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Terrestrial mercury cycling in Northern Michigan: Honeysuckle Creek watershed and Burt Lake

HONORS THESIS

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Abstract

Mercury (Hg), a potent environmental toxicant, affects the cognition and health of both human and aquatic ecosystem populations. Despite regulation-driven decreases in atmospheric mercury levels, Burt Lake is among the list of mercury-impaired lakes in Michigan due to high concentrations of Hg in the lake's fish. Transport and sourcing of mercury to 17,120 acre Burt Lake were explored in Honeysuckle Creek watershed, a first order watershed in which the land is now largely undeveloped forest and peatland resting on roughly 100 meters of unconsolidated sediment.

Water samples from Honeysuckle Creek watershed were collected from the lake, groundwater, and one stream input to the lake during July 27-August 6, 2015 and analyzed for total Hg (THg), methylmercury (MeHg), dissolved organic carbon (DOC), and carbon isotopes ($\delta^{13}C$). Conductivity, pH and temperature data were collected in the field. Surface water discharge, along with groundwater table levels, were quantified.

THg and MeHg in the stream are flushed from the soils during storm event on August 2nd. Unfiltered THg concentrations range from 2.6 ngL^{-1} to 14.2 ngL^{-1} in the stream and 0.01 ngL^{-1} to 13.8 ngL^{-1} in the lake. Filtered THg levels in the groundwater table north of the stream rise as a result of this storm along with the water table reaching 2.9 ngL^{-1}, while the water south of the stream remains constant. DOC levels in the lake and stream remain consistent at baseflow, and lower than DOC levels in groundwater, while $\delta^{13}C_{DOC}$ values in the system are confined to a range of -22 to -28 ‰.

Taking both aforementioned chemical and physical aspects, current work has demonstrated patterns in water flow and constituent concentrations during baseflow and storm events for the stream, lake and groundwater. While further exploration is needed in order to determine the sites of methylation and calculate a THg and water budget, the results indicate that Honeysuckle Creek is acting as a legacy mercury source to Burt Lake, providing an additional and more consistent source of mercury other than rainwater.

1. Introduction

The presence of mercury in the environment leads to adverse human and ecosystem effects. The organic form of mercury, methylmercury, can cross the blood-brain barrier, thus acting as a neurotoxin (Harris et al., 2007). Individuals who consume methlymercury-contaminated fish experience neurological symptoms ranging from impairment of speech, vision, hearing, and gait to death (Eto, 2002), while affected fetuses experience extreme effects such as cerebral palsy, seizures, and developmental challenges (ATSDR, 1999). Methylmercury also affects fish populations and those that feed on fish, such as birds, resulting in behavioral, cognitive, hormonal, and reproductive changes (Scheuhammer et al., 2007). The effects of mercury on other ecosystem components such as terrestrial plants or soil microbes, is largely unknown perhaps due to the lack of studies in the field (Chibuike and Obiora, 2014). The mercury cycle has been largely disturbed by anthropogenic activity (ASTDR, 1999; Selin 2009; Bank, 2012) and increased concentrations of the heavy metal travels by means of the hydrologic cycle, entering the system through precipitation and ending up in large water bodies.

Climate change projections for the Midwest call for increased precipitation events and an increase in the severity of these storms (Magnuson et al., 1997; Wuebbles and Hayhoe, 2004). Increased storms will lead to increased runoff and erosion rates due to increasing discharge. Increased erosion will mobilize organic matter into streams and rivers, which are major transport systems of mercury to larger water bodies (Bank 2012; Shuster et al., 2008).

1.1 Sources, species, and cycling of mercury

Although mercury is naturally emitted by volcanoes along tectonic plate boundaries or hot spots from mantle plumes, this naturally-occurring mercury does not provide a substantial input to the hydrosphere, atmosphere and biosphere in Michigan (EPA and MDEQ, 2013). Instead, anthropogenic emissions accounts for a large portion of both global emissions, and emissions delivered to Michigan (Selin, 2009; Harris et al., 2007; EPA and MDEQ, 2013). Globally, 80% of anthropogenic emissions are released into the atmosphere from coal fired powerplants, artisanal gold mining and smelting, and fossil fuel production, while approximately 15% are fed into soils from fertilizers, fungicides and municipal waste, and the remaining 5% results from industrial wastewater that feeds directly into water sources (ATSDR, 1999). The atmospheric emissions cause mercury to serve as a truly global pollutant.

Anthropogenic sources release a variety of different species of mercury: elemental mercury (Hg^0) oxidized mercury (Hg^{2+}), and particulate mercury (Hg^P). Once emitted, Hg^0 can have an atmospheric

lifetime of 0.5-1 years, allowing it to travel long distances, whereas relatively soluble Hg^{2+} and Hg^{P} serve as localized contaminants that are deposited within 1000 km of the source (Selin, 2009; Cohen et al., 2004). Atmospheric deposition of mercury occurs as wet deposition (precipitation) or dry deposition in which plants scavenge Hg^{0} and Hg^{2+} through their stomata (Bank, 2012). As leaves fall and accumulate, mercury is assimilated into the soil matrix, which can retain as much as 80% of the mercury in a watershed. Over time, the "legacy" Hg can be delivered to adjacent water bodies by stream and groundwater discharge, delaying the recovery of aquatic ecosystems (Hintelmann et al., 2002; Bank, 2012). In anoxic environments with sulfur reducing bacteria, such as peatlands and lake sediments, Hg^{0} is methylated into methlymercury (MeHg), the most toxic form of mercury in the environment as it can bioaccumulate to up to a million times the original concentration in the aquatic food web (EPA and MDEQ, 2013).

The two main export mechanisms of mercury once in the environment are volatilization, and transportation by streams, in which mobilized mercury typically has a strong correlation to total organic carbon (TOC) and dissolved organic carbon (DOC) (Bank, 2012).The Hg cycle of deposition, accumulation and reemission reaches its final sink in the deep ocean—the cycle takes an estimated 10,000 years (Selin, 2009).

1.2 Mercury in the Great Lakes region

Sediment cores of both the Great Lakes and inland lakes in the region have shown decreased mercury concentrations in recent years, (Drevnick et al., 2012; UNEP, 2013). The decrease is attributed to regulation-driven declines in atmospheric mercury emissions in the United States over the last twenty years (Selin et al., 2009). Despite an initial decrease in concentrations in fish and bird species, mercury levels in these species are again on the rise in some parts of the Great Lakes region (Evers et al., 2011). As of 2013, out of the 4,709 water bodies in Michigan assessed for impairment, 743 of them (16%) were impaired due to mercury concentrations in the fish, in the water column, or both (EPA and MDEQ, 2013). The high content of vegetation and organic matter in soils in the Great Lakes region allow the widespread forests and peatlands in the area to be particularly efficient at Hg sequestration (Grigal, 2003). The sequestration of mercury in landscapes has been tied to watershed size (Harris et al., 2007) and percent organic matter in the soil (Grigal, 2003). In order to best inform further policy and initiatives to decrease Hg concentrations in aquatic ecosystems, increased resolution of storage, cycling, and transport of Hg is needed. Transport of mercury by streams is already recognized as a main mechanism to deliver THg to larger water bodies, however, relatively few studies have looked at the movement of THg from groundwater inputs to larger water

systems such as inland lakes (Vidon et al., 2013), which is a significant source of water to many lakes in the region (Travick et al., 2009).

1.3 Burt Lake and Honeysuckle Creek

Burt Lake, in Cheboygan County Michigan (Figure 1), is among the state's list of Hg impaired lakes due to high concentrations in the lake's fish (EPA and MDEQ, 2012).

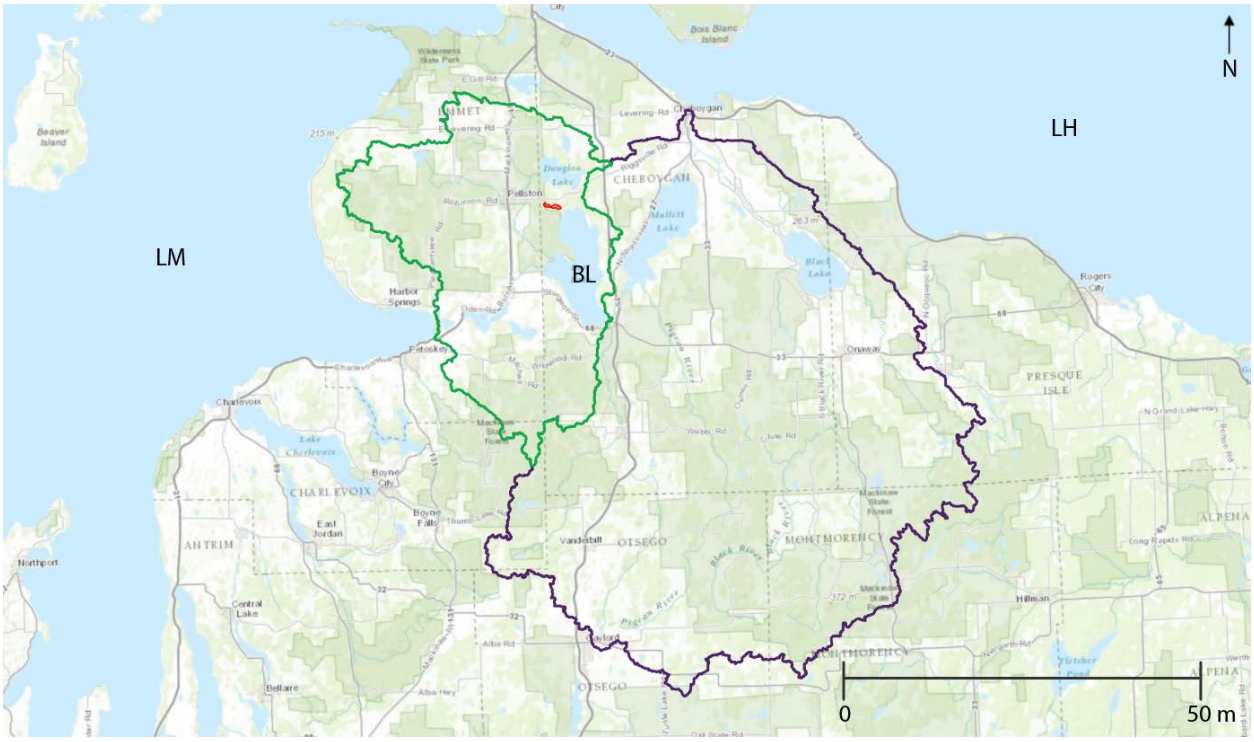

Figure 1: The study area of Burt Lake (BL) and Honeysuckle Creek watershed (in red), which is roughly 130 acres. These study sites are located in northern Michigan, just south of the University of Michigan Biological Station. The study site is located between Lake Michigan (LM) and Lake Huron (LH). The green represents Burt Lake's watershed and the purple the Cheboygan River's Watershed

Burt Lake spans over 17,000 acres and its watershed totals over 250,000 acres. Almost half of the lake's coastline is undeveloped, while the remaining half is residential (Tip of the Mitt Watershed Council, 2012). Honeysuckle Creek watershed was once logged but is now an undeveloped forest owned by the University of Michigan Biological Station. The interface of the watershed and Burt Lake is comprised mostly of muck, while the rest of the lowland is peat, and the mid and upper watershed is a mixture of sand and loamy sand (Nave, unpublished). The area contains over 100 meters of unconsolidated sediment before reaching limestone bedrock. The subtle topography of

the study site complicates remote delineation of Honeysuckle Creek watershed, however the area is estimated as 130 acres.

Coupled stream and groundwater analysis of Honeysuckle Creek watershed allows for exploration of a series of chemical and physical questions: 1) Compared to stream water, does groundwater transport more organic carbon and mercury from the terrestrial landscape to the adjacent lake system? 2) Does the efflux change significantly after a storm event? 3) What does the groundwater table look like? And 4) How does stream water discharge and groundwater flow change from baseflow and in response storm events?

2. Methods

2.1 Sampling preparation and procedure

All sample bottles and equipment were prepared by sitting in a 1% Citranox bath overnight, triple rinsed with Milli-Q water, set into a 10% hydrochloric acid bath overnight, triple rinsed with Milli-Q water, and set under a laminar flow hood to dry. Once dry the equipment was double bagged in clean, resealable plastic bags.

Sampling procedure followed a clean-hands, dirty hands structure following the United States Geological Survey's National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, 2006). The clean hands individual wore gloves and dealt with any clean equipment including the inner bag of sampling equipment, sample bottles, tubing and collection flask if needed. All sample bottles were rinsed with the native water by the clean hands individual at least once by filling the collection bottle part way, capping the bottle, turning it over at least three times, uncapping the bottle, and pouring the liquid out. Clean hands changed gloves between stations or once he/she touched anything not considered clean. The dirty hands individual opened the outer bag of the equipment, and dealt with any equipment not sanitized (i.e. hand pump, water table recorder, tape measure, etc).

Once collected, the samples were placed on ice until reaching the laboratory where they were stored in the refrigerator until filtration. All groundwater samples were filtered in order to measure the dissolved constituents in the water. Both unfiltered and filtered THg and MeHg samples were collected to measure both the mercury bound to particulate matter and the dissolved mercury component.

2.2 Groundwater sampling

In order to adequately sample the groundwater both in chemical and physical properties, a set of piezometers were installed along the 50-meter study site equally distributed on either side of Honeysuckle Creek. A series of six shallow PVC onshore piezometers were located along a S-W verging transect, herein referred to as sampling piezometers. Three additional onshore piezometers, further to the west of the aforementioned transect, were installed in order to help quantify groundwater flow, and will be referred to as parameter piezometers (Figure 2).

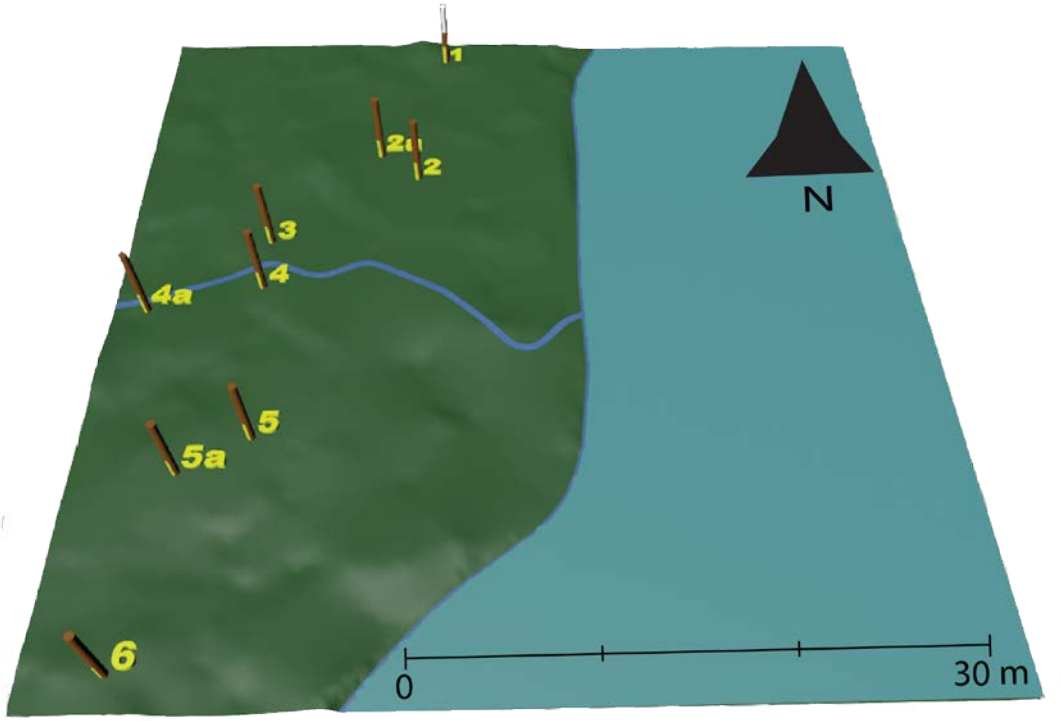

Figure 2: The well field of the Honeysuckle Creek study site. Piezometers 1-6 are the sampling piezometers, while 2a, 4a, and 5a are parameter piezometers. Parameter piezometers were installed to provide increased resolution of water table height, pH and specific conductivity. After installation, all piezometers were pumped on three different dates to remove any artifact sediment from installation.

