Photo by Darin Howard

Analysis of the Asylum Lake Water Column:

Assessing the Extent of Nutrient Input and Road Salt Contamination

By

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Introduction

Asylum Lake, owned by Western Michigan University in Kalamazoo, Michigan, is a glacier formed kettle lake, similar to thousands around the state. Located in the southwest corner of Kalamazoo, Asylum Lake is surrounded by many sources of anthropogenic pollution including various shopping centers, gas stations, and restaurants as well as a major highway. Due to its propinquity to pollution sources, some concern has arisen regarding the condition of the lake and the eutrophication of the lakes ecosystem. Cari Delong, the WMU Natural Areas Manager, has stated that "water quality in the lake is a concern due to heavy stormwater loads and eutrophication…A 2008 study commissioned by the Asylum Lake Policy and Management Council characterized both Asylum and Little Asylum lakes as eutrophic due to high levels of phosphorous, nitrogen, and chlorophyll" (Harmse, 2011).

Eutrophication, as defined by the United States EPA, is "the natural and artificial addition of nutrients to a water body, which may result in depleted oxygen levels". Eutrophication is a naturally occurring process, however on many occasions this process is accelerated and worsened by various human activities. Asylum Lake is exposed to drainage systems, road salts, and other point-source and non point-source pollutants. Therefore, the lake suffers from increased input of limiting nutrients. These nutrients are naturally found in very small concentrations, limiting the growth of photosynthetic plants and organisms.

The main limiting nutrient of concern is phosphorus (P). When excess phosphorous is added to a body of water, such as Asylum Lake, photosynthetic organisms no longer compete for the nutrient; instead, the organisms thrive and choke the water with plant life and algae. The large biomass of plants in the water use photosynthesis during the daytime hours

consuming carbon dioxide (CO_2) and sunlight to produce oxygen and sugars. During the night the same plants use aerobic respiration, a process that consumes oxygen, as there is no sunlight for the photosynthetic chemical reaction. When this excess of plant biomass, specifically in cases of large algal blooms, dies and decays, large amounts of bacteria that function in decomposition conduct respiration, depleting the dissolved oxygen levels in the hypolimnion (depths near the lake bottom) creating hypoxic and sometimes anoxic conditions. The resulting lack of dissolved oxygen can be responsible for devastating die-offs of the lake biota.

The presence of dissolved iron (FeII), manganese (Mn), and sulfide indicates anaerobic respiration is occurring in the absence of oxygen. The redox reactions that occur in these conditions have a variety of effects on the lake ecosystem including changes in pH and the creation of potentially toxic conditions for various life forms. Similarly, the presence of chloride can indicate pollution from septic systems and road salts. Such pollution can lead to dense waters in the hypolimnion that do not mix during equinox seasons, reducing the availability of oxygen and nutrients to the ecosystem biota. Therefore, it is important to assess these various parameters in order to determine the health of Asylum Lake, the extent of the eutrophication, and to possibly identify sources of pollution and nutrient input that contribute to the growing problem.

Methods
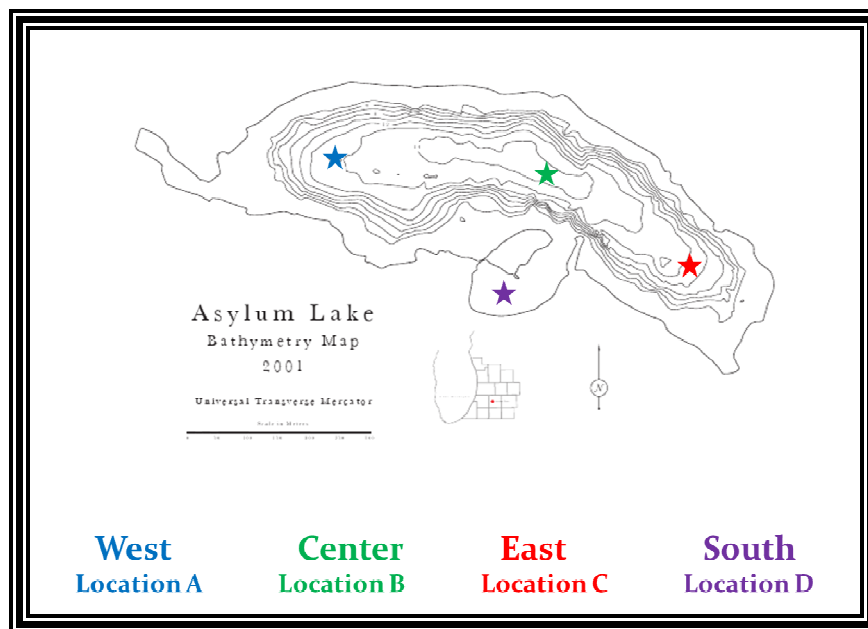
The focus of our study at Asylum Lake is to assess several parameters that indicate the presence of eutrophication and the presence of pollutants at various locations and depths around the lake. To begin, we chose four locations around the lake for testing: one near the west bank of the lake (Location A), one in the middle (Location B), one near the east bank (Location C), and a final location in the shallow marsh area to the south of Location B (Location D). Each location had varying depths; therefore we chose to test the water column at every meter up to 6 meters at Locations A and C, to 14 meters at Location B in the deepest portion of the lake, and only the surface waters of Location D, where the water was less than a meter deep. These locations are shown on the map of Asylum Lake above.

We were able to collect our data on three separate days: October 22nd, November 3rd, and November 13th. For each location we tested for ten different parameters: temperature, pH, conductivity, dissolved oxygen (DO), phosphate (PO_4^{-3}), iron (FeII), manganese (Mn), sulfide,

chloride, and water transparency (Secchi disk). A Van Dorn sampler was used to collect water samples from every meter in the water column. The water was poured from the Van Dorn into large open vials and then quickly analyzed with the pH probe, conductivity probe, and DO probe (each calibrated appropriately).

Next we gathered water samples in sealed containers for the remaining parameters to be analyzed in the lab. These samples were filtered *in situ* in order to remove particulates and other matter that could change UV/Vis results. Three water samples were collected at every meter per location:

1. The first sample was for UV/Vis analysis of manganese and phosphate as well as for IC analysis for chloride.

2. The second sample was a replicate of the first that helped to reduce the impact of errors or corrupt data, and made finding mistakes we made in the testing process easier to identify.

3. The third sample was for iron (FeII) which reacts with oxygen to form iron (FeIII), therefore, when we pulled the sample out of the VanDorn sampler, we immediately introduced concentrated nitric acid to the sample to slow or prevent the iron reduction reaction. The third sample was only used for FeII on the first day. For the remaining sampling days, a trap solution was prepared in the vials for the third sample in order to trap sulfide for subsequent analysis.

The UV/Vis spectrophotometer was used to obtain absorbance readings for iron (FeII), phosphate (PO_4^{-3}), and manganese (Mn). For manganese, the formaldoxime method was used for UV/Vis preparation and analysis. For phosphate, the ascorbic acid method was used for

UV/Vis preparation and analysis. For iron (FeII), the FerroZine method was used for preparation and analysis. Finally, for sulfide, the methylene blue method was used. All associated standards, concentrations, dilutions, and reagents were used per common guidelines. The IC (ion chromatograph) was then used to obtain concentrations of chloride.

On October 22nd, our first sampling day, we obtained information on temperature, pH, and conductivity *in situ* using probes and a Clinefinder, as well as water transparency readings using a Secchi disk for all four locations. Iron (FeII), manganese, phosphate, and chloride were measured in the lab using the UV/Vis and IC, respectively. On November 3rd, our second day of sampling, we only sampled at Locations B and D. For these two locations, we tested for the same parameters as our first day October 22nd, with the addition of dissolved oxygen using an *in situ* DO probe and the FeII sample was replaced with sulfide samples at Location B. On November 13th, our final day of sampling, we tested Locations A and C, using the same techniques and equipment as November 3rd. We also tested Location B for dissolved oxygen and sulfide, in order to compare our results for that location with the previous sampling day.
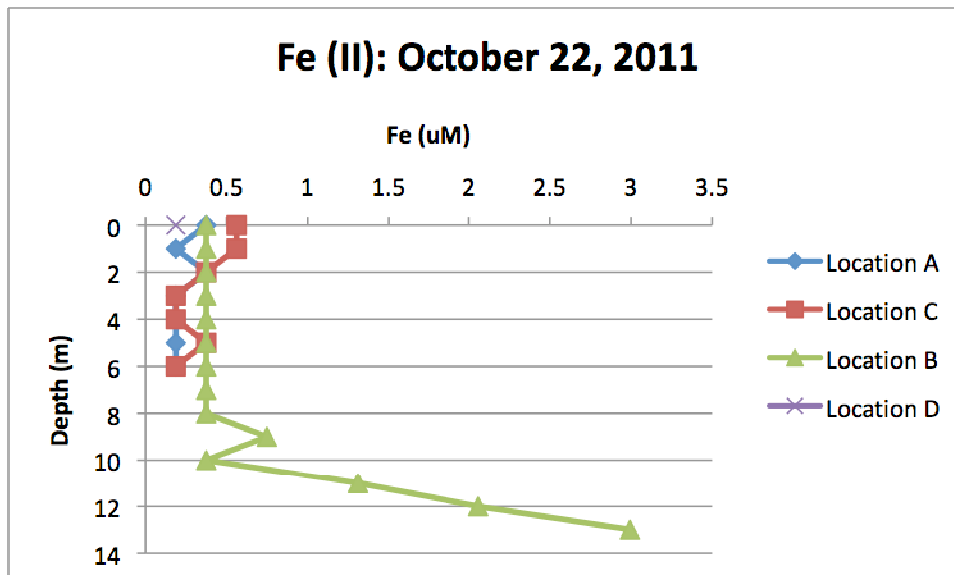
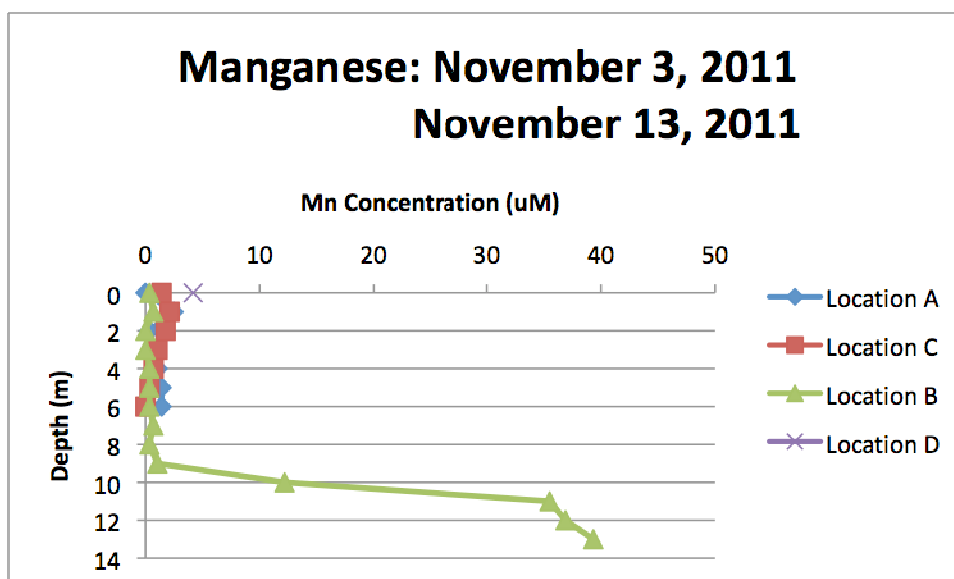Figure 1: Fe(II) concentration (µM) profile for October 22, 2011.

Figure 2: Manganese concentration (µM) profile for November 3, 2011 and November 13, 2011 as a function of depth. Locations B and D were tested on November 3 and locations A and C were tested November 13.
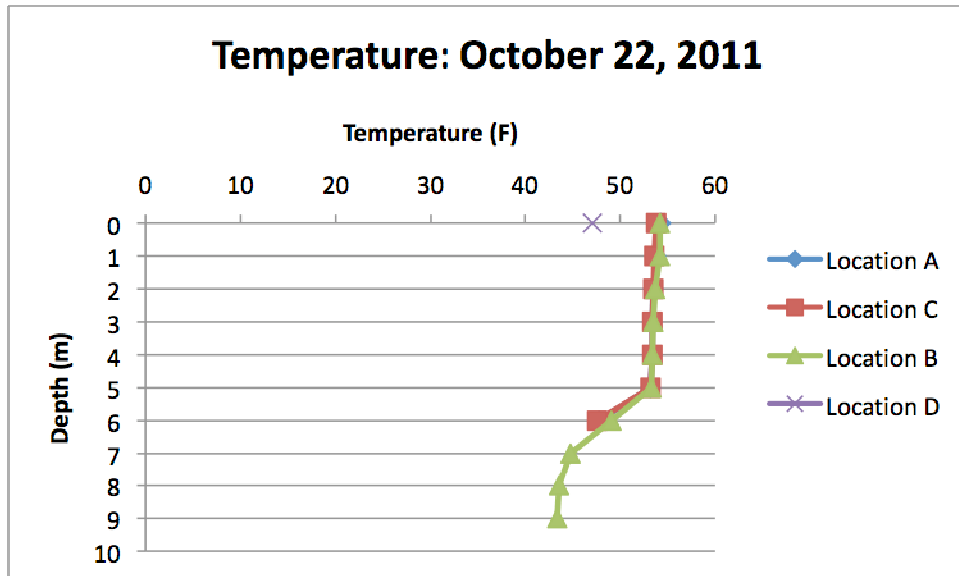
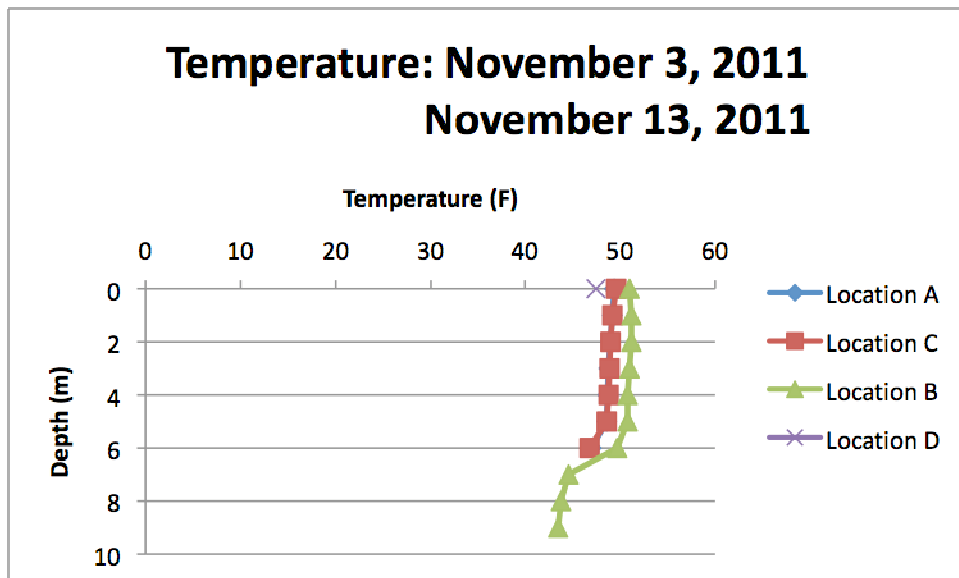Figure 3: Water column temperature (°F) profile for October 22, 2011.

Figure 4: Water column temperature (°F) profile for November 3, 2011 and November 13, 2011. Locations B and D were tested on November 3 and locations A and C were tested November 13.
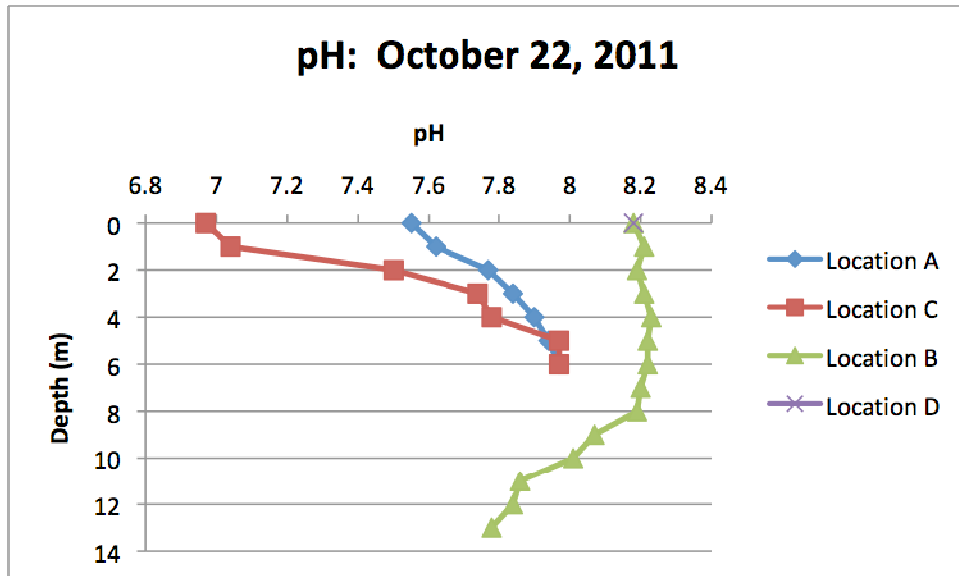
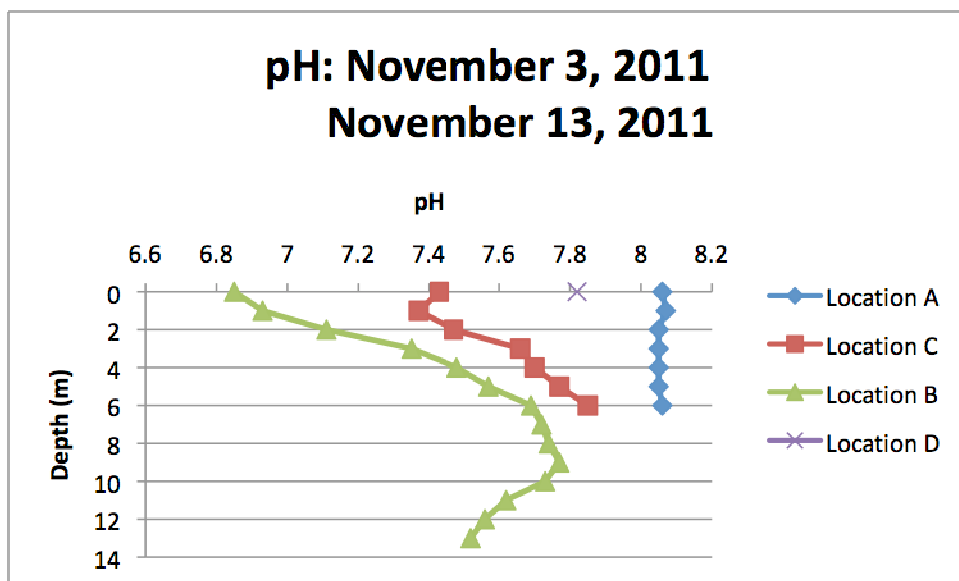Figure 5: Water column pH profile for October 22, 2011.

