

# The Spatial Distribution and Fate of Trace Metals in Ombrotrophic Peat Bogs

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## Abstract:

Atmospheric deposition of heavy metals and other pollutants has substantially increased due to human activities over the past several hundred years. For some metals such as lead and mercury, these changes have been well studied because of their potentially harmful impact to human and ecosystem health. However, some aspects of metal transport and storage in the environment are still not well understood; for example, metal mobility in acidic wetlands and peat bogs is complex and not well constrained. Sediment cores from an ombrotrophic peat bog in the S-2 Watershed in Marcell Experimental Forest, Northern Minnesota were examined to determine potential drivers of the element mobilization or remobilization in a wetland/bog environment. Sediments and porewaters were analyzed for metal concentration, and core transects showed clear trends in the metal concentration from upland sites higher in the watershed to the peat bog. The trends were then compared with the hydrology of the watershed, as well as background studies of the elements to determine their potential fate. Evidence suggests some elements such as mercury are actively being transported through the watershed system in relation with the watershed's hydrologic flow, whereas lead does not appear to be mobile from the uplands into the peatlands, but may be mobile in the peatlands in correspondence with the pH and anoxic condition of the watershed.

## **Acknowledgements**

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## **Introduction:**

The atmospheric deposition of trace metals has been substantially altered by anthropogenic sources. Although these alterations have been discovered and documented quite thoroughly over the past few decades, their potential impacts on different environments are still not well understood. Various metals, such as lead (Pb) and mercury (Hg), are harmful to organisms at elevated concentrations. These elevated concentrations can result in the nervous system disruptions, cancer, and birth defects (EPA, 2010). Too often, we find this problem of harmful trace metal concentrations in a water source when it is too late, without any chance of prevention. In order to prevent unnecessary contamination in the future, an understanding of trace metal fate in different types of environments is crucial.

Elements act very different from each other after deposition to wetland environments. Some elements, such as Pb, have been assumed to immobile after deposition (Appleby, 2005), while others are remobilized, but only under certain conditions. Others, such as highly soluble major cations, may remain mobile long after deposition.

In the case of wetlands, Hg mobility is very important to understand due to potential for methylation to more toxic form of methylmercury. Wetlands are ideal for Hg methylation due to anoxic conditions and low pH. Under those conditions, sulfate-reducing bacteria convert Hg into methylmercury (MeHg) ( $\text{CH}_3\text{Hg}$ ) as a byproduct (Mitchell, 2008). MeHg is a very hazardous species of Hg and is able to bioaccumulate, meaning that concentrations in animal tissue increase higher in the food chain (Baird, 2008). This effect is particularly strong in aquatic

food webs, where there is less of a potential for MeHg to photo-degrade back to less harmful forms of Hg. This can have a detrimental impact on humans, who sometimes consume large quantities of aquatic foods (Baird, 2008). Hg transport in wetlands must be understood because of the potential to be a supplier of MeHg to downstream environments including lakes and oceans.

The study of how trace elements act in peatlands is not only important because of potentially harmful impacts, but also to scientific studies on other topics.  $^{210}\text{Pb}$  dating is often used in peat bog studies as way to establish chronologies in recent sediments, because Pb binds strongly to organic matter and many researchers assume Pb is immobile in these bogs (Appleby, 2005). Others in the scientific community have doubts about the immobility of Pb in peat bogs. If in fact Pb is remobilized after deposition, it could cast doubt on peat chronologies and accumulation rates based on  $^{210}\text{Pb}$  dating (Urban, 1990).

This study focuses specifically on the elements Pb, Hg, and MeHg in ombrotrophic peat bogs. These peatlands have the potential to reveal more detail about the fate of trace metals since they contain three distinct sub-environments in relatively close proximity to one another. Higher elevations of the watershed contain an upland environment consisting of nutrient rich mineral soils developing on glacial till. The uplands connect to the lagg, which is where the first of the peat material is found. The lagg is defined by peat material that lies on top of the nutrient rich mineral soils. Farther out into the center of the peatland is the bog. The bog is ombrotrophic meaning that it receives all of its nutrients from the atmosphere and does not receive any surficial runoff or subsurface flow from the uplands and lagg (Kolka, 2011). These

three sub-environments also vary in pH, vegetation, oxidation, and nutrient availability shown in Table 1. Because the three environments are in close proximity to each other, samples can be collected from transects that include all three, allowing for the study of the element concentrations at points along the transects where varying conditions can be compared.

**Table 1.)** Display of information about the S-2 Wetland/Bog environments (Kolka). Photos from Emily Seelen’s study.

<b>Upland</b>	<b>Lagg</b>	<b>Bog</b>
<ul style="list-style-type: none"> <li>• 6.5-ha forest of aspen</li> <li>• Oxic</li> <li>• pH = 5 to 7</li> <li>• More nutrient rich, mineral soil of glacial till</li> </ul>	<ul style="list-style-type: none"> <li>• Saturated organic soils</li> <li>• Adler Vegetation</li> <li>• O<sub>2</sub> exposure at the surface; anoxic below the water table</li> <li>• pH = 3.5 to 5.5</li> <li>• Poor to intermediate nutrient status</li> </ul>	<ul style="list-style-type: none"> <li>• 3.2 ha black spruce [Picea mariana]</li> <li>• Organic peat soil</li> <li>• Ombrotrophic</li> <li>• O<sub>2</sub> exposure at the surface; anoxic below the water table</li> <li>• pH = 3.5 to 4.5</li> <li>• Nutrient-poor</li> </ul>
		

Previous works have analyzed major cation and trace metal concentrations in the porewaters of these transects. This is only one component of these complex wetland systems,

and more information is needed in order to gain a better understanding of trace metal mobility.

