wetlands, 24(1):207-211. 2004

Branfireun BA, Heyes A, Roulet NT (1996) The hydrology and methylmercury dynamics of a Precambrian shield headwater peatland. Water Resources Research (32)1785-1794.

Cliffs Natural Resources, Inc. (2013) 2012 Water Appropriation Permit 1963-0691 Mitigation & Monitoring Plan Annual Report. Memo to Michael Liljegren at MN DNR Waters dated 2/4/2013.

Coleman-Wasik JK, Mitchell, CPJ, Engstrom DR, Swain EB, Monson BA, Balogh SJ, Jeremiason JD, Branfireun BA, Eggert SL, Kolka RK, Almendinger JE (2012) Methylmercury declines in a boreal peatland when experimental sulfate deposition decreases. Environmental Science and Technology (46)6663-6671

Compeau GC, Bartha R (1985) Sulfate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediment. Applied and Environmental Microbiology (50) 498-502.

Compeau G, Bartha R (1984) Methylation and demethylation of mercury under controlled redox, pH, and salinity conditions. Applied and Environmental Microbiology (48)1203-1207

Fitzgerald WF, Engstrom DR, Mason RP, Nater, EA. (1998) The case for atmospheric mercury contamination in remote areas. Environmental Science and Technology (32)1-7.

Gilmour CC, Riedel GS, Ederington MC, Bell JT, Benoit JM, Gill GA, Stordal MC (1998) Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry (40)327-345.

Gilmour CC, Henry EA, Mitchell R (1992) Sulfate stimulation of mercury methylation in freshwater sediments. Environmental Science & Technology (26) 2281-2287

Gustin MS, Chavan PV, Dennett KE, Marchand EA, Donaldson S (2006) Evaluation of wetland methyl mercury export as a function of experimental manipulations. J. Environ Qual (35)2352-2359.

Helms J R, Stubbins A, Ritchie JD, Minor EC, Kieber DJ, Mopper K (2008) Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, Limnol. Oceanogr., (53)955-969.

Harmon SM, King, JK, Gladden JB, Chandler GT, Newman LA (2004) Methylmercury Formation in a Wetland Mesocosm Amended with Sulfate. Environmental Science & Technology (38) 650-656

Hintelmann H, Keppel-Jones K, Evans RD (2000) Constants of mercury methylation and demethylation rates in sediments and comparison of tracer and ambient mercury availability. Environmental toxicology and chemistry, 19(9), 2204-2211.

Hsu-Kim H, Kucharzyk KH, Zhang T, Deshusses MA (2013) Mechanisms regulating mercury bioavailability for methylating microorganisms in the aquatic environment: A critical review. Environmental Science & Technology (47) 2441-2456.

Hurley JP, Benoit JM, Babiarz CL, Shafer MM, Andren AW, Sullivan JR, Hammond R Webb DA (1995) Influences of watershed characteristics on mercury levels in Wisconsin rivers. Environmental Science Technology (29) 1867-1875

Jeremiason JD, Engstrom DR, Swain EB, Nater EA, Johnson BM, Almendinger JE, Monson BA, Kolka RK (2006) Sulfate Addition Increases methylmercury production in an experimental wetland. Environmental Science and Technology (40)3800-3806

Kelley MJ, Berndt ME (2013) An updated isotopic analysis of sulfate cycling and mixing processes in the St. Louis River Watershed.

Kerin EJ, Gilmour CC, Roden E, Suzuki MT, Coates JD, Mason RP, (2006) Mercury methylation by dissimilatory iron reducing bacteria. Appl. Environ. Microbiol. (72)7919-7921.

Khwaja AR, Bloom PR, Brezonik PL (2006) Binding constants of divalent mercury (Hg2+) in soil humic acids and soil organic matter. Environmental Science and Technology (40) 844-849

Mitchell CPJ, Branfireun BA, Kolka RK (2009) Methylmercury dynamics at the upland-peatland interface: Topographic and hydrogeochemical controls. Water Resources Research. (45)W02406

Mitchell CPJ, Gilmour CC (2008) Methylmercury production in a Chesapeake Bay salt marsh. Journal of Geophysical Research: Biogeosciences 113-G2. 2005–2012

Mitchell CPJ, Branfireun BA, Kolka RK (2008a) Assessing sulfate and carbon controls on net methylmercury production in peatlands: an in situ mesocosm approach. Applied Geochemistry (23)503-518.

Mitchell CPJ, Branfireun BA, Kolka RK (2008b) Spatial characteristics of net methylmercury production hotspots in peatlands. Environmental Science and Technology (42)1010-1016.

Mitchell CPJ, Branfireun BA (2005) Hydrogeomorphic controls on reduction-oxidation conditions across boreal upland-peatland interfaces. Ecosystems (8)731-747.

Miller CL, Mason RP, Gilmour CC, Heyes A (2007) Influence of dissolved organic matter on the complexation of mercury under sulfidic conditions. Environmental Toxicology and Chemistry (26) 624-633.

Morel FMM, Kraepiel AML, Amyot M (1998) The chemical cycle and bioaccumulation of mercury. Ann Rev Ecol Syst (29)543-566.

Parks JM, Johs A, Podar M, Bridou R, Hurt RA, Smith SD, Tomanicek SJ, Qian Y, Brown SD, Brandt CC, Palumbo AV, Smith JC, Wall JD, Elias DA, Liang L (2013) The genetic basis for bacterial mercury methylation. Science. DOI: 10.1126/science.1230667

Skyllberg U, Bloom PR, Qian J, Lin CM Bleam WF (2006) Complexation of mercury(II) in soil organic matter: EXAFS evidence for linear two-coordination with reduced sulfur groups. Environmental Science and Technology (40) 4174-4108.

St. Louis V, Rudd J, Kelley C, Beaty K, Bloom N, Flett R (1994) Importance of wetlands as sources of methylmercury to boreal forest ecosystems. Canadian Journal of Fish and Aquatic Sciences (51)1065-1076.

Stumm W, Morgan JJ (1996) Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters. Wiley & Sons.