Figure 6: Water column pH profile for November 3, 2011 and November 3, 2011. Locations B and D were tested on November 3 and locations A and C were tested November 13.
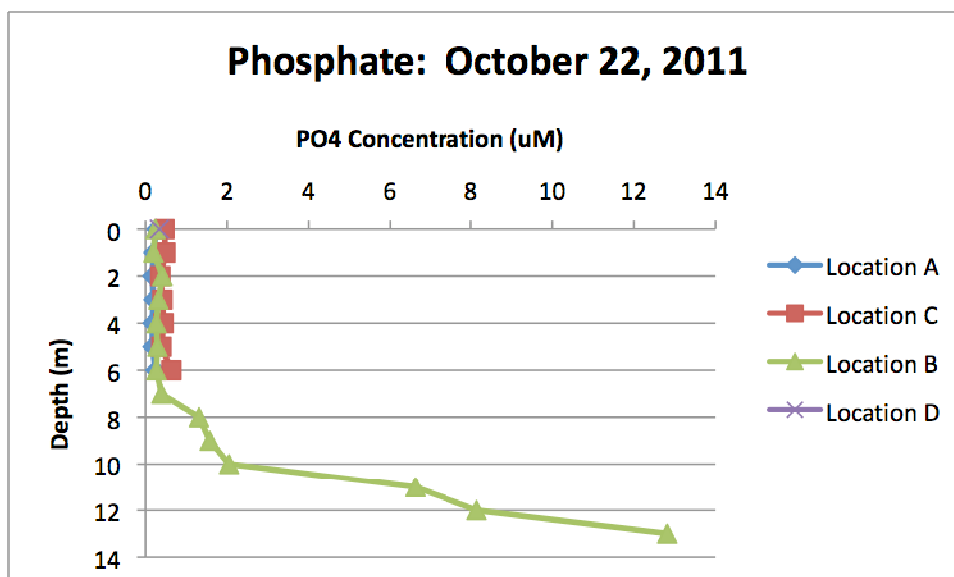
Figure 7: Phosphate concentrations (µM) profile for October 22, 2011.
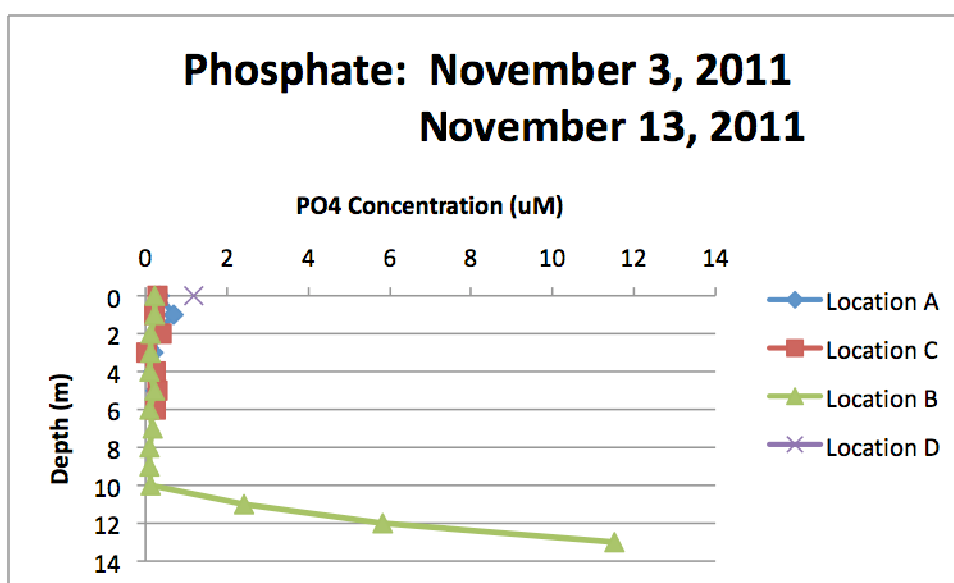

Figure 8: Phosphate concentrations (µM) profile for November 3, 2011 and November 13, 2011. Locations B and D were tested on November 3 and locations A and C were tested November 13.

Figure 9: Dissolved oxygen (% saturation) profile for November 3, 2011.
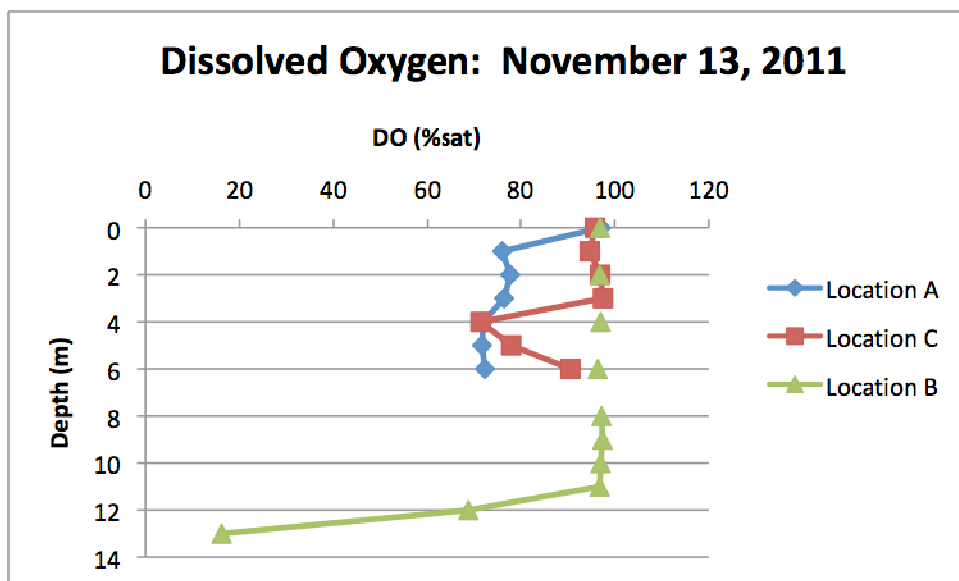
Figure 10: Dissolved oxygen (% saturation) profile for November 13, 2011.
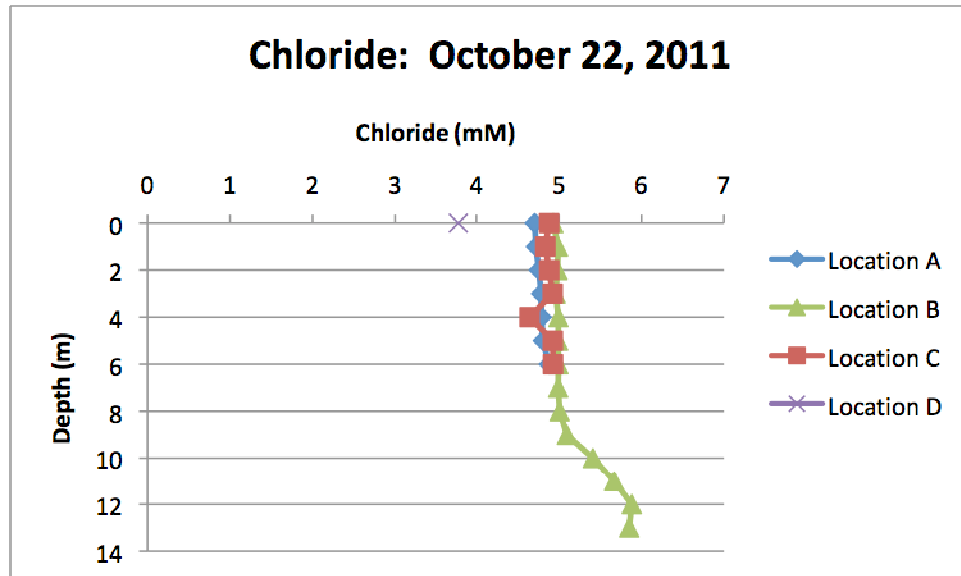
Figure 11: Chloride concentrations (mM) profile for October 22, 2011.
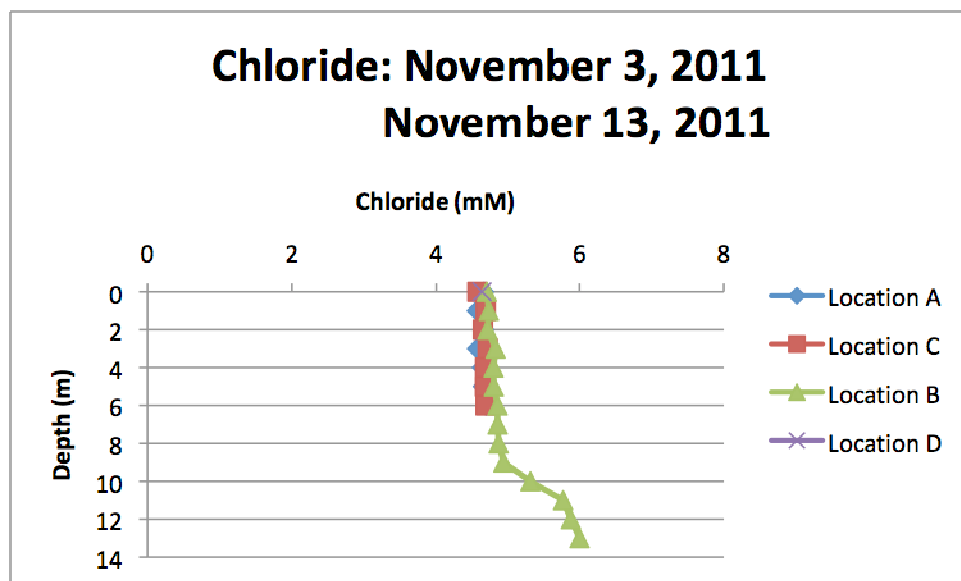
Figure 12: Chloride concentrations (mM) profile for November 3, 2011 and November 13, 2011. Locations B and D were tested on November 3 and locations A and C were tested November 13.
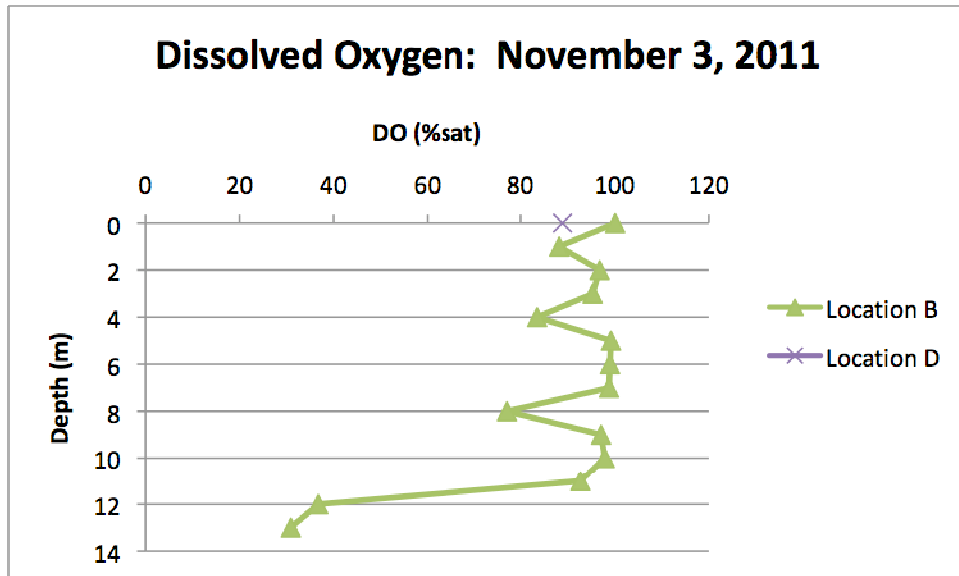
Figure 13: Conductivity (uS) profile for October 22, 2011.

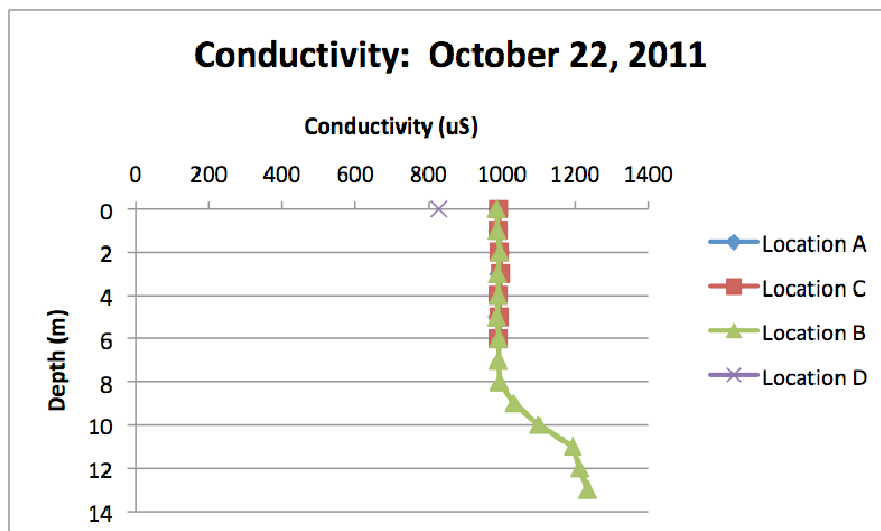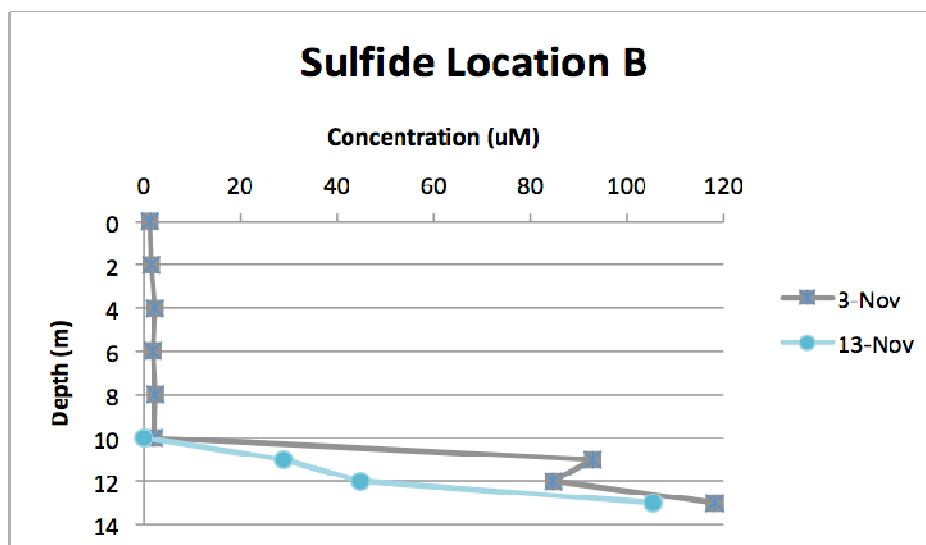Figure 14: Sulfide concentrations (µM) profile at location B for November 3, 2011 and November 13, 2011.

Location	Secchi Disc Reading (m)
A	3.5
B	3.5
C	3.25

Table 1: Secchi Disc readings for October 22, 2011.

Discussion

Dissolved Oxygen (DO): We discovered that the oxygen levels in the lake decrease with depth, especially at location B. The decrease in DO levels could be attributed to aerobic respiration at depth. An excess of nutrients in the lake leads to an increase in organic matter, which in turn increases the amount of aerobic respiration to the point where DO levels are almost completely depleted (as low as 16 % sat). In the hypolimnion, hypoxic or anoxic conditions are thus present, resulting in a variety of redox reactions. Also, there were no obvious differences in DO levels between locations or sample days. Location B is the only location to experience extreme drops in DO.

Sulfide: We only found sulfide at location B, likely because locations A, C, and D were not deep enough to result in anoxic conditions. However, the sulfide concentrations reached alarming levels: up to 120 µM. Concentrations did not significantly change between sampling days. Sulfide in the lake is formed through anaerobic respiration and levels tend to decrease in the presence of Fe(II) because sulfide and Fe(II) combine to form pyrite precipitates. Therefore, Fe(II) concentrations are limited in the hypolimnion of Asylum Lake where sulfide exists in large concentrations. In the epilimnion and metalimnion (upper and middle layers of the lake, respectively), sulfide levels remain extremely low, increasing at the exact depth (11 m) where DO levels drop.

Fe(II): The dissolved Fe(II) levels do not exceed 4 µM at any location in Asylum Lake and only increase at location B when DO levels drop. Fe(II) is produced through anaerobic redox reactions that reduce Fe(III) into Fe(II). Dissolved Fe(II) concentrations are likely low because when sulfide combines with Fe(II) to form pyrite, dissolved Fe(II) levels decrease. Also, the high

pH of Asylum Lake limits the solubility of iron, which could also explain the low observed

concentrations (Shaw et al, 2004).

Phosphate: The phosphate levels in Asylum Lake increase with depth from 0 µM to

roughly 15 µM at location B. All other locations did not show significant levels of PO_4^{-3}, likely

due to the presence of oxygen in those locations. Phosphate increases with depth because

anaerobic respiration at the bottom releases phosphate from the sediments into the water

column: phosphate attaches to Fe(III) and when Fe(III) is reduced into Fe(II), the phosphate is

released (Shaw et al, 2004). We see phosphate levels increase as the DO levels decrease at

about 11m.