During a two-week period from July 27th to August 6th, samples were collected for analysis of total mercury (THg) or all mercury species, MeHg, DOC and $\delta^{13}C_{DOC}$ from the sampling piezometers on five different dates, including the day after a storm event. Before starting the sampling process, water level was recorded by using a fishing bobber, to which the prerecorded measurement of the piezometer that was above the soil was later subtracted. After water level was taken, clean hands put on gloves, and would insert a roughly 160 cm, ¾ inner diameter Teflon tube into the piezometer. Clean tubing was used for each sampling piezometer. Leaving the flask in the double ziploc bags, clean hands attached the tubing to the special Teflon fitting for a 500 mL volumetric filter flask and the Tygon tubing from the hand pump to the sidearm of the filter flask. The dirty hands would begin to pump the piezometer, taking out roughly 50-100 mL for the sample rinse. Clean hands rinsed the filter flask by lightly swirling the piezometer water in the flask before dumping it. After the rinse, dirty hands would begin to pump until the piezometer was dry or until more than the needed 250 mL was collected. Clean hands would pour the sample volume into the

sample bottle, a 250 mL amber glass bottle, after completing a native rinse of the bottle. Clean hands placed and secured the bottle in the inner bag, while dirty hands would secure the outer bag.

One procedural blank was taken for both sets of analysis. One method blank was taken to measure potential contamination of the fishing bobber used for taking water table height.

After the sampling piezometers were pumped, a YSI ODO water quality probe was inserted to measure the temperature. Once all mercury samples were collected, one of the piezometer tubes and the filtration flask were used to pump all parameter wells. These samples were collected in 150 mL Citranox washed plastic sample bottles to be tested in the lab for specific conductance, using an Oaklon ECTester 11+ probe, and pH, using a Mettler Toledo SevenCompact meter.

2.3 Surface water sampling

A Parshall flume was leveled with a gravel bed and installed according to USGS guidelines of constricting flow to the flume entrance by piling sandbags on either side of the bank (Figure 3).

Figure 3: The Parshall flume installed to measure discharge on Honeysuckle Creek. The stream samples were taken just downstream of this flume. The photo was taken downstream and the flume measured a half a foot wide.

During the two week sampling period, samples were collected in five different locations along the stream for two dates. A total of seven dates at a single sampling site downstream of the flume were recorded, including multiple samplings during one storm event. All grab samples were taken at the middle of the stream, with the bottle opening facing upstream (U.S. Geological Survey, 2006). One replicate was taken during the two-week sampling period.

Gauge height was recorded using the water height in the Parshall flume at a specified location. These heights were then converted to discharge using empirically determined charts from the USGS.

Lake water samples were collected at four dates, including multiple samplings during a storm event, that parallel stream sampling. All samples were taken roughly 15 meters from shore, and are integrative of the sampling area. Samples were taken from a canoe to reduce disruption of sediments. Two replicates were taken of lake samples during the two-week sampling period.

Temperature of both stream and lake water was recorded, while sample volume was collected to test for conductance and pH in the laboratory with the tools and equipment in the above groundwater sampling section.

2.4 Water filtration and analysis

Filtered samples were filtered using the USGS method for particulate filtration of field samples (USGS, 2006). Filters were prepped by combusting them at 550°C for six hours in a muffle furnace. A Teflon union was placed on a 500 mL filtration flask, and after rinsing the union with Milli-Q water, a 47 mm quartz glass fiber filter was placed on the filter holder using Teflon forceps. The filter was rinsed with Milli-Q water, and a small portion of sample volume before filtering the volume kept for analysis. For the piezometers, only filtered sample volumes were processed for THg, MeHg DOC, and $\delta^{13}C_{DOC}$, while the stream and lake samples were analyzed for unfiltered and filtered THg, and MeHg, then filtered DOC and $\delta^{13}C_{DOC}$. Unfiltered and filtered samples were transferred to 40 mL glass amber vials and THg and MeHg samples were acidified with 200 μg of trace metal grade hydrochloric acid. All work was done under a clean laminar flow hood setting.

Once prepared for analysis, samples were stored in the refrigerator. THg and MeHg samples were transported to Ann Arbor, MI on ice. All THg samples were run within roughly two weeks of collection and MeHg samples were run during the summer of 2015.

Unfiltered and filtered THg was analyzed at the Radiogenic Isotope clean lab at University of Michigan, Ann Arbor using a Brooks Rand MERX following method EPA 1631 (EPA, 2002) for THg. Approximately 25 mL of the sample was used for this analysis and 0.100 mL of 30% Hydroxylamine and 20% Stannous Chloride were added to each sample vial. In total 103 samples were run.

Unfiltered and filtered MeHg was analyzed at the same facility at University of Michigan, on the Brooks Rand MERX analyzer. All samples underwent vapor distillation, following EPA Method 1630 (EPA, 1998) in order to remove any organic particulate matter that would skew the data. Roughly 30 mL of sample was placed in one set acid washed Teflon distillation tubes, and 2 mL of reagent was added to each tube. The reagent was made of 7.805 grams of copper sulfate, 5 grams of potassium chloride and 25 mL of sulfuric acid. In the second set of distillate tubes, roughly 5 mL of

deionized water (DI water) was measured. Initial weights of the distillation tubes, along with the starting sample weight, were recorded. After preparation, sample tubes were placed into a distillation block connected to a hot plate, which maintained a temperature of 125°C, and the distillation tubes in a metal distillation block in an ice bath. The sample and distillation tubes were connected by Teflon caps with tubes to carry the distillate vapor from the sample tube to the distillation tube. Nitrogen gas flowed through the samples to aid this process. The samples were left to vaporize for roughly two hours, or until roughly 80% of the sample volume carried over to the distillate tube. In total, six method blanks were added to the distillation process, and two spiked blanks. The final weight of the distillation tube was recorded, and samples were kept cold until sample preparation.

Approximately 25 mL of distillate (exact weight was recorded) was added to the 40 mL amber glass vials used with the Brook Rand MERX analyzer. The samples were diluted with DI water up to the neck of each vial, approximately 15 mL, then 300 μL of acetate buffer, and 50μL of sodium tetraethylborate were added. DI water was added to the samples until a positive meniscus formed, then each sample was capped with septum caps. A series of procedural blanks were analyzed during each run. The calibration curve was formed from a series of methylmercury chloride standards. Multiple check standards of methylmercury hydroxide were included in each run, along with certified reference material of fish digestate.

DOC and $\delta^{13}C_{DOC}$ were analyzed at the University of Michigan Biological Station using an Aurora 1030W TOC Analyzer in conjunction with a Delta^{PLUS} XP stable isotope mass spectrometer. At the beginning of the run, one blank and a 5-point calibration curve were developed using tanic acid. After every ten samples two check standards of tanic acid and sucrose were measured to account for drift of concentration and isotopic signature. Seventy-one samples were analyzed, where all sample values are an average of three draws. Values are reported as per mil (‰) deviations from the PDB standard.

Ion chromatography and inductively coupled plasma-optical emissions spectrometry were carried out at Washington and Lee University. The water samples used for analysis were both surface water and groundwater samples were collected on August 14. These samples were all filtered with a 0.20 μm filter at the University of Michigan Biological Station and then shipped to Washington and Lee overnight. Two of the samples bottles, P1 and P2A, broke during storage of the sample bottles and were filtered a second time before analysis.

2.5 Statistical analysis

All statistical processing of the data was completed using IBM SPSS software. All sampling dates were treated as independent variables and piezometers were grouped into north and south of the stream, averaging their values. All data were checked for normal distribution before running statistical analysis.

2.6 Software modeling

Interpolated 2D visual groundwater levels and concentrations were created in ArcMap by importing the physical and chemical results into the attribute table of a point feature, then running the Geostatistical Analyst toolbox for the Geostatistical Wizard Kernal Smoothing method. Surfaces were created for SpC, THg, MeHg, DOC, $\delta^{13}C_{DOC}$, and water table level. The stream was input as a barrier to interpolation methods in order to best represent the dichotomy between the groundwater north and south of the stream. The values were interpolated following an exponential kernal function, which follows equation 1 where *r* is the centered radius at a point, and *h* is the bandwidth. For consistency and for their visual appeal the bandwidth was set at 22.26, and the radius at 22.

$$e^{-3(\frac{r}{h})} \quad \text{Equation 1.}$$

Groundwater flow was modeled using the EPA's SMARTe on site calculator, which uses the x, y, and head (water table elevation) to fit a plane to the groundwater surface, determining the flow and magnitude of groundwater. The north and the south planes were calculated separately.

2.7 Hydraulic conductivity

Methods for estimating hydraulic conductivity for organic dominated soils involve quantifying texture or grain size, and percent organic matter. Soil cores were taken near the piezometers (Figure 4) and sent to Washington and Lee from the University of Michigan Biological Station for further analysis.

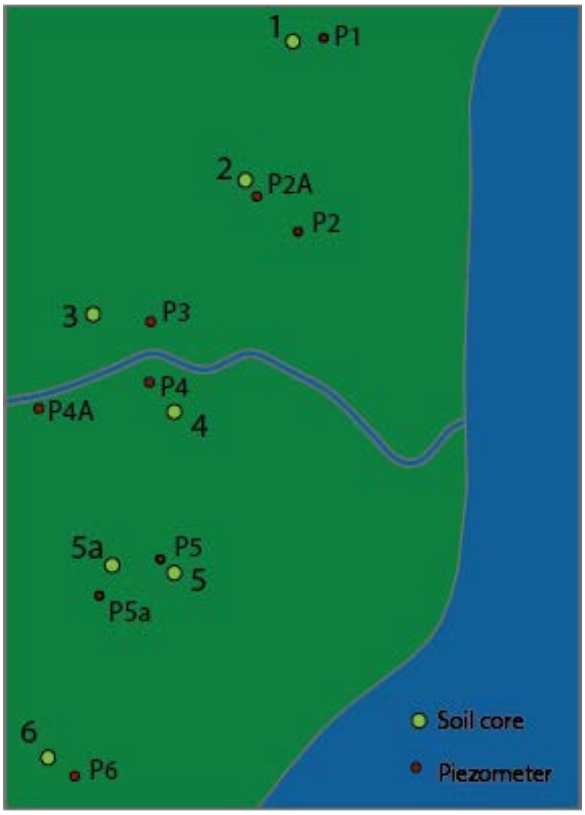

Figure 4: Distribution of the seven soil cores taken and their proximity to the sampling piezometers. The cores are named in relation to the closest piezometer.

In order to quantify grain size, all soils were sieved using a Ro-Tap Sieve Shaker with the distribution of sieves from 2mm-0.038 mm, decreasing by half increments with the exception of moving from 0.25-1mm due to a missing sieve. The samples passed through a 4mm sieve before using the Ro-Tap set up to remove larger debris. Each sample was weighed and then saved in either clean plastic bags or small plastic vials.

Soils <2mm in diameter were dried in an oven at 105°C overnight, weighed, combusted at 360°C in a muffle furnace for two hours, and weighed after combustion following the loss on ignition method outlined by Salehi et al. (2011). These methods determined the percent carbon in each soil core in particles <2mm. Soils with large fractions for particular soil size were kept separate for the combustion process, and the percent loss was then averaged for each particle size.

Equations 2 and 3, modified from Jutras and Arp (2011), were used to determine the hydraulic conductivity of each soil type. In equation 2, Dp is the mean particle density of the soil, Db is the bulk density of the soil, SAND is the fraction of the soil that is sand, DEPTH is the mean depth of the soil horizon, and OM is the fraction of the soil that is organic carbon. In equation 3, Ksat is saturated hydraulic conductivity, Dp is mean particle density, Db is bulk density, and SAND is the fraction of the soil that is sand.

$$Dp = \frac{(1+6.38(OM)-1.23}{(1-\exp(-0.0106Depth))} + 1.23 + 0.75SAND \quad \text{Equation 2.}$$

$$log_{10}\, Ksat = -0.98 + 7.94\, log_{10}\,(Dp - Db) + 1.96SAND \quad \text{Equation 3.}$$

2.8 Soil core carbon isotopes

A fraction of the sieved and unsieved soil cores were set aside for stable isotope analysis. The soils were homogenized and ground with mortar and pestle, placed on glass watches, and then dried at roughly 60°C for 48 hours. Ten samples with known isotopic compositions that were run at the University of Michigan Biological Station, and were used to calibrate the Washington and Lee mass spectrometer with the University of Michigan Biological Station mass spectrometer, were also dried with these samples. The ground and dried samples were kept in plastic vials inside a dissector. The amount of sample volume that would be appropriate was determined using the University of California Davis's Stable Isotope Facility online Sample Weight Calculator, in which the expected percent carbon for each soil type was entered to get the amount of sample that should be run. The mass need for each soil type ranged from 1 mg to almost 16 mg. These samples were weighed on the microbalance in 5x9 pressed flat bottom tin cups, using tools and surfaces that were cleaned with ethanol between each sample. Each sample was tin-balled, along with a duplicate, recording each weight. Samples were analyzed in order, from highest carbon content to lowest. Each run started with a sample to bypass the column in elemental analyzer (EA) in order to equilibrate the machine to the chemistry of the samples, a series of blanks (balled tin cups) and standards. A set of standards and reference materials were analyzed between every 12 samples, in order to check for instrument drift. The standard used was 0.5 mg and 1 mg of Acetanilide, and the reference materials were USGS 40 L-Glutamic Acid and USGS 41 L-Glutamic Acid. Values are reported as per mil (‰) deviations from the PDB standard.

3. Results

3.1 Chemical hydrology

Groundwater

Table 1 summarizes the range and average values for the groundwater concentrations of THg, MeHg, DOC, and $\delta^{13}C_{DOC}$ along with water quality parameters of temperature, specific conductance, and pH. Full results are available in Appendix 1.