The goal of this study was to analyze trace metals in sediment cores along transects, and compare the results with the previous works on porewater transects. This comparison will show how trace metal concentrations (specifically Hg and Pb) relate between the porewater and sediment cores, with the end goal of gaining further insight to Hg and Pb mobility.

**Location:**

The ombrotrophic bog examined in this study is located in the Marcell Experimental Forest (MEF), in Northern Minnesota (Figure 1a). The MEF is an 890-ha tract of land about 20 miles north of Grand Rapids that has been reserved for long term research (NRS, 2011). The MEF contains six separate watersheds each consisting of a mineral soil upland and a peatland section. Also, each watershed has a stream that acts as a discharge for the water in the bog.

This study focused on the S-2 watershed (Figure 1b).

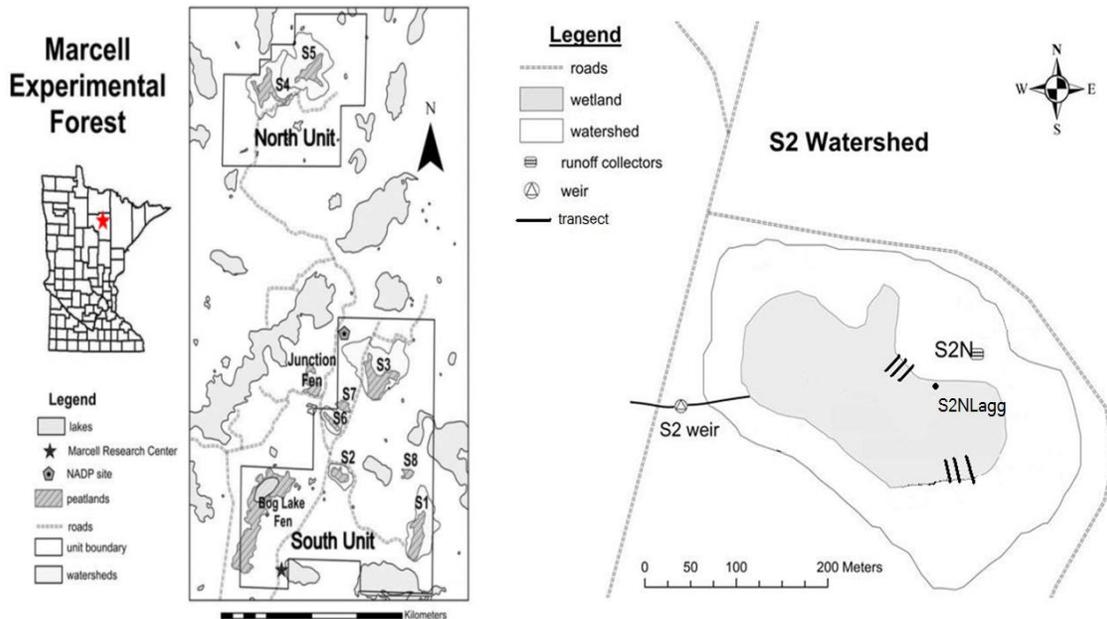


Figure 1. (a) Location of the Marcell Experimental Forest in relation to Minnesota (on left). (b) Image of the S-2 watershed (on right).

The S-2 watershed contains 3.24-ha of peat deposit (organic rich) and 6.48-ha of mineral soil (glacial till) uplands (Kolka, 2011). The S-2 watershed is used as a control for experiments regarding fertilizers, burning, grazing, and many other studies (NRS, 2011). This watershed was chosen specifically because it has also been used for a study on trace metal analysis in the peat porewater, which will later be incorporated into this study.

### **Geologic Setting**

In relatively recent geologic history, Northern Minnesota has been influenced by various glacial advances and retreats of lobes branching from the Laurentide Ice Sheet (Minnesota Geological Survey, 1997). With these glacial advances came the sculpting of the land, along with the deposition of various glacial tills. It is important to understand the geologic setting because it determines the hydrologic characteristics that are or could be found today (Verry, 2011). Figure 2 shows that the S-2 Watershed sits on several different layers of glacial till. The top layer of till consists primarily of sand that has a depth of 30-100cm (Kolka, 2011). This layer allows subsurface water to run from the uplands to the lagg area. Below this layer is a layer of mostly clay which is less permeable and acts as a barrier for the subsurface flow. However, some runoff is lost from the system by seeping through the clay layer.