Manganese: We observed manganese levels in Asylum Lake to increase with depth from

levels below detection to roughly 40 µM at location B, while not showing significant levels at

any other location. Manganese is created through anaerobic respiration as organisms use

manganese to breathe once DO levels in a lake are depleted. We see manganese levels increase

dramatically as DO levels decrease significantly.

Temperature: The temperature profile for each location shows the thermocline at about

six meters for all sampling days. The temperature decreases with depth and remains fairly

consistent throughout the sampling period. In an oligotrophic (nutrient poor) lake we would see

DO levels increasing as the water temperature decreases, but in Asylum Lake we see the

opposite, indicating eutrophic conditions.

pH: The general pH trend of all 3 days and all locations is that the pH decreases with

depth. The high pH at the top is probably due to photosynthesis removing CO_2 from the water

and producing oxygen. The low pH at the bottom is likely due to redox reactions occurring at

depth. The pH at location B on November 3 shows a low pH at the surface that increases to a

depth of 8 m and decreases below that. November 3 was overcast and the low pH at the

surface is likely due to decreased photosynthesis. The drop in pH at 8m is likely a result of

oxygen diffusing from the surface to the bottom waters. The diffusing oxygen will oxidize

reduced solutes (sulfide, ammonia, ferrous iron) in the anoxic zone of the lake, which will cause

a drop in pH.

Chloride/Conductivity: Both chloride and conductivity stay constant, with chloride at

roughly 5 mM and conductivity at roughly 1000 µS, until 8m and then increases with depth,

with chloride reaching roughly 6 mM and conductivity reaching upwards of 1250 µS. The major

source of chloride likely comes from road salt that is carried into the lake by urban runoff. Road

salt is 60% chloride ion and thus is a major contributor to chloride in northern urban lake

ecosystems. Septic systems, fertilizers, and animal waste might also contribute to chloride

levels in Asylum Lake. High chloride levels could potentially lead to denser bottom waters that

prevent the lake from turning over in the fall and spring, leading to persistently lower dissolved

oxygen levels throughout the hypolimnion in all seasons (Keseley, S. IAPPO).

Conclusion

Analysis of the Asylum Lake water column yielded interesting results that certainly

support claims that the lake ecosystem is eutrophic and suffering from nutrient and pollutant

input from a variety of anthropogenic sources. Analyses of phosphate, iron, manganese,

sulfide, and chloride were all completed. Due to the severe drop in dissolved oxygen in the

hypolimnion of Asylum Lake, this eutrophic lake is in danger of biota die-off events, increased

sulfide toxicity, and possibly the discontinuation of nutrient mixing during the fall and spring.

Locations A, C, and D all lacked obvious eutrophication indicators due to their shallow

depths, allowing oxygen to diffuse throughout the water column at these locations. However,

chloride does appear in fairly heavy concentrations throughout each of these locations,

indicating probable pollution from storm water drains, septic systems, and road salts. Location

B, located at the center of the lake, was deep enough to undergo stratification and thus yields a

distinct epilimnion, metalimnion, and hypolimnion. At 11 meters, in the hypolimnion, the data

show a deep decrease in dissolved oxygen coupled with heavy increases in iron (FeII),

manganese (MnII), phosphate (PO_4^{-3}), and especially sulfide. The presence of these

constituents reveals that anaerobic respiration is occurring in this part of the lake column. Such

conditions create an environment that is deadly to many forms of lake biota. Chloride also

increased in the hypolimnion of Location B, which could potentially increase the density of the

water and prevent fall and spring mixing. The water column temperature profile showed the

continued presence of a thermocline by November 13th. More data is needed to determine if

the chloride has reached high enough concentrations to prevent mixing and thus the retention

of the thermocline.

Alarming as these results may be, funding was recently procured in an effort to aid in

the health of Asylum Lake. Secchi disc readings, taken on a sunny October afternoon, yielded

good water transparency of 3.5 meters. According to the water clarity index provided by Byron

Shaw, 3.5 meters indicates good water clarity (Shaw et al, 2004). Although these promising

results may be due to a current lack of an algal bloom, which would cloud the waters, they

could also indicate that Asylum Lake may respond well to treatments if the eutrophic conditions have not yet clouded the water to persistently poor clarity conditions.

Asylum Lake is certainly undergoing eutrophication and likely suffering from road salt pollution, indicated by the high concentrations of chloride throughout the entire water column. Steps must be taken to prevent further input of nutrients and pollutants if the lake ecosystem is to survive and thrive. Further data must be collected to determine if Asylum Lake mixes in the spring and fall. However, if mixing still occurs, and nutrient and pollutant input is reduced, Asylum Lake may yet recover.

Error Analysis

A few complications arose during the sampling and analysis of our lake water columns. They are as follows:

1. Manganese data from October 22, 2011 had to be thrown out due to issues with the standards resulting is concentrations a thousand times larger than expressed every other sampling day.

2. The use of probes *in situ*, especially the DO probe, yielded possible errors. The DO probe was prone to air bubbles that altered some data and calibration problems resulted in DO results being scraped for October 22, 2011. The pH probe only received a 2-point calibration on October 22, 2011, possibly changing the results for that day slightly. Every other sampling day, both DO and pH probe complications were rectified.

3. The removal of water samples from the water column in Asylum Lake creates the risk of reactions when the sample comes in contact with the atmosphere. To combat this, the samples were filtered and sealed as quickly as possible. However, certainly we could not prevent all reactions from occurring. An *in situ* probe that records data within the water column, without having to remove samples, would be the most accurate method.

4. Some lab complications occurred with standards and dilutions for manganese and phosphate, however, because we took replicates, we did not lose good data as the replicates were done correctly.

References

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Shaw, B., Mechenich, C., & Klessig, L. (2004). Understanding lake data. *University of Wisconsin Extension*, RP-03, 0-17.

Asylum Lake:
Sediment and Pore Water Analyses

Photograph of Asylum Lake, September 2011.

By: Carol Beaver, Andrew Johnson, and Lacie Muller

December 9, 2011

Introduction

Asylum Lake Preserve is a 274-acre site near Kalamazoo, Michigan. It consists of two bodies of water, Asylum Lake and Little Asylum Lake, with a connecting stream. It is used for research and education, as well as recreational activities such as swimming and fishing. With the lakes playing such a vital role in the community, water quality has become a major concern as signs of deterioration have become more apparent. According to a study by Kieser and Associates (2008), storm water inputs from drains located near Drake Road and Stadium Drive have been contributing excess nutrients and pollution to the lake.

In the fall of 2011, a study on the condition of Asylum Lake was performed by an environmental field geochemistry class. The purpose of this class was to determine if eutrophication was taking place. Eutrophication is the process of nutrient loading that leads to excessive algal blooms. As the algae die off and decompose at the bottom of the lake, bacteria consume the oxygen, which leads to anoxic conditions. The absence of oxygen may lead to fish kills and other undesirable events. Water quality and clarity may also be affected by the decomposition occurring in the lake. As a consequence, aquatic plants cannot perform photosynthesis and die when turbid water blocks sunlight.

In spite of the many negative effects associated with eutrophication, not all organisms suffer when a lake turns eutrophic. Anoxic conditions benefit microorganisms such as anaerobic bacteria. Anaerobic bacteria do not "breathe" oxygen to create energy. They use nitrate (NO_3^-), manganese IV (MnIV), ironIII (FeIII), and sulfate (SO_4^{-2}) to "breathe". As a result, nitrite, Mn(II), Fe(II), and sulfides (S^-) are produced. If anoxic conditions are present, they can be found through chemical testing. Therefore, eutrophic conditions may be assessed. For this study, analyses were performed on sediment and pore waters of Asylum Lake in order to determine its trophic state.

Materials and Methods

Field Site

Pore water and sediment samples were taken from four sites on the southern side of Asylum Lake. Sediment samples were taken at the west side of the lake (West), and three more sites centrally located at the lake (Mid, Peeper, and East). All sites are shown in Figure 1. In addition, pore water analysis was done at two sites, the West Site and the Peeper Site.

Figure 1. Map of sampling sites at Asylum Lake. The sites are represented as follows: Green: West; Purple: Mid; Red: Peeper; Blue: East.

Sediment Sampling and Analysis:

For sediment analysis, samples were collected with a Russian peat corer on October 20, 2011. Russian peat corers were used to prevent the compression of core samples taken from wetlands, a common occurrence with end-filling corers. Next, 5 cm depths sliced from the cores were packed in Ziploc bags with most of the air eliminated from the bags. The core depths for each site were as follows: 45 cm deep for the West core, 30 cm deep for the Mid core, 40 cm deep for the Peeper core, and 30 cm deep for the East core. Core depths varied due to the hardness of the sediment. Difficulty in pushing the peat corer into the sediment prevented the sampler from taking samples of a consistent depth. Besides the differences in depth, sediments were submerged under various depths of water. The West site core was beneath 18 cm of water, the Mid site was beneath 18 cm of water, the Peeper site was beneath 40 cm of water, and the East site was beneath 25 cm of water. In addition, sediments from the West and Peeper sites were taken within 3 meters of the pore water samples. The East and Mid site samples were not taken near pore water samples.

After collection from the site, the samples were transported to the lab where pore waters were centrifuged off the soil within 4 hours, and frozen for further sampling. The sediment was then dried to a constant weight in the oven for 4 days at 90 $°C$. After the initial drying, it was weighed, dried at 550$°C$ for 2 hours, then reweighed according to

Heiri et al. (2001). Organic matter of the sediment was then analyzed by loss on ignition. The loss-on-ignition was calculated as follows: (Initial mass of sediment-final mass of sediment)/ initial mass of sediment * 100. Greater loss on ignition indicates higher organic matter content.

Pore waters from the sediment samples were analyzed for Fe(II), using the UV/Vis spectrophotometric ferrozine method. Dried sediment samples were extracted with 0.5 M HCl or ascorbic acid and analyzed for Fe(II) (HCl extraction only) and total Fe by using a reducing agent (hydroxylamine to reduce Fe(III) to Fe(II)), which was measured by the UV/Vis spectrophotometric ferrozine method.

Pore Water Sampling and Analysis

All pore water samples were taken anaerobically from a dialysis equilibrator (peeper). Peepers were 50 cm long, with 35 sample chambers at 1-2 cm intervals. Peepers were assembled under DDI water in a plexiglas box in the laboratory and allowed to degas with N_2 for 2 days. After degassing, they were placed in vinyl bags and transported to the lake under constant nitrogen gas pressure and insert into the sediment. The peepers were extracted once the DDI water had equilibrated with the surrounding pore water for approximately 3 weeks. After removal from the sediment, peepers were immediately placed within a nitrogen-filled bag and sealed. Two peepers (#1 and #2) were placed at the West site and one was placed at the Peeper site. The peepers at the West site were inserted into the sediments on September 7, 2011 and retrieved on September 29, 2011. Samples from these peepers were collected and analyzed during a class exercise. The peeper at the Peeper site (#1) was inserted into the sediments on October 20, 2011 and retrieved on November 13, 2011. The Queens group collected the data for that peeper. No peeper samples were inserted at the East or the Mid site. A positive nitrogen pressure was kept within the bag as individual samples were extracted with a syringe. After extraction, fluid from each chamber was filtered and analyzed within 6 hours of collection.

Fluid from the equilibrated peeper chambers were analyzed for pH, alkalinity, Fe(II), phosphate, sulfate, Mn(II), ammonium, and chloride. The pH of each section of the pore water within the peeper was sampled in the lab using a Fischer pH meter. The pH meter was calibrated using a 3-point calibration (pH 4.00 to pH 7.00 to pH 10.00 in that order). After calibration, each sample was measured for pH. All other parameters were measured in the laboratory using a UV/Vis spectrophotometer, except for sulfate and chloride, which were analyzed using ion chromatography (IC). Alkalinity (sodium bicarbonate) of each section of the peepers was analyzed using the bromophenol blue method. Fe(II) of the pore water within the peeper was measured using the ferrozine

method. Dissolved phosphate was measured using the ascorbic acid method. Dissolved Mn(II) was measured using the formaldoxime method, and ammonium was analyzed in the lab using the hypochlorite method.

Results and Discussion

Sediment Core Analysis

Loss on Ignition

Loss on ignition was used to assess the amount of organic carbon of the sediments. As seen in figure 2, the Peeper site contained the most organic matter. At the surface, the Peeper Site was calculated to have an LOI of 65.8%. It decreased to 9.8% at 40 cm. The West site ranged from 30.6% at the surface to 14.7% at 45 cm, and the Mid site ranged from 15.0% at the surface to 2.8% at 45 cm. The East Site was the only site that increased in LOI. It was 4.7% at the surface, and increased to 11.1% at 30 cm.

The Peeper site may have had the highest percentage of organic material due to the greater amount of vegetation surrounding the area. Trees are on the south side, and cattails and more aquatic vegetation lie to the north. In fact, Kieser and Associates classified this area as a wetland. The reason for less organic matter at the other three sites may be that they are exposed to less vegetation. The West and the Mid site are also more exposed to the open lake, so dead vegetation may not have as much of an opportunity to accumulate there. As for the East site, it may contain less organic carbon due to erosion of soil from the bank eroding east of the site. Erosion may be depositing sediments with a higher mineral content on top of the organic material, possibly decreasing the organic carbon content.

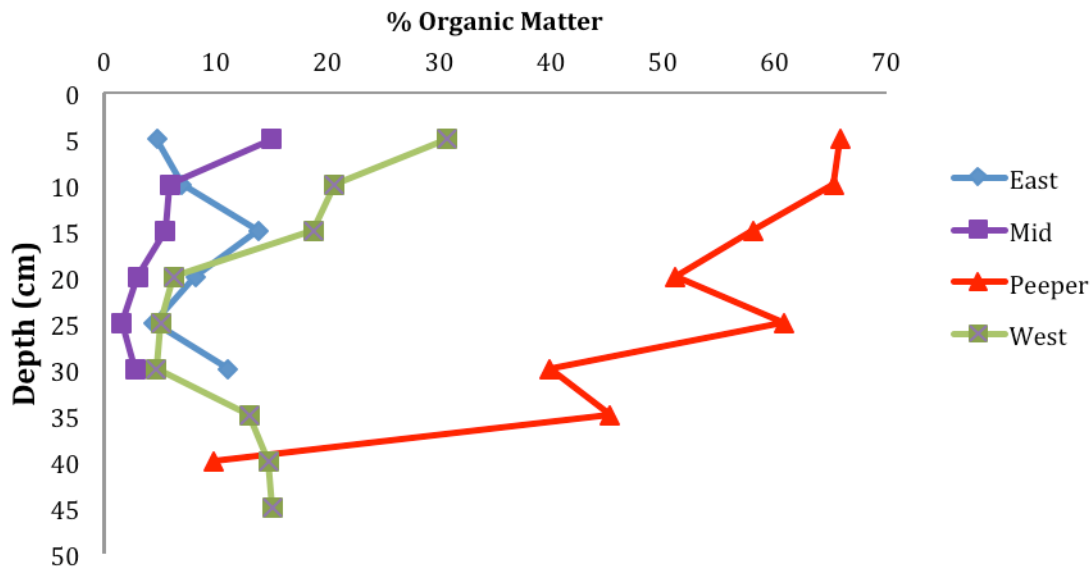## % Organic Matter of Sediment Core Samples by Loss on Ignition

Figure 2. Loss on ignition as a function of depth for four core samples from Asylum Lake.

Pore Water Iron Extraction

Figure 3 displays the concentration of Fe(II) in sediment core pore water, which ranged from 0.6 to 10.2 μM at the sediment surface. The West, Mid and Peeper sites each increased in concentration of Fe(II) with depth for the first 20 cm. While Fe(II) at East site increased with depth overall, it fluctuated wildly between 0.6 and 10 μM Fe(II) throughout the entirety of the 30 cm core. Interestingly, at 20 cm in the peeper core, the Fe(II) concentration decreased to approximately 1 μM, and stabilized for the lower 20 cm. In addition, the Mid and East sites had the highest concentrations of Fe(II) at the greatest depth of 9.4 and 10.2 μM, respectively.

The presence of Fe(II) suggests that Fe reducing conditions are occurring in these sediments, which is an indicator of anoxic conditions. If oxygen was present, it would

oxidize Fe(II) to Fe(III), eliminating its presence in the pore water. However, the actual concentrations of Fe(II) in this graph may not be accurate. Because the pore water was centrifuged out of the sediments, some of the Fe(II) may have been retained in the sediment, or reoxidized during centrifugation, which would give inaccurate results.
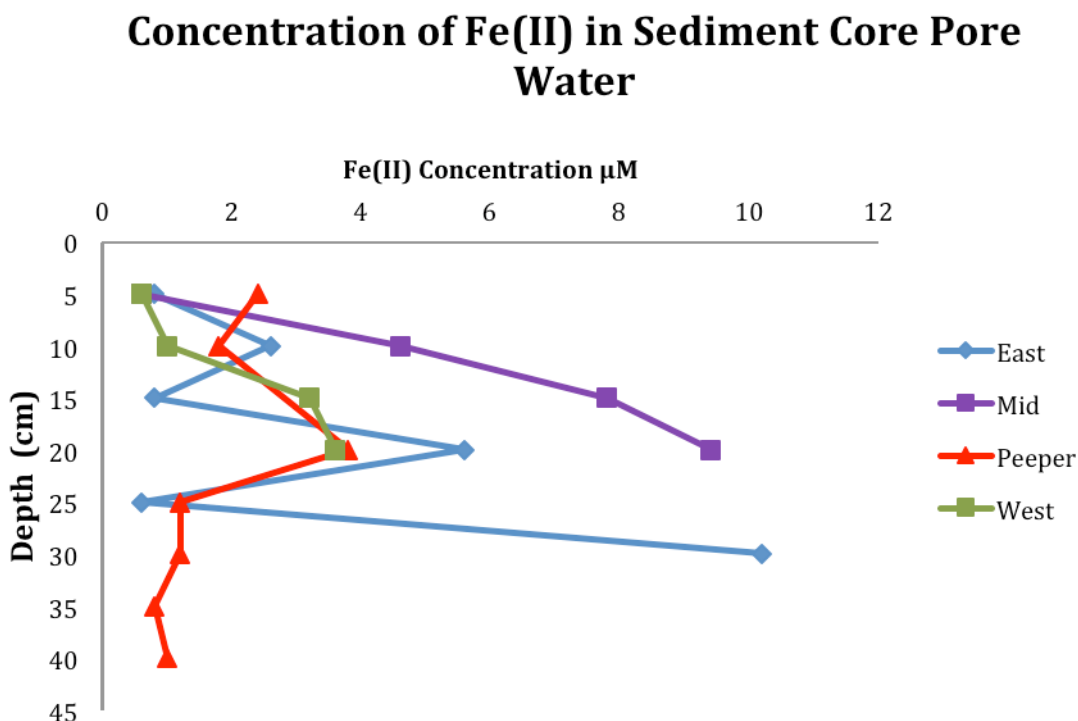

Figure 3. Fe(II) from pore water centrifuged from sediment cores, as a function of depth.