US EPA (1997) Mercury Study Report to Congress EPA-452/R97-004, Office of Air, Washington, DC

Appendix A – Raw data tables

Long Lake Creek - Plot 2 (nearshore) Solid Phase (1 of 2)

		5/15/2012									7/24/2012								
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)		
Analytes																			
AVS	umol/kg	69164	97047	68713	103317			321460$^+$			141752	51378	3674	200200			113676		
%C-Organic	[]	66.2	68.7	67.0	70.6			64.0			64.0	67.1	66.0	63.97			67.1		
%C-Calcite	[]	7.6	8.2	9.1	8.8			10.8			8.5	9.3	8.7	8.52			9.3		
%C-Inorganic	[]	26.2	23.1	24.0	20.7			25.2			27.5	23.7	25.3	27.51			23.7		
Mercury Analysis		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]	7.65	2.02	0.44	6.24			5.21			6.52	0.92	0.31	3.92	0.81	0.45	8.62	2.13	0.58
THg	[ng/g]	69.66	68.16	79.23	96.28			96.37			85.02	105.94	160.08	101.48	84.52	86.91	76.02	104.54	117.11
% MeHg	[]	10.98	2.97	0.55	6.48			5.41			7.67	0.87	0.20	3.86	0.96	0.52	11.34	2.04	0.49
K_{meth}	$[d^{-1}]$	0.090	0.059	0.013	0.147			0.098			0.161	0.046	0.006	0.193	0.037	0.016	0.331	0.101	0.015
K_{demeth}	$[hr^{-1}]$	0.036	0.035	0.036	0.026			0.044			0.035	0.052	0.067	0.041	0.043	0.082	0.041	0.023	0.056
K_m/K_d	[]	2.49	1.68	0.36	5.70			2.23			4.63	0.89	0.09	4.66	0.87	0.19	8.09	4.33	0.27
Elemental		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)
%C	[]										1.78	2.20	2.13	2.02			1.99		
%N	[]										37.34	31.73	32.41	37.55			41.01		
C/N ratio	[]										21.0	14.4	15.2	18.7			20.7		
Metals Extract		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)
Fe	[mg/kg]										22.0	7.0	4.3		22.8			20.7	
Al	[ppm]										11.0	14.9	32.9		-18.5			10.8	
Mn	[ppm]										1.7	-0.4	-0.7		0.7			1.8	
Zn	[ppm]										0.5	-0.8	-0.8		-0.8			0.5	
Ca	[ppm]										13.2	13.9	13.9		14.0			13.8	
K	[ppm]										1.0	-38.1	-38.1		-36.7			1.3	
Mg	[ppm]										8.9	10.5	12.5		11.7			10.3	
Na	[ppm]										144.0	-49.5	-49.0		-49.0			142.3	

$^+$Outlier excluded from 0-4 cm average

Long Lake Creek - Plot 2 (nearshore) Solid Phase (2 of 2)

											SUMMARY STATISTICS		
		10/6/2012									Top 0-4 cm 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
Analytes													
AVS	umol/kg	111894	72008	46142	40730			18408			93211	136814	50363
%C-Organic	[]	71.3	69.8	70.7	75.4			72.9			67.3	65.5	72.9
%C-Calcite	[]	7.5	10.8	8.6	5.2			5.5			9.2	8.9	6.6
%C-Inorganic	[]	21.2	19.4	20.7	19.4			21.7			23.5	25.6	20.4
Mercury Analysis		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)	Top 4 cm Avr		
MeHg	[ng/g]	13.64	7.27	1.22	13.47	3.22	0.52	8.84	5.60	2.53	5.43	3.82	8.67
THg	[ng/g]	87.23	125.17	165.47	83.96	114.93	132.17	50.40	63.29	95.48	87.19	92.92	87.49
% MeHg	[]	15.64	5.81	0.74	16.04	2.81	0.39	17.55	8.84	2.65	6.29	4.46	11.11
K_{meth}	$[d^{-1}]$	0.032	0.020	0.008	0.022	0.011	0.007	0.021	0.036	0.009	0.11	0.14	0.02
K_{demeth}	$[hr^{-1}]$	0.054	0.081	0.093	0.075	0.097	0.096	0.067	0.073	0.094	0.04	0.04	0.07
K_m/K_d	[]	0.58	0.24	0.09	0.29	0.12	0.08	0.32	0.49	0.09	3.34	3.91	0.34
Elemental		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)	Top 4 cm Avr		
%C	[]											2.00	
%N	[]											37.70	
C/N ratio	[]											19.0	
Metals Extract		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)			
Fe	[mg/kg]											19.4	
Al	[ppm]											1.8	
Mn	[ppm]											1.1	
Zn	[ppm]											*0	
Ca	[ppm]											13.8	
K	[ppm]											*0	
Mg	[ppm]											10.6	
Na	[ppm]											46.9	

$^{+}$Outlier excluded from 0-4 cm average

* values negative

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

		5/15/2012									7/24/2012								
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)		
Analytes																			
AVS	umol/kg	47563	30599	11673	509^{+}			13574			6327	12054	9007	1044^{+}			3937		
%C-Organic	[]	73.1	73.4	80.7		75.7			76.6		66.0	79.4	75.9	76.57			81.09		
%C-Calcite	[]	4.5	7.4	6.5		2.7			3.6		8.7	3.9	5.8	3.45			3.2		
%C-Inorganic	[]	22.4	19.3	12.8		21.6			19.8		25.3	16.6	18.4	19.97			15.74		
Mercury Analysis		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]	18.31	11.64	3.49	11.46			13.33			17.93	11.39	8.62	20.52	8.70	4.71	14.81	5.77	1.90
THg	[ng/g]	63.85	84.15	116.12	78.15			109.89			109.76	138.96	159.18	104.09	104.07	122.72	137.33	140.15	166.02
% MeHg	[]	28.67	13.83	3.01	14.66			12.13			16.34	8.19	5.42	19.71	8.36	3.84	10.78	4.12	1.14
K_{meth}	[d^{-1}]	0.091	0.088	0.026	0.074			0.068			0.005	0.132	0.106	0.026	0.076	0.023	0.113	0.048	0.021
K_{demeth}	[hr^{-1}]	0.037	0.031	0.047	0.023			0.014			0.035	0.025	0.027	0.025	0.047	0.049	0.002	0.032	0.045
K_m/K_d	[]	2.48	2.83	0.56	3.13			4.83			0.15	5.35	3.92	1.02	1.61	0.47	48.51	1.48	0.47
Elemental		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)
%C	[]										2.06	2.23	2.00	2.29			2.15		
%N	[]										51.29	38.88	40.60	36.14			44.0		
C/N ratio	[]										25.0	17.4	20.3	15.7			20.45		
Metals Extract		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)
Fe	[mg/kg]										22.4	11.9	7.5		11.9			21.6	
Al	[ppm]										-25.5	-21.1	9.9		-18.5			-21.5	
Mn	[ppm]										-0.4	-0.7	0.3		-0.7			-0.4	
Zn	[ppm]										-0.8	-1.0	0.3		-0.9			-0.9	
Ca	[ppm]										13.3	15.3	18.7		15.9			13.9	
K	[ppm]										-14.9	-27.1	0.1		-42.8			-27.4	
Mg	[ppm]										7.7	8.9	10.7		8.9			8.2	
Na	[ppm]										-52.6	-53.9	141.7		-54.4			-53.1	

$^{+}$Outlier excluded from calculation of 0-4 cm average

Long Lake Creek - Plot 3 (upland) Solid Phase (2 of 2)