### **S-2 hydrology**

Figure 2 shows a cross section of a transect extending from the bog to the uplands. In this figure, the path of runoff is indicated by the white arrows. The S-2 watershed contains negligible amounts of surface runoff, so only the shallow subsurface runoff was focused on. This image shows how the bog section of the wetlands is ombrotrophic, because there is no

input from the runoff. Instead, the runoff either enters the lagg or slowly seeps downward into deeper ground waters. It is important to note that once the runoff reaches the lagg, it gradually flows through the lagg around the bog until it reaches the weir to the west (Figure 1b). This happens because the bog is at a slightly higher elevation (dome like) causing flow to actually enter the lagg from the bog.

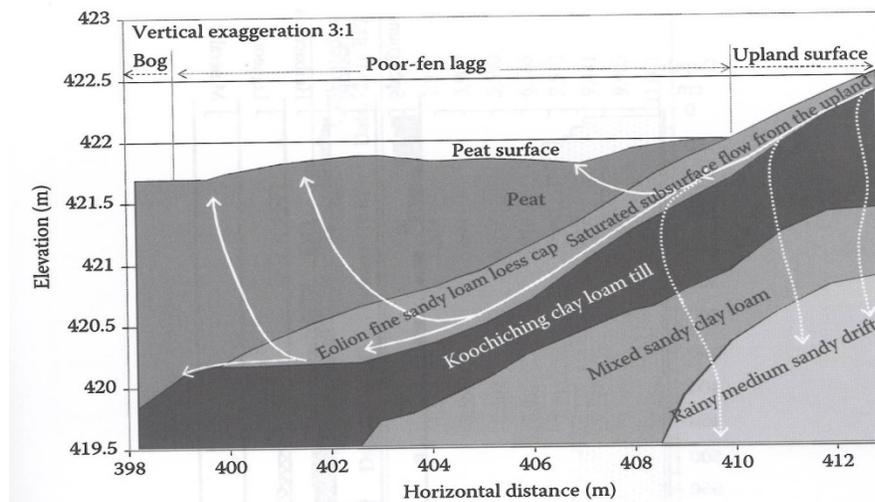


Figure 2.) Displayed is a cross section of a transect containing flow directions and soil boundaries in Marcell Experimental Forest's S-2 watershed. The flow path of runoff is indicated by the white arrows. The solid arrows represent saturated flow and the dotted arrows represent unsaturated flow. (Verry, 2011. Figure 4.8)

Topographic characteristics also play an important hydrologic role in the S-2 Watershed. Depending on the transect position, upland topography may control the amount of sub-surface flow that will enter the lagg. Upland contours that are concave relative to the transect cause an increase in flow to the lagg because the flow converges as elevation decreases. Convex upland contours will have the opposite impact on the flow, and parallel upland contours should have no impact on flow.

## Methods:

The sampling strategy for this study was to take sediment cores along two transects, each extending from the uplands into the bog. One of the transects was located on the north side of the bog (Transect A), and one on the south side (Transect B). Sampling took place during August and November of 2011. Cores were collected at even intervals of 2.5 meters (Transect A) or 6 meters (Transect B). Depth measurements and core description were taken at each site. The core samples were immediately sectioned and placed in plastic zip lock bags. The peat cores were separated into two sections based on saturation, whereas the upland cores were sectioned by different soil horizons. Due to the small amount of the organic rich layer in the upland cores, a second sub-sample from each soil horizon was taken as a replicate.

Samples were taken to a lab at Gustavus Adolphus College for further processing. First, the samples were weighed and dried in an oven at about 70 degrees Celsius for three days. Once dried, the samples were weighed again, which provided sample saturation levels. Then samples were ground up and homogenized using a mortar and pestle. Trace metals were extracted by taking a tenth of a gram of each sample, and placing it in a centrifuge tube with 10ml of 0.5 M HCl. The sample tubes were placed in a water bath at 85°C for 30 minutes. After the digestion, 200 uL of the sample solution was pipetted into a second centrifuge along with 9.7 mL of 2% HCl and 100 uL of internal standard. MeHg digestion required .25 grams of sample added to 2 mL of 25% KOH in a methanol solution. Samples were then placed into a 60°C oven for 4 hours and eventually diluted with 8 mL of MilliQ and 200 uL of MeHg standard. THg samples were processed by placing .25 grams in 8 mL of HNO<sub>3</sub> and microwaving for 5 minutes.

500 uL of sample were then placed in 9.5 mL of MilliQ. Finally, all the samples were prepared to be analyzed using an ICP-MS (inductively coupled plasma mass spectroscopy). Using the ICP-MS, concentrations of Hg, MeHg, and Pb were analyzed.

Total organic matter (TOM) was measured for all sediment samples by loss on ignition. Approximately .25 grams sediment was placed in a crucible and burned at 550°C. Samples were then weighed again to find the percentage of organic material.

## **Results:**

### **Sediment Core Descriptions:**

The peat cores were dark brown to black in color and with a composition mostly of organic matter. One peat core at the bog end of transect B contained a bright orange staining at 26-29 cm deep. The upland cores had a dark brown organic rich layer about 4-5 cm thick, followed by an abrupt transition to a tan/gray sandy composition deeper in the core.