Total Fe Extracted from Sediment
Figure 4 represents the concentration (µg/g) of ascorbate-extracted Fe(II) in the sediment at each depth. Ascorbate is intended to extract the Fe(III) in solids readily available to microorganisms for Fe reduction. Due to an error in processing, some of the cores at the sediment surface were not analyzed. The concentrations at 15 cm, for which all cores were analyzed, ranged from about 35 µg/g Fe to almost 250 µg/g Fe. In the East core and West core, the Fe level spiked at 25 cm and 30 cm respectively. The Peeper and the Mid sites had the greatest concentrations at the surface. In addition, the West site was 248 µg/g at 15 cm, increased to 352 µg/g at 30 cm, and decreased to 211 µg/g at 40 cm. The Mid site had an initial concentration of 315 µg/g at the surface and decreased to 20 µg/g at 25 cm. The Peeper site was 144 µg/g at 10 cm, and gradually decreased to 84 µg/g at 35 cm, with a peak of 114 µg/g at 30 cm. The East site started at 35 µg/g and increased to 173 µg/g, with a peak of 106 µg/g at 10 cm.

Overall, the Peeper and Mid sites decreased in concentration, the West site remained fairly constant, while the East site increased with depth.

The stacked bar for each depth represents the total Fe extracted from sediment core samples. It includes Fe(II) extracted by HCl, Fe(III) extracted by HCl, as well as the ascorbate extractable Fe. HCl extracts the Fe that is not easily accessible by anaerobic bacteria. Fe(II) extracted by HCl includes FeS, which can form when Fe(II) comes in contact with sulfide, while Fe(III) may be associated with organic matter of crystalline oxides. Four sediment core samples were analyzed and the range of total Fe in the sediment was approximately 1000 µg/g to 8000 µg/g. The West site decreased from 5852 µg/g at 15 cm to 3565 µg/g at 40 cm. The Mid site decreased from 4896 µg/g at the surface to 3292 µg/g at 25 cm, with a peak at 10 cm. The Peeper site was 3289 µg/g at 10 cm, increased to 7761 µg/g at 30 cm, and dropped down to 3289 µg/g at 35 cm. The East site gradually increased in total Fe, starting at 1043 µg/g to 5300 µg/g, with a peak at 6794 µg/g.

Due to errors in testing, further analysis may be necessary in order to assess the Fe reduction in Asylum Lake. Typically, Fe removed by ascorbate would be the largest pool of Fe, but it is not the largest on these graphs. It is possible that the ascorbate extraction did reduce all of the easily extractable Fe, and that the rest of that Fe was extracted by HCl. As a result, the total Fe would be correct, however, the Fe easily accessible by bacteria would be underrepresented in that total. However, based purely on the comparison of sediment cores it is apparent that the Peeper, Mid, and West sites have high levels of total Fe and Fe(II). The overall availability of Fe(II) in solution does suggest the anaerobic respiration of bacteria breaking down organic matter is occurring.
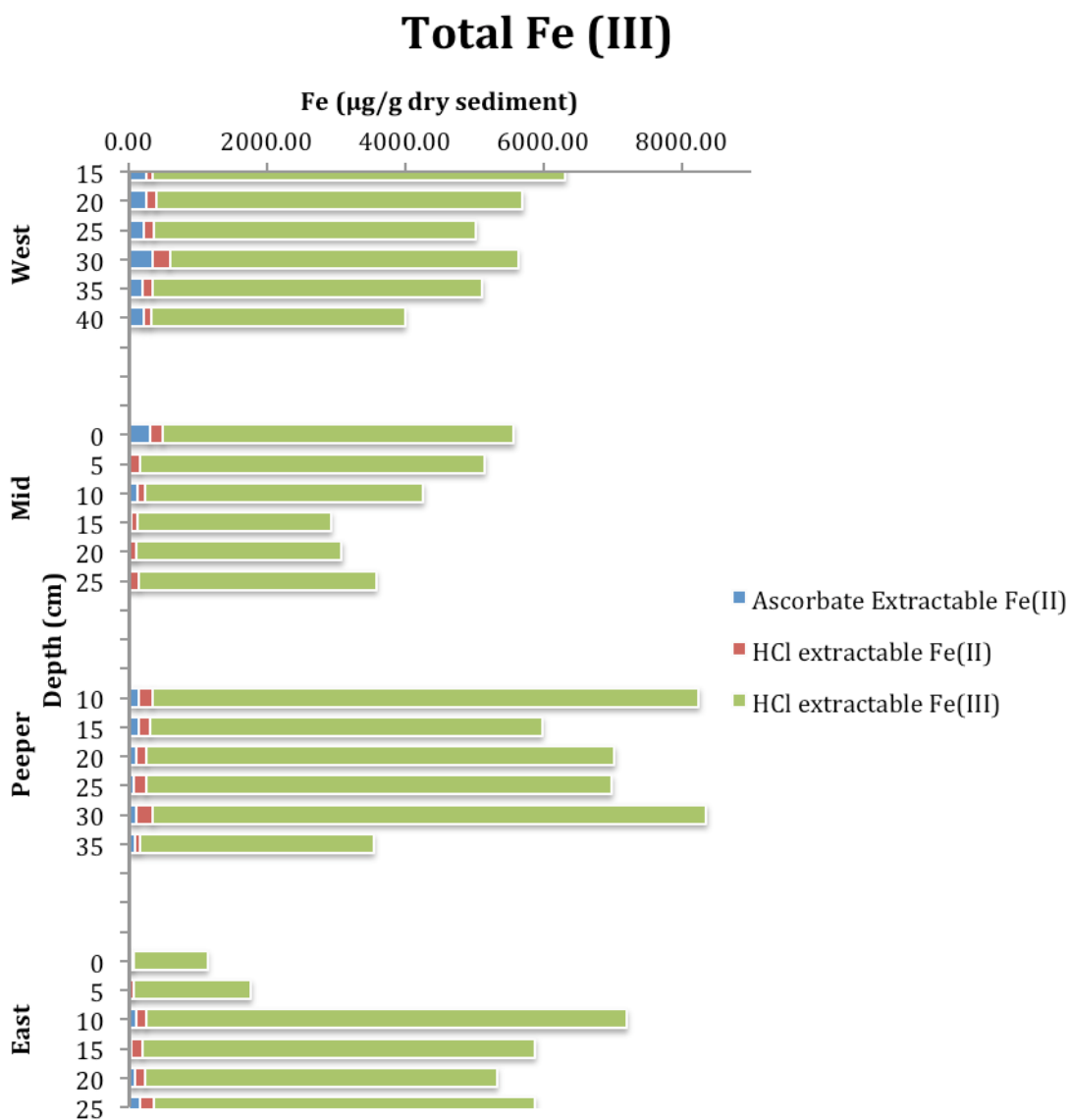
Total Fe (III)

Fe (µg/g dry sediment)

Figure 4. Total Fe from sediment cores as a function of depth. Due to a processing error, some of the most surficial samples from the cores were not analyzed.

Peeper Pore Water Analysis
pH

The pH of the solution extracted from the three peepers installed at Asylum Lake fluctuated with depth, but overall stayed in the range of 6.2 to 7.2 (Figure 5). At the top of the peeper 1 profile, the pH is 6.3, with an immediate drop to 6.5 at 1 cm and gradually increasing to a pH of 7 at 49 cm. Peeper 2 has a pH of 6.3 at the surface and fluctuates for the upper 15 cm between 6.2 and 7.2 before leveling out to 6.8 at 48 cm

depth. Peeper 3 has a pH of 6.5 at the surface, which gradually decreases to a pH of 6.3 at 50 cm depth.

Aerobic respiration lowers pH, while anaerobic respiration increases pH. One would expect that the pH would increase as less oxygen became available. For example, Peeper 1 increases in pH with depth overall, except for a possible outlier at 1 cm. The other two peepers decrease with depth. A possible reason as to why the pH decreases in these peepers, which also display signs of anoxic conditions, may be that the roots from nearby vegetation are supplying the sediment with oxygen which quickly reacts with the reduced solutes in the pore waters. The Peeper site had tree roots that could have been adding oxygen to the sediment.
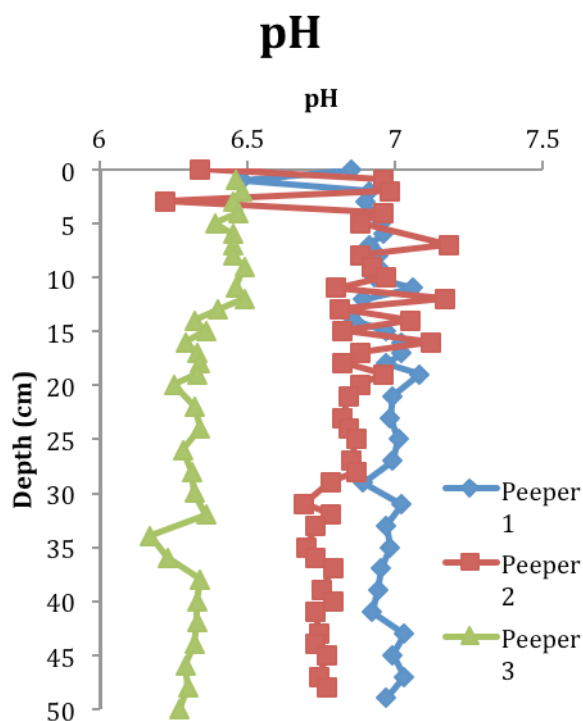

Figure 5. pH of pore waters as a function of depth.

Manganese

The manganese (II) profiles for both peeper 1 and 3 appear to have similar trends of increasing concentration with depth (Figure 6). Peeper 1 has an overall lower concentration of manganese, as it is below detection limits near the surface and

reaches a maximum of 20 µM at depth. Peeper 3 has a surficial concentration of 30 µM and increases to a maximum of 78 µM at 42 cm, but then decreases to 67 µM at 50 cm.

In the absence of oxygen, manganese (IV) is reduced to manganese (II). According to their profiles, peeper 3 has a greater concentration, which correlates to more organic matter decomposing in anoxic conditions via manganese reduction.
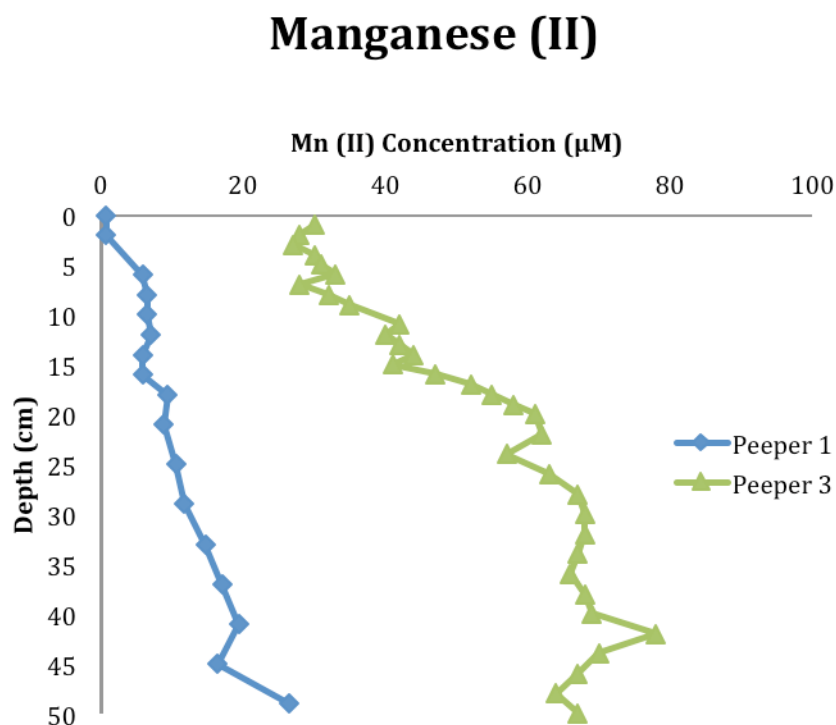
Manganese (II)

Figure 6. Manganese(II) concentration as a function of depth.

Fe(II)

Fe(II) concentrations from pore water analysis are approximately 18 µM at the surface for all three peepers. Fe(II) in Peeper 1 decreases to below detection limits at 12 cm, and gradually increases to approximately 65 µM at 40 cm, decreasing to 45 µM at 45 cm. Fe(II) in Peeper 2 decreases to below detection limits between 2 and 18 cm, gradually rising to 20 µM at 35 cm, and decreasing to ~5 µM at 46 cm depth. Fe(II) in Peeper 3 decreases from 18 µM near the surfce to 8 µM at 5 cm, increasing to 85 µM at

42 cm. Below this, Fe(II) decreases to 55 µM at 48 cm and increases again to 85 µM at 50 cm.

Peeper 3 had the greatest concentrations of Fe(II), suggesting that the greatest amount of Fe reduction takes place at this site, which was probably the most reducing of the peeper sites. High levels of organic matter deposition, consistent with eutrophic conditions in Asylum Lake, are probably creating the anoxic environment, which selects for anaerobic bacteria capable of reducing Fe(III).
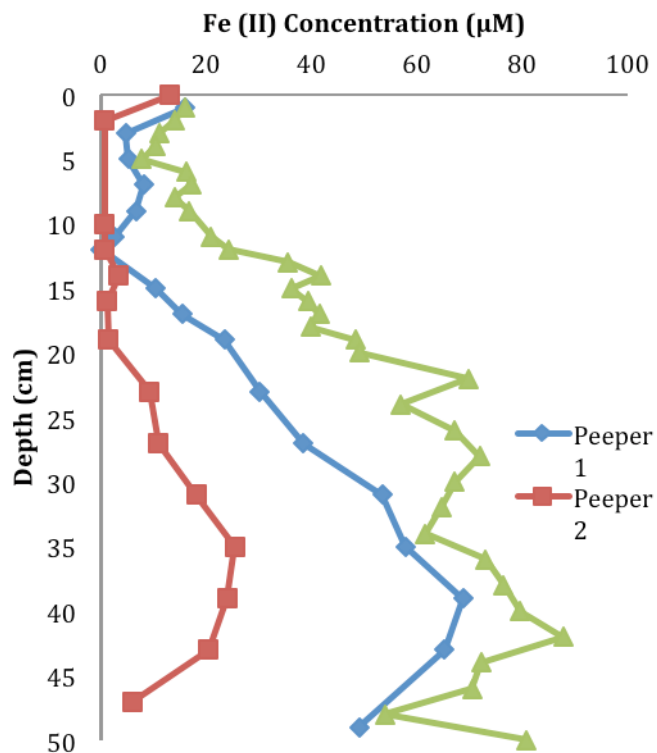
Iron (II)

Figure 7. Fe(II) concentration in porewaters as a function of depth.

Phosphate

The phosphate profiles of peepers 1 and 3 have similar trends, as phosphate increases slightly with depth in they both (Figure 8). Phosphate concentrations at the surface of Peeper 1 are 9 µM, increasing to a concentration of 15 µM at 49 cm depth. A significant spike in phosphate concentration is noted at 33 cm, with a concentration of 33 µM.

Peeper 3 has a phosphate concentration of 16 µM near the surface, which increases to a maximum of 24 µM at 26 cm, dropping to 23 µM at 50 cm depth. Phosphate data for peeper 2 was not available.

Phosphates adsorbed to Fe(III) and Mn(IV) oxides are released upon reduction of Fe(III) to Fe(II) and Mn(IV) to Mn(II) in anoxic conditions. Peeper 3 has a greater concentration of phosphate than peeper 1. This indicates that more Mn(IV) and Fe(III) reduction are occurring, which happen in anoxic conditions, and is also consistent with the higher levels of Mn(II) and Fe(II) observed at this site (Figures 6 and 7).
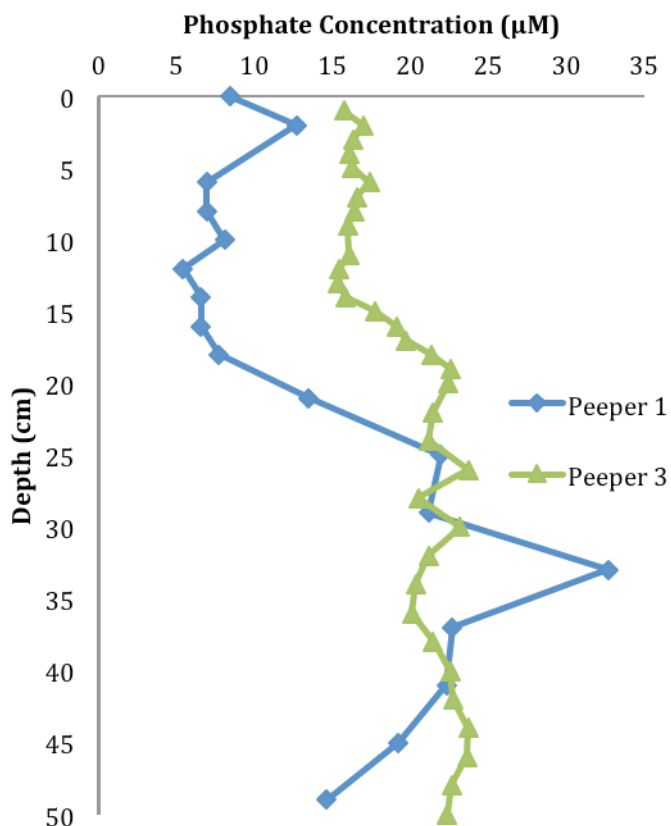
Phosphate

Figure 8. Phosphate concentrations from pore water as a function of depth.