Table 1: The range and averages of temperature, specific conductivity, pH, filtered total mercury, dissolved organic carbon and the carbon isotopic values for the groundwater. Below these values are broken into north and south.

Groundwater	Temperature (°C)	Specific Conductance (µs/cm)	pH	Filtered THg (ng/L)	DOC (mgC/L)	δ13C (‰ vs. PDB)
Maximum	14	453	8	2.88	29.6	-22.40
Minimum	11	232	6.8	0.00	0.24	-26.98
Average	12	315	7.5	0.52	11.4	-25.92

Groundwater North	Temperature (°C)	Specific Conductance (µs/cm)	pH	Filtered THg (ng/L)2	DOC (mgC/L)	δ13C (‰ vs. PDB)
Maximum	13.80	395	7.9	2.88	28.08	-26.20
Minimum	12.10	232	6.9	0.46	1.67	-28.60
Average	12.77	288	7.3	1.26	14.90	-27.43

Groundwater South	Temperature (°C)	Specific Conductance (µs/cm)	pH	Filtered THg (ng/L)2	DOC (mgC/L)	δ13C (‰ vs. PDB)
Maximum	14.40	359	8.0	0.26	29.61	-22.32
Minimum	12.10	320	7.4	0.00	0.24	-27.41
Average	12.88	336	7.8	0.06	5.16	-24.91

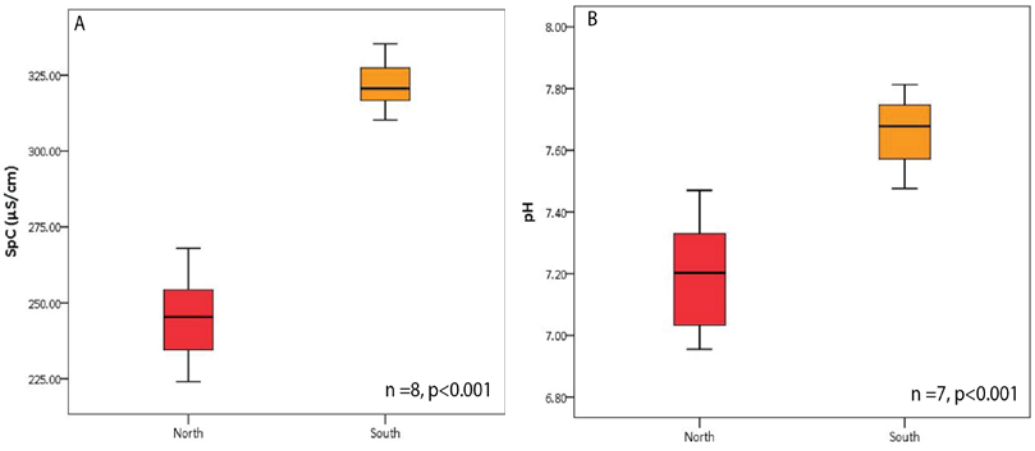

Figure 5: Box plots showing the statistically significant differences between the wells north of the stream (P1, 2 and 3) and those south of the stream (P 4, 5 and 6). A shows the differences in specific conductivity,

Significant differences were found between the north (P1, P2, P2a, and P3) and south piezometers (P4, P4a, P5, P5a, and P6) in specific conductance (n=8, p<0.001) and pH (n=7, p=0.001) (Figure 5).

Overall, north piezometers have significantly lower specific conductance and pH values than the south grouping of piezometers. Temperature and THg values are not statistically significantly different (n=8, p=0.121 and n=5, p=0.112 respectively). Average values of DOC are higher in the

north piezometers, with a slightly lower $\delta^{13}C_{DOC}$ values (Table 1). Temperature, water table, specific conductance, and pH are not significantly correlated with THg concentrations in neither the north nor south piezometers.

There is a large increase in THg, and after the August 2nd storm event in the north piezometers (Figure 6). DOC values are highest in the groundwater with close proximity to the stream (Figure 7). The $\delta^{13}C_{DOC}$ values show a delayed response to the storm event (Figure 8). The spatial SpC data

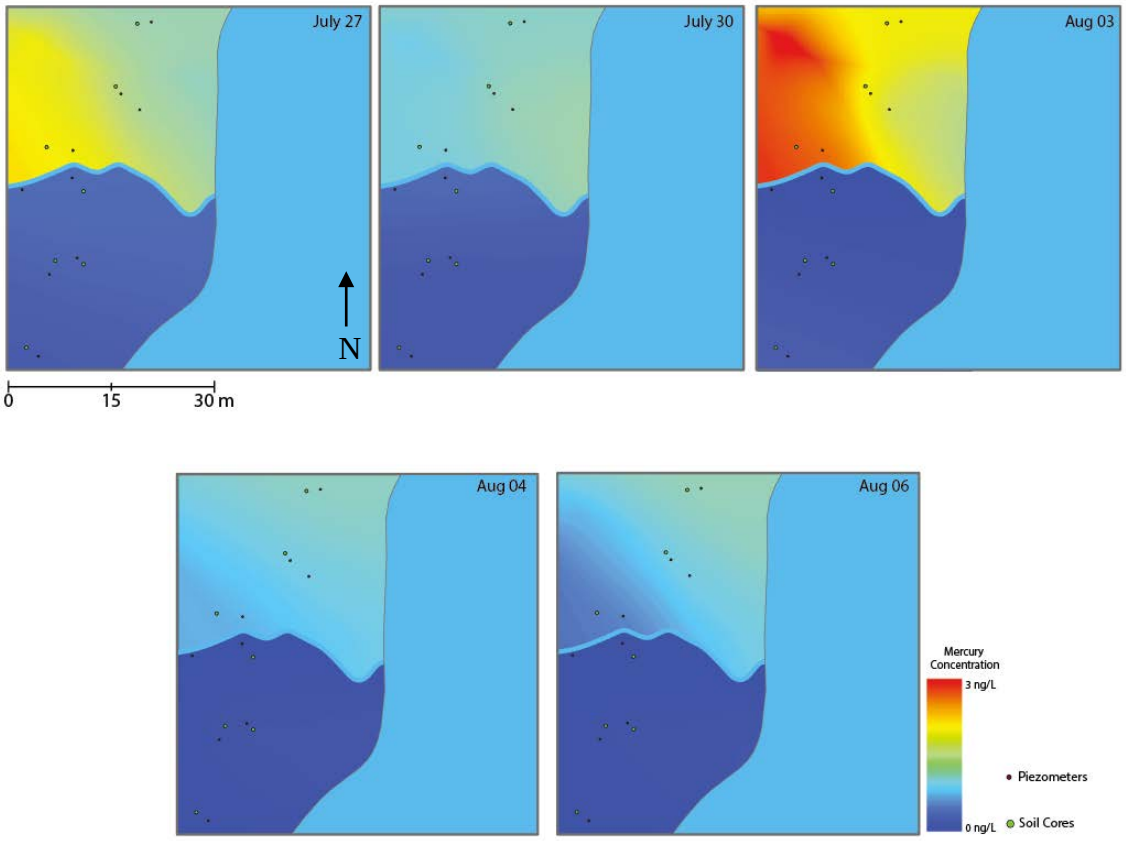

Figure 6: Interpolated filtered THg concentrations in groundwater. The mercury concentrations spike on August 3rd, a day after the storm event, and then return to lower concentrations. Notice that mercury concentrations only rise on the north side,

show low conductivity values on August 4th (Figure 9). Filtered MeHg interpolation values are variable, however are mostly very low (Appendix 5). Major dissolved anion, cation, and trace element data are shown in Tables 4 and 5 respectively. The IC results show two grouping of data, one set of data shows that the groundwater south of the stream has little in common with surface water bodies, while the north groundwater is similar to the stream and the lake (Figure 10). The major ion data shows dissolution of carbonate bedrock (Figure 11).

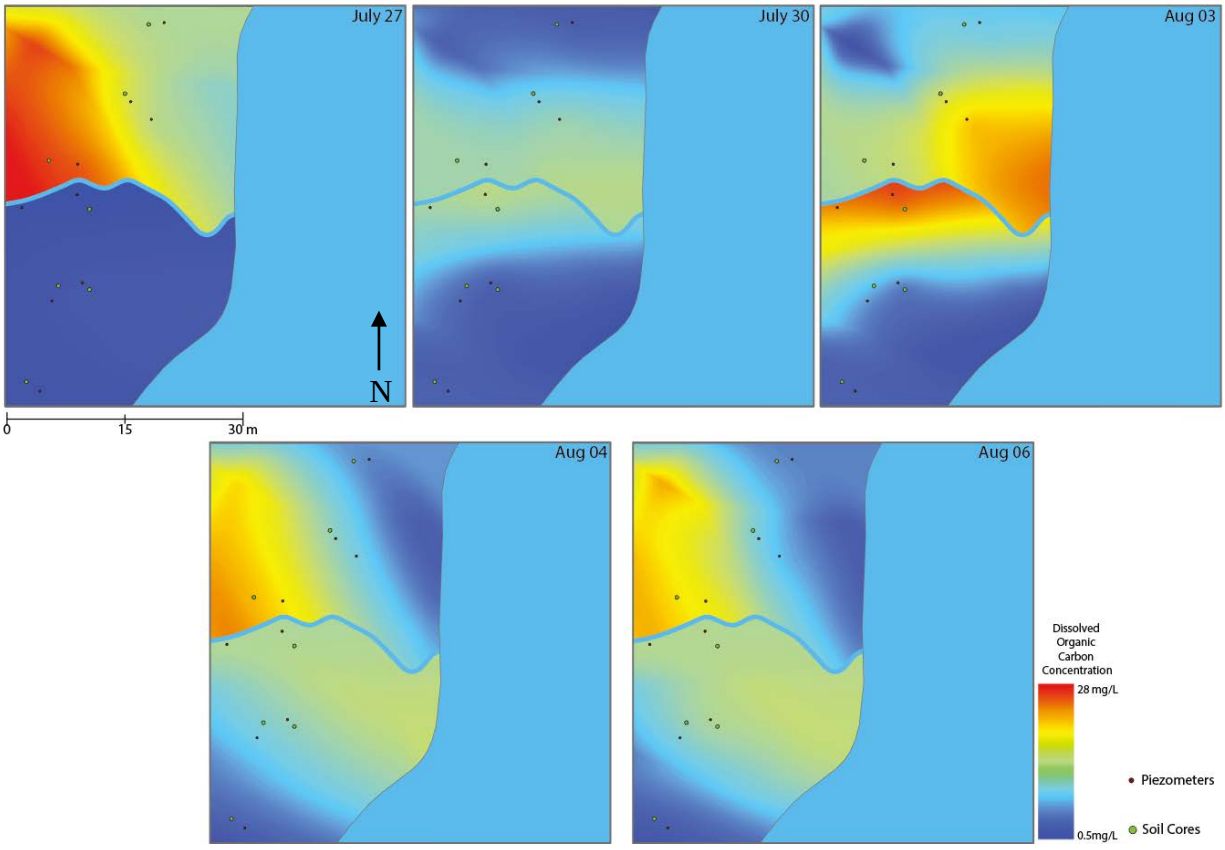

Figure 7: Interpolated DOC concentrations for the groundwater table. The DOC starts out high, on the north side. The concentrations then seem to increase after the storm, but mostly by the stream.

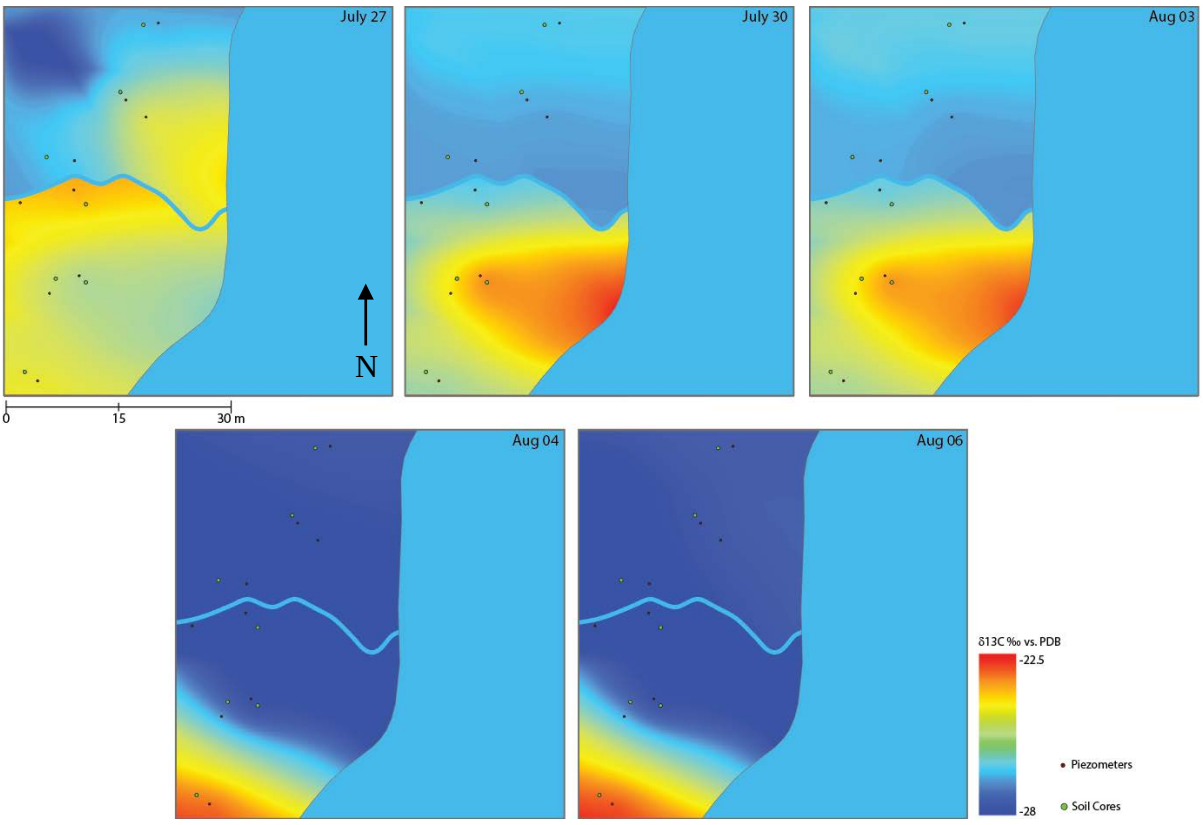

Figure 8: Interpolated $\delta^{13}C$ groundwater values.