### **Watershed Hydrology**

Table 2 displays the average saturation percentage between each different sample type (peat surface, peat depth, upland organic layer, and upland clastic), as well as the percent difference between both transects in the same month and the same transect during both months. Both peat samples types are highly saturated with H<sub>2</sub>O ranging from 80 to 90 percent. The peat surface and depth samples show a strong correlation between each transect and each month by having less than a 10% difference. Overall though, the peat samples in transect B had

a slightly higher saturation percentage. There is also a much higher variation between the upland organic and clastic samples. It is important to note that some water may have been accidentally discarded when transferring sectioning the cores in the field.

Percent H <sub>2</sub> O Saturation of Sample				
Column1	Surface Peat Sample	Depth Peat Sample	Upland Soil O layer	Upland Soil Clastics
Aug Transect A	84.6	80.9	68.3	12.5
Aug Transect B	90.5	85.8	66.8	22.8
Nov Transect A	89.2	88.6	30.2	13.3
Nov Transect B	90.3	90.0	46.8	13.8
% difference Aug	-7.0	6.0	2.1	-82.0
% difference Nov	-1.2	1.6	-54.6	-3.1
% difference A	-5.4	9.5	55.7	6.6
% difference B	0.28	4.9	29.9	39.5

Table 2 represents the average percent saturation level of each different sample type (peat surface and depth samples, upland organic layers, and clastic) for each transect sampled in August and November. The percent difference in August and November compares transects A and B in the featured month. The percent difference of A and B compares the featured transect in August and November.

Water table levels for throughout 2011 are shown in figure 3. Water levels appear higher in the spring and summer months. Between August and September there was a 4 inch decrease in the water table elevation.

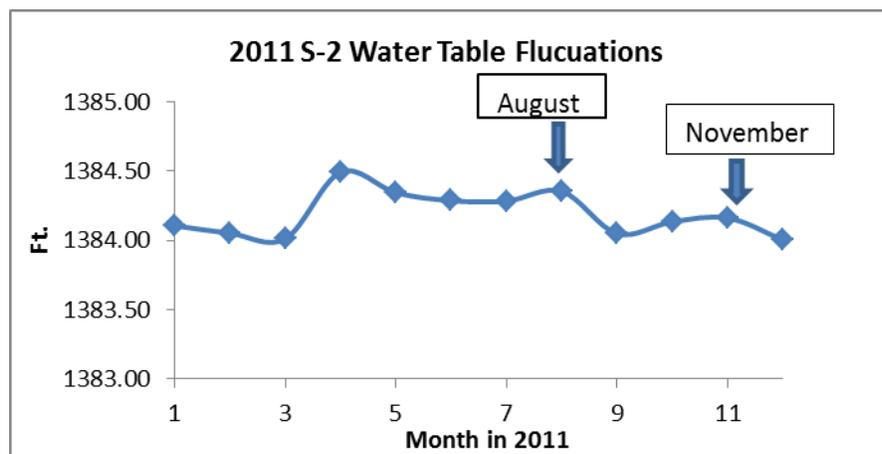


Figure 3.) The variation of the S-2 bog water table in feet over the 2011 year (1 being January and 12 being December). August and November mark the times when samples were acquired.

### Metals in Porewater Transects:

Porewater transects were first analyzed for major cation (Na, Ca, and Mg) concentrations. Figure 4 displays concentrations in transects A and B in August. Transect B shows almost a 50% increase in concentration from the upland to the bog for Na, Mg, and Ca. The northern Transect A shows a slight decrease in concentration of major cations from upland to bog, but the decrease is substantially less than the first transect. Also, the sub-surface flow collector samples for both transects contain major cation concentration that are all nearly a half of the concentration found in the first upland samples