Ammonium

The profiles of peepers 1 and 2 show consistently small amounts of ammonium (NH_4^+) throughout the entire depth. In contrast, Peeper 3 displays fluctuation in ammonium

concentrations, which are much greater, ~810 μM near the surface with a maximum spike in concentration of 980 μM at 17 cm depth. A gradual, overall decline in ammonium concentration occurs between 20 and 50 cm depth, to a minimum of 240 μM at 50 cm.

Peeper 1 and 2 were located in the same area, which does not appear to be as reducing as the location of Peeper 3. High concentrations at near the surface of Peeper 3 suggest that ammonification is occurring. In the presence of oxygen, the ammonium would have converted to nitrate. Because it does not, anoxic conditions must be present throughout the depth profile of Peeper 3.
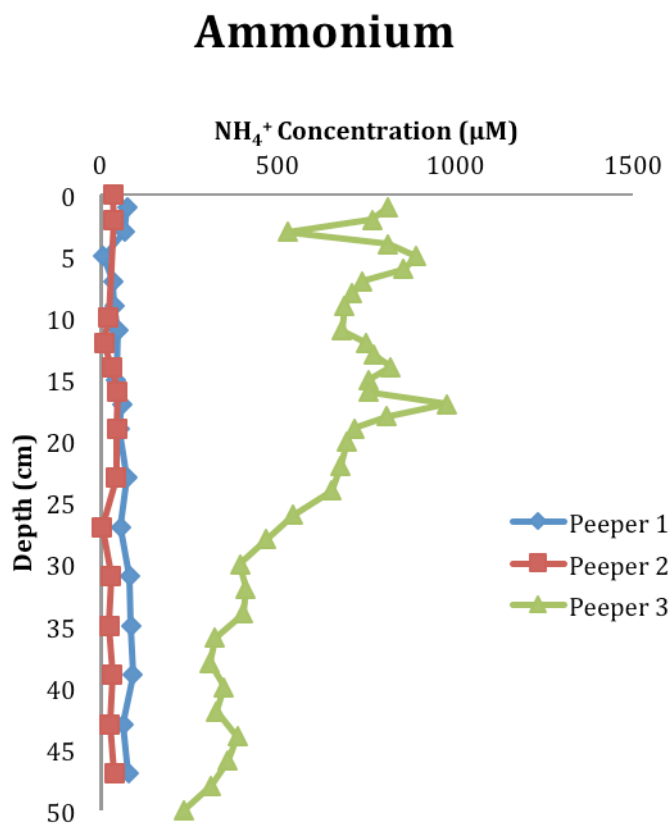

Figure 8. Ammonium (NH_4^+) concentration of pore water as a function of depth.

Sulfate

Sulfate concentration for Peepers 1 and 2 are higher than Peeper 3 throughout the profiles. Peeper 1 has a surficial concentration of approximately 15 ppm sulfate, decreasing to 10 ppm at 20 cm, increasing to over 20 ppm at 35 cm, and decreasing

back down to 14 ppm at 46 cm depth. Peeper 2 has a surficial concentration of 16 ppm, increasing to 20 ppm at 15 cm, and decreasing to 16 ppm at 45 cm. In contrast, Peeper 3 has a much lower surficial concentration of 8 ppm, which decreases to approximately 4 ppm for most of the measured profile.

The sulfate concentration in peeper 3 may be lower because of the reduction of sulfate to sulfide (H_2S) under anoxic conditions by anaerobic bacteria. Furthermore, if Fe(II) is present, it can react with sulfides, precipitate, and diffuse downward in the sediments. If this process is occurring, it could result in less sulfide being evident in the pore water than might be expected from the lowered concentration of sulfate relative to the Peeper 1 and 2 sites.
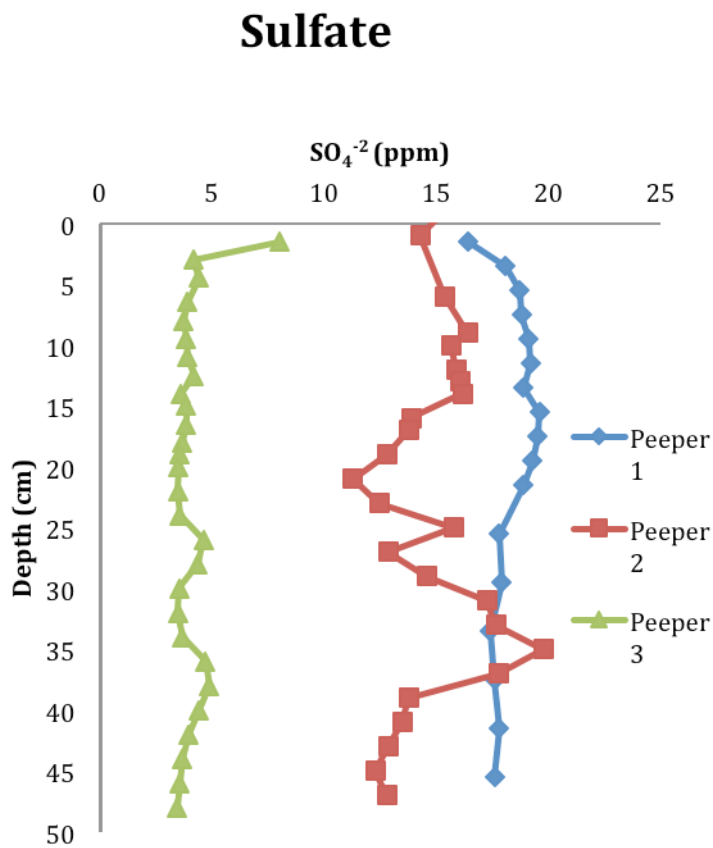
Sulfate

Figure 9. Sulfate concentration of pore water as a function of depth.

Chloride

Chloride concentrations for Peeper 3 were approximately 50 ppm higher than the concentrations of chloride for Peepers 1 and 2. Peepers 1 and 2 have chloride concentrations of approximately 100 ppm throughout the entire depth of the peepers. The concentration of peeper 3 was approximately 155 ppm for the entire depth.

The presence of chloride at all three sites suggests that road salts have leached into the lake, because there are likely no significant natural reservoirs of chloride present at Asylum Lake. Perhaps surprisingly, Peeper 3, which is located farthest from Drake and Stadium Drive, has the greatest accumulation of chloride. This could indicate that a plume of chloride moves from west to east in the groundwater and shallow sediments around Asylum Lake. Further testing is needed in order to determine whether the chloride is having an effect on lake conductivity or turnover or biogeochemical processes within the sediments.
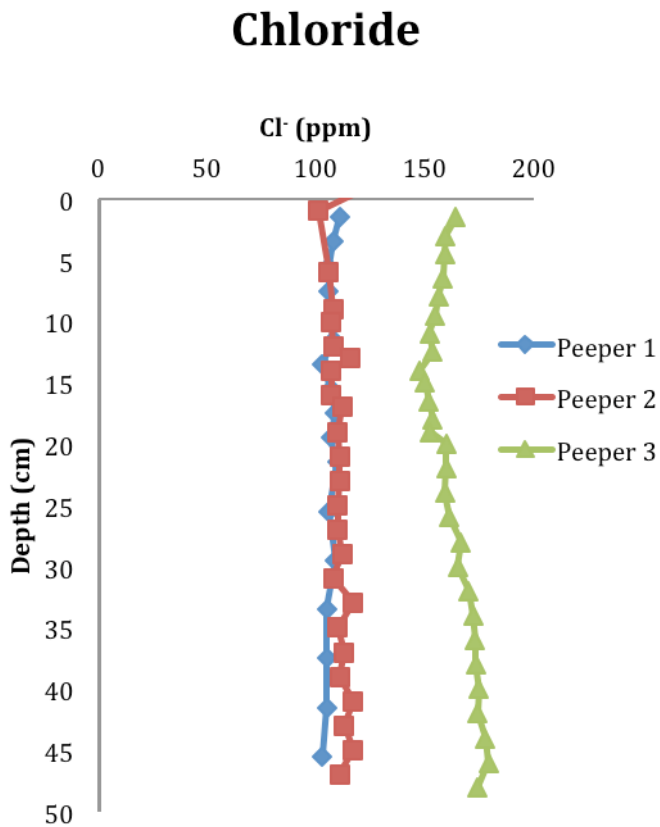

Figure 10. Chloride concentration as a function of depth.

Conclusion

After analysis of sediments and pore water, we conclude that Asylum Lake is showing signs of eutrophication and road salt contamination. The high percentage of organic matter, especially at the Peeper Site, suggests that eutrophication is occurring. Further, the presence of Fe(II), Mn(II), phosphate, and ammonium in the pore water also are consistent with eutrophication and high deposition of organic matter, because those redox-sensitive species are found in anoxic water and sediment. Other contamination, such as chloride from road salts, appears to have leached into the lake, but its ultimate impact is unknown.

Eutrophication, once it takes control of a lake ecosystem, can be difficult if not impossible to eliminate. Diagnosing the problem, and reducing nutrient loading and other contamination, may lessen the severity of its effects on lake ecology.

References

Heiri O., Lotter A.F., and Lemcke G. (2001) Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. Journal of Paleolimnology **25**: 101-110.

Western Michigan University**:** Water Quality Evaluation of Asylum Lake and Little Asylum Lake With Management Recommendations, Kieser & Associates, LLC. 536 E. Michigan Ave, Suite 300 Kalamazoo, MI 49007. 2008.

Autumn Turnover, Water Column Mixing, and Shore Sediments Report for Asylum Lake

November 2011

Western Michigan University

Nicole Dickerman

Joe Kreft

Jesse Torma

TA: Ryan Sibert

GEOS 5500

Kings group

Introduction

Our analysis of Asylum Lake focused on water temperature, organic matter content of the surrounding lake sediments, and chloride and sulfide ions in the water column. We expect to find a build-up of chloride ions due to road salt contamination, patterns of fall turnover and lake mixing, and increased organic carbon build up due to eutrophication.

Methods and Materials

Soil Sampling Procedure

Russian peat corer	Plastic bags and spatula
Ruler, metric	Cooler with ice packs
Apple iPhone 4, GPS	

The soil sediment core samples were taken using a Russian peat corer. Extracted samples were divided up based on depth in centimeters into 5cm subsections of each core after a "top section" was established. The samples were placed into labeled zip-lock bags using a

spatula and then sealed with as little air in the bags as possible. The samples were then put into a cooler for transport back to the lab. GPS location readings were recorded at each sampling site. Once in the lab, the samples were placed in a refrigerator for storage until work-up and analysis could be performed.

Water Column Sampling Procedure

Canoe, 2-person	Vertical Van Dorn sampler
Temperature probe, °F	Auto-pipette, 100-1000 µL
2.5 M HNO_3	Secchi disk
Cooler with ice packs	20mL plastic sampling vials
Bathymetric map of Asylum Lake	5mL vials with 500µL trap solution
HTC EVO 4G, GPS	

      Using the bathymetric map of Asylum Lake, we paddled out to our chosen sites. We anchored the canoe and took a GPS reading of our location before beginning our sampling. The temperature probe was lowered into the water column at 2ft intervals, and the temperature reading was recorded. The Van Dorn sampler was lowered into the water column at 2m intervals to gather water samples for IC and ICP-OES analyses in 20mL sampling vials. Each vial was filled to the very top. ICP-OES vials had 3 drops 2.5 M HNO_3 added before capping. These samples were placed into vials unfiltered. When the water coming out of the sampler smelled of sulfur, samples were taken for the sulfide test. These samples were taken every meter. 500µL of water sample was added to the 5mL vials of trap solution. A Secchi depth reading for water transparency was taken, but the results were most likely inconclusive given the time of year, time of day, and weather.

IC Procedure

Centrifuge	25mm, 0.45µm syringe filters
Syringe	15mL polycarbonate centrifuge tubes
5mL Dionex tubes and caps	

Samples taken from the deeper portions of the lake contained a greater amount of sediment and required centrifuging to remove the large particulates. All samples were filtered using a syringe-filter into a clean 15mL polycarbonate centrifuge tube, then put into 5mL Dionex plastic tubes, and the special cap was inserted in the top of the tube using a cap-installing tool. The samples were then refrigerated until the IC instrument was available for testing.

ICP-OES Procedure

Centrifuge   15mL polycarbonate centrifuge tubes

Syringe   25mm, 45µm syringe filters

2.5 M HNO_3

The ICP-OES samples had three drops of 2.5 M HNO_3 added to the top of them in the container in the field when collected. Once in the lab the samples with sediment in them were centrifuged, decanted and filtered with a syringe filter into a clean plastic vial. The samples without excessive sediments in them were syringe filtered into clean plastic vials without centrifugation. 1mL of the sample was added to a clean 15mL centrifuge tube, then 5mL of DDI water and 4mL of the 2.5 M HNO_3. These were refrigerated until they were run on the ICP machine.

Loss on Ignition (LOI) Procedure

Oven   Crucible and Tongs

Balance   Centrifuge

Gloves

In the lab, samples were transferred into 15mL centrifuge tubes and centrifuged for 6 minutes. The liquid was decanted then the uncapped tubes were left to dry in an oven at 105°C for 72 hours. The dried solids were collected and placed in pre-weighed crucibles and weighed (DW_{105}). Samples in the crucibles were placed in a pre-heated (550 °C) muffle oven for two hours. The samples were removed, allowed to cool and re-weighed in the crucibles (DW_{550}). Organic matter content could then be calculated by the loss on ignition according to the equation (Craft et al., 1991)

$$Organic\ Carbon = 0.04 \times LOI_{550} - 0.0025 * LOI_{550}^2$$

A subset of these samples was also analyzed for inorganic matter content by heating again to 950°C for two more hours (DW_{950}). Samples were then removed, allowed to cool and re-weighed. Inorganic carbonate was calculated with the equation:

$$Original\ Carbonate\ Content = LOI_{950} * 1.36$$

(Heiri et al., 2001) were used to compute the inorganic carbon content of these samples.

Data Tables and Graphs

Map of sampling sites

W2
42.267385,-85.647494

W.1
42.266739,-85.646820

W.3
42.267929,-85.645660

N.1
42.268616,-85.641632

E1
+42° 15' 54.27", -85° 38' 9.61"

SE1
42.264954,-85.636215

S.1
42.266037,-85.641022

S.2
42.265808,-85.641205

S.3.
42.265976,-85.642593

WEST LAKE SAMPLE SITE (11-2-11)
42.267896,-85.643550

EAST LAKE SAMPLE SITE - (11-2-11)
42.267456,-85.639109

SE CREEK OUTLET SAMPLE (11-2-11)
42.264382,-85.635965

WEST LAKE SAMPLE SITE (11-10-11)
42.267719,-85.643014

Asylum Lake
Bathymetry Map
2001

Universal Transverse Mercator

Scale in Meters
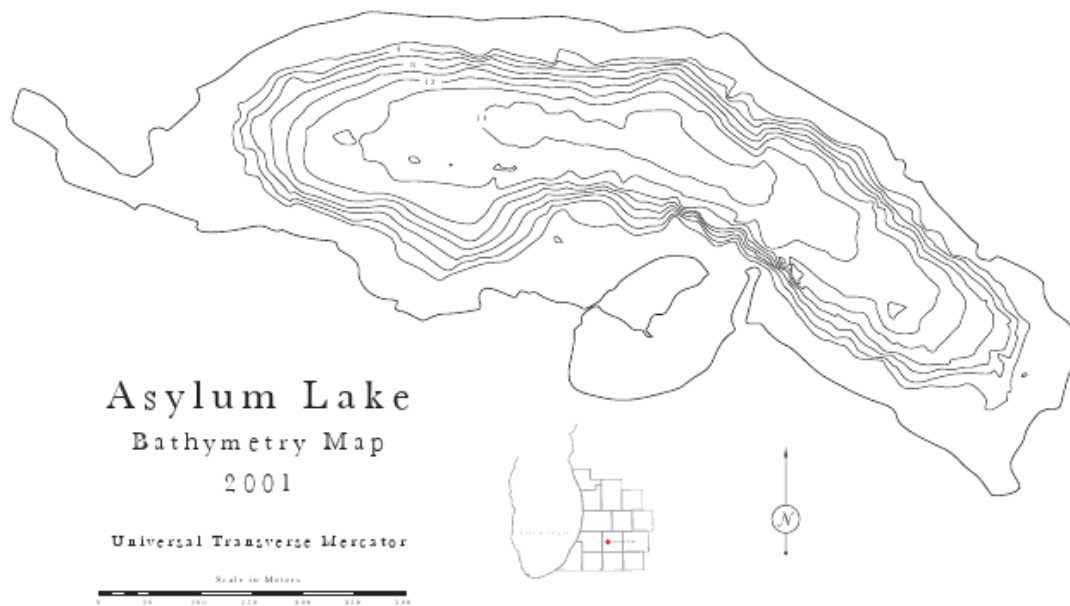
Soil Sampling

Name: Nicole Dickerman and Joe Kreft

Date: October 22, 2011

Time: 10:24 am

Location: West End of Asylum Lake-Under ~20 cm of water

GPS coordinates: 42.266739, -85.646820

Temperature: 41° F

Weather: Slightly Moist, Blue Skies

Sample #: W1

Description: top 15 cm is fluffy mush; rest of the core collected in 5 cm increments

Time: (Not recorded)

Location: West End of Asylum Lake, very close to Drake Rd.-Under ~20 cm of water.

GPS coordinates: 42.267385, -85.647494

Temperature: 41° F

Weather: Slightly Moist, Blue Skies

Sample #: W2

Description: Black to brown

Time: 11:38 am

Location: North-West side of Asylum Lake-Under ~20 cm of water

GPS coordinates: 42.267929, -85.645660

Temperature: 47° F

Weather: Slightly Moist, Blue Skies

Sample #: W3

Description: all black; drier than the others; more roots

Time: 12:00 pm

Location: North side of Asylum Lake-Under ~20 cm of water

GPS coordinates: 42.268616, -85.641632

Temperature: 47° F

Weather: Slightly Moist, Blue Skies

Sample #: N1

Description: not much swamp; more lake; split samples by soil appearance: 0-9cm fluff, 9-15cm loose, moist sediment; 15-23cm and 23-31cm compacted organic sediment

Time: 12:26 pm

Location: East side of Asylum Lake-Under ~20 cm of water

GPS coordinates: 42.265075, -85.636003

Temperature: 47° F

Weather: Slightly Moist, Blue Skies

Sample #: E1

Description: North East side is less marsh-like. Could not get very good samples.