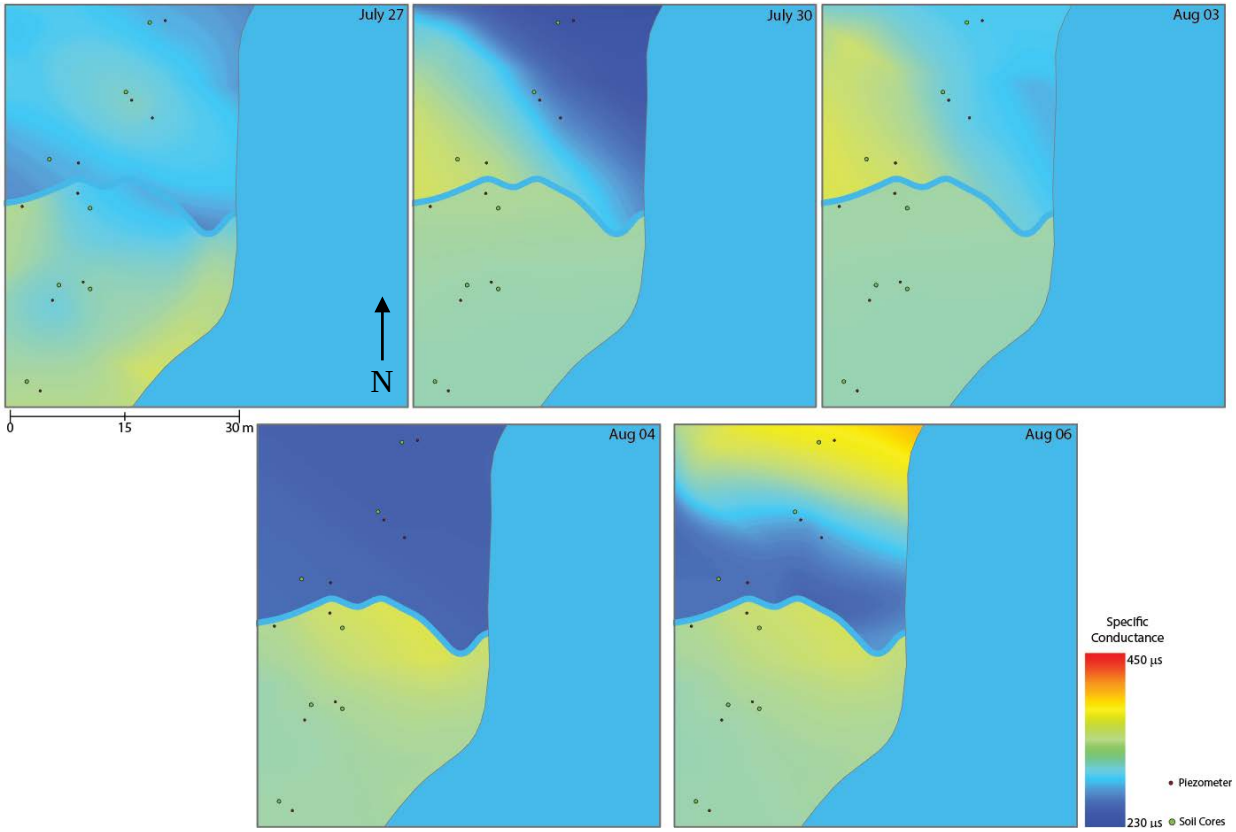

Figure 9: Interpolated groundwater values for specific conductance.

Table 4: The concentrations of major dissolved ions at two locations at the stream, three locations at the lake where lake 1 was taken from the center of the lake, lake 2 was taken where the samples are typically taken and lake 3 was taken at the south end of Burt Lake and all piezometers.

Sample	Ammonium	Calcium	Lithium	Magnesium	Potassium	Sodium	Bromide	Fluoride	Nitrate	Chloride	Nitrite	Phosphate	Sulfate
stream 1 8/12/15 10:28	BDL	29.60	BDL	14.39	0.58	6.80	BDL	0.07	0.22	5.60	BDL	0.07	4.06
stream 3 10:37	BDL	30.39	BDL	14.90	0.63	6.55	BDL	0.07	0.32	5.27	BDL	0.08	4.00
lake 1 mid-lake 9:43	BDL	33.29	BDL	13.27	0.63	8.82	BDL	0.07	0.15	9.75	BDL	0.06	10.11
lake 2 study area 9:33	BDL	32.82	BDL	13.62	0.59	8.88	BDL	0.08	0.11	9.97	BDL	0.14	9.95
lake 3 indian river 13:53	BDL	30.69	BDL	12.44	0.59	8.66	0.13	0.09	0.52	14.07	BDL	0.07	9.46
P1 10:47	BDL	8.86	BDL	4.66	0.49	3.15	0.06	BDL	0.33	1.75	BDL	0.09	3.41
P2 11:07	BDL	33.61	BDL	12.31	0.81	7.55	0.13	BDL	0.09	11.17	BDL	0.29	2.72
P2A 11:16	BDL	7.64	BDL	4.02	0.31	3.60	BDL	BDL	BDL	2.60	0.08	0.09	0.62
P3 11:19	BDL	27.95	BDL	10.47	0.46	6.09	0.14	BDL	0.19	7.05	BDL	0.26	0.97
P4 11:27	BDL	26.54	BDL	20.75	1.07	12.59	0.05	0.34	0.12	2.66	BDL	0.33	9.93
P4A 11:27	BDL	31.66	BDL	15.42	0.67	3.73	0.28	0.11	0.18	0.74	0.33	0.10	8.73
P5 11:57	BDL	26.09	BDL	18.04	0.88	10.22	0.14	0.25	0.08	2.89	BDL	0.28	3.69
P5A	BDL	24.81	BDL	14.85	0.66	8.73	0.18	0.20	0.10	4.11	BDL	0.69	2.25
P6 12:00	BDL	25.82	BDL	18.48	0.85	7.35	0.18	0.25	0.05	1.32	BDL	0.10	2.86

BDL=Below detection limit

Table 5: The concentrations of trace elements at two locations at the stream, three locations at the lake where lake 1 was taken from the center of the lake, lake 2 was taken where the samples are typically taken and lake 3 was taken at the south end of Burt Lake, and all the piezometers. All concentrations are reported in ppb. The elements observed are expected in this undeveloped system with limestone bedrock.

Sample	Al	Fe	Na	K	Cr	Mn	Co	Cu	Sr	Zn	Cd	Ti	Pb	Ni	V
stream 1 8/12	2.40	26.9	6285	918	BDL	4.05	BDL	BDL	54.0	3.76	BDL	BDL	BDL	BDL	BDL
stream 3	2.32	28.7	6075	920	BDL	5.56	BDL	BDL	46.2	4.14	BDL	BDL	BDL	BDL	BDL
lake 1 midlake	1.72	2.36	7728	992	BDL	4.59	BDL	15.37349	178	2.96	BDL	BDL	BDL	BDL	BDL
lake 2 study area	1.74	9.02	7575	996	BDL	5.91	BDL	BDL	139	6.01	BDL	4.91	BDL	BDL	BDL
lake 3 indian rive	BDL	5.74	7369	970	BDL	4.02	BDL	BDL	128	6.51	BDL	4.48	BDL	BDL	BDL
P1	BDL	12.5	2631	536	BDL	6.20	BDL	BDL	17.8	17.3	BDL	5.55	BDL	BDL	BDL
P2	3.28	28.4	6865	1226	BDL	6.36	BDL	BDL	57.4	71.0	BDL	5.91	BDL	BDL	BDL
P2a	BDL	15.85	2864	357	BDL	15.2	BDL	BDL	24.3	16.3	BDL	5.77	BDL	BDL	BDL
P3	4.03	96.4	5306	632	BDL	16.5	BDL	BDL	54.0	34.6	BDL	6.64	BDL	BDL	BDL
P4	1.88	32.2	10763	1645	BDL	7.08	BDL	BDL	329	4.28	BDL	4.19	BDL	BDL	BDL
P4a	2.58	20.4	3632	1234	BDL	22.0	BDL	BDL	93.9	22.1	BDL	4.48	BDL	BDL	BDL
P5	2.04	18.4	8635	1325	BDL	13.9	BDL	BDL	226	2.31	BDL	5.38	BDL	BDL	BDL
P5a	2.44	24.1	7486	1040	BDL	23.4	BDL	BDL	102	3.16	BDL	6.04	BDL	BDL	BDL
P6	1.90	6.66	6642	1389	BDL	23.8	BDL	BDL	406	BDL	BDL	BDL	BDL	BDL	BDL

BDL=Below detection limit

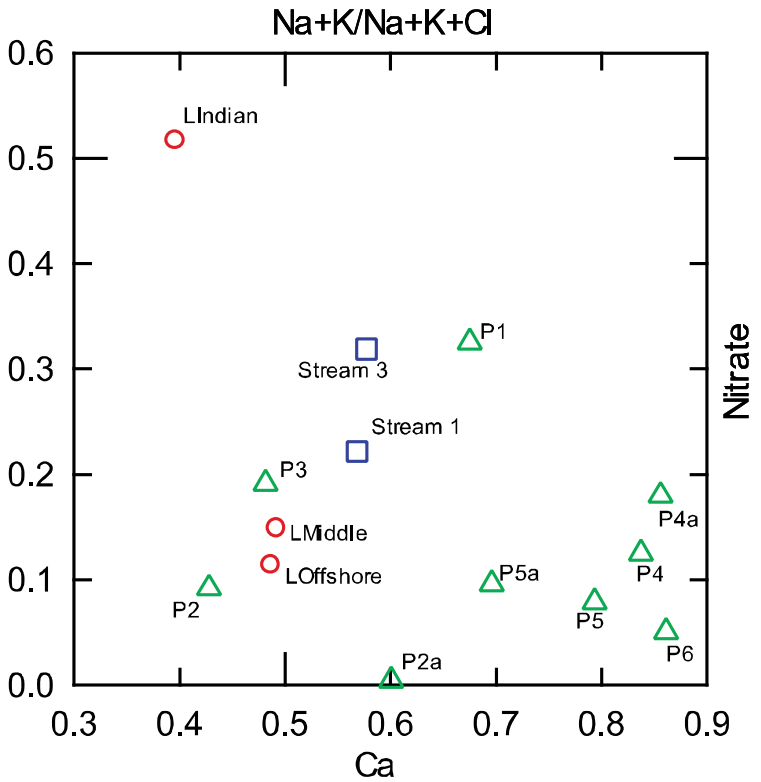

Figure 10: IC data of major dissolved ions vs. nitrate. The more nitrate the sample has in it, the more influence the sample is by anthropogenic surface activity. There are three main groups: a high salt ion and low nitrate ion made of the south piezometers, a middle group with mid salt ions and mid nitrate values and a low salt high nitrate value at the Indian River sample site.

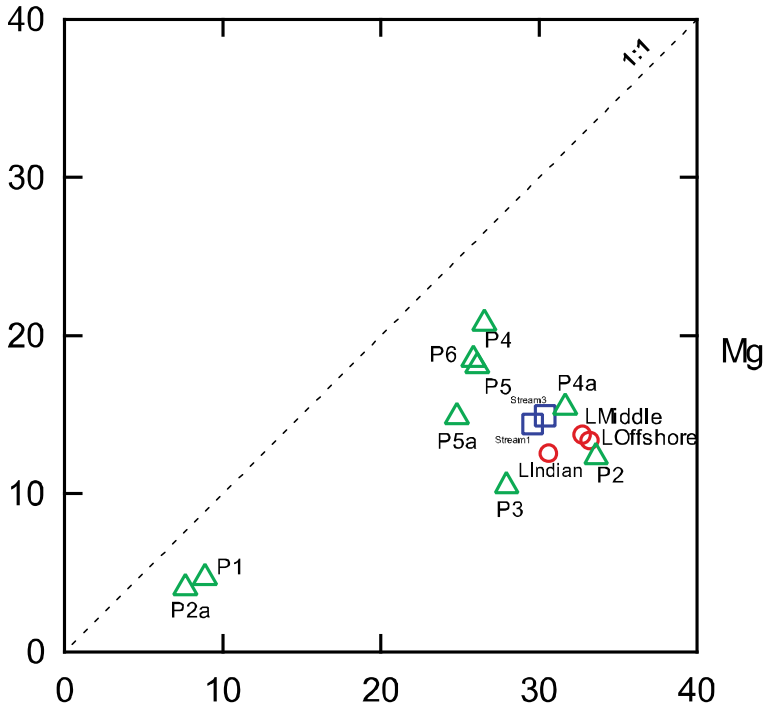

Figure 11: IC data of calcium vs magnesium. All of the samples fall below the Ca, Mg unity line meaning they are dissolved mostly dolostone bedrock.

Surface water

Table 2 summarizes the range and average values for concentrations of THg unfiltered and filtered, unfiltered MeHg, DOC, and $\delta^{13}C_{DOC}$, discharge (Q) and HgFlux along with water quality parameters of temperature, specific conductance, and pH for Honeysuckle Creek. HgFlux was calculated by taking *THg (unfiltered)*Q=HgFlux*. These results are tabulated in full in Appendix 2.

Table 2: The range and averages of temperature, specific conductivity, pH, unfiltered total mercury, and methylmercury, dissolved organic carbon and the carbon isotopic value, discharge and mercury flux for the stream. Here the maximum account for the storm events, and the minimum for baseflow conditions.

Stream	Temperature (ºC)	Specific Conductance (µs/cm)	pH	Unfiltered THg (ng/L)	Filtered THg (ng/L)	MeHg (ng/L)	DOC (mgC/L)	δ13C (‰ vs. PDB)
Maximum	14.6	324	8.1	2.6	0.95	2.895	5.54	-24.45
Minimum	13.2	288	7.1	14.2	0.62	0.168	4.37	-27.53
Average	14.1	307	7.7	6.4	0.79	0.819	4.96	-25.99

On average, there are higher values of DOC, MeHg and HgFlux during the August 2nd storm event than at baseflow (Figure 12).

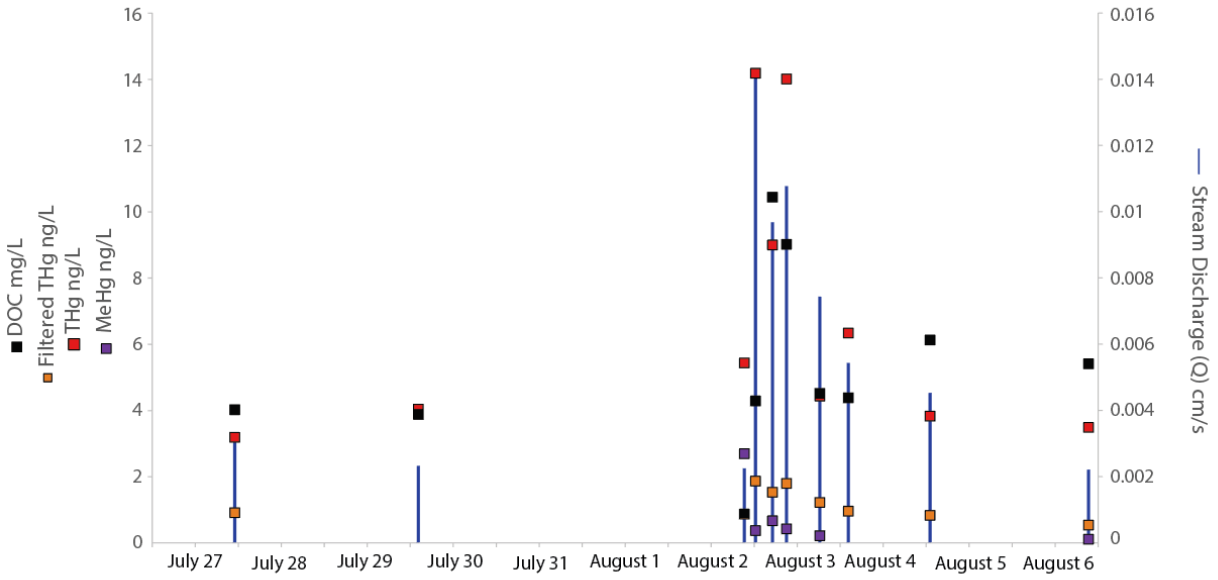

Figure 12: Discharge, DOC, filtered THg, unfiltered THg and MeHg in Honeysuckle Creek. Discharge increased with the storm event, and with that increased discharge there is an increase, or a peak in all other parameters. Total unfiltered mercury is greater than filtered mercury concentrations and the dissolved organic carbon peak does not increase as dramatically either.