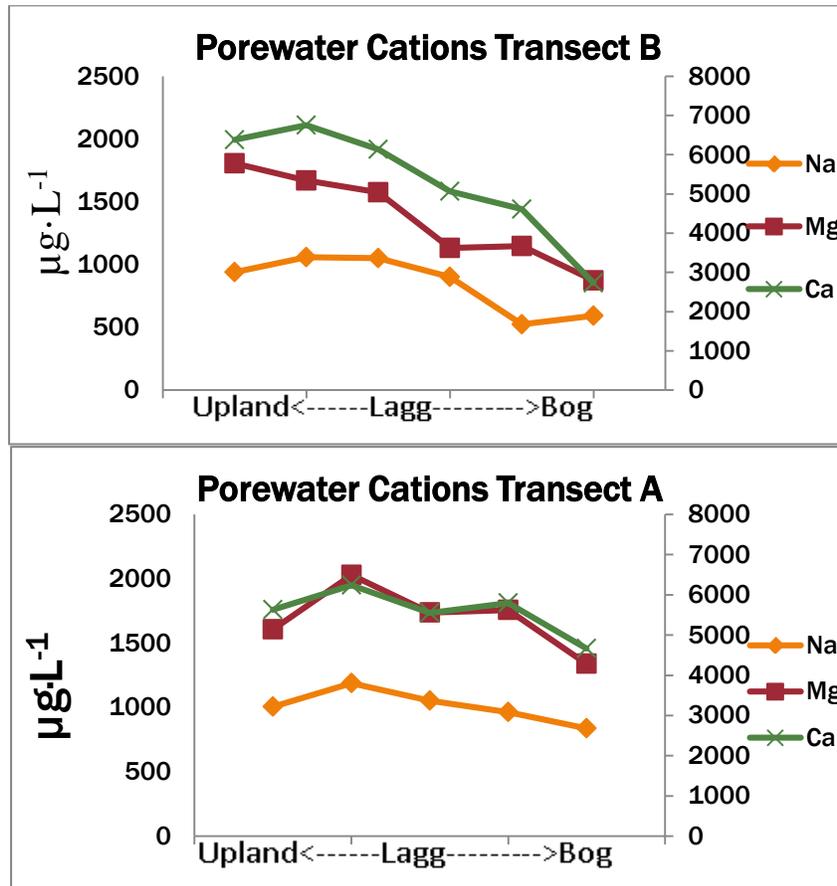


Figure 4.) Graphs display major cations concentrations(µg/L) in porewater transects A and B collected in August. The left axis is a scale for Mg and Na, and the right axis represents Ca. Transects are shown in the direction of upland to the left and bog to the right.

The porewater concentrations for total mercury (tHg) on these same transects showed a strong decrease in concentration from upland to bog as well (figure 5). The magnitude of decrease was much higher than the cations, finding only a quarter of first upland concentration out in the bog. Sub-surface collectors again showed the concentration of tHg to be nearly half that of the concentration found in the first upland sample for both transects.

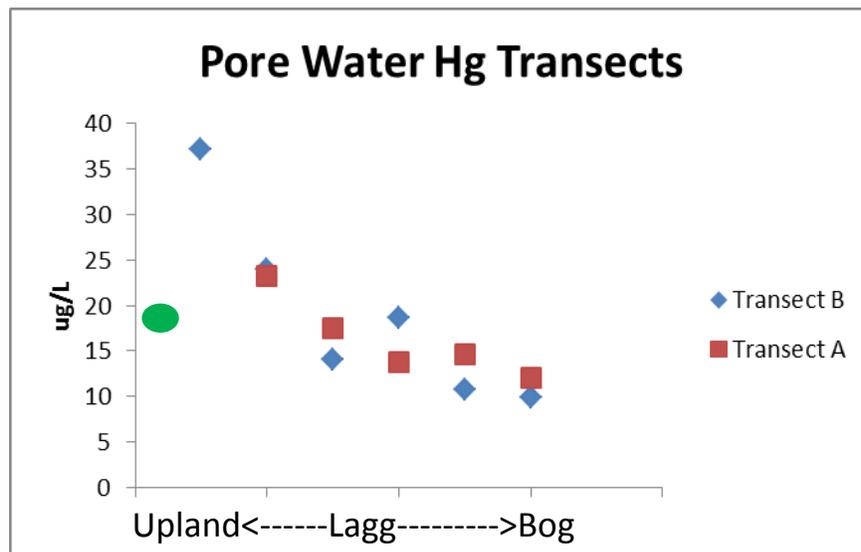


Figure 5.) Represents tHg concentrations (ug/L) for transects A and B in August. The green oval represents tHg concentrations in the shallow sub-surface collector. Transects are shown in the direction of upland to the left and bog to the right.

Pb concentration along these transects show a much different trend (Figure 6). Here, there is a decrease in concentration from the uplands to the lagg area, and a larger increase going out farther into the bog. Not only did the trend in Pb not match the trends of the previous metals, the sub-surface runoff collectors showed very low (10%) concentrations compared to the concentrations of the first upland samples.

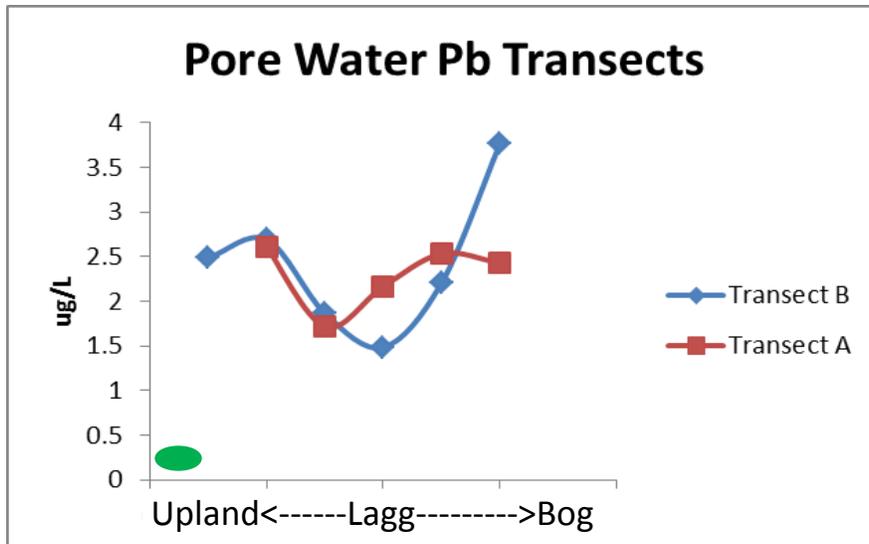


Figure 6.) Represents tHg concentrations ( $\mu\text{g/L}$ ) for transects A and B in August. The green oval represents tHg concentrations in the shallow sub-surface collector. Transects are shown in the direction of upland to the left and bog to the right.