0-6cm top fluff; 6-18cm sediments obtained are more compacted

Time: (Not recorded)

Location: South-East side of Asylum Lake-Under ~20 cm of water

GPS coordinates: 42.264954, -85.636215

Temperature: 47° F

Weather: Slightly Moist, Blue Skies

Sample #: SE1

Description: Split visual distinction

Time: (Not recorded)

Location: South side of Asylum Lake-marsh-core not under water.

GPS coordinates: 42.266037, -85.641022

Temperature: 47° F

Weather: Slightly Moist, Blue Skies

Sample #: S1

Description: Small sediment grab from the middle of the peninsula

Time: (Not recorded)

Location: South side of Asylum Lake-Under ~20 cm of water

GPS coordinates: 42.265808, -85.641205

Temperature: 47° F

Weather: Slightly Moist, Blue Skies

Sample #: S2

Description: 36cm core; clayey in the last 6cm

Time: (Not recorded)

Location: South side of Asylum Lake-Under ~20 cm of water

GPS coordinates: 42.265976, -85.642593

Temperature: 47° F

Weather: Slightly Moist, Blue Skies

Sample #: S3

Description: Very clayey, last 25cm more soil-like

Water Column Sampling

Name: Joe Kreft & Jesse Torma

Date: November 02, 2011

Time: 4:30 pm

Location: West side of Asylum Lake

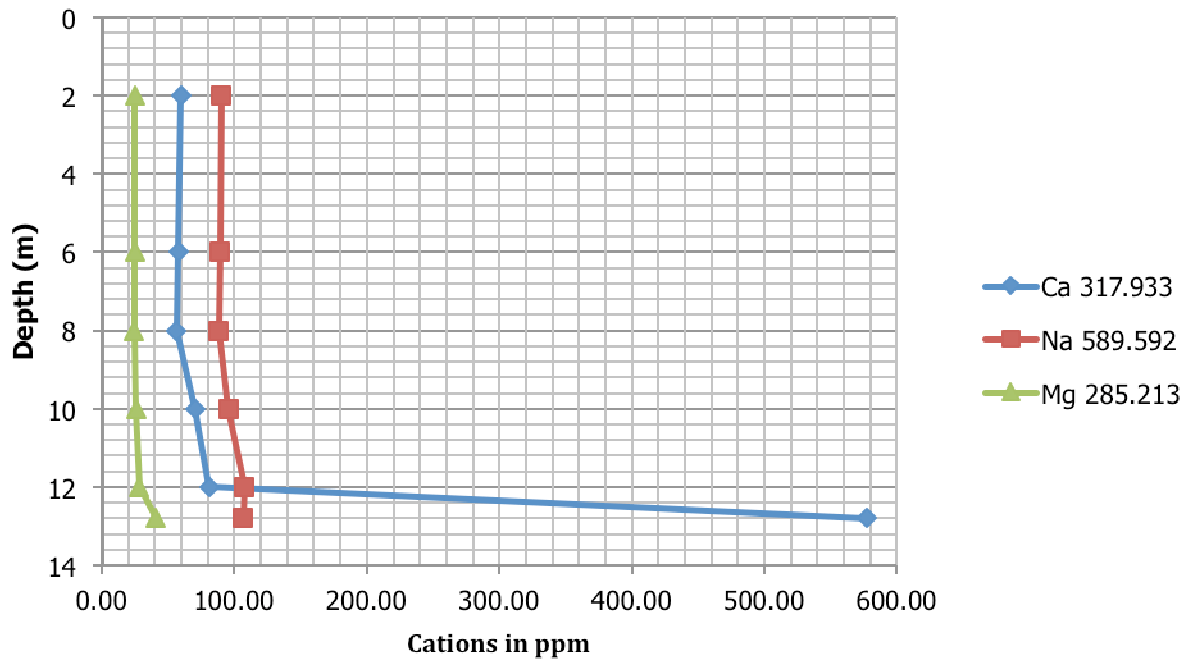GPS coordinates: 42.267896, -85.643550

Temperature: 63° F

Weather: Overcast

Samples taken: 6 IC, 3 Sulfide, and Temperature

IC Sample	Depth (m)	IC Sample	Depth (m)	Sulfide Sample Depth (m)	
1	2	4	8	8	10
2	4	5	10	9	11
3	6	6	11		

ICP-OES Data:

Cation Concentrations 11-2-2011

Temperature (11-2-11)

West Site

Depth (m)	°C
0.61	10.94
1.22	10.67
1.83	10.67
2.44	10.67
3.05	10.61
3.66	10.56
4.27	10.56
4.88	10.56

5.49	10.56
6.10	10.44
6.71	10.44
7.32	10.39
7.92	10.33
8.53	10.33
9.14	10.11
9.75	9.89
10.36	9.50
10.97	8.06
11.58	7.00
12.19	7.22

Depth (m)

2
4
6

Temp readings

Sample
1
2
3
4
5
6
7

51.7

4
6
8
10
12
14
16

Time: 5:51 pm

Location: East side of Asylum Lake

GPS coordinates: 42.267456, -85.639109

Temperature: 63° F

Weather: Overcast

Samples taken: 7 IC, 7 ICP-OES, Secchi depth, and 2 Sulfide

IC Sample	Depth (m)	ICP-OES	Depth (m)	Sulfide	Secchi depth
1	2	1	2	Sample	
2	4	2	4	Depth (m)	3m@5:40pm
3	6	3	6	12	
4	8	4	8	12.8	
5	10	5	10		
6	12	6	12		
7	12.8	7	12.8		

Time: 6:44 pm

Location: Creek outlet East of Asylum Lake

GPS coordinates: 42.264382, -85.635965

Temperature: 63° F

Weather: Overcast

Samples taken: 1 IC, 1 ICP-OES

Sulfide Ion Data:

West Samples (m)	S^{2-} Concentration (mol/L)	East Samples (m)	S^{2-} Concentration (mol/L)
8	1.96E-05	12	1.80E-03
9	3.36E-05	12.8	2.99E-03
10	7.56E-05		
11	2.25E-03		

Name: Joe Kreft and Jesse Torma

Date: November 10, 2011

Time: 3:47 pm

Location: West side of Asylum Lake

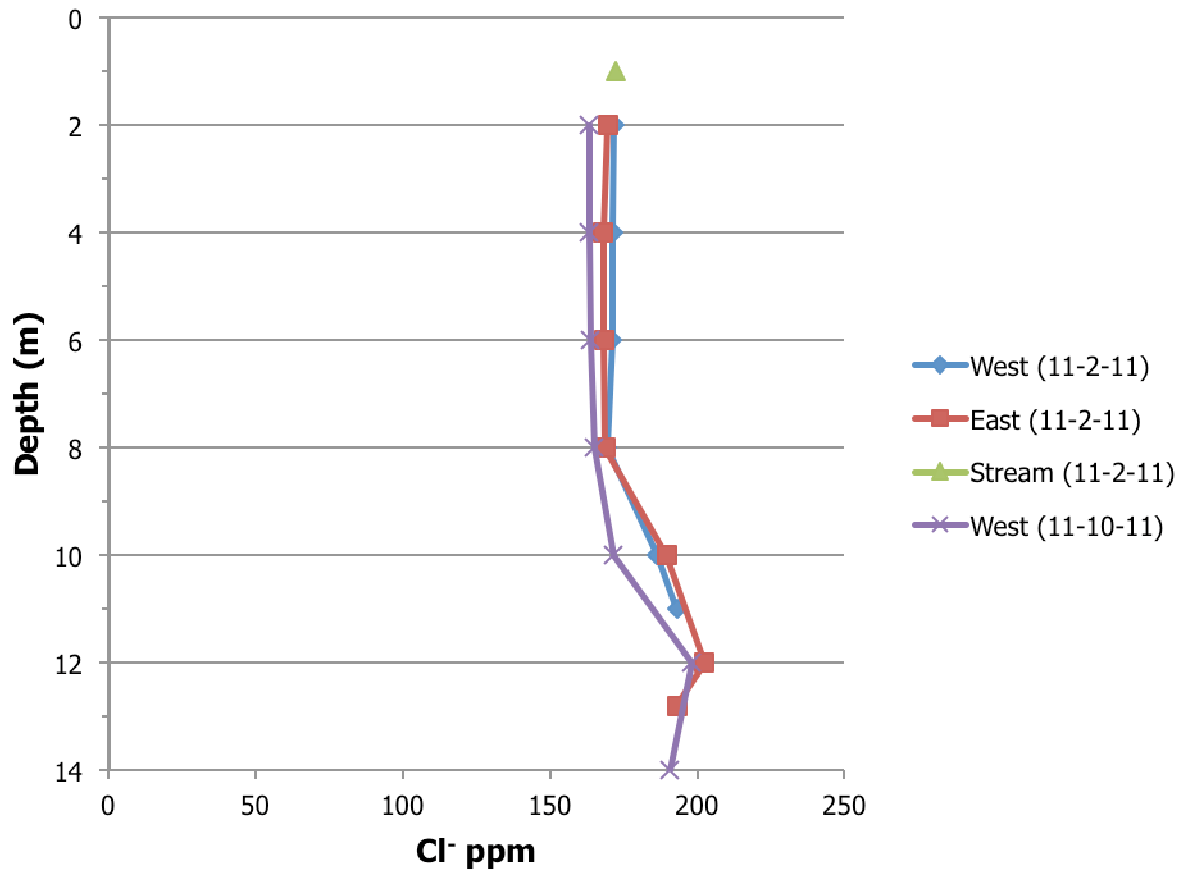GPS coordinates: 42.267719, -85.643014

Temperature: 33° F

Weather: Windy, Snowing

Samples taken: 6 IC, 3 Sulfide (not used)

Sample	Depth (m)	Sample	Depth (m)	Sulfide Sample Depth (m)	
1	2	5	10	12	
2	4	6	12	13	
3	6	7	14	14	
4	8			(samples expired, not used)	

IC Data:

Chloride Ions in ppm

Depth (m) vs. Cl⁻ ppm

Legend:
- West (11-2-11)
- East (11-2-11)
- Stream (11-2-11)
- West (11-10-11)

Temperature (11-10-11)

West Site

Depth (m)	ºC
0.61	10.00
1.22	10.00
1.83	10.00
2.44	10.00
3.05	10.00
3.66	10.00
4.27	10.00
4.88	10.00
5.49	10.00
6.10	10.00
6.71	10.00
7.32	9.89
7.92	9.83
8.53	9.67
9.14	9.56
9.75	9.56
10.36	9.44
10.97	8.00

11.58	7.22
12.19	6.89
12.80	6.78
13.41	6.67

Temperature Profiles from 11/2/11 and 11/10/11 at West Sampling Site:

Loss On Ignition Results: 550°C

Loss on Ignition Results: 950°C
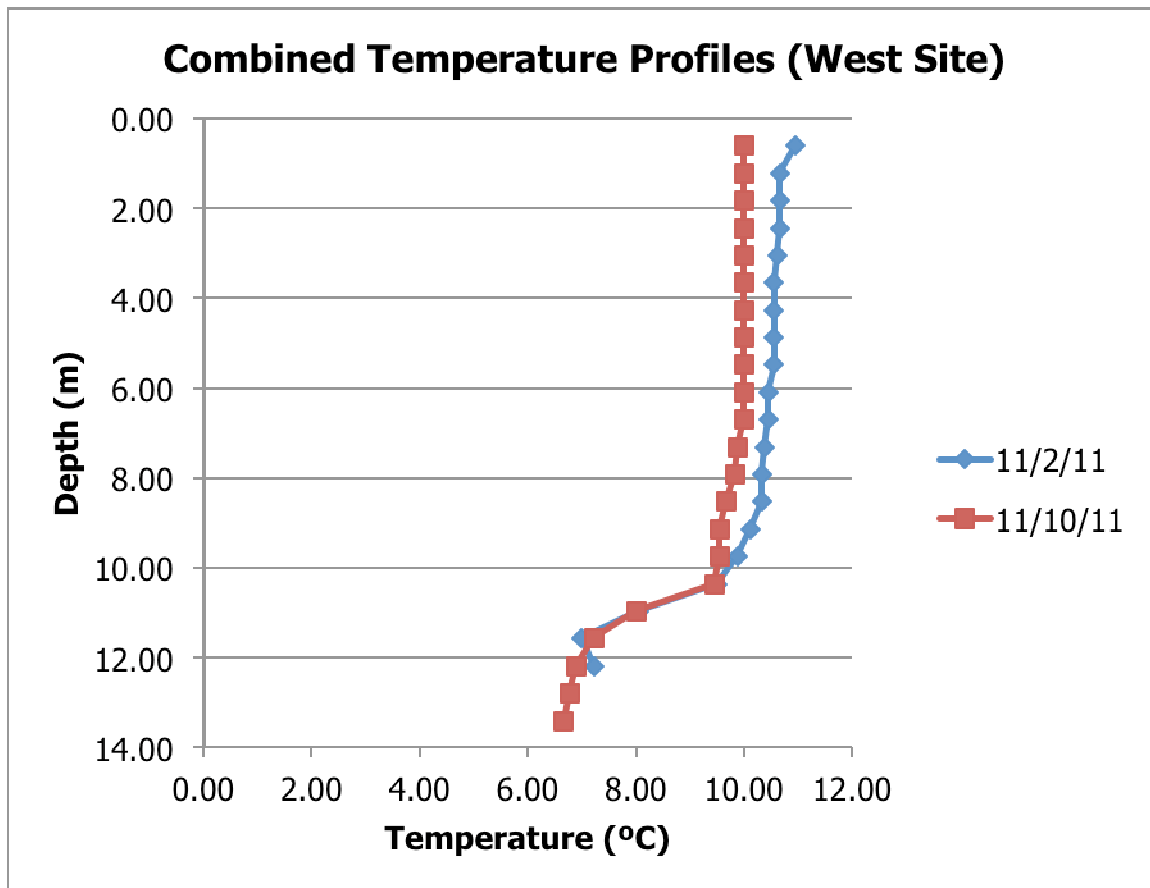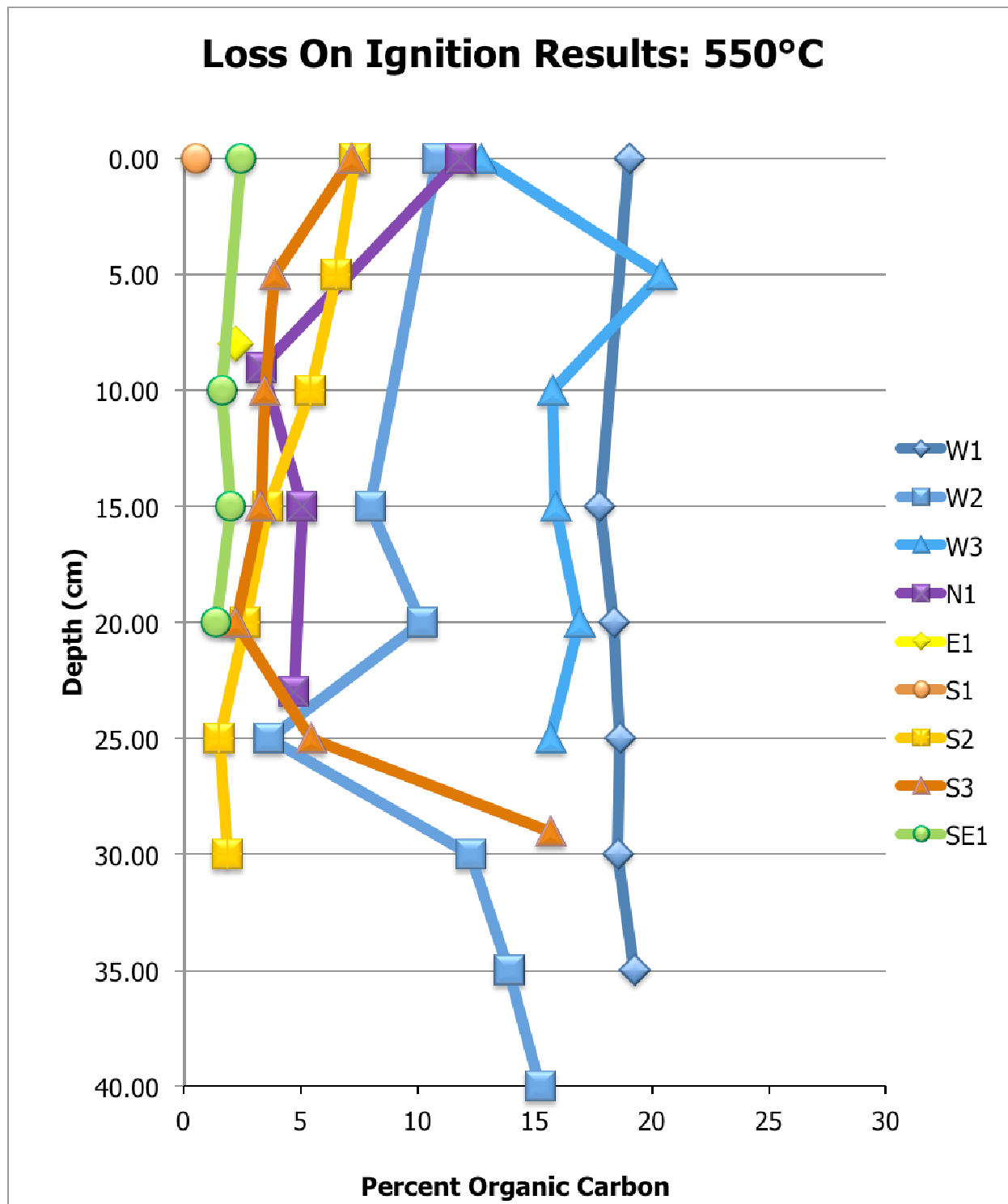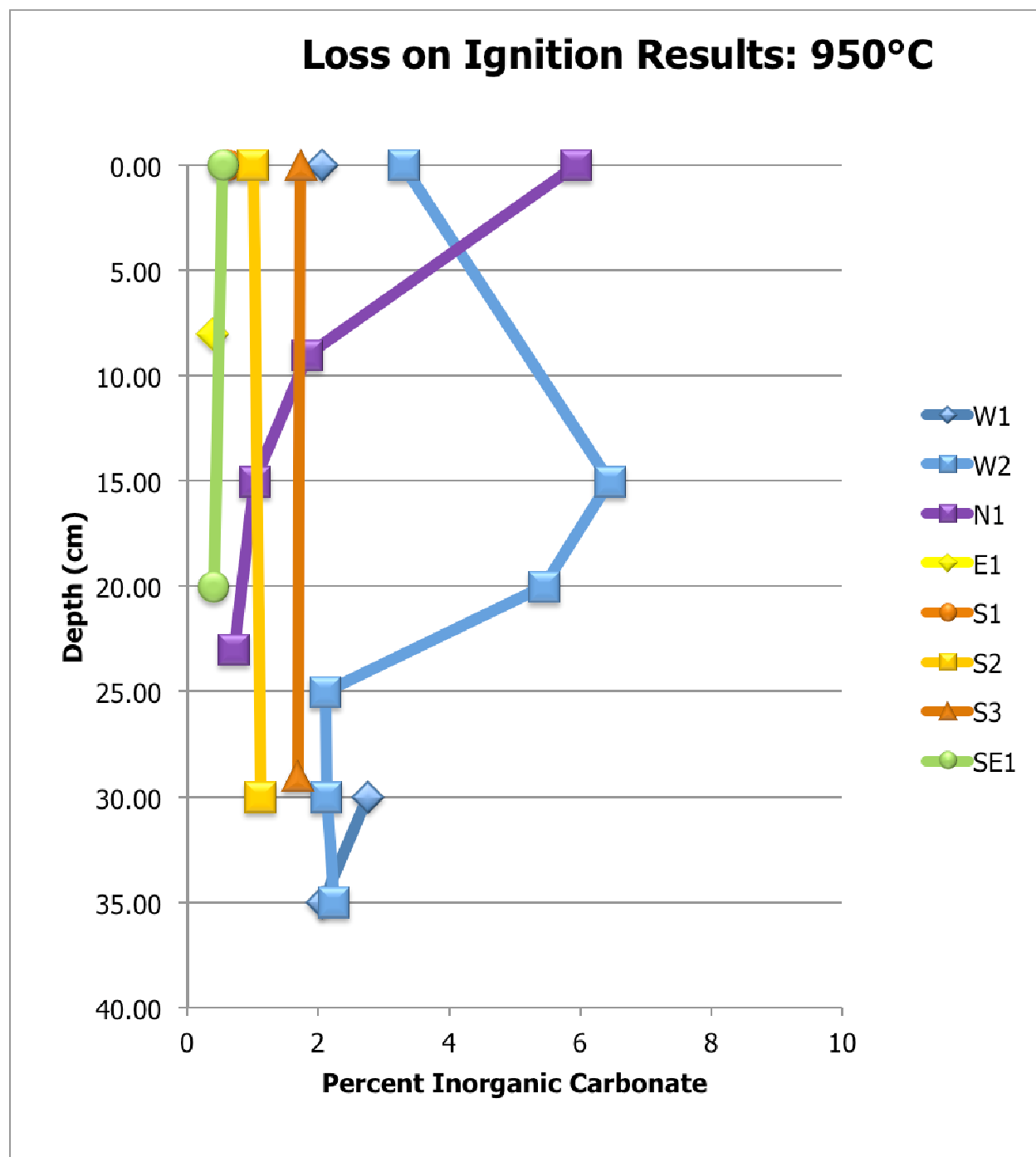
Interpretation