Filtered THg was found to be significantly higher during the storm event ($p=0.021$), while particulate (unfiltered-filtered) THg was almost significantly higher ($p=0.051$).

The stream has significantly lower concentrations of filtered THg than the north group of piezometers (0.003), and has on average higher concentrations of THg than the south group of piezometers, but no significant difference was found.

Table 3 summarizes the range and average values for concentrations of THg unfiltered and filtered, MeHg, DOC, and $\delta^{13}C_{DOC}$, along with water quality parameters of temperature, specific conductance, and pH for Burt Lake. These results are tabulated in full in Appendix 3.

Table 3: The range and averages of temperature, specific conductivity, pH, unfiltered total mercury, filtered total mercury, dissolved organic carbon and the carbon isotopic values for the lake. Similar to the stream the maximum accounts for the storm values and the minimums for normal baseflow conditions.

Lake	Temperature (ºC)	Specific Conductance (µs/cm)	pH	Unfiltered THg (ng/L)	Filtered THg (ng/L)	DOC (mgC/L)	δ13C (‰ vs. PDB)
Maximum	24	339	8.6	13.8	0.62	8.5	-26.33
Minimum	21	324	8.4	0.01	0.01	4.4	-26.80
Average	22	330	8.5	1.7	0.21	5.0	-26.71

During the August 2nd storm event, THg unfiltered peak, and average levels increase (Figure 13), however there were no significant differences found between baseflow and storm particulate ($p=0.41$) and filtered THg ($p=0.28$). Stream and lake major dissolved ion and trace element

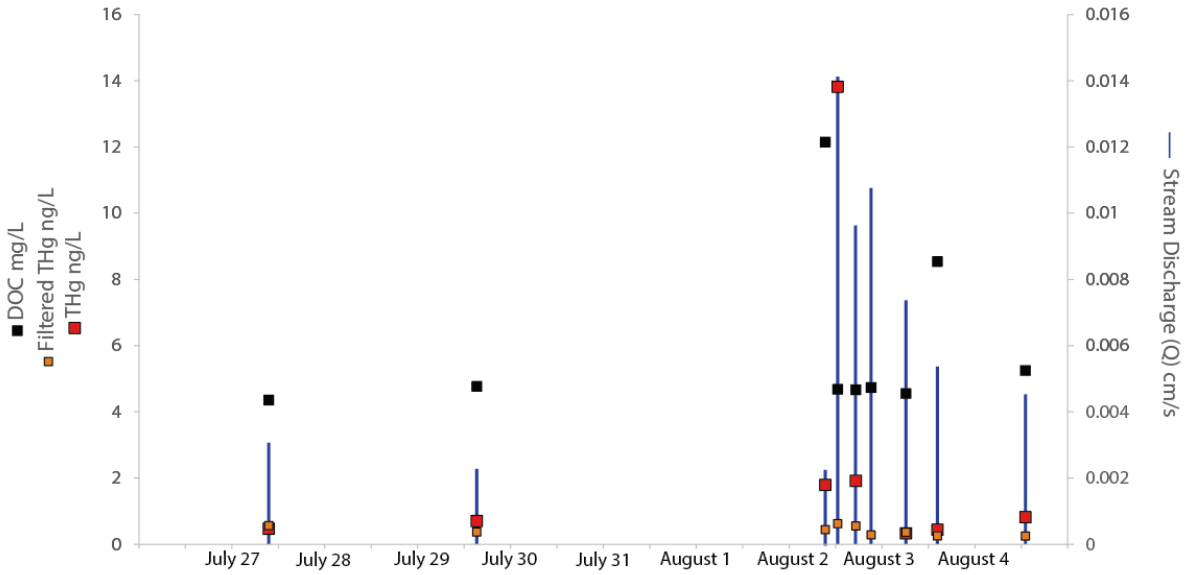

Figure 13: DOC, filtered THg, and unfiltered THg plotted against stream discharge in order to track the impact of the storm event. Concentrations of all constituents are much lower than the stream values, except for one peak during the storm event.

concentrations are shown in Tables 4 and 5 respectively.

Reported mercury concentrations in rain water are from the Mercury Deposition Network (MDN) for the station at Douglas Lake, just north of Burt Lake. The data from 2014 is the only data

available, and will be used to estimate the input of mercury to the Burt Lake environment from precipitation. On average, the concentration of rain during a storm event is about 10 ngL^{-1}. The data download from the MDN are tabulated for the months of July and August for 2014 in Appendix 4. Weekly precipitation data, gathered from Weather Underground at the Pellston airport site roughly 7.5 miles from Honeysuckle Creek for July and August of 2014 and for the sampling period are tabulated in Appendix 4.

3.2 Physical hydrology

Water table measurements show that on July 27th, prior to the storm event, the water table is gently sloping from south to north (Figure 14).

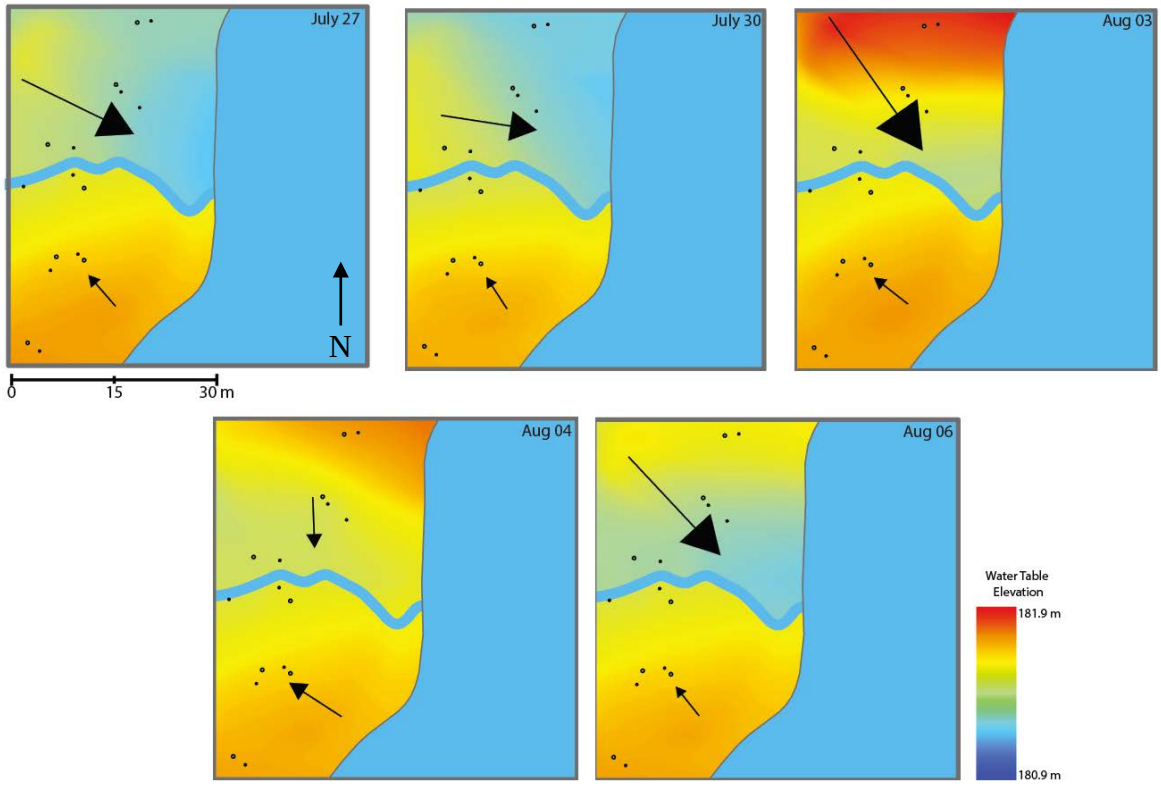

Figure 14: Interpolated groundwater water table elevation. The most notable observation is that the south side is usually high and less variable, while the north side is more dynamic, as it is low before the August 2 storm event, and then increased by 37 cm as a result of the storm. The arrows denote the water flow path and their size indicate magnitude. The north increased in magnitude due to the storm event, and also changes flow path direction.

After the rain event the north piezometers, P1-P3, record an increase in water table elevation of 37 centimeters, whereas the south group, especially P5 and P6, remain relatively constant during the precipitation event. The water flow arrows calculated by the EPA's online SMARTe tool based on

the orientation of a best-fit triangulation show that groundwater movement in the north is of much greater magnitude, and increases in magnitude after the storm event. In the north, the water flows mostly southeast toward the lake or the mouth of the stream. At slower magnitudes, the water flow moves east toward the lake. When the water table is higher in the north during the storm events, the water table moves in a southward direction toward the stream. Groundwater on the south side, flows northwest, again towards the stream, at a much slower magnitude relative to the north side. During the storm events, the magnitude increases slightly, while the direction seems relatively constant.

Stream discharge increased during the storm event from a baseflow of approximately 0.003 cubic meters per second to a peak of 0.014 cubic meters per second and returned to baseflow conditions within roughly four days. (Figure 13). Baseflow conditions in this study are all data collected on date other than August 2nd and 3rd, while stormflow conditions are data collected on August 2nd and 3rd.

3.3 Soil core analysis

There are two main groupings of soils types, those mostly comprised as sand, and those made of silt. Most of the soil cores taken south of the stream fall under the sand classification (Figure 15). Those soils that are mostly comprised of silt and clay also have at least 20% organic

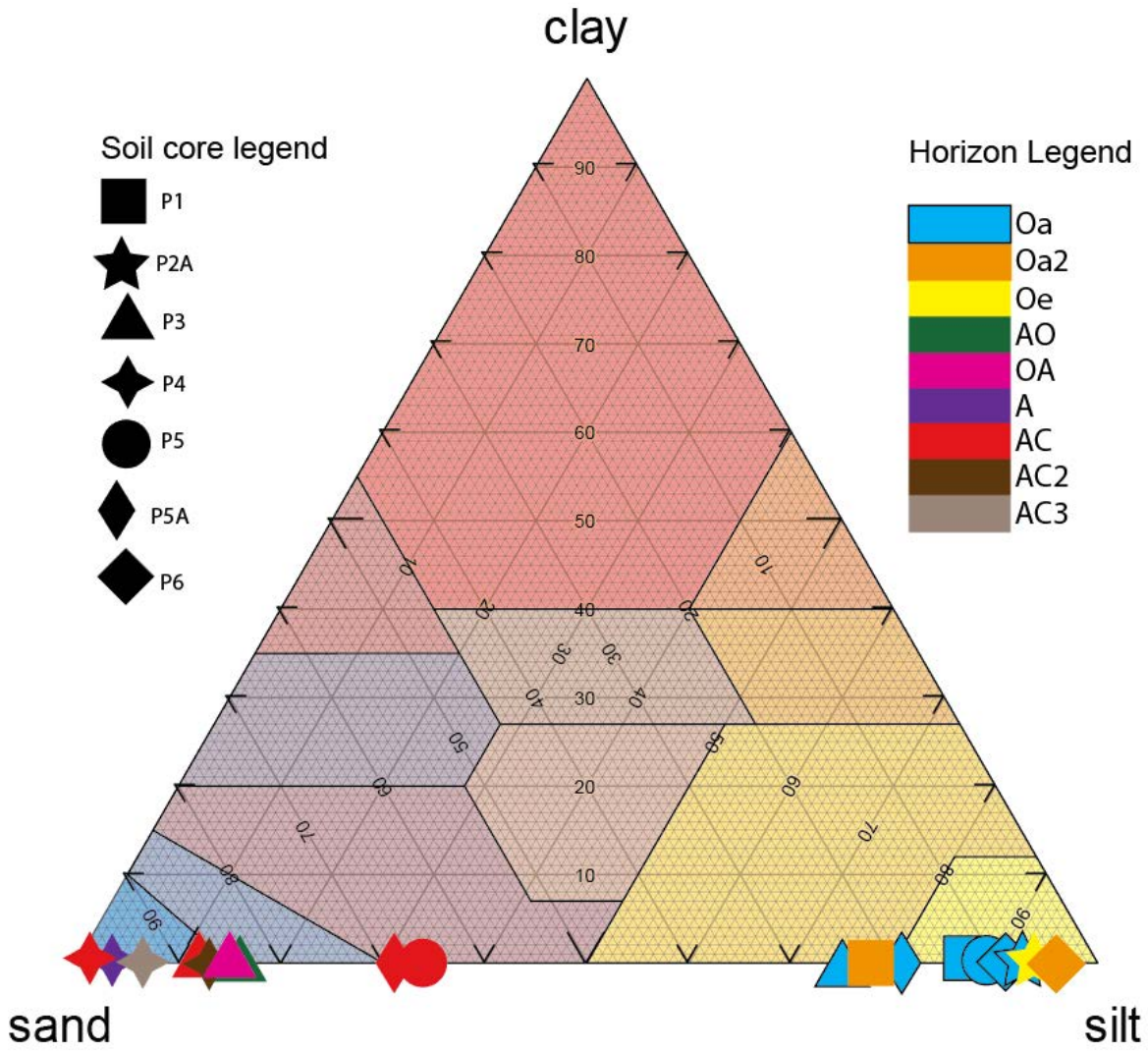

Figure 15: Triangular plot of sand, clay and silt. All of the piezometers have essentially no clay in then, and are either split into sand dominated soils or silt dominated. Piezometers 5 and 5A verge more towards a combination of these two soil types.

composition, referred to as organic rich soils, where soils made of sand have less than 10% organic composition are referred to as mineral soils (Figure 16). The percent organic carbon in the soils averages 40.0% for organic soils, but reaches a maximum of 60.2%. The average for mineral soils, or soils mostly comprised of sand, is 8.5%, but is as low as 3.2%. The hydraulic conductivity varies

from $9.3x10^{-3}$ to $1.3x10^{8}$ $cmday^{-1}$. The $\delta^{13}C$ value of the soils ranged from -29.92 ‰ to -16.00‰, seemingly with organic rich soils being lighter than mineral rich soils (Table 6).