											SUMMARY STATISTICS		
		10/6/2012									Top 4 cm 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
Analytes													
AVS	umol/kg	24396	17609	8777	41585			1518$^+$			26327	6564	31294
%C-Organic	[]	73.9	79.3	72.1	74.6			78.8			75.2	76.8	76.7
%C-Calcite	[]	4.4	4.8	6.7	6.8			3.5			4.1	4.3	5.0
%C-Inorganic	[]	21.8	15.9	21.2	18.6			17.7			20.7	18.9	18.4
Mercury Analysis		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]	11.52	5.78	2.82	10.56	10.86	4.70	18.44	17.10	13.11	13.3	13.2	12.4
THg	[ng/g]	86.71	101.81	98.28	51.01	92.35	118.53	112.98	117.88	145.5	87.3	122.4	93.8
% MeHg	[]	13.28	5.68	2.87	20.70	11.76	3.96	16.32	14.51	9.01	16.0	11.3	13.7
K_{meth}	$[d^{-1}]$	0.019	0.017	0.018	0.024	0.025	0.021	0.025	0.031	0.020	0.077	0.067	0.023
K_{demeth}	$[hr^{-1}]$	0.068	0.074	0.095	0.062	0.081	0.097	0.065	0.048	0.090	0.024	0.028	0.066
K_m/K_d	[]	0.27	0.23	0.19	0.38	0.31	0.22	0.38	0.64	0.22	3.54	9.69	0.37
Elemental		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)		Top 4 cm Avr	
%C	[]											2.20	
%N	[]											41.75	
C/N ratio	[]											19.1	
Metals Extract		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)			
Fe	[mg/kg]											16.89	
Al	[ppm]											0*	
Mn	[ppm]											0*	
Zn	[ppm]											0*	
Ca	[ppm]											14.69	
K	[ppm]											0*	
Mg	[ppm]											8.49	
Na	[ppm]												

$^+$Outlier excluded from calculation of 0-4 cm average

* Measured values negative

Long Lake Creek - Upstream (1 of 1)

Measured by DNR

Parameter	Units	5/16/2012	6/6/2012	6/26/2012	7/17/2012	7/31/2012	8/14/2012	8/27/2012	9/10/2012	9/19/2012	9/24/2012	10/2/2012	10/9/2012	10/16/2012	10/30/2012
pH	[]	7.64	7.72	7.84	7.62	7.71	7.67	7.71	7.82	7.93	7.85	7.89	8.04	7.99	8.03
Temp	[°C]	5.87	8.28	9.51	9.84	11.88	8.14	7.68	7.02	6.61	6.12	6.62	6.07	9.22	5.28
LDO	[mg/L]	11.57	9.5	10.24	8.65	8.92	9.7	10.73	10.08	12.27	12.24	12.92	13.12	12.39	13.67
Conductivity	[µS/cm]	866	953	1002	1419	849	1020	1025	1022	1070	1024	1032	1032	876	953
ORP	[mV]				78	50	24	77	-133	104	23	38	2	95	142
Water Table*	[ft]														
Analytes															
Sulfate	[mg/L]	246.4	262.2	280.6	291.3	197.3	273.8	298.7	306.3	519.0	520.2	528.2	532.2	384.5	
Nitrate	[mg/L]	3.13	3.24	5.23	5.61	6.71	6.37	7.42	6.82	0.31	0.58	0.76	0.72	0.22	
Phosphate	[mg/L]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Chloride	[mg/L]	3.0	2.7	2.3	2.2	2.6	2.5	2.4	2.6	39.2	39.5	38.9	38.5	31.8	
Ferrous Iron	[mM]	0.001	0.000	0.000	0.001	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	
DOC	[mg/L]	5.9	5.5	4.1	5.0	4.4	5.8	4.0	4.3	1.8		1.6	1.7	1.4	1.5
SUVA	[$Lm^{-1}mg^{-1}$]	2.4	2.4	2.5	2.6	2.4	2.2	2.1	2.0	1.5		1.3	1.0	1.0	
Mercury Analysis															
MeHg	[ng/L]	0.02	0.37	0.05	0.08	0.05	0.09	0.07	0.03	0.01	0.00	0.02	0.03	0.02	0.01
THg	[ng/L]	2.30	1.27	0.99	3.29	1.07	0.63	0.44	0.33	0.22	0.24	0.22	0.23	0.18	0.18
% MeHg	[]	0.9	29.1	5.1	2.4	4.7	13.6	16.8	8.4	2.5	0.0	9.1	11.1	8.4	5.2
Metals															
Fe	[ppm]	0.0287	0.0125	0.01076	0.0307455	0.0155915	0.0371865	0.0344655	0.0116914	0.001498	0.0173035	-0.006608	-0.003719	0.0152295	0.01156333
Al	[ppm]	0.0018	0.0001	0.00296	0.00448845	0.0038379	0.00042149	0.00999715	-0.0039561	-0.0019671	0.00811265	-0.001951	-0.001121	0.00167256	0.00364833
Mn	[ppm]	0.0651	0.036	0.019	0.144555	0.0540205	0.188295	0.321375	0.233755	0.818725	0.96431	1.0587	0.69135	0.399215	0.50957667
Zn	[ppm]														
Ca	[ppm]	63.8045	60.4275	58.4105	66.9055	51.164	68.993	76.2055	68.279	89.712	89.565	88.065	87.9255	67.199	84.161
K	[ppm]	14.4785	15.73	17.241	18.3385	14.757	17.6655	17.8725	15.9855	11.406	11.814	11.721	11.879	10.85	11.6473333
Mg	[ppm]	130.4	147.595	153.59	155.55	135.015	153.775	161.165	146.225	174.47	176.485	175.335	175.59	133.59	169.47
Na	[ppm]	27.755	25.2855	27.6435	34.3245	23.4725	35.5115	40.273	38.358	27.938	28.553	28.357	28.445	24.027	27.8583333

Long Lake Creek - Downstream (1 of 1)