Chloride

Elevated chloride levels were noted in all water samples collected at all sites. The levels detected, near the bottom of the lake of ~200ppm, are nearing the EPA's National Water Quality Criteria: "aquatic organisms and their uses should not be affected unacceptably if the four-day average concentration of dissolved chloride, when associated with sodium, does not exceed 230 mg/L more than once every three years on the average," (Benoit, 1988). However, the Michigan Department of Environmental Quality has stricter environmental controls stating, "the waters of the state designated as a public water supply source shall not exceed 125 mg/L of chlorides as a monthly average." (MI DEQ, 2006). Many people in the area have city water, so the status of Asylum Lake as a public water supply source would need to be verified. The two main water-sampling sites resulted in chloride depth profiles that were very similar. There was a consistent concentration in the top 6-8 m, which then increased somewhat abruptly below 8m depth. Our initial hypothesis was that the west end of the lake would have a greater concentration of these ions due to road salt (NaCl and $CaCl_2$) washing in from Drake Avenue because it is heavily salted (as is US-131) and has a gully that drains run-off into the west side of the lake. Data in this study, however, indicates more Cl^- at the east lake site compared to the western study site. One possible source for this increase to the east could be the runoff from Stadium Drive. Another possibility is the effect of groundwater traveling from west to east, possibly concentrating suspended ions in the east portion of the lake. The bulk of the Cl^- measured in November is likely road salt runoff from last winter or prior years.

The third water sample site was a surface sampling of the creek water flowing out from the south east end of Big Asylum Lake to Little Asylum Lake taken from a drain pipe under the trail in the woods. The concentration of chloride ions for this sample is plotted together with the lake water column depth profiles, from which it can be seen that the concentration is similar to those in the top 6 m of the lake sites. This suggests that the concentration flowing out of the surface waters of the lake is not as elevated as those observed at greater depths in the water column.

Sulfide Ion Content

Our data shows significant dissolved sulfide build up in the bottom 2-3 m of Asylum Lake. Due to the highly reactive nature of sulfide ions in the presence of oxygen, the high concentration of sulfide ions in the bottom of the lake means there is a complete lack of oxygen there. This data combined with the temperature profile leads us to believe Asylum Lake is slow to turn over in the very bottom layer of the lake, if it turns over at all. Further testing and sample gathering would be required to determine lake turnover given our small window of observation. Our standards were not as precise (calculated linearity) as we would have liked, so the accuracy of our calculated sulfide ion concentration consequently suffered; however, the test merely quantitatively describes what our noses could qualitatively describe. The presence of sulfide is undeniable, and worthy of further investigation.

Carbon Content in the Sediment Cores

The graphs show a trend of more carbon content in the west side of the lake. This is expected because Asylum Lake is more marsh-like on the west side than the east side of the lake. Given more time, the sediments could be tested for total Fe content, and the pore water that was discarded could have been saved to test for Fe and Mn levels. All of which should be tested for reproducibility next year.

Conclusions

The data gathered in the study is not enough to tell us whether or not Asylum Lake is eutrophic. The presence of dissolved species such as sulfide indicates a state of anoxia at the bottom of the lake in the late summer and early fall so this merits further attention because this indicates possible eutrophication. What we are seeing from the trends of chloride concentrations is that there are indications that chloride is definitely collecting in the lake. This can further exacerbate a eutrophic lake so monitoring this lake in the future may be a prudent action to take. There seems to be a disruption in the lakes seasonal over-turn cycle but the data collected is not sufficient yet to say state this conclusively. If this was studied further and found to be true, then more specifically the top of the lake would be mixing reasonably well but below that depth the water might not be mixing especially not with the top lake water. This situation leaves the bottom of the lake with less ability to support plant and animal life but the top of the lake is oxygenated. Ultimately we can hypothesize further that the road salt running off the

roads and into Asylum Lake is having a negative effect on the geochemistry of the lake, but without a thorough investigation we cannot yet draw conclusions in full about its effect on the lake.

Calcium and sodium combined with chloride could be coming from nonpoint sources such as chlorine treated water or bleach from washing machines, not just road salt, so all sources should be considered. Regardless, elevated chloride levels are present in the lake water.

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GEOS 5020

Environmental Field Geochemistry

Department of Geosciences

Western Michigan University

1. Introduction

According to Louis et al. (2009), "The principal water quality problems encountered in lakes come from the processes of eutrophication, sedimentation, and contamination. Eutrophication is the process by which lakes are enriched with nutrients, essentially phosphorus and nitrogen. Sedimentation is the deposition and accumulation of both organic and inorganic matter in lake bottoms. Contamination is the process by which a health hazard is created when harmful substances are added to a lake", and further, "The term eutrophication refers to the natural and artificial addition of nutrients to lake waters and the effects of these added nutrients. Eutrophication is an aspect of lake aging; it is a process that increases the rate at which lakes disappear or become unsuitable for human use. Man-made eutrophication, in contrast to natural eutrophication, is rapid, but can be reduced or reversed by restricting or limiting the rate of supply of nutrients to the lake".

This report covers our research activity of water quality evaluation of Asylum Lake. Asylum Lake is located in Kalamazoo County, Michigan; in southwest Kalamazoo, north of Parkview Avenue and east of Drake Road. The lake is a glacial kettle lake formed during the last ice age. Asylum Lake has a surface area of approximately 46.5 acres and maximum depth of 54.5 ft. This lake is largely groundwater fed, with 51.9% of its annual inflow from groundwater, another 39.2% enters from the stormwater and other runoff, and the smallest contribution is 8.9% from direct rainfall (Kieser & Associates, 2008).

2. Sampling Locations

This report will reference our two testing locations in the lake. The first testing location was at the west end of the lake near Drake Rd in a deep (~13 m) part of the lake. This location will be referred to as "West Site". Our second testing location was at the east end of the lake in

a shallow area approximately 6 meters deep. This location will be referred to as "East Site". These locations can both be seen on the map in Figure 1.

Figure 1. Location map. (Google Earth).

3. Objectives

Our goal in conducting these tests is to determine if Asylum Lake shows signs of eutrophication and/or road salt contamination. We set out to do this by testing the pH,

temperature, dissolved oxygen levels, conductivity, sulfide levels, iron(II) levels, phosphate levels, and chloride levels in the lake column at the two test sites.

4. Methods

Our testing was conducted from October 23, 2011 through December 2, 2011 with samples being collected on October 23, 2011 and November 13, 2011.

Sample collection: water column samples were collected from the two sites using a Van Dorn water sampler at 1 meter intervals from the surface to the lake bottom (figure 2). Samples were collected in 25 mL plastic sample bottles. Two samples were taken from each depth, one bottle was acidified with nitric acid to preserve the sample for later testing and other bottle was filled and remained un-acidified (none of the samples were filtered).

In situ measurements: temperature, dissolved oxygen, and pH were measured in the field using field probes.

In lab measurements: conductivity was measured in the lab using field probes. Sulfide, phosphate, and iron (II) levels were measured using UV/Vis spectrophotometry. Chloride was measured using ion chromatography.

Figure 2: Water Sampling at Asylum Lake, Oct. 23, 2011.

5. Results and Discussion

After all the measurements were completed, the data was reassembled into graphs to represent the trends of different concentrations or values with depth.

5.1. Temperature

Temperature was measured at both locations of the lake for each sample. There was a slight decrease of the temperature with depth reaching 7.7^{o}C in the deeper, cooler part of the lake column (figure 3, 4). The relatively constant temperatures in the upper portion of the lake is because mixing. The results obtained from the second round of measurements (Nov. 13) show that the temperature dropped 5°C at the surface since the first measurements. This is because Nov 13 was a windy day and a snow shower took place just before the sampling (Nov. 10).

5.2. pH

The pH values ranged from 7.2 to 8.0 in the West profile; most of the values fit between the 7.8 and up to 8.0 range. Plotting the profiles shows an increase of pH values below the surface to a depth of 10 m, then an increase in the bottom waters below 10 m (figure 5). This increase at bottom depth could be associated with the reduced solutes, which are produced by anaerobic degradation reactions in the bottom waters.
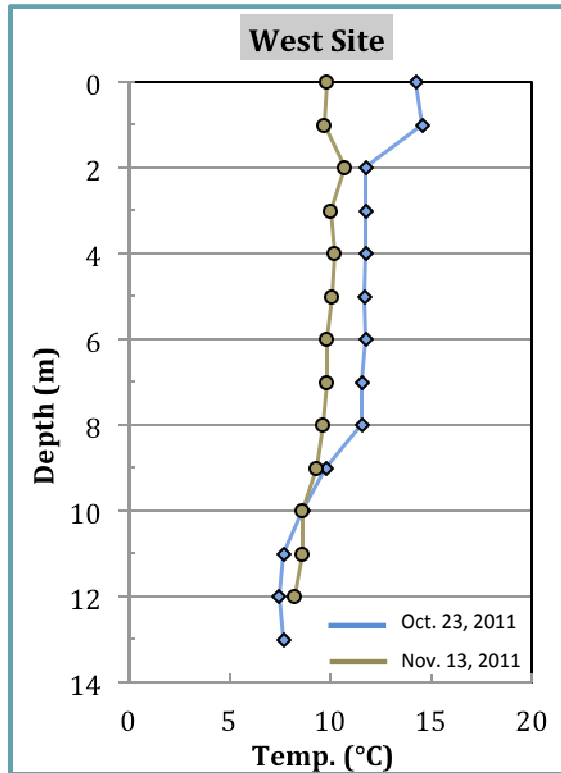
Figure 3: Temperature profiles at west site.
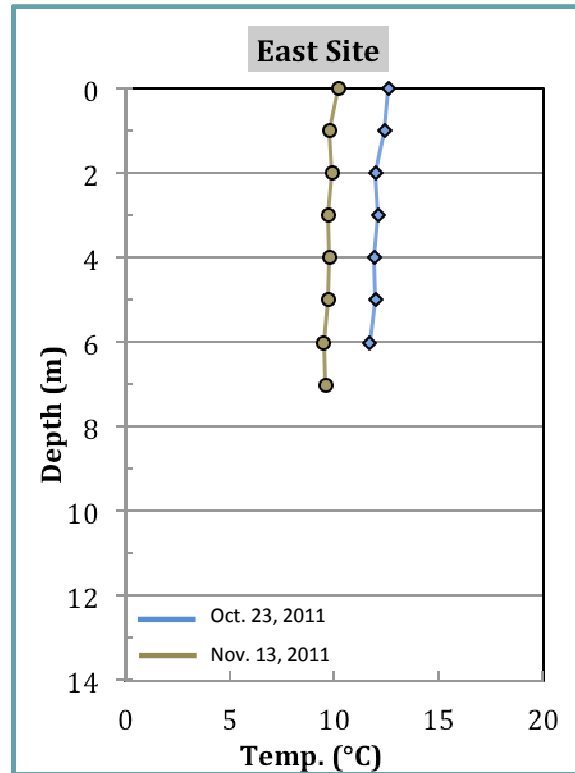
Figure 4: Temperature profiles at east site.

Figure 5: pH profiles at east and west sites.
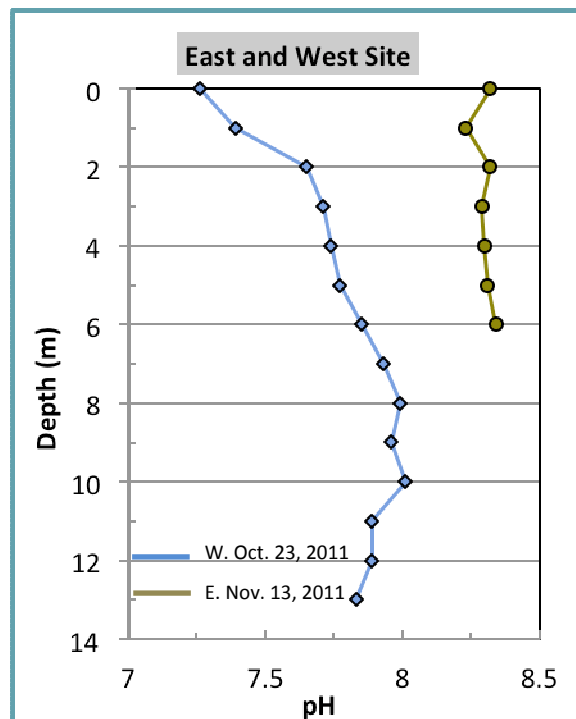
5.3. Dissolved Oxygen

Dissolved Oxygen (DO) was measured in mg/L. The values ranged from 10.96 mg/L at the surface to 9.47 mg/L in the bottom waters without any large difference in the values at the two sites. The depth profile shows a slight difference between the surface and bottom waters, which could be due to incomplete mixing of the lake waters (figure 6, 7). The slight increase of the DO at both sites in the second round of measurements is probably due to the cooling of the lake waters.
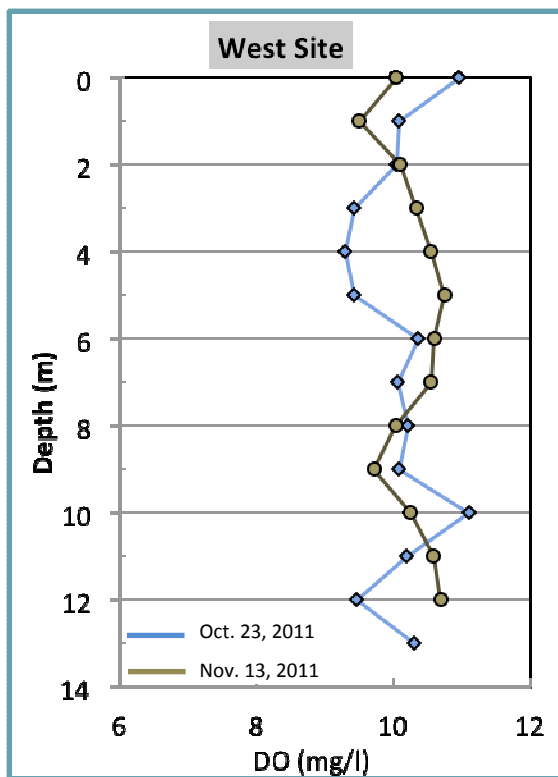
Figure 6: DO profiles at west site.
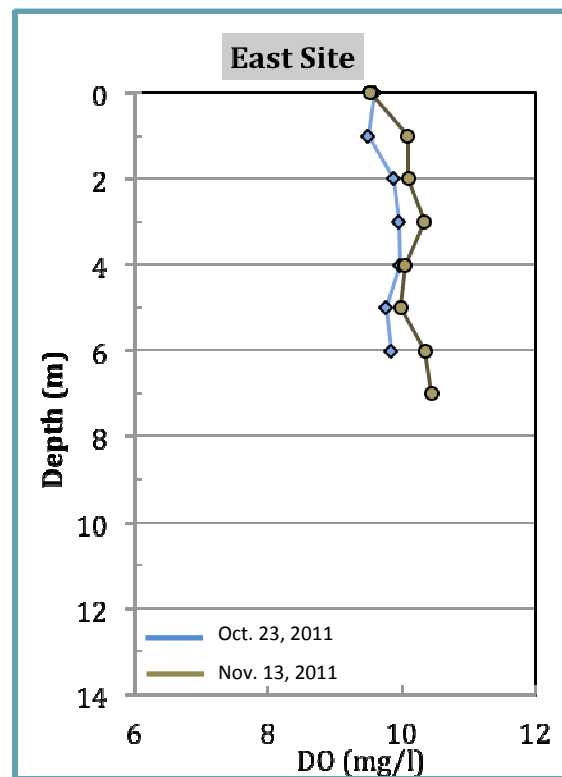
Figure 7: DO profiles at east site.