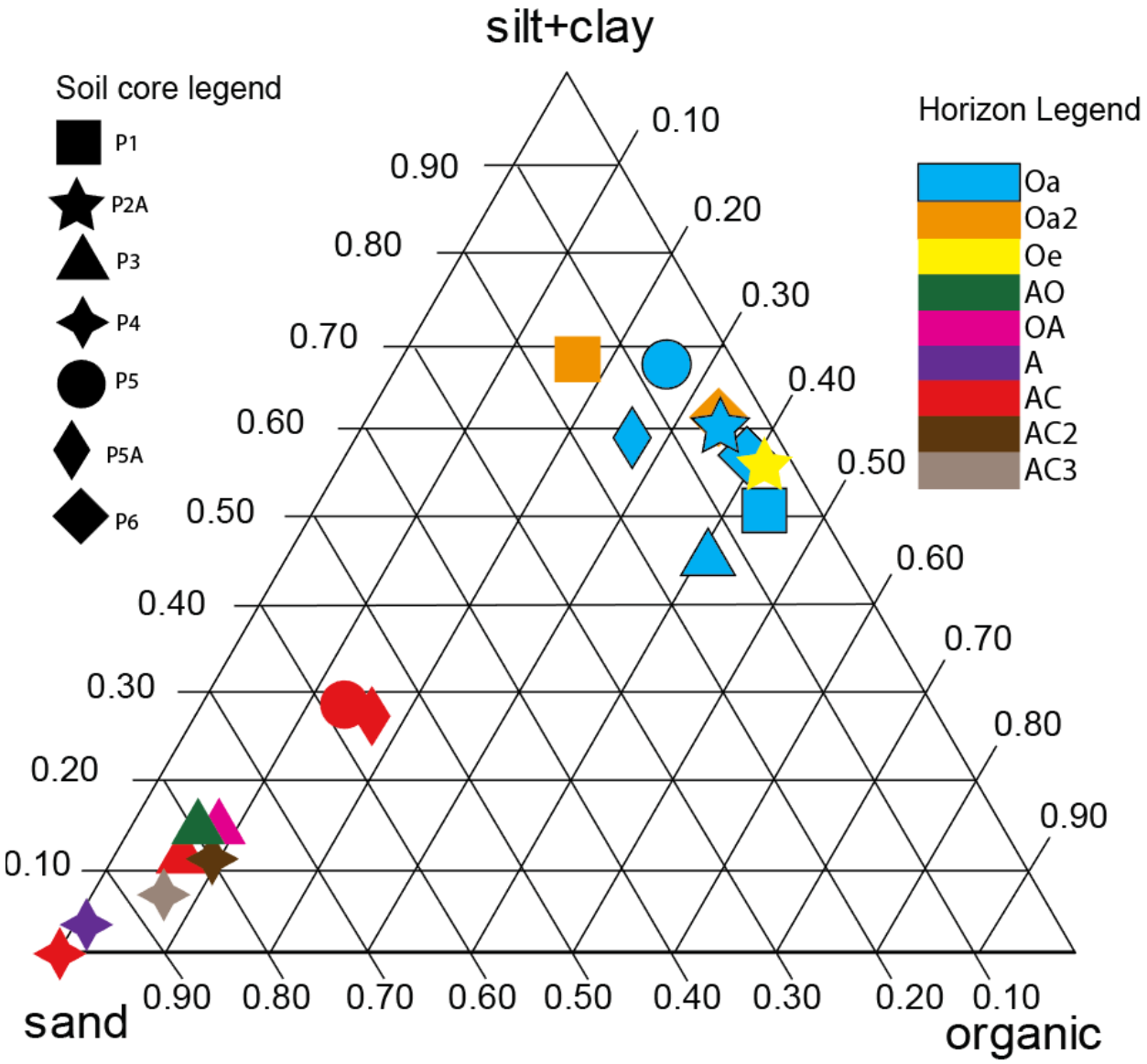

Figure 16: Triangular plot of sand vs. sand+clay vs. organic matter. Most of the high organic matter soils are mostly fine grains, whereas the mineral soils do not have a lot of organic matter.

Table 6: The isotopic values, hydraulic conductivity and percent organic carbon for each soil core taken.

Piezometer	Horizon	δ13C (‰ vs. PDB)	Ksat (cm/day)	% OC
1	Oa1	-26.71	0.04	48.42
1	Oa2	-27.49	0.79	57.82
2A	Oa1	-26.49	0.06	57.41
2A	Oe1	-23.83	0.02	45.84
3	AO	-27.02	13547946	18.28
3	AC	-25.46	3627437	7.83
3	Oa	-25.09	0.36	52.79
4	A	-22.42	1189405	14.89
4	AC	-20.76	67891060	0.24
4	AC2	-29.38	2566250	37.86
4	AC3	-16.61	133096919	N/A
5	Oa	-25.53	0.01	25.44
5	AC	-19.82	1905	8.39
5A	Pa1	-25.77	0.2	36.38
5A	AC1	-23.11	20950	2
6	Oa1	-28.89	0.01	72.36
6	Oa2	-27.22	0.02	67.43

4. Discussion

The preliminary investigation of the physical and chemical hydrology of the Honeysuckle Creek and greater Burt Lake watersheds presented here suggests that: 1) The highest mercury concentrations are delivered to Burt Lake in the form of unfiltered THg by the stream during storm conditions, however the north group of piezometers have higher concentrations of filtered THg and DOC than Honeysuckle Creek 2) Both the stream and groundwater THg concentrations increase as a result of the August 2nd storm event 3) The water table has a high south to low north during normal conditions 4) The discharge and water table elevation north of the stream increase as a result of the storm event.

Groundwater samples were analyzed for filtered or dissolved concentrations of THg, MeHg, DOC and $\delta^{13}C$ where surface water, stream and lake samples, were analyzed for both filtered and unfiltered THg and MeHg, which would incorporate the species bound to particulate matter. The concentrations of THg found in the system are representative of the expected concentrations for the region, which are typically 10ngL^{-1} (Hurley et al., 1995). The soils north of the stream show much higher percent organic carbon concentrations, with the exception of the soil core taken by piezometer 6 (the southernmost piezometer) which also has high organic carbon content.

4.1 Mercury cycling under baseflow conditions

The concentrations of filtered THg and DOC in the groundwater north of the stream (piezometers 1,2 and 3) are higher than the groundwater sampled on the south side of the stream. DOC concentrations remain high in samples from piezometers that are close to the stream (3 and 4). The water table on the north side is lower than on the south. The changes in THg and SpC concentrations show that the water table north of the stream is more dynamic than the south side. The graduate work of Rich Fiorella at the University of Michigan confirms this hypothesis as $\delta^{18}O$ isotope analysis of groundwater collected from the sample site shows a shorter residence time for the groundwater north of Honeysuckle Creek than south of the creek suggesting that the water moves more quickly through the shallow subsurface north of the stream (Fiorella, personal communication). Furthermore, higher concentrations of dissolved nitrate and higher levels of dissolved chloride relative to sodium and potassium in the groundwater north of the stream suggests that these waters are more responsive to interaction with the terrestrial landscape. They are also similar in composition to water sampled from the stream and the lake, suggesting the groundwater north of the stream does not spend long amount of time under the ground (Figure 10). The north piezometers have more filtered THg than the stream or the lake.

At baseflow conditions, there is more than 2 ngL^{-1} of unfiltered THg in the stream, meaning that THg is entering the stream from another source other than precipitation. Further studies are needed to determine if the secondary source of THg is coming from the soils that have sequestered past THg concentrations, or from litterfall that has scavenged more recent THg emissions. The filtered THg concentrations, are much lower than the unfiltered THg. DOC concentrations are lower than the concentrations in the piezometers north of the stream and do not effectively explain THg the low concentration, contrary to what is observed in other systems (Watras et al., 1998; Brigham et al., 2009). Typically, poorly correlated THg and DOC relationships are found in systems that are not wetlands, and where THg input is primarily from the atmosphere (Ravichandran, 2004). However, for Honeysuckle Creek watershed, particulate organic carbon (POC) may play a larger role in THg transport in surface waters than DOC, which is typically a small fraction of organic carbon transported, but has been shown to account for 50-80% of THg transport in peatland watersheds (Kolka et al., 1998). The lake shows much lower concentrations of unfiltered THg than the stream, however DOC concentrations are roughly the same.

4.2 Mercury cycling under stormflow conditions

In the groundwater, there is an increase in filtered THg concentrations in the groundwater north of the stream on August 3. The water table on the north rises as a result of the storm as well, suggesting that the groundwater responds to storm events while the groundwater to the south of the stream does not. Unfiltered THg concentrations in Honeysuckle Creek peak with discharge, while unfiltered THg increases slightly, suggesting that the THg leaving the watershed during storm events is bound to particulate matter. Unfiltered MeHg in the groundwater has its highest concentrations during the storm, before dropping back down roughly zero ngL^{-1}. Understanding of MeHg in the system is limited due to the low sampling resolution. At the peak of the storm, the concentrations of unfiltered THg in the lake also increases before returning to baseflow concentrations much more quickly than the stream. This peak in THg is likely due to increased turbidity during the stream that caused particulate matter to be suspended into the water column. Particulate matter increasing THg concentrations would support particulate bound THg dominating the system.

Rain concentrations are estimated to bring in water with ~10 ngL^{-1} of unfiltered THg, however, the concentration of unfiltered THg in the stream are higher during the storm event, suggesting that there is an additional source of THg to the stream than precipitation (Figure 17). THg concentrations of water in the lake are lower than the average in the precipitation suggesting that not all of the THg delivered by the stream is measured in the lake water column. This may be a

result of the mercury bound to particulate matter settling to the lake bed, a likely site of methylation (Bank, 2012).

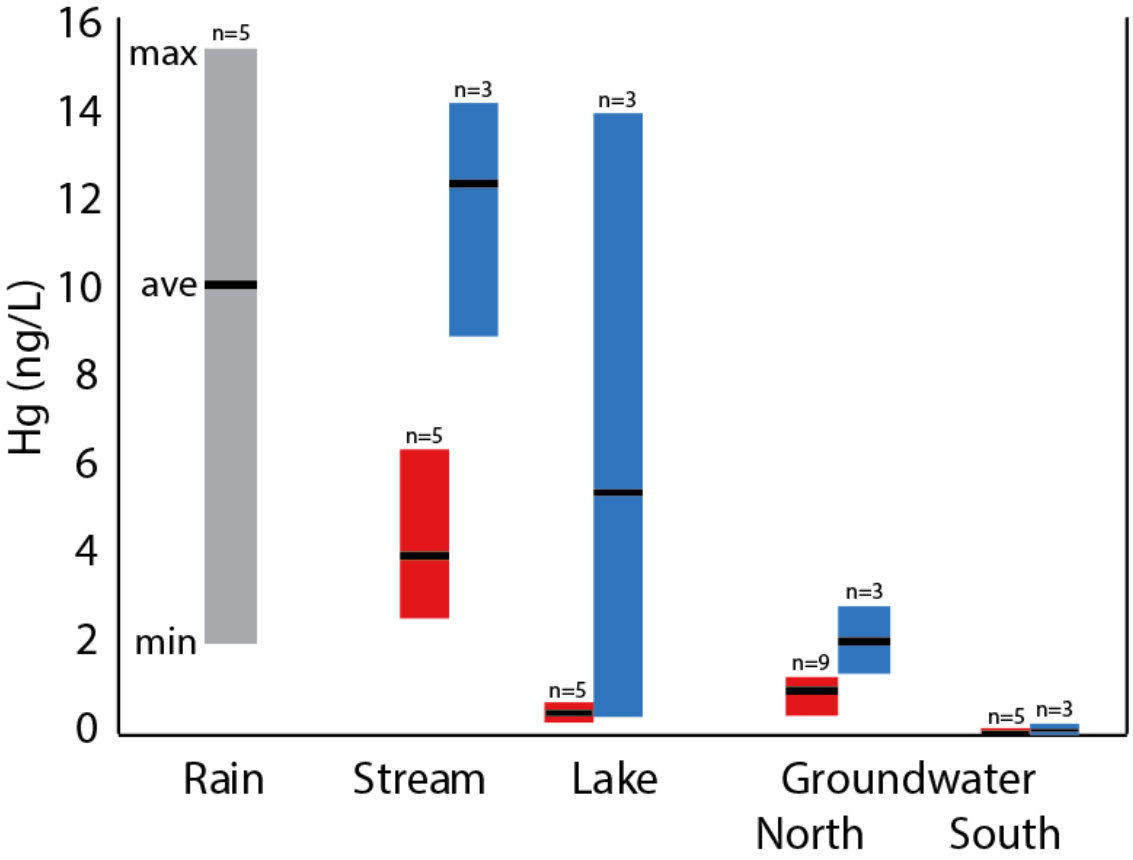

Figure 17: Summary of Hg concentrations in the Burt Lake watershed. The rain data, in grey, is from the Mercury Deposition Network (MDN) and is marked as an average of 10 ngL^{-1}. The stream and lake dare are unfiltered mercury, where the red are samples taken during baseflow and blue is storm are sampled taken during the August 2nd storm. The groundwater is filtered mercury where blue is the storm event. For each system the storm averages and ranges are much greater than baseflow. Also, the groundwater (filtered mercury) is much lower than the stream or lake (unfiltered) range.

4.3 Additional sources of mercury to Burt Lake

The groundwater and the stream serve as lines of evidence that Honeysuckle Creek watershed is participating in terrestrial THg cycling and the soils act as a legacy source of THg to the system. The interpolated groundwater maps show that the groundwater on the north side of the stream increases in filtered THg concentrations and water table height as effect of the storm (Figures 6 and 14), however the conductivity during this peak date (August 3rd) remains high. If the

precipitation was bringing the THg to cause the peak THg concentration, the conductivity would be low, as rain typically has a low conductivity (Koch et al., 1985; Sanders 1998). Conductivity decreases substantially in the groundwater to the north of Honeysuckle Creek on August 4th, when THg concentrations in this area have already returned to their pre-storm conditions (Figure 9), suggesting that the THg in the groundwater is coming from a terrestrial sources. While the SpC and the pH of the groundwater north and south of the stream are significantly different and allow for separate treatment of the groundwater table, this variability does not explain why the systems have different mercury concentrations. Higher mercury concentrations in the north may be a result of two factors: more contiguous organic rich soils, which may provide a source of THg, and greater fluctuations in the water table which brings oxygen to deeper THg-containing soil horizons, exposing larger volumes of THg containing soils to oxidizing conditions, allowing for more soluble species that can enter the groundwater when the water table rises (Grigal, 2003). Since the residence time of the north groundwater table is shorter, this soluble mercury is delivered to the lake, where it has an increased likelihood of methylation in the anoxic lake bed. Soluble THg in the stagnant groundwater south of the stream may be more susceptible to volatilization into the atmosphere, leaving less THg in the system other than what is bound to the soils (Bollen and Biester, 2008). Moreover, the $\delta^{13}C$ values in the system show that the north of the stream piezometer water and soils have a more similar values than the variability of the south soils cores, which do not correspond to the water (Figure 18). This suggests that the carbon in the groundwater on the north side of the stream is more in equilibrium with the soil, suggesting that this soil, or in the least similar soil types, are providing the THg to that groundwater. Due to the southeast flow of groundwater during storms (Figure 14) the THg may be sourced from soils northwest of the study site. Further studies are needed to determine the THg concentration in the soils to the north and west of the study site.