#### Metals in Solid Transects:

It is important to note that the solid core transects were not taken along the same transects as the porewater samples, although they were close as possible and that they are normalized to total organic matter (TOM). Also, major cations were not analyzed in the solid transects due to their highly soluble characteristics. Figure 7 displays tHg normalized to TOM. Again, there is a definite decrease in concentration from the upland to the bog. This figure differs from the pore water figures in the way it shows the same transect for both August and November instead of both transects in August. The magnitude of decrease from upland to bog is nearly 4-fold which was the same result found in the porewater transects. Concentrations of Pb in the solid core samples show a decrease in the lagg and increase back into the bog (Figure 7), like the porewater transects (Figure 6). However, the degree of decrease in the lagg was much larger in November than August.

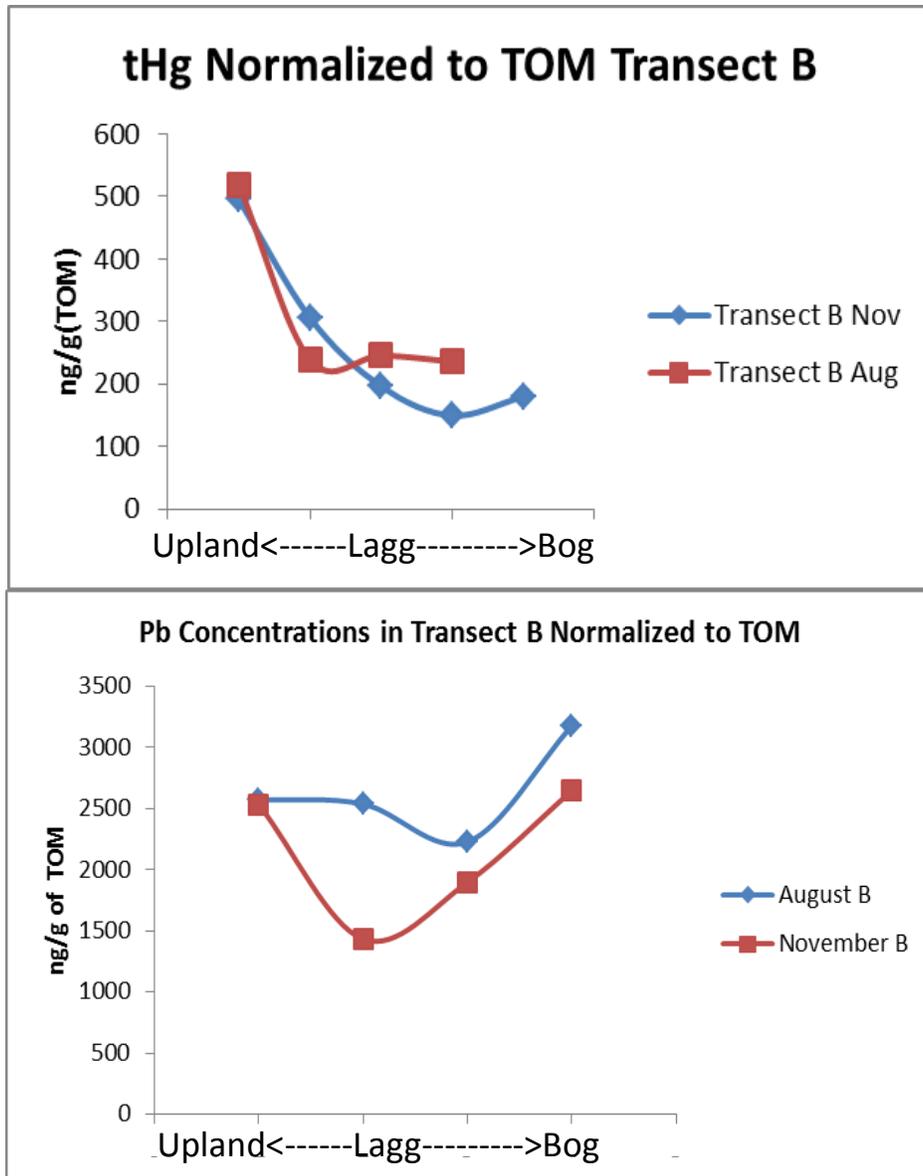


Figure 7.) Represents tHg(top) and Pb(bottom) concentrations normalized to TOM (ng/g of TOM) in solid phase sediment cores in Transect B for August and November. Transects are shown in the direction of upland to the left and bog to the right.

**Discussion:**

The porewater transects show a substantial decrease in concentration from the upland to the bog in both the major cations and tHg. This combined with the elevated concentrations of major cations and tHg in the sub-surface collectors, indicates that these metals are in fact

being mobilized from the uplands to the lagg. Major cations are very soluble in water and as precipitation falls on the uplands, it collects the cations and transports them in sub-surface flow to the lagg. This is shown by the concentrations of major cations measured in the sub-surface runoff collectors. The upland soils concentrate the cations in the upland runoff and as they enter the more dilute environment of the lagg, concentrations decrease. Because none of this flow is reaching the bog, and in fact some of the bog water is flowing into lagg itself, an even larger decrease in concentration should be found in the bog. This could potentially explain the decreasing concentrations from the uplands to the bog.