Measured by DNR

Parameter	Units	5/16/2012	6/6/2012	6/26/2012	7/17/2012	7/31/2012	8/14/2012	8/27/2012	9/10/2012	9/19/2012	9/24/2012	10/2/2012	10/9/2012	10/16/2012	10/30/2012
pH	[]	7.80	7.55	7.33	7.77	7.92	7.94	7.93	7.85	7.61	7.65	7.86	7.93	7.89	7.98
Temp	[^{o}C]	15.16	19.48	21.55	25.97	24.53	18.15	18.2	12.65	9.67	7.91	8.73	5.19	8.47	3.88
LDO	[mg/L]	7.51	5.37	3.08	3.48	6.15	4.99	2.34	3.63	4.55	6.87	8.75	10.07	10.76	12.56
Conductivity	[µS/cm]	610	540	527	831	792	875	911	830	1166	1071	1119	1013	947	778
ORP	[mV]				-99	-65	-61	59	-71	121	-62	26	2	89	142
Water Table*	[ft]														
Analytes															
Sulfate	[mg/L]	135.1	78.4	74.3	140.2	143.1	170.6	185.0	197.7	482.5	494.3	519.3	518.9	412.3	
Nitrate	[mg/L]	2.16	0.03	0.00	0.00	0.01	0.06	0.03	0.02	-0.01	0.01	0.07	0.13	0.00	
Phosphate	[mg/L]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Chloride	[mg/L]	9.1	3.7	2.4	5.3	5.5	6.6	7.6	9.1	35.4	37.4	38.4	38.3	32.8	
Ferrous Iron	[mM]	0.001	0.013	0.012	0.002	0.001	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.000	
DOC	[mg/L]	19.4	31.3	31.5	25.2	20.3	16.4	16.6	17.9	5.9	4.2	2.9	2.8	2.7	2.4
SUVA	[$Lm^{-1}mg^{-1}$]	3.3	4.6	4.4	4.1	3.7	3.3	3.3	3.1	3.3	2.6	2.5	2.6	2.5	
Mercury Analysis															
MeHg	[ng/L]	0.26	1.32	2.26	1.01	0.27	0.19	0.38	0.12	0.24	0.09	0.07	0.09	0.11	0.07
THg	[ng/L]	1.17	5.63	6.61	3.87	2.17	1.05	0.96	0.74	0.73	0.40	0.40	0.53	0.47	0.30
% MeHg	[]	22.2	23.4	34.2	26.1	12.4	17.7	39.7	16.3	33.1	23.5	16.3	17.0	22.7	21.9
Metals															
Fe	[ppm]	0.0834	0.7315	0.64312	0.114935	0.063102	0.053626	0.057168	0.036796	0.0471835	0.027314	0.0079488	-0.000391	0.0181995	0.01539033
Al	[ppm]	0.0072	0.1334	0.10508	0.021506	0.00944465	0.00674145	0.015464	0.011632	0.00385345	0.0021729	0.0011227	0.0028758	0.003509	0.0017441
Mn	[ppm]	0.1149	0.0949	0.16331	0.37441	0.190615	0.261675	0.621065	0.2782	0.1031	0.053865	0.0306765	0.03376	0.0207885	0.0065547
Zn	[ppm]														
Ca	[ppm]	42.122	27.2505	27.915	44.1175	44.242	49.0685	50.201	41.982	85.5945	86.898	88.214	87.2525	71.952	69.424
K	[ppm]	6.6571	4.9712	5.59115	8.6052	7.98545	9.0285	9.76515	9.54255	11.0175	11.12	11.3975	11.484	10.934	10.812
Mg	[ppm]	61.262	47.6885	52.1625	80.871	84.024	96.468	107.71	98.8015	165.295	166.395	170.875	170.05	140.175	137.59
Na	[ppm]	14.328	9.047	9.19875	17.0705	17.5575	21.645	24.316	24.044	27.758	27.9665	28.2445	28.0695	25.1135	24.5713333

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

		5/15/2012			6/25/2012			7/10/2012			7/24/2012			8/7/2012			8/22/2012		
Parameter	Units	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
pH	[]																		
Temp	[^{o}C]																		
LDO	[mg/L]																		
Conductivity	[mS/cm]																		
ORP	[mV]																		
Water Table*	[ft]																		
Analytes																			
Sulfate	[mg/L]	132.7	131.9	153.2	8.9	1.8	39.2	0.7	9.0	1.2	8.7	1.1	0.9	5.2	8.2	8.7	8.6	8.4	
Nitrate	[mg/L]					0.2	0.4				0.5	0.6	0.6	1.7		0.4		0.3	
Phosphate	[mg/L]			0.3								0.2		17.1	3.7	3.4	1.0		
Chloride	[mg/L]										6.2				0.5		23.5		
Ferrous Iron	[mM]	0.047	0.018	0.015	0.068	0.002	0.017	0.113	0.017	0.065	0.056	0.117	0.194	0.050	0.020	0.044	0.017	0.016	0.015
Sulfide	[mmol]	105.5	56.8	48.8	14.4	6.6	5.8	6.0	37.5	17.5	40.6	10.8	11.0	28.2	45.1	31.6	15.0	22.0	65.3
Ammonium	[mg/L]	0.1	0.0	0.0				0.2	0.0	0.0									
DIC	[mg/L]	86.0	44.2	47.8	85.4	91.2	61.3	51.4	66.9	65.4	83.6	108.1	74.7	58.8	66.5	43.7	83.7	66.6	98.1
DOC	[mg/L]	18.3	19.3	13.4	43.6	62.7	35.7	63.0	39.6	60.5	38.8	82.4	62.6	39.7	47.3	35.4	58.9	46.5	39.2
SUVA	[Lm^{-1}mg^{-1}]	6.5	6.2	8.7	6.3	5.9	4.8				4.9	8.0	4.9	5.1	5.1	4.9	4.2	4.8	4.6
Mercury Analysis																			
MeHg	[ng/L]	0.013^{+}	0.070^{+}	0.64	0.92	2.70	1.27	1.75	0.70	0.58	1.30	1.68	0.94	1.82	1.72	1.19	1.16	1.51	1.10
THg	[ng/L]	1.23	0.69	0.74	2.79	4.52	3.91	6.33	4.27	3.81	2.92	5.88	2.84	2.97	3.15	2.31	3.15	2.76	1.39
% MeHg	[]	#VALUE!	#VALUE!	86.03	32.83	59.64	32.55	27.59	16.33	15.24	44.35	28.49	32.97	61.41	54.53	51.40	36.98	54.80	78.82

$^{+}$Outlier excluded from 0-4 cm average

Long Lake Creek - Plot 2 (nearshore) Sediment Porewater (2 of 2)