The presence of MeHg in the system also indicates that the terrestrial mercury cycling, in particular methylation is occurring in Honeysuckle Creek watershed. While MeHg concentrations are variable in the groundwater, the presence of filtered MeHg and unfiltered MeHg in the stream during the storm event shows that Honeysuckle Creek is participating in biotic reprocessing of atmosphere delivered THg. MeHg involves anoxic conditions and sulfur reducing bacteria, therefore precipitation cannot deliver MeHg (Gilmore et al., 1992).

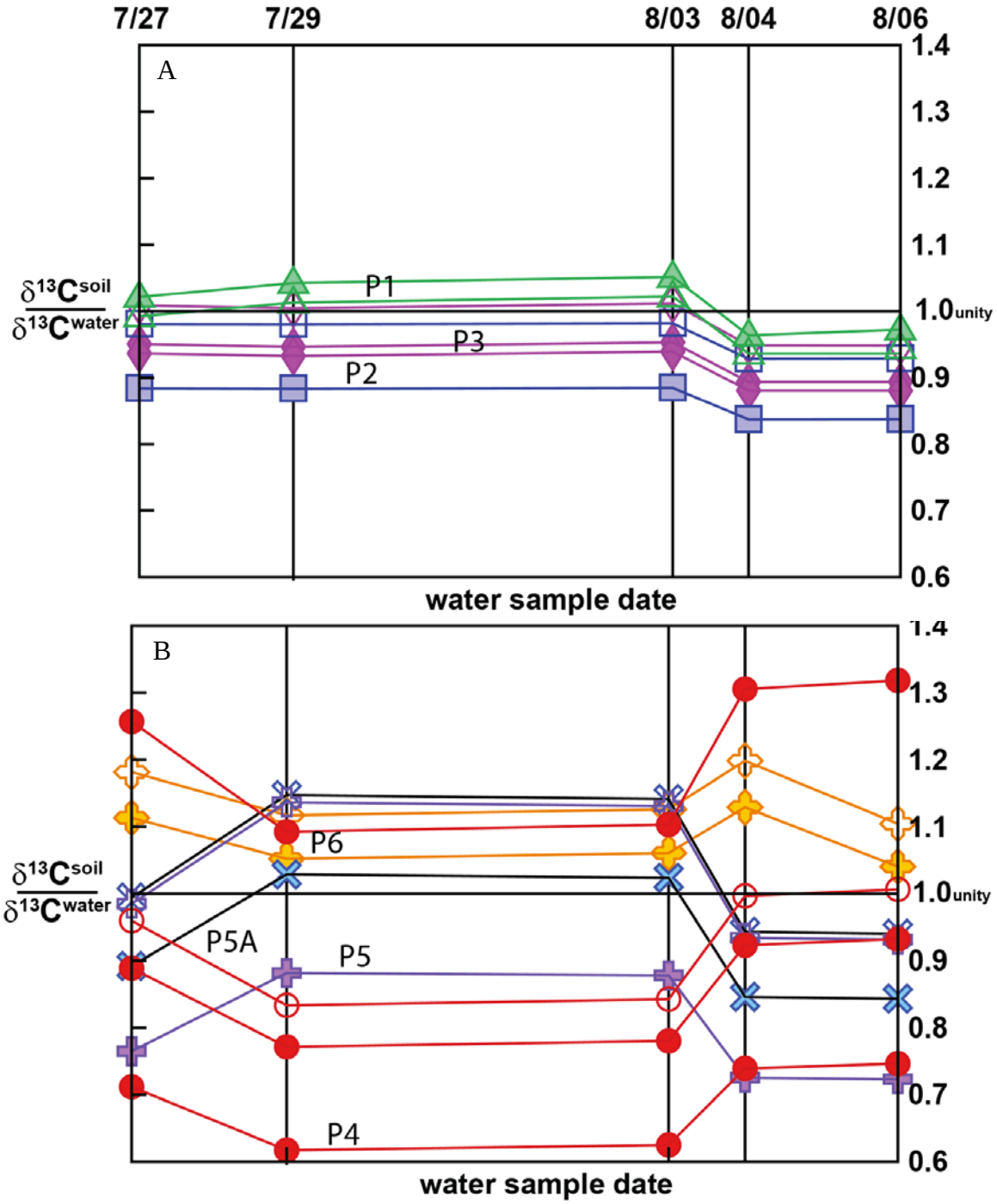

Figure 18: Comparisons between the carbon isotope value of the soil over the water in A: the north piezometers and B: the south piezometers. The piezometers are in like colors, and the multiple lines are different soil horizons. The unity line represents were the soil and water signatures are most similar. In the north there is more unity between the soils and the water. The carbon isotope values in the south are much more variable.

5.4 Future research

In order to better understand the THg dynamics, higher sampling resolution of MeHg is needed. Currently, THg concentrations are quantified for all reservoirs, however in order to understand where the methylation is occurring and what interactions are most import, more MeHg samples must be run. For the lake, all unfiltered MeHg samples were lost due to analytical failure; these analyses would have paralleled the stream analysis and may have brought insight to how much MeHg is entering the water column.

The volume of the reservoirs in the system are needed to determine both mercury and water budgets for Honeysuckle Creek watershed. For the stream, this is quantified by the Parshall flume, however volumes are unknown for the rest of the water bodies, Burt Lake and the groundwater. Sample collection of throughfall, or litterfall that reaches the forest floor, must be analyzed for THg and MeHg concentrations as they are considered a large input of THg to forested systems, sometimes even greater than precipitation (Grigal, 2002). Calculating the THg budget for the system would allow for determination of whether a consistent base flow source of large stormflow event are larger providers of THg and MeHg to Burt Lake.

Seasonal variations should be observed in this system. Northern Michigan experiences a large amount of snowfall, and various seasons that have the potential to impact the THg dynamics of the landscape. Snowmelt has been shown to provide a substantial amount of THg to like systems in the Upper Midwest (Babiarz et al., 1998)

Due to the relationship the THg and MeHg has with organic soils and particulate matter in the Honeysuckle Creek watershed, THg exports from Honeysuckle Creek watershed will only increase with climate change. As Midwest climate predictions call for increased severe storm events in the Midwest, the storms will lead to increased erosion that will liberate more soil, and therefore more THg. Remediation of soils with low levels of THg and MeHg must be considered for the recovery of aquatic communities. Bioremediation, or mercury removal by means of microbial activity, and phytoremediation, or removal by plants provide two *in situ* and non-destructive remediation techniques that show promise for THg remediation and would be suitable for undeveloped watersheds like that of Honeysuckle Creek (Lefebvre et al., 2007; Favas et al., 2014).

5. Conclusion

The chemical and physical hydrology of the stream, lake and shallow groundwater in Honeysuckle Creek watershed shows that Hg concentrations increase in all reservoirs as a result of The August 2nd storm event. The interpolated groundwater values for THg and SpC show that this THg is likely not delivered to the system by the rainfall. Similar carbon isotope values of the soil and the groundwater on the north side of the stream, along with higher concentrations of unfiltered rather than filtered THg in the stream suggest that this THg is sourced from the watershed's organic rich soils. Honeysuckle Creek watershed is serving as a legacy Hg source to Burt Lake.

During the summer months, THg and MeHg are flushed from the terrestrial landscape into Burt Lake. In order to locate the source of methylation to target appropriate sites for remediation sampling resolution must be increased. THg and MeHg sampling of the vegetation and throughfall, along with volumes of all reservoirs, including Burt Lake and the shallow groundwater must be obtained into to create a THg budget.

Small watershed studies allow for observation and collection of high resolution spatial and temporal relationships. These data can lead to greater understanding of complex terrestrial Hg cycling dynamics, which can then be extrapolated to similar and larger scale areas. This study of Honeysuckle Creek watershed can be applied to many small watershed feeding into Burt Lake or other small watersheds that make up a part of a large watershed in the Great Lakes region. Understanding the interactions between the stream, lake, and groundwater interfaces are needed, especially when looking at contaminant cycling in a watershed.

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Appendix 1: Groundwater

Piezometer	date	Temperature (ºC)	Conductivity (µs/cm)	pH	Water Table Height (m)	DOC (mg/L)	δ13CDOC	HgT filtered (ng/L)	MeHg (ng/L)
p-meter 1	27-Jul-2015	13.5	342	6.9	181.33062	13.41	-26.98	1.252604167	0.254524378
p-meter 2	27-Jul-2015	12.5	275	7.4	181.18062	11.22	-26.95	1.256837243	0.069774323
p-meter 3	27-Jul-2015	12.9	275	7.7	181.431624	28.08	-26.79	2.126032301	0.116706982
p-meter 4	27-Jul-2015	12.9	348	8.0	181.521356	0.29	-23.41	0.413086707	0.497667337
p-meter 5	27-Jul-2015	12.4	330	7.4	181.664433	2.55	-25.92	0.343492371	0.031623798
p-meter 6	27-Jul-2015	12.8	320	7.8	181.727091	1.18	-24.45	0.192276272	1.066695339
p-meter 1	30-Jul-2015	12.1	298	7.5	181.236853	1.67	-26.35	1.117191062	0.189110685
p-meter 2	30-Jul-2015	12.9	232	7.9	181.24062	13.76	-26.87	1.302501544	
p-meter 3	30-Jul-2015	12.5	264	7.1	181.516624	12.22	-26.82	0.978342046	0.041775897
p-meter 4	30-Jul-2015	14.4	352	7.8	181.475356	15.61	-26.87	0	0.090664605
p-meter 5	30-Jul-2015	12.8	333	7.4	181.648433	0.24	-22.40	0.163047069	0.039201705
p-meter 6	30-Jul-2015	13.1	322	7.8	181.697091	3.51	-25.79		0.064876166
p-meter 1	3-Aug-2015	13.2	324	7.1	181.899853	6.81	-26.20	2.034025519	0.035370403
p-meter 2	3-Aug-2015	12.6	292	7.3	181.42062	25.40	-26.92	1.372174533	0.038825449
p-meter 3	3-Aug-2015	12.2	285	7.3	181.474624	13.06	-26.72	2.875077395	0.059784587
p-meter 4	3-Aug-2015	13.2	358	8.0	181.555356	29.61	-26.68	0.008997231	
p-meter 5	3-Aug-2015	12.8	328	7.7	181.694433	0.37	-22.58	0.079288604	0.025548126
p-meter 6	3-Aug-2015	12.9	322	7.9	181.709091	3.48	-25.66	0.262459551	0.034466357
p-meter 1	4-Aug-2015	13.7			181.764853	22.09	-28.60	1.172301743	
p-meter 2	4-Aug-2015	12.4	255	7.3	181.55862	12.86	-28.46	0.929368942	
p-meter 3	4-Aug-2015	12.8	261	7.1	181.472624	15.06	-28.49	0.691612657	
p-meter 4	4-Aug-2015	13.0	359	8.0	181.523356	1.64	-22.54	0	
p-meter 5	4-Aug-2015	12.1	332	7.9	181.656433	4.40	-27.33	0.101620263	
p-meter 6	4-Aug-2015	12.5	327	8.0	181.709091	2.09	-24.11	0.008618133	
p-meter 1	6-Aug-2015	13.8	395	6.9	181.600853	19.87	-28.35	1.2347661	0.178351861
p-meter 2	6-Aug-2015	12.3	275	7.3	181.26062	13.32	-28.45	1.004740036	0.034949762
p-meter 3	6-Aug-2015	12.1	263	7.0	181.370624	14.69	-28.50	0.463535619	0.084938425
p-meter 4	6-Aug-2015	13.1	353	8.0	181.509356	1.68	-22.32	0	0.63573253
p-meter 5	6-Aug-2015	12.3	332	7.7	181.657433	5.02	-27.41	0.083533191	
p-meter 6	6-Aug-2015	13.1	324	7.9	181.710091	5.71	-26.16	0.004022058	0.010983418

Appendix 2: Stream

flume (site 2)	date	Temperature °C	Conductivity (µs/cm)	pH	Gage height (cm)	DOC (mg/L)	δ13CDOC	HgT filtered (ng/L)	HgT unfiltered (ng/L)	MeHg (ng/L)
stream	27-Jul-2015	14.4	323	8.16	5	4.01	-26.2	0.906	3.184	
stream	29-Jul-2015	16.6	300	8.25	4.0	3.9	-25.88		4.031	no result; bad run
stream	2-Aug-2015	N/A	N/A	N/A	3.8	0.9	-23.85	0.868	5.427	no result; bad run
stream	2-Aug-2015	N/A	N/A	N/A	12.5	4.3	-24.36	1.863	14.180	2.895
stream	2-Aug-2015	N/A	N/A	N/A	9.7	10.4	-26.63	1.526	8.993	0.571
stream	2-Aug-2015	N/A	N/A	N/A		9.0	-26.44	1.792	14.005	0.874
stream	3-Aug-2015	N/A	N/A	N/A	8.3	4.5	-26.70	1.215	4.431	0.627
stream	3-Aug-2015	N/A	N/A	N/A	6.8	4.4	-24.46	0.951	6.332	0.417
stream	4-Aug-2015	14.4	288	8.14	4.5	6.1	-27.60	0.822	3.824	no result; bad run
stream	6-Aug-2015	14.6	310	8.10	4.3	5.5	-27.52	0.619	3.570	0.168
stream (dup)	6-Aug-2015	14.6	310	8.10	4.3	5.4	-27.51	0.636	2.579	0.182

Appendix 3: Lake

Lake	Date	Temperature °C	Conductivity (µs/cm)	pH	DOC (mg/L)	δ13CDOC	HgT filtered (ng/L)	HgT unfiltered (ng/L)	MeHg (ng/L)
lake	27-Jul-2015	24.0	326	8.6	4.36	-26.79	0.563	0.470	
lake (dup)	27-Jul-2015	24.0	326	8.6	4.79	-27.01	0.479	0.615	
lake	29-Jul-2015	N/A	325	8.6	4.68	-26.74	0.299	0.701	
lake (dup)	29-Jul-2015	N/A	325	8.6	4.77	-26.88	0.370	0.461	
lake	2-Aug-2015	N/A	N/A	N/A	12.14	-26.47	0.437	0.441	0.063
lake	2-Aug-2015	N/A	N/A	N/A	4.68	-26.73	0.620	13.819	no result; bad run
lake	2-Aug-2015	N/A	N/A	N/A	4.67	-26.74	0.550	1.917	no result; bad run
lake	2-Aug-2015	N/A	N/A	N/A	4.74	-26.59	0.286	0.375	no result; bad run
lake	3-Aug-2015	23.2	324	8.54	4.56	-26.81	0.365	0.328	no result; bad run
lake	3-Aug-2015	23.2	324	8.54	8.54	-26.33	0.257	0.442	no result; bad run
lake	4-Aug-2015	23.3	324	8.5	5.25	-28.24		0.251	