The variation in the magnitude of decreasing cation concentrations are likely influenced by the topographic features of the uplands. The larger decrease in Transect B (Figure 4) may be due to concave upland features. These features cause increased amounts of sub-surface flow to enter the lagg. This increased sub-surface flow could potentially transport more cations, but Figure 4 shows close to the same initial cation concentrations for both transects A (parallel upland features) and B (concave upland features). This means that the increased sub-surface flow is not bringing more cations, resulting in greater dilution and decreasing concentrations through the transect because of the input of more water.

If the above scenario is correct, tHg is also being transported from the uplands into the lagg. The evidence for this is that the trends in tHg concentrations are very similar to the trends found with the soluble major cations. However, this raises the question of why the tHg concentrations decreased by about twice as much as the cations, moving from upland to bog. One answer might be that the characteristics of the bog and lagg determine mobility. As

mobile tHg in the runoff enters the lagg, it enters a new set of geochemical and hydrological conditions. From the upland to lagg, pH decreases from 5-7 to 3.5-5.5, and in addition, the lagg is anoxic. These conditions promote the growth of sulfate-reducing bacteria, which in turn promote mercury methylation. Figure 8 shows the concentration of tHg in the sediment, and the proportion of tHg that is MeHg. However, the results do show that there are negligible amounts of MeHg in the upland, and that MeHg is found in the lagg and bog. This shows that a portion of the tHg is being methylated once it enters the peatland conditions. Also, a higher percent of the tHg is MeHg in the month of August. This cannot be explained by the current data, but may be influenced by temperature or water table levels, since both were lower in November. However, more sediment samples would need to be analyzed for MeHg before we could be certain of these conclusions.

Another reason for tHg concentrations to decrease by a larger magnitude than the cation concentrations may be the percentage of TOM. THg, unlike base cations, binds to organic matter which is more prevalent in the lagg than the upland soils. This would cause more tHg to transfer from the porewater to the organic matter in the sediments, resulting in decreasing concentrations in the porewater throughout a transect.

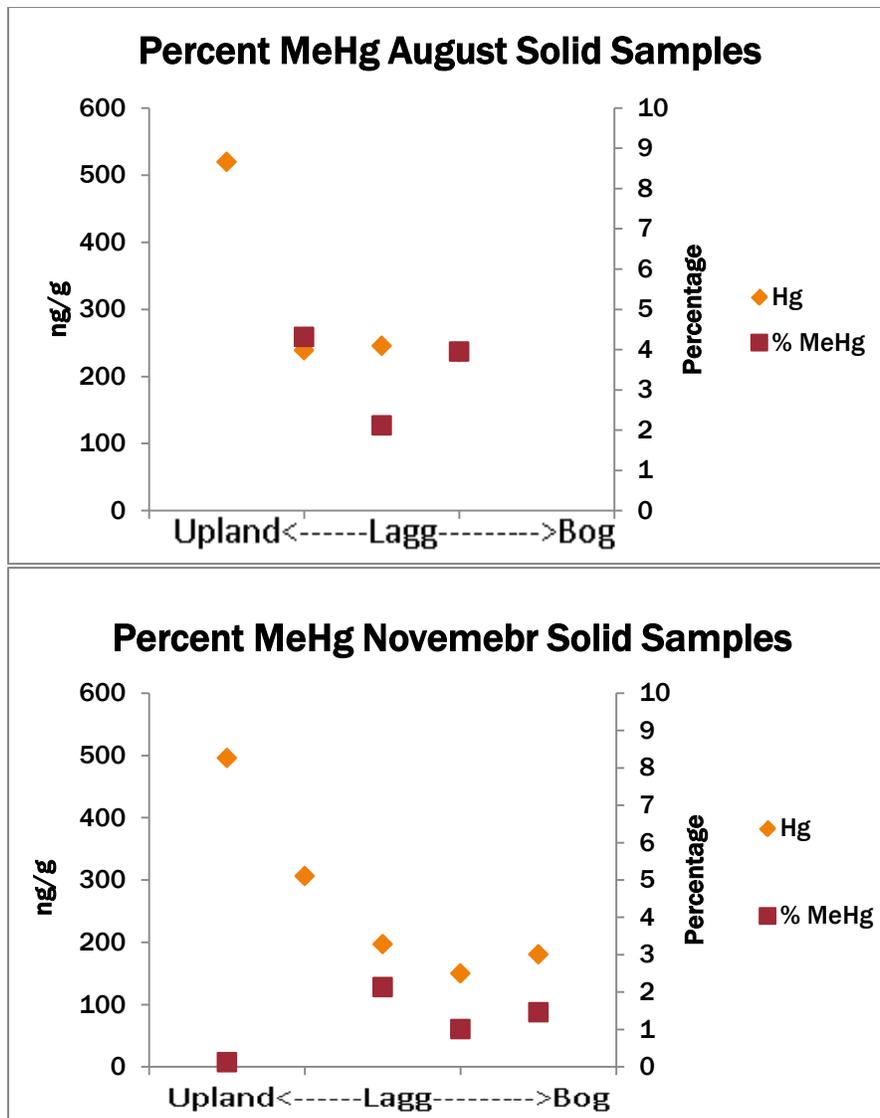


Figure 8.) Diamonds represents tHg solid phase sediment core concentrations normalized to TOM (ng/g TOM) in transect B in August(top) and November(bottom). Squares represent the percent of of tHg that is MeHg (right axis) of the same samples. Missing squares are due to lack of data. Transects are shown in the direction of upland to the left and bog to the right.