SUMMARY STATISTICS

		9/17/2012			10/6/2012			Average							
Parameter	Units	A	B	C	A	B	C	5/15/2012	6/25/2012	7/10/2012	7/24/2012	8/7/2012	8/22/2012	9/17/2012	10/6/2012
pH	[]							7.05		7.1	6.53	6.39	6.66	7.4	
Temp	[^oC]							19.7		26.3	25.7	17.84		12.6	
LDO	[mg/L]							5.48		2.01	0.5	1.2			
Conductivity	[mS/cm]							785		254.6	700.1	743	720	1210	
ORP	[mV]							322		177	83	-95			
Water Table*	[ft]									0.86	1.2	1.22	1.31	-0.14	
Analytes															
Sulfate	[mg/L]	310.6	238.8	286.0	475.8	326.0	331.6	139.3	16.6	3.6	3.6	7.4	8.5	278.5	377.8
Nitrate	[mg/L]	0.5	0.2	0.2	4.8	5.3	4.7		0.2		0.6	0.7	0.2	0.3	4.9
Phosphate	[mg/L]	0.9						0.1			0.1	8.1	0.5	0.3	
Chloride	[mg/L]		12.7								6.2	0.5	23.5	12.7	
Ferrous Iron	[mM]	0.007	0.026	0.009	0.004	0.001	0.050	0.027	0.042	0.065	0.122	0.038	0.016	0.014	0.018
Sulfide	[mmol]	10.3	2.1	59.8	2.8	0.7	15.8	70.4	8.9	20.3	20.8	35.0	34.1	24.0	6.4
Ammonium	[mg/L]							0.0		0.1					
DIC	[mg/L]	86.1	56.4	85.6	105.0	101.2	98.5	59.3	79.3	61.3	88.8	56.3	82.8	76.0	101.6
DOC	[mg/L]	22.6	31.2	19.5	2.9	13.5	13.7	17.0	47.3	54.4	61.3	40.8	48.2	24.4	10.0
SUVA	[$Lm^{-1}mg^{-1}$]	3.7	3.9	3.5	15.3	10.0	5.1	7.1	5.7		5.9	5.1	4.5	3.7	10.1
Mercury Analysis															
MeHg	[ng/L]	0.29	0.19	0.37	0.44	0.52	0.29	0.64	1.63	1.01	1.30	1.58	1.26	0.28	0.42
THg	[ng/L]	1.53	2.55	1.89	1.05	1.97	0.88	0.89	3.74	4.80	3.88	2.81	2.43	1.99	1.30
% MeHg	[]	18.74	7.47	19.58	42.19	26.60	33.60	72.07	41.67	19.72	35.27	55.78	56.87	15.26	34.13

[+] Outlier excluded from 0-4 cm average

Long Lake Creek - Plot 3 (upland) Sediment Porewater (1 of 2)

		5/15/2012			6/25/2012			7/10/2012			7/24/2012			8/7/2012			8/22/2012		
Parameter	Units	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
pH	[]																		
Temp	[^{o}C]																		
LDO	[mg/L]																		
Conductivity	[mS/cm]																		
ORP	[mV]																		
Water Table*	[ft]																		
Analytes																			
Sulfate	[mg/L]	111.9	119.4	127.4	2.4	5.3	33.7	0.7	0.6	0.5	4.4	6.1	1.0	52.5	18.6	12.0		5.5	9.1
Nitrate	[mg/L]										0.3	0.6	0.4	1.7					
Phosphate	[mg/L]													1.3				1.6	
Chloride	[mg/L]												4.1						
Ferrous Iron	[mM]	0.027	0.028	0.028	0.062	0.084	0.036	0.137	0.130	0.091	0.068	0.043	0.063	0.027	0.017	0.035	0.016	0.022	0.038
Sulfide	[mmol]	33.6	12.0	17.5	2.0		1.7	4.4	7.4	19.9	31.7	124.3	8.3	50.5	93.5	33.7	6.2	42.5	
Ammonium	[mg/L]	0.2	0.1	0.1				0.0	0.1	0.3									
DIC	[mg/L]	11.1	13.6	13.7	22.8	58.9	53.8	58.6	46.0	38.9		28.3	49.3	39.7	39.2	39.7		60.5	43.5
DOC	[mg/L]	44.5	43.2	41.3	71.8	61.5	39.1	127.6	101.9	114.4		64.1	57.8	53.4	69.6	50.8		67.3	55.8
SUVA	[$Lm^{-1}mg^{-1}$]	5.4	5.6	5.2	4.7	5.2	5.6					4.5	4.6	4.5	7.5	4.9		3.6	5.1
Mercury Analysis																			
MeHg	[ng/L]	0.87	0.01^{+}	0.44	2.25	3.36	3.97	3.27	1.90	5.27	0.49	0.60	3.59	0.88	0.81	0.76	1.25	0.44	0.63
THg	[ng/L]	1.99	1.73	1.47	7.04	8.30	9.25	9.17	6.32	12.84	3.63	4.93	7.61	3.07	2.18	2.00	1.36	1.36	2.23
% MeHg	[]	43.68	0.58	29.68	31.95	40.48	42.89	35.61	30.03	41.07	13.38	12.14	47.25	28.52	37.24	38.23	92.26	32.65	28.45

$^{+}$Outlier excluded from 0-4 cm average

Long Lake Creek - Plot 3 (upland) Sediment Porewater (2 of 2)

SUMMARY STATISTICS

		9/17/2012			10/6/2012			Average							
Parameter	Units	A	B	C	A	B	C	5/15/2012	6/25/2012	7/10/2012	7/24/2012	8/7/2012	8/22/2012	9/17/2012	10/6/2012
pH	[]							6.49		7.06	7.04	6.38	6.42	7.55	
Temp	[^{o}C]							14.9		21.1	24.95	17.69		11.4	
LDO	[mg/L]							2.6		0.65		0.08			
Conductivity	[mS/cm]							453		293.6	388.1	471	410	1231	
ORP	[mV]							276		37	248	-88			
Water Table*	[ft]									1.8	2.07	2.05	2.11	0.69	
Analytes															
Sulfate	[mg/L]	497.9	353.5	488.7	448.7	217.1	447.8	119.5	13.8	0.6	3.8	27.7	7.3	446.7	371.2
Nitrate	[mg/L]	0.4	0.3	0.3	4.1	4.5	5.2				0.5	0.6		0.3	4.6
Phosphate	[mg/L]	1.5	0.6	0.9								0.4	0.8	1.0	
Chloride	[mg/L]										4.1				
Ferrous Iron	[mM]	0.008	0.010	0.011	0.123	0.024	0.078	0.028	0.061	0.120	0.058	0.026	0.025	0.010	0.075
Sulfide	[mmol]	12.9	5.1	1.1	12.3	61.6	0.9	21.0	1.9	10.6	54.8	59.2	24.4	6.3	24.9
Ammonium	[mg/L]							0.1		0.1					
DIC	[mg/L]	107.0	51.5	88.2	100.2	67.1	98.6	12.8	45.2	47.8	38.8	39.5	52.0	82.2	88.6
DOC	[mg/L]	5.0	24.7	16.6	7.1	26.1	8.2	43.0	57.5	114.6	61.0	58.0	61.5	15.4	13.8
SUVA	[$Lm^{-1}mg^{-1}$]	3.7	3.5	3.6	1.5	2.2	7.2	5.4	5.2		4.6	5.6	4.4	3.6	3.6
Mercury Analysis															
MeHg	[ng/L]	0.30	0.30	0.84	0.43	0.26	0.51	0.65	3.19	3.48	1.56	0.82	0.78	0.48	0.40
THg	[ng/L]	1.73	3.21	5.42	4.45	2.24	4.44	1.73	8.20	9.44	5.39	2.41	1.65	3.45	3.71
% MeHg	[]	17.33	9.42	15.55	9.65	11.51	11.39	36.68	38.44	35.57	24.26	34.66	51.12	14.10	10.85