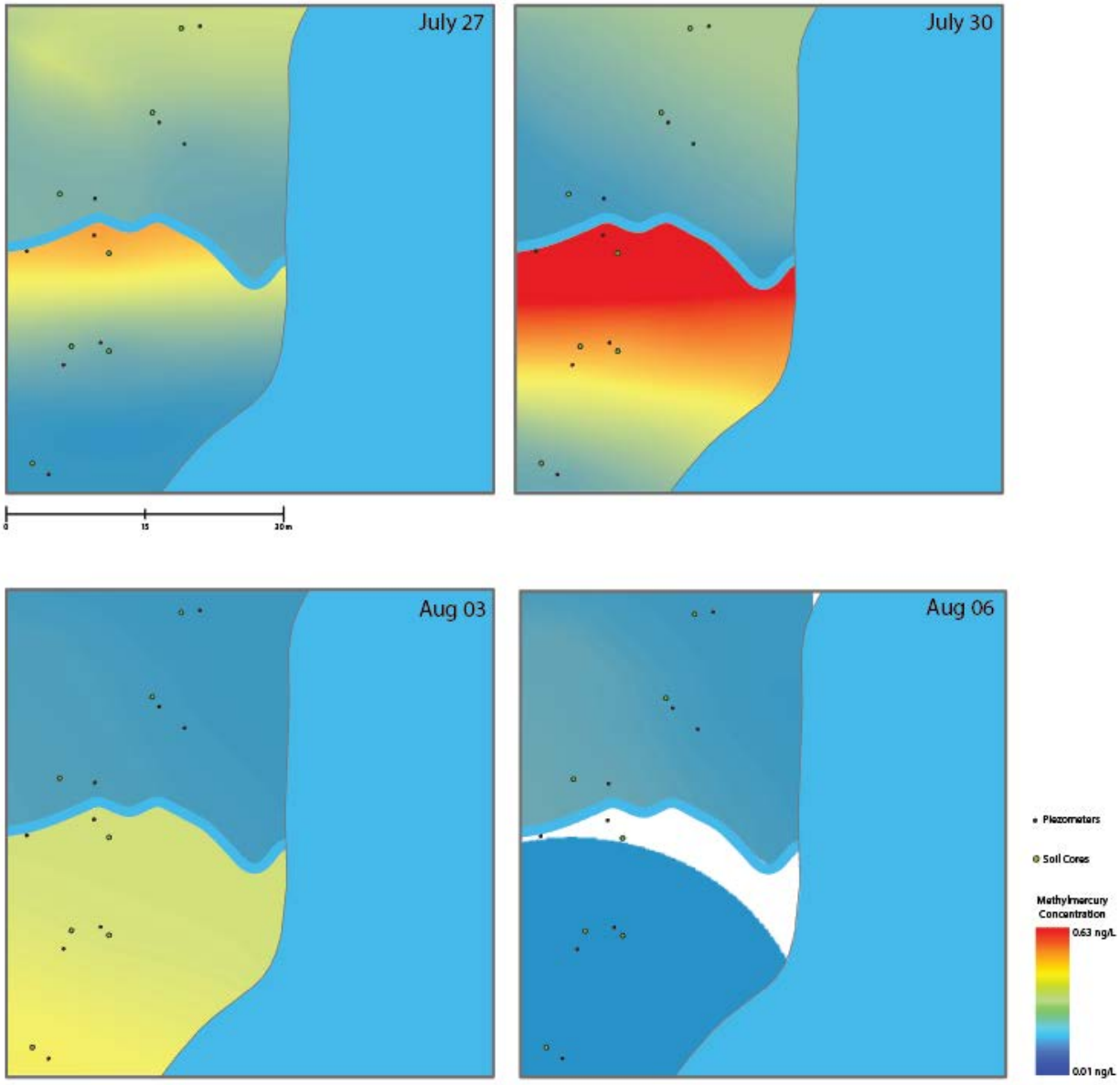
Appendix 4: Mercury Deposition Network (MDN) and Precipitation

Date on	Date off	HgConc (ng/L)
7/1/2014 19:50	7/8/2014 14:00	10.89
7/8/2014 14:15	7/16/2014 12:37	10.29
7/16/2014 12:48	7/22/2014 13:30	--
7/22/2014 13:45	7/29/2014 14:00	15.52
7/29/2014 14:11	8/5/2014 15:05	--
8/5/2014 15:15	8/12/2014 17:30	2
8/12/2014 17:38	8/19/2014 14:15	12.32
8/19/2014 14:25	8/26/2014 14:30	9.55
8/26/2014 14:40	9/2/2014 14:17	4.87

Summer 2014 Weekly Precipitation Data			
Week	**Precip (In)**	**Precip (m)**	**Precip (cm)**
7/1-7/8	0.77	0.020	1.96
7/8-7/16	1.24	0.031	3.15
7/16-7/22	0.72	0.018	1.83
7/22-7/29	0.17	0.004	0.43
7/29-8/5	0.01	0.000	0.03
8/5-8/12	1.01	0.026	2.57
8/12-8/19	1.28	0.033	3.25
8/19-8/26	0.11	0.003	0.28
8/26-9/2	1.09	0.028	2.77

Sampling Period Precipitation			
Date	**Precip (in)**	**Precip (m)**	**Precip (cm)**
17-Jul	0.00	0.00	0.00
18-Jul	0.00	0.00	0.00
19-Jul	0.00	0.00	0.00
20-Jul	0.00	0.00	0.00
21-Jul	0.00	0.00	0.00
22-Jul	0.00	0.00	0.00
23-Jul	0.00	0.00	0.00
24-Jul	0.00	0.00	0.00
25-Jul	0.11	0.00	0.28
26-Jul	0.00	0.00	0.00
27-Jul	0.00	0.00	0.00
28-Jul	0.00	0.00	0.00
29-Jul	0.00	0.00	0.00
30-Jul	0.00	0.00	0.00
31-Jul	0.00	0.00	0.00
1-Aug	0.00	0.00	0.00
2-Aug	0.46	0.01	1.17
3-Aug	0.00	0.00	0.00
4-Aug	0.01	0.00	0.03
5-Aug	0.00	0.00	0.00
6-Aug	0.00	0.00	0.00

Appendix 5: MeHg interpolation of groundwater



References

ATSDR (1999). Toxicological Profile for Mercury (Update). US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, GA.

Babiarz, C. L., Benoit, J. M., Shafer, M. M., Andren, A. W., Hurley, J. P., & Webb, D. A. (1998). Seasonal influences on partitioning and transport of total and methylmercury in rivers from contrasting watersheds. *Biogeochemistry*,*41*(3), 237-257.

Bank, M. S. (2012). Mercury in the Environment. Berkeley: University of California Press.

Becker, M. W. (2006), Potential for Satellite Remote Sensing of Ground Water. *Groundwater, 44:* 306–318.

Boelter, DH. (1969), Division S-6 Soil and Water Management and Conservation. *Soil Science Society American Procedure, 33:* 606-609.

Bollen, A., Wenke, A., & Biester, H. (2008). Mercury speciation analyses in HgCl 2-contaminated soils and groundwater—Implications for risk assessment and remediation strategies. *Water research*, *42*(1), 91-100.

Brigham, M. E., Wentz, D. A., Aiken, G. R., & Krabbenhoft, D. P. (2009). Mercury cycling in stream ecosystems. 1. Water column chemistry and transport. *Environmental science & technology*, *43*(8), 2720-2725.

Cohen, M., Artz, R., Draxler, R., Miller, P., Poissant, L., Niemi, D., ... & McDonald, J. (2004). Modeling the atmospheric transport and deposition of mercury to the Great Lakes. *Environmental Research*, *95*(3): 247-265.

Chibuike, G. U., & Obiora, S. C. (2014). Heavy metal polluted soils: Effect on plants and bioremediation methods. *Applied and Environmental Soil Science.*

Drevnick, P.E., Engstrom, D.R., Driscoll, C.T., Swain, E.B., Balogh, S.J., Kamman, N.C., Long, D.T., Muir, D., Parsons, M.J., Rolfhus, K.R., Rossmann, R., 2012. Spatioal and temporal patterns of mercury accumulations in lacustrine sediments across the Laurentian Great Lakes Region. *Environmental Pollution, 161:* 252-260.

EPA (2002). Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry.

EPA (1998). Method 1630, Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry.

Eto, K. (2000), Minamata disease. *Neuropathology, 20:* 14–19.

Evers, D. C., Wiener, J. G., Basu, N., Bodaly, R. A., Morrison, H. A., & Williams, K. A. (2011). Mercury in the Great Lakes region: bioaccumulation, spatiotemporal patterns, ecological risks, and policy. *Ecotoxicology*, *20*(7): 1487-1499.

Favas, P. J., Pratas, J., Varun, M., D'Souza, R., & Paul, M. S. (2014). Phytoremediation of soils contaminated with metals and metalloids at mining areas: potential of native flora. *Environmental Risk Assessment of Soil Contamination*, 485-517.

Gilmour, C. C., Henry, E. A., & Mitchell, R. (1992). Sulfate stimulation of mercury methylation in freshwater sediments. *Environmental Science & Technology*, *26*(11), 2281-2287.

Grigal, D. F. (2002). Inputs and outputs of mercury from terrestrial watersheds: a review. *Environmental Reviews*, *10*(1), 1-39.

Grigal, D. F. (2003). Mercury sequestration in forests and peatlands. *Journal of Environmental Quality*, *32*(2): 393-405.

Harris, R. C., Rudd, J. W., Amyot, M., Babiarz, C. L., Beaty, K. G., Blanchfield, P. J., ... & Tate, M. T. (2007). Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. *Proceedings of the National Academy of Sciences*, *104*(42): 16586-16591.

Hintelmann, H., R. Harris, A. Heyes, J. P. Hurley, C. A. Kelly, D. P. Krabbenhoft, S. Lindberg, J. W. M. Rudd, K. J. Scott, and V. L. St. Louis (2002). Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. *Environmental Science and Technology* 36: 5034–5040.

Holmer, M., and Storkholm, P., 2001. Sulphate reduction and sulpher cycling in lake sediments: a review. *Freshwater Biology, 46*: 431-451.

Hurley, J. P., Benoit, J. M., Babiarz, C. L., Shafer, M. M., Andren, A. W., Sullivan, J. R., ... & Webb, D. A. (1995). Influences of watershed characteristics on mercury levels in Wisconsin rivers. *Environmental Science & Technology*, *29*(7), 1867-1875.

IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp

Jutras, Marie-France and Arp, Paul A. (2011). Determining Hydraulic Conductivity from Soil Characteristics with Applications for Modelling Stream Discharge in Forest Catchments, Hydraulic Conductivity - Issues, Determination and Applications, Prof. Lakshmanan Elango (Ed.)

Koch, W. F., Marinenko, G., & Paule, R. C. (1986). Development of a standard reference material for rainwater analysis. *Journal of Research of the National Bureau of Standards*, *91*(1).

Lee, D. R. (1977). Device for Measuring Seepage Flux in Lakes and Estuaries, *Limnology and Oceanography*, 22(1): 140–147.

Lefebvre, D. D., Kelly, D., & Budd, K. (2007). Biotransformation of Hg (II) by cyanobacteria. *Applied and environmental microbiology*, *73*(1), 243-249.

Magnuson, J. J., Webster, K. E., Assel, R. A., Bowser, C. J., Dillon, P. J., Eaton, J. G., ... & Schindler, D. W. (1997). Potential effects of climate changes on aquatic systems: Laurentian Great Lakes and Precambrian Shield Region. *Hydrological processes*, *11*(8), 825-871.

Ravichandran, M. (2004). Interactions between mercury and dissolved organic matter—a review. *Chemosphere*, *55*(3), 319-331.

Salehi, M. H., Beni, O. H., Harchegani, H. B., Borujeni, I. E., & Motaghian, H. R. (2011). Refining soil organic matter determination by loss-on-ignition. Pedosphere, 21(4), 473-482.

Sanders, L. L. (1998). *Manual of field hydrogeology*. Prentice Hall.

Scheuhammer AM, Meyer MW, Sandheinrich MB, Murray MW(2007). Effects of environmental methylmercury on the health of wild birds, mammals, and fish. *AMBIO: A J. Hum. Environ.* 36:12–19.

Selin, N (2009). Global Biogeochemical Cycling of Mercury: A Review. *The Annual Review of Environment and Resources. 34:*43–63.

Schuster, P.F., Shanley, J.B., Marvin-Dipasquale, M., Reddy, M.M., Aiken, G.R., Roth, D.A, Taylor, H.E., Krabbenhoft, D.P., DeWild, J.F., 2009. Mercury and Organic Carbon Dynamics During Runoff Episodes from a Northeastern USA Watershed. *Water, Air, and Soil Pollution, 187, 1-4:* 89-108.

Schuster, P. F., Shanley, J. B., Marvin-Dipasquale, M., Reddy, M. M., Aiken, G. R., Roth, D. A., ... & DeWild, J. F. (2008). Mercury and organic carbon dynamics during runoff episodes from a northeastern USA watershed. *Water, Air, and Soil Pollution*, *187*(1-4), 89-108.

Tip of the Mitt Watershed Council, 2012. Burt Lake Tributary Monitoring Study. *Tip of the Mitt Watershed Council.* Cheboygan, MI.

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., ... & Weyhenmeyer, G. A. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography*,*54*(6part2): 2298-2314.

UNEP Global Mercury Assessment (2013). Global Mercury Assessment 2013: Sources Emissions, Releases and Environmental Transport. United Nations Environment Programme.

U.S. Environmental Protection Agency (EPA). (2002). Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry.

U.S. Environmental Protection Agency (EPA) and Michigan Department of Environmental Quality (MDEQ) 2013. Statewide Michigan Mercury TMDL. Public Review Draft.

U.S. Geological Survey, 2006, Collection of water samples (ver. 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4.

Verry, Elon S., et al. "Physical properties of organic soils." *Peatland Biogeochemistry and Watershed Hydrology at the Marcell Experimental Forest (eds Kolka RK, Sebestyen SD, Verry ES, Brooks KN)* (2011): 135-176.

Vidon, P. G., Mitchell, C. P., Jacinthe, P. A., Baker, M. E., Liu, X., & Fisher, K. R. (2013). Mercury dynamics in groundwater across three distinct riparian zone types of the US Midwest. *Environmental Science: Processes & Impacts*, *15*(11): 2131-2141.

Watras, C. J., Back, R. C., Halvorsen, S., Hudson, R. J. M., Morrison, K. A., & Wente, S. P. (1998). Bioaccumulation of mercury in pelagic freshwater food webs. *Science of the Total Environment*, *219*(2), 183-208.

Wuebbles, D. J., & Hayhoe, K. (2004). Climate change projections for the United States Midwest. *Mitigation and Adaptation Strategies for Global Change*, *9*(4), 335-363.