Partition coefficients were calculated by dividing the tHg in the sediment by tHg in the porewater, all normalized to organic matter. The same was done for MeHg (figure 9). Again we faced the challenge of limited data, but overall there is an increase of tHg and MeHg in the solid samples relative to the porewater samples from upland to bog. That is, some mechanism is increasing the tendency for tHg and MeHg to bind to TOM farther out into the bog. Based on

the current data, the reason for this cannot be determined, but may be due to different types of organic and dissolved organic matter, and should be an area of future research.

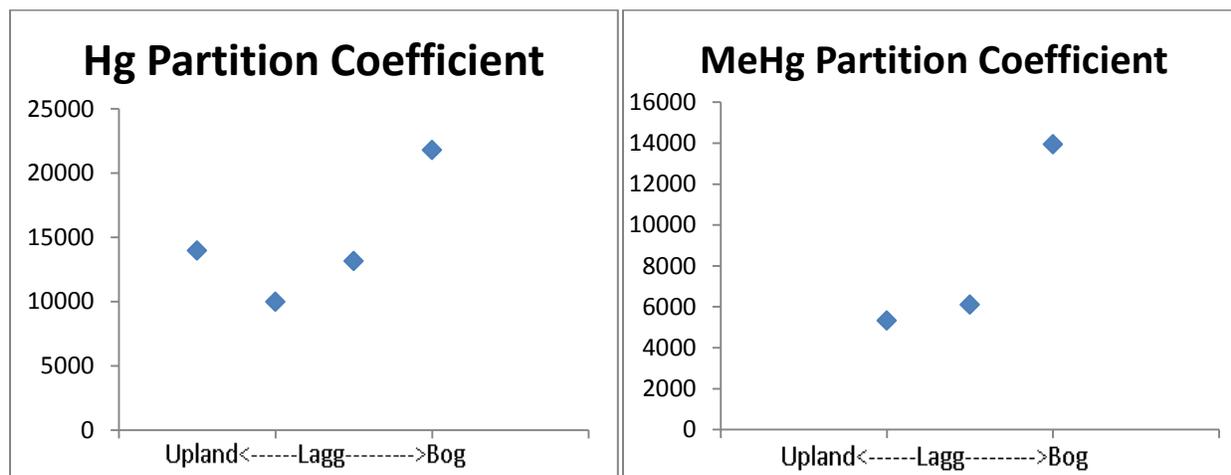


Figure 9.) Partition coefficients of tHg and MeHg are shown by taking the sediment concentrations normalized to TOM, and dividing by porewater concentrations for Transect B in August. MeHg upland sample is missing due to lack of data. Transects are shown in the direction of upland to the left and bog to the right.

Pb concentrations tell a very different story than Hg. In both the porewater and sediment samples, Pb concentrations were higher in the upland, decreased in the lagg and then increased in the bog. First, Pb appears to be almost completely immobile from the uplands into the lagg. This is shown by the very low concentration of Pb found in the sub-surface collectors. If Pb was completely immobile, concentrations throughout the transects would be expected to not vary much. Instead, the lagg is clearly depleted in Pb relative to the upland and bog. It has been suggested that Pb may become mobile in anoxic conditions with a low pH. We speculate that the decrease in pH in the lagg, combined with anoxia, is mobilizing Pb. pH was measured in the transects but the data are not yet available, so we cannot provide a definite answer.

## Conclusion:

This study was the first to compare peat porewater transects to peat sediment transects. However, this was a preliminary study, and more transects should be analyzed in the future to support and add to the findings of this paper. The results of this paper show that Hg is actively being transported from the uplands into the peatlands, where conditions allow for the production of MeHg. Therefore, the peatlands are an active source of MeHg. Even though this is a natural process, the burning of coal and various other operations, have increased the amount of Hg in the atmosphere. This results in increased Hg deposition and transport into conditions that produce MeHg. Further study must be done to increase understanding of how Hg behaves once it reaches the peatlands.

Also, this study shows that Pb is almost completely immobile in the uplands due to minimal concentrations in sub-surface flow which would transport Pb between the uplands and peatlands. Evidence from both the porewater and sediment samples in the lagg suggest that some component of the lagg is having an impact on Pb and may be causing it to remobilize. A lack of watershed data, such as pH levels and flow rates, stopped any conclusion that could be made for Pb mobility in the peatlands. If Pb is being mobilized in peatlands, it could impact originally deposited Pb concentrations, which would result in inaccurate  $^{210}\text{Pb}$  dating.

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