[+] Outlier excluded from 0-4 cm average

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

		5/15/2012									7/24/2012								
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)		
Analytes																			
AVS	umol/kg										1365	1546	1695	2053			817		
%C-Organic	[]											91.1	90.5		89.4			86.3	
%C-Calcite	[]											3.0	2.5		2.1			2.6	
%C-Inorganic	[]											5.9	7.0		8.5			11.1	
Mercury Analysis		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]										9.66	4.55	6.42	11.30	6.23	3.64	14.13	21.60	18.02
THg	[ng/g]										57.94	87.46	111.27	78.65	92.09	136.90	94.90	123.08	148.15
% MeHg	[]										16.67	5.21	5.77	14.37	6.76	2.66	14.89	17.55	12.16
K_{meth}	[d^{-1}]										0.231	0.141	0.081	0.320	0.122	0.059	0.144	0.139	0.100
K_{demeth}	[hr^{-1}]										0.001	0.028	0.042	0.018	0.034	0.046	0.035	0.030	0.035
K_m/K_d	[]										245.83	4.98	1.93	17.62	3.54	1.28	4.09	4.58	2.87
Elemental		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)
%C	[]														2.10			2.42	
%N	[]														42.62			48.04	
C/N ratio	[]														20.3			19.9	
Metals Extract		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)
Fe	[mg/kg]											2.1	1.8		3.4			5.1	
Al	[ppm]											5.0	10.9		3.5			21.8	
Mn	[ppm]											-0.1	0.0		0.2			0.0	
Zn	[ppm]											0.1	0.2		0.1			0.1	
Ca	[ppm]											3.8	8.8		10.6			11.0	
K	[ppm]											9.8	42.4		0.0			14.7	
Mg	[ppm]											2.2	5.0		5.5			4.8	
Na	[ppm]											-16.9	-13.6		2.6			-17.1	

West Two River - Plot 2 (nearshore) Solid Phase (2 of 2)

SUMMARY STATISTICS

		10/6/2012									Top 0-4 cm 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
Analytes													
AVS	umol/kg	536	1072	1057	736			1485				1442	1008
%C-Organic	[]	90.6	88.4	87.0		88.3			88.4			88.9	88.7
%C-Calcite	[]	2.7	2.6	3.0		2.6			2.3			2.3	2.5
%C-Inorganic	[]	6.6	9.0	10.0		9.1			9.3			9.8	8.7
Mercury Analysis		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)	Top 4 cm Avr		
MeHg	[ng/g]	5.22	5.04	3.47	8.33	15.13	4.13	6.35	3.99	0.88		11.25	7.34
THg	[ng/g]	104.51	109.79	134.37	67.95	107.15	170.96	38.38	95.12	111.57		89.02	87.15
% MeHg	[]	5.00	4.59	2.58	12.26	14.12	2.42	16.53	4.19	0.79		12.57	9.45
K_{meth}	$[d^{-1}]$	0.036	0.075	0.042	0.020	0.108	0.042	0.006	0.017	0.023		0.18	0.04
K_{demeth}	$[hr^{-1}]$	0.033	0.015	0.049	0.016	0.027	0.014	0.032	0.031	0.046		0.02	0.03
K_m/K_d	[]	1.10	5.04	0.86	1.24	4.07	2.88	0.19	0.55	0.50		6.96	2.03
Elemental		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)	Top 4 cm Avr		
%C	[]											2.26	
%N	[]											45.33	
C/N ratio	[]											20.1	
Metals Extract		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)			
Fe	[mg/kg]											4.3	
Al	[ppm]											12.6	
Mn	[ppm]											0.1	
Zn	[ppm]											0.1	
Ca	[ppm]											10.8	
K	[ppm]											7.4	
Mg	[ppm]											5.2	
Na	[ppm]											*0	

* values negative

West Two River - Plot 3 (upland) Solid Phase (1 of 2)

		5/15/2012									7/24/2012								
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)		
Analytes																			
AVS	umol/kg										83	159	169	167			124		
%C-Organic	[]											94.8	94.3					90.7	
%C-Calcite	[]											1.6	1.2					1.1	
%C-Inorganic	[]											3.6	4.5					8.2	
Mercury Analysis		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]										8.17	8.33	26.67	8.34	9.93	8.67	7.98	7.64	13.22
THg	[ng/g]										107.31	115.02	131.11	84.92	120.44	134.45	114.35	151.10	188.43
% MeHg	[]										7.62	7.25	20.34	9.83	8.25	6.45	6.98	5.05	7.02
K_{meth}	$[d^{-1}]$										0.139	0.191	0.115	0.182	0.182	0.113	0.243	0.127	0.078
K_{demeth}	$[hr^{-1}]$										0.024	0.034	0.057	0.019	0.036	0.044	0.016	0.055	0.028
K_m/K_d	[]										5.85	5.57	2.02	9.80	5.10	2.59	14.88	2.30	2.75
Elemental		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)
%C	[]																	2.09	
%N	[]																	46.06	
C/N ratio	[]																	22.0	
Metals Extract		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)
Fe	[mg/kg]											3.3	3.6					4.0	
Al	[ppm]											3.8	9.5					8.8	
Mn	[ppm]											-0.1	0.0					0.0	
Zn	[ppm]											0.0	0.3					0.1	
Ca	[ppm]											2.3	3.9					2.9	
K	[ppm]											15.2	22.6					36.4	
Mg	[ppm]											1.5	2.3					1.9	
Na	[ppm]											-21.3	-20.2					-19.1	

West Two River - Plot 3 (upland) Solid Phase (2 of 2)

SUMMARY STATISTICS

		10/6/2012									Top 0-4 cm 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
Analytes													
AVS	umol/kg	327	734	1261	348			155				137	345
%C-Organic	[]	90.6	88.4	87.0		88.3			88.4			90.7	88.7
%C-Calcite	[]	2.7	2.6	3.0		2.6			2.3			1.1	2.5
%C-Inorganic	[]	6.6	9.0	10.0		9.1			9.3			8.2	8.7
Mercury Analysis		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)	Top 4 cm Avr		
MeHg	[ng/g]	18.93	20.45	28.33	9.42	16.96	13.29	12.79	18.87	6.42		8.40	16.24
THg	[ng/g]	164.01	161.98	109.81	122.03	175.65	134.37	168.17	198.17	129.28		115.52	165.00
% MeHg	[]	11.54	12.63	25.80	7.72	9.65	9.89	7.61	9.52	4.97		7.49	9.78
K_{meth}	$[d^{-1}]$	0.017	0.028	0.035	0.009	0.007	0.027	0.004	0.014	0.020		0.18	0.015
K_{demeth}	$[hr^{-1}]$	0.019	0.039	0.056	0.013	0.002			0.003	0.001		0.03	0.016
K_m/K_d	[]	0.90	0.71	0.64	0.67	3.16			4.50	15.58		7.25	1.99
Elemental		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)	Top 4 cm Avr		
%C	[]											2.09	
%N	[]											46.06	
C/N ratio	[]											22.0	
Metals Extract		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)			
Fe	[mg/kg]											4.0	
Al	[ppm]											8.8	
Mn	[ppm]											0.0	
Zn	[ppm]											0.1	
Ca	[ppm]											2.9	
K	[ppm]											36.4	
Mg	[ppm]											1.9	
Na	[ppm]											*0	

$^{+}$Outlier excluded from 0-4 cm average

* values negative

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

		7/10/2012			7/24/2012			8/7/2012			8/22/2012		
Parameter	Units	A	B	C	A	B	C	A	B	C	A	B	C
pH	[]												
Temp	[^{o}C]												
LDO	[mg/L]												
Conductivity	[mS/cm]												
ORP	[mV]												
Water Table*	[ft]												
Analytes													
Sulfate	[mg/L]		0.4	0.9	1.2	1.0	1.1	0.7	0.5	0.3	0.8	3.8	3.1
Nitrate	[mg/L]		0.2		1.5	1.8	0.4	0.3	0.1		0.2	0.1	0.2
Phosphate	[mg/L]						0.3	2.3			0.8		
Chloride	[mg/L]				1.5							0.3	
Ferrous Iron	[mM]	0.047	0.047	0.008	0.030	0.070			0.011	0.003	0.008	0.010	0.009
Sulfide	[mmol]	2.8	15.8	12.3	13.6	3.2	13.6	4.1	3.4	3.6	3.9	4.1	0.3
Ammonium	[mg/L]	0.0	0.0	0.1									
DIC	[mg/L]	31.4	33.3	22.2	25.2	26.2	24.0	12.8	16.1	11.7	21.1	15.9	19.2
DOC	[mg/L]	69.7	24.6	26.4	31.1	34.8	19.9	42.4	34.7	43.1	43.7	28.7	34.8
SUVA	[$Lm^{-1}mg^{-1}$]				5.1	8.0	4.9	4.7	4.7	4.8	4.8	4.4	4.2
Mercury Analysis													
MeHg	[ng/L]	5.63	3.07	1.87	1.65	2.87	0.94	1.38	0.30	0.34	0.90	0.52	0.68
THg	[ng/L]	10.28	6.78	4.63	4.16	5.79	2.51	3.56	2.44	2.43	2.65	1.95	2.65
% MeHg	[]	54.76	45.28	40.44	39.60	49.48	37.56	38.67	12.15	13.83	33.96	26.72	25.73

West Two River - Plot 2 (nearshore) Sediment Porewater (2 of 2)

SUMMARY STATISTICS

		9/17/2012			10/6/2012			Average					
Parameter	Units	A	B	C	A	B	C	7/10/2012	7/24/2012	8/7/2012	8/22/2012	9/17/2012	10/6/2012
pH	[]							6.24		6.04	6.07	6.1	
Temp	[^{o}C]							30.23		18.3	14.5		
LDO	[mg/L]							2.71		0.1			
Conductivity	[mS/cm]							59.2		112.3	130.2	188.6	
ORP	[mV]							304		40		75	
Water Table*	[ft]								2.27	3.66	2.82	3.09	
Analytes													
Sulfate	[mg/L]	1.8		1.8	9.7	9.3		0.4	1.1	0.5	2.6	1.8	9.5
Nitrate	[mg/L]	0.6		0.7	0.6	0.2		0.1	1.3	0.1	0.1	0.7	0.4
Phosphate	[mg/L]	1.2		1.2	0.2				0.1	0.8	0.3	1.2	0.1
Chloride	[mg/L]				0.2				1.5		0.3		0.2
Ferrous Iron	[mM]	0.004	0.027	0.021	0.006			0.034	0.050	0.007	0.009	0.017	0.006
Sulfide	[mmol]	4.9	11.6	3.3		1.9	3.9	10.3	10.2	3.7	2.8	6.6	2.9
Ammonium	[mg/L]				0.0			0.0					0.0
DIC	[mg/L]	19.0		31.2	14.5	13.6		29.0	25.1	13.6	18.7	25.1	14.0
DOC	[mg/L]	32.9		24.8	24.8	21.7		40.2	28.6	40.1	35.7	28.8	23.2
SUVA	[$Lm^{-1}mg^{-1}$]	3.3		4.2	3.7	3.3			6.0	4.7	4.5	3.7	3.5
Mercury Analysis													
MeHg	[ng/L]	0.21	0.31	0.38	2.35			3.52	1.82	0.67	0.70	0.30	2.35
THg	[ng/L]	2.40	2.21	2.31	4.51			7.23	4.15	2.81	2.42	2.31	4.51
% MeHg	[]	8.77	13.86	16.30	52.06			46.83	42.21	21.55	28.81	12.98	52.06

West Swan River - Plot 3 (upland) Sediment Porewater (1 of 2)

		7/10/2012			7/24/2012			8/7/2012			8/22/2012		
Parameter	Units	A	B	C	A	B	C	A	B	C	A	B	C
pH	[]												
Temp	[^{o}C]												
LDO	[mg/L]												
Conductivity	[mS/cm]												
ORP	[mV]												
Water Table*	[ft]												
Analytes													
Sulfate	[mg/L]	0.4	0.5		0.4	1.1	0.4	0.3	0.3		0.4	0.3	0.4
Nitrate	[mg/L]		0.1		0.4	0.5	0.4	0.0	0.1	0.3	2.7	0.2	
Phosphate	[mg/L]					0.4				0.1	2.3	1.4	
Chloride	[mg/L]						3.9	0.3					
Ferrous Iron	[mM]	0.080	0.081	0.072	0.082	0.094	0.119	0.058	0.058	0.082	0.028	0.044	0.034
Sulfide	[mmol]	1.8	1.6	1.3	2.2	0.5	0.9	0.6	1.9	2.1	2.8	2.1	2.1
Ammonium	[mg/L]	0.0	0.0	0.3									
DIC	[mg/L]	25.7	21.8	20.9	8.8		8.3	13.5	7.7	6.3	8.0	9.0	12.2
DOC	[mg/L]	89.9	71.9	105.6	56.9		71.8	72.7	74.1	78.3	63.0	109.2	81.2
SUVA	[Lm^{-1}mg^{-1}]				9.0		8.2	8.0	8.1	8.0	5.0	5.3	5.2
Mercury Analysis													
MeHg	[ng/L]	0.72	2.66	0.91	1.05	1.02	1.16	1.02	0.83	0.91	1.11	1.64	1.64
THg	[ng/L]	7.88	7.33	9.33	9.38	6.92	8.71	7.37	6.24	8.14	5.39	5.59	3.75
% MeHg	[]	9.19	36.34	9.74	11.17	14.73	13.32	13.82	13.28	11.23	20.58	29.38	43.86

West Swan River - Plot 3 (upland) Sediment Porewater (2 of 2)

		9/17/2012			10/6/2012			SUMMARY STATISTICS Average					
Parameter	Units	A	B	C	A	B	C	7/10/2012	7/24/2012	8/7/2012	8/22/2012	9/17/2012	10/6/2012
pH	[]							5.23		5.32	5.53		
Temp	[^{o}C]							25.05		16.18			
LDO	[mg/L]							1.14		0.12			
Conductivity	[mS/cm]							24		126.6	72.1		
ORP	[mV]							327				120	
Water Table*	[ft]								2.33	2.65	2.83	3.04	
Analytes													
Sulfate	[mg/L]	1.0	0.2	0.3	2.7	2.2	2.6	0.5	0.6	0.2	0.4	0.5	2.5
Nitrate	[mg/L]	1.4	0.1	0.1	0.3	0.5	0.5	0.0	0.4	0.1	1.0	0.5	0.4
Phosphate	[mg/L]	0.4	0.5	0.5					0.1	0.0	1.2	0.5	
Chloride	[mg/L]				0.1	4.8	0.1		3.9	0.3			1.6
Ferrous Iron	[mM]	0.044	0.034	0.054	0.032	0.024	0.036	0.078	0.098	0.066	0.035	0.044	0.031
Sulfide	[mmol]	1.5		1.2	1.4	1.7	1.3	1.6	1.2	1.5	2.3	1.4	1.5
Ammonium	[mg/L]				0.0	0.3	0.2	0.1					0.2
DIC	[mg/L]	9.4	12.3	13.1	2.5	2.8	1.1	22.8	8.6	9.2	9.7	11.6	2.1
DOC	[mg/L]	61.4	70.3	72.2	49.4	52.9	54.8	89.1	64.4	75.0	84.5	68.0	52.4
SUVA	[Lm^{-1}mg^{-1}]	4.9	4.8	4.8	4.5	3.9	3.9		8.6	8.0	5.2	4.8	4.1
Mercury Analysis													
MeHg	[ng/L]	0.54	0.16	0.61	0.41	0.84	0.30	1.43	1.08	0.92	1.47	0.44	0.52
THg	[ng/L]	3.88	3.02	3.74	3.10	4.37	3.82	8.18	8.34	7.25	4.91	3.54	3.76
% MeHg	[]	14.00	5.46	16.20	13.25	19.28	7.78	18.42	13.07	12.78	31.27	11.89	13.43

West Swan River - Plot 2 (nearshore) Solid Phase (1 of 1)

SUMMARY STATISTICS

		5/15/2012									Top 0-4 cm 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
Analytes													
AVS	umol/kg	666	146	481	609			875			630		
%C-Organic	[]	40.7	31.2	58.9		31.529			43.96		37.2		
%C-Calcite	[]	3.0	2.6	1.8		2.0213			2.0949		2.3		
%C-Inorganic	[]	56.3	66.1	39.3		66.449			53.945		60.5		
Mercury Analysis		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)	Top 4 cm Avr		
MeHg	[ng/g]	4.46	2.18	0.96	2.64			2.31			2.76		
THg	[ng/g]	105.74	121.38	143.70	129.86			135.56			126.33		
% MeHg	[]	4.22	1.80	0.67	2.03			1.71			2.25		
K_{meth}	$[d^{-1}]$	0.244	0.108	0.065	0.176			0.183			0.178		
K_{demeth}	$[hr^{-1}]$	0.037	0.034	0.069	0.069			0.057			0.054		
K_m/K_d	[]	6.52	3.16	0.94	2.55			3.23			3.54		

West Swan River - Plot 3 (upland) Solid Phase (1 of 1)

SUMMARY STATISTICS

		5/15/2012									Top 0-4 cm 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
Analytes													
AVS	umol/kg	1390	598	120	474			201			557		
%C-Organic	[]	42.3	37.0	22.6		41.7			40.453		40.61		
%C-Calcite	[]	2.3	2.4	2.9		2.1862			2.5198		2.4		
%C-Inorganic	[]	55.4	60.5	74.5		56.113			57.027		57.0		
Mercury Analysis		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)	Top 4 cm Avr		
MeHg	[ng/g]	6.06	2.16	1.92	3.24			4.09			3.81		
THg	[ng/g]	122.45	140.49	115.21	133.89			149.57			138.31		
% MeHg	[]	4.95	1.54	1.67	2.42			2.73			2.80		
K_{meth}	$[d^{-1}]$	0.064	0.075	0.039	0.125			0.090			0.095		
K_{demeth}	$[hr^{-1}]$	0.035	0.041	0.040	0.040			0.029			0.036		
K_m/K_d	[]	1.81	1.84	0.98	3.14			3.12			2.69		

West Swan River - Plot 2 (nearshore) Sediment Porewater (1 of 1)

SUMMARY STATISTICS

		5/15/2012			Average
Parameter	Units	A	B	C	5/15/2012
pH	[]				
Temp	[^{o}C]				
LDO	[mg/L]				
Conductivity	[mS/cm]				
ORP	[mV]				
Water Table*	[ft]				
Analytes					
Sulfate	[mg/L]				
Nitrate	[mg/L]				
Phosphate	[mg/L]				
Chloride	[mg/L]				
Ferrous Iron	[mM]				
Sulfide	[mmol]	5.5	4.7	5.8	5.3
Ammonium	[mg/L]	0.5	3.2	4.8	
DIC	[mg/L]	59.7	219.4	117.1	132.1
DOC	[mg/L]	36.2	31.0	47.0	38.0
SUVA	[Lm^{-1}mg^{-1}]	9.3	22.7	12.3	14.8
Mercury Analysis					
MeHg	[ng/L]	0.26	0.38	0.30	0.31
THg	[ng/L]	1.91	2.79	2.58	2.43
% MeHg	[]	13.65	13.54	11.76	12.99

West Swan River - Plot 3 (upland) Sediment Porewater (1 of 1)

		5/15/2012			Average
Parameter	Units	A	B	C	5/15/2012
pH	[]				
Temp	[^{o}C]				
LDO	[mg/L]				
Conductivity	[mS/cm]				
ORP	[mV]				
Water Table*	[ft]				
Analytes					
Sulfate	[mg/L]				
Nitrate	[mg/L]				
Phosphate	[mg/L]				
Chloride	[mg/L]				
Ferrous Iron	[mM]				
Sulfide	[mmol]	8.0	6.9	7.6	7.5
Ammonium	[mg/L]	0.1	0.1	0.2	
DIC	[mg/L]	23.9	11.6	31.3	22.3
DOC	[mg/L]	20.6	15.2	17.6	17.8
SUVA	[Lm^{-1}mg^{-1}]	13.1	10.3	9.3	10.9
Mercury Analysis					
MeHg	[ng/L]	0.29	0.04	0.01	0.11
THg	[ng/L]	2.94	2.31	1.55	2.26
% MeHg	[]	9.92	1.81	0.65	4.13