5.4. Phosphate

Phosphate concentrations remain nearly constant with depth from the surface to a depth of 11-12 m in the west deep side of the lake. Beneath 11 - 12 m, close to the lake bottom, the phosphate levels increase to the maximum level. In contrast, in the east shallow side of the lake the depth profile shows constant low levels with depth (figure 8,9). The two profiles suggest that the fall turnover of the lake mixes the phosphate, but the west deep side of the lake shows incomplete turnover. The significant increase in dissolved phosphate beneath depth 11 m in the deep part of the west lake side is due to the decomposition of organic matter and the reductive dissolution of Fe (III) oxides. Phosphate is released from the sediments under anoxic conditions and is remixed with the surface water during turnover periods.
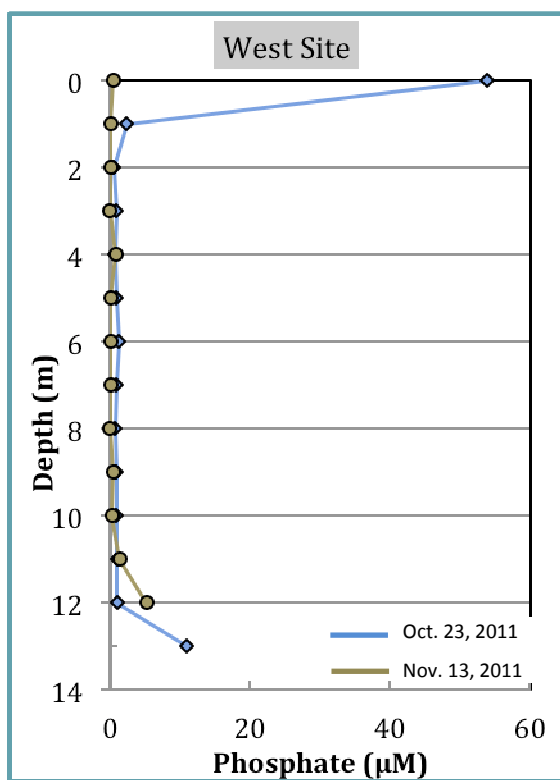
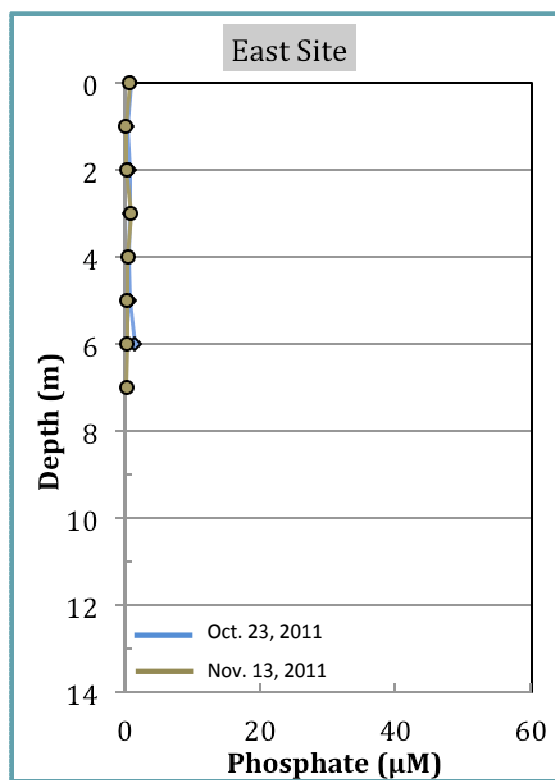Figure 7: Phosphate profiles at west site.

Figure 8: Phosphate profiles at east site.

5.5. Sulfide

Sulfide was measured in the two locations during the two dates of sampling. A sulfur smell was detected at depth 10 - 13 meters in the west site of the lake. The depth profile of sulfide shows an extreme increase of sulfide concentrations from 4.2 to 120 µM within 3 meters, from depth 10 to 13 m (figure 9, 10). This significant increase is due to anaerobic respiration (sulfate reduction in the absence of oxygen producing sulfide) and the decomposition of the dead alga and organic matter. Another possible source is sulfide releasing from the organic rich, anoxic sediments of the lake bottom. Sulfide reacts with dissolved ferrous (FeII) to form FeS, which gives a black color to the sediments.
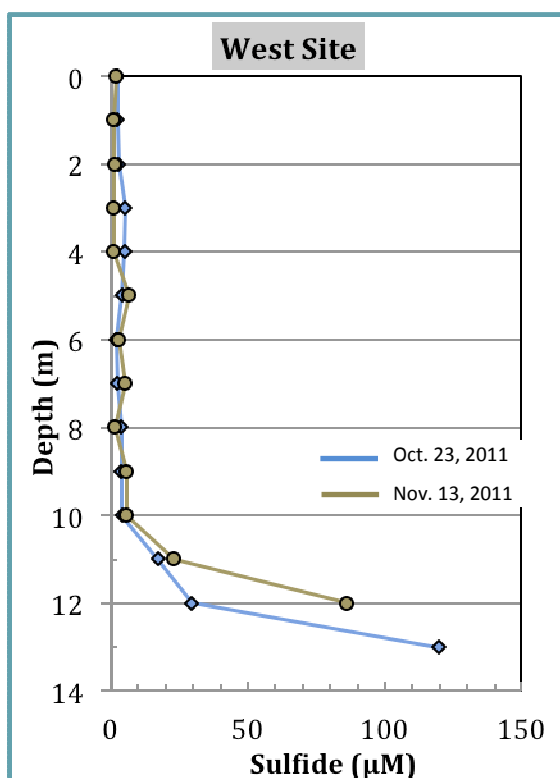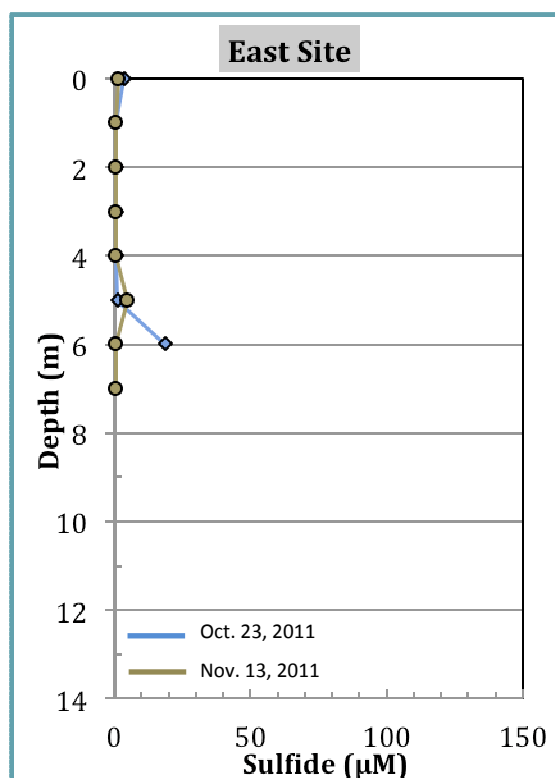
Figure 9: Sulfide profiles at west site.

Figure 10: Sulfide profiles at east site.

5.6. Iron (II)

Iron(II) concentrations shows a poorly defined trend from the surface to depth 10 meter, with values near detection limits ranging from 0.56 to 1.49 µM (figure 11, 12). The depth profile of the iron (II) shows an increase in the concentrations in the bottom waters, this could be due to the reductive of Fe (III) coupled to anaerobic degradation of organic matter.

5.7. Salinization (conductivity and chloride).

Conductivity and chloride were measured to indicate whether the lake is salinized or showing high levels of salts. The west location has a surface reading of 411 µS/cm and has a gradually increasing trend to converge around 1200 µS/cm in the bottom waters. The East location, though, has a higher surface reading of 900 µS/cm and a peak at 1043 µS/cm in the deepest waters (figure 13, 14). The scatter of the depth profile may be due to water mixing and the wind activities. Chloride levels show a consistent increase with depth with a range of about 150 – 200 ppm in the West location (figure 15). The maximum concentration is at the bottom waters of the lake at 207.6 ppm. Buildup of chloride towards the bottom of the lake results in the steadily increasing trend with depth of the profile.

There is a remarkably high concentration of chloride at the two test sites, with higher concentrations in the west side than the east side of the lake. Engemann (1977) reported high levels of chloride concentrations during winter time, ranging between 82 to 120 ppm. The excessive chloride levels detected today indicate the gradual increase of chloride concentrations of the lake waters and the continuous addition of salts into the lake waters. Road salt is likely the main reason for the high levels of the chloride concentrations and the lake salinization overall. Road salt are assumed to enter the lake from the stormwater runoff during winter from the surrounding Drake Road, Stadium Drive, and the heavily traffic highway (US131) located to the west of the lake. Chloride concentrations as high as 19,000 mg/l were measured in stormwater runoff during winter by Hildebrandt and Wood (1978) due to the extensive salting of the roads in the area.
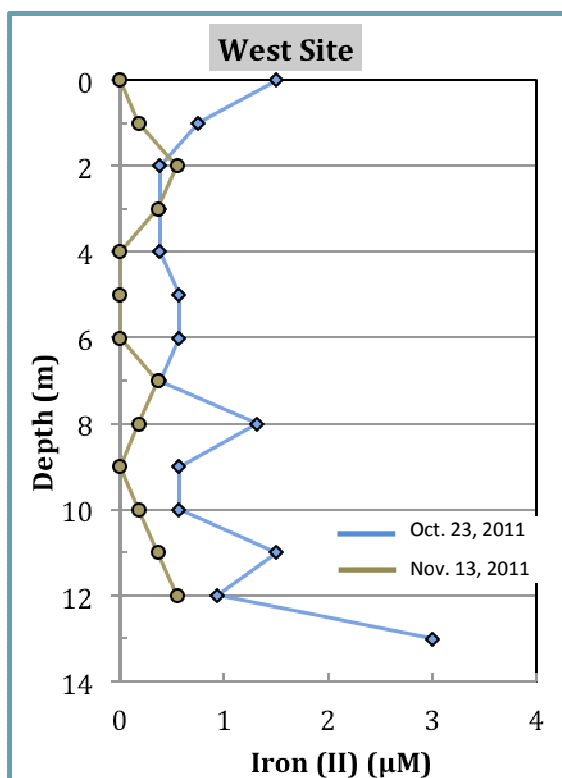
Figure 11: Iron (II) profiles at west site.
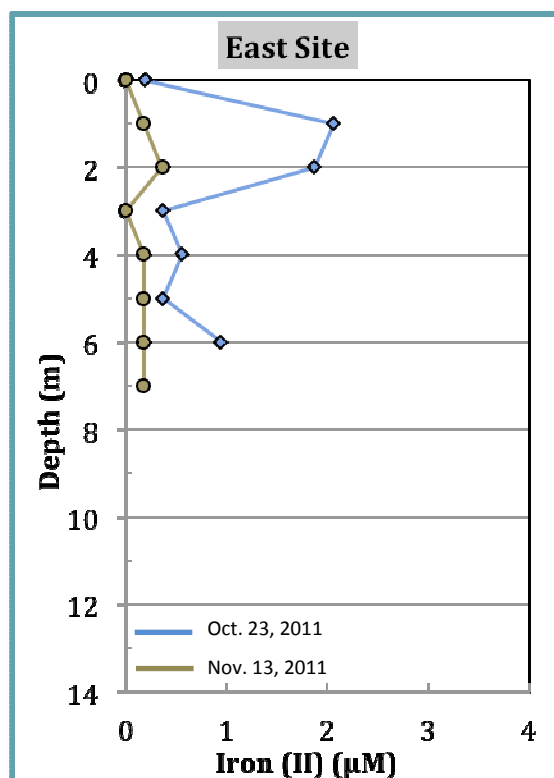

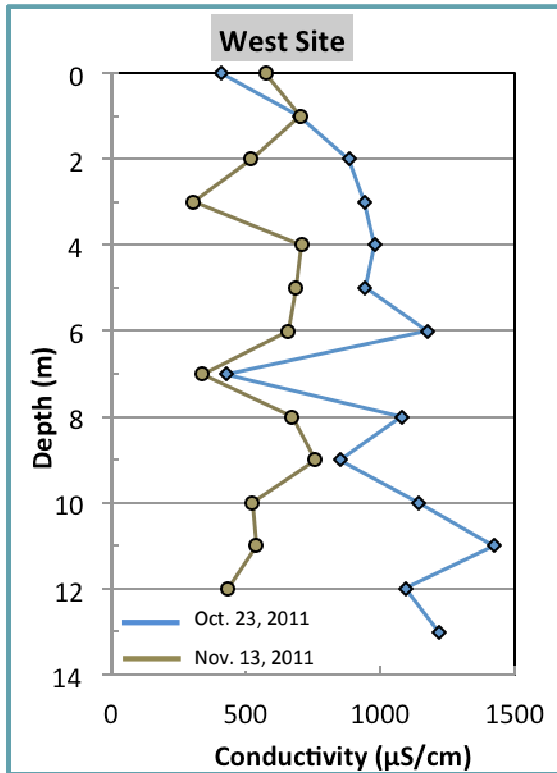Figure 12: Iron(II) profiles at west site.

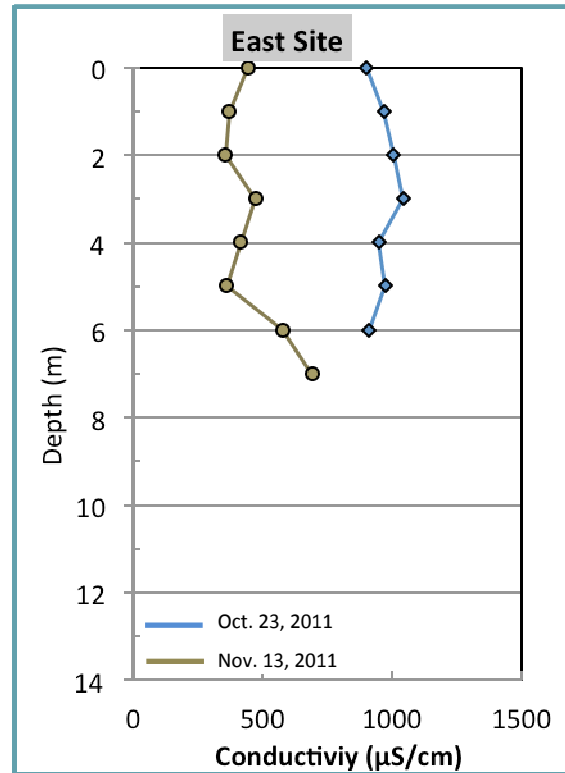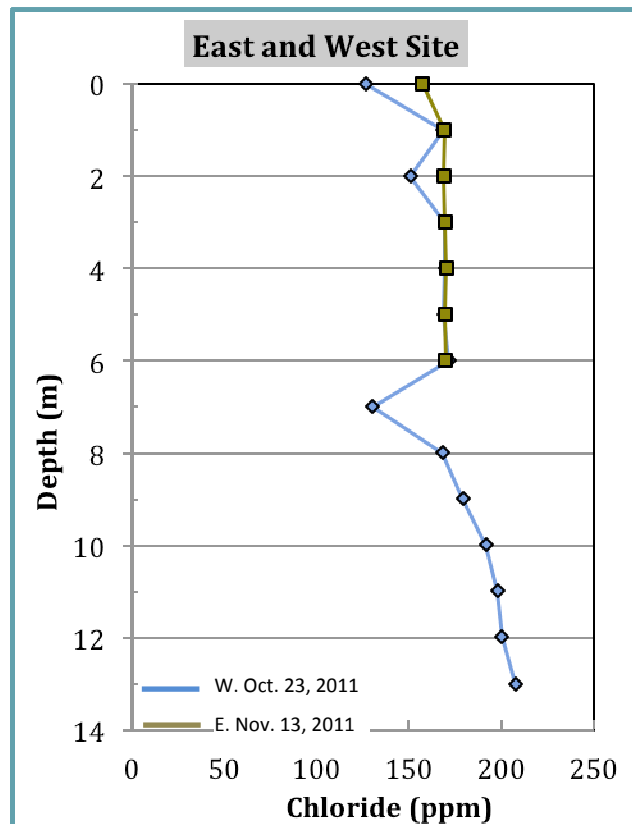Figure 13: Conductivity profiles at west site.

Figure 14: Conductivity profiles at west site.

Figure 15: Chloride profiles at east and west sites.

6. Conclusion

The obtained data shows that the lake water is not completely mixed, which could indicate a delay in fall turnover, or even the absence of the fall turnover event. This means that oxygen may not be introduced to the anoxic bottom waters. This could affect aquatic biota of the lake, and especially those near the anoxic bottom waters. Seasonal research is needed to further investigate the possible delay or absence of the lake water mixing. The elevated salinity may be causing delays in lake water mixing, as high conductivity and chloride levels occur in the deeper waters. Road salts from surrounding main roads could easily drain into Asylum Lake or into groundwater that would eventually end up in the lake. Additional inputs of these "salts" to a lake could start to affect the natural geochemistry processes in the water and eventually disturb the whole ecosystem. Although the dissolved oxygen is not showing a sharp decrease at the bottom water, increasing Fe (II), phosphate and sulfide at the bottom depth indicates reducing conditions (anoxic bottom waters). Elevated phosphate levels indicate external, anthropogenic sources of phosphate, likely from the stormwater flow into Asylum Lake from surrounding roads and neighborhoods, which might be sources of fertilizers, detergents and other phosphate-rich wasters.

7. Recommendations

◆ Follow up studies in the Asylum Lake and its watershed is necessary for more evaluation of the lake water.

◆ Control the nutrients and pollutants by establishing a strong stormwater management plan.

◆ Properly functioning wastewater disposal systems are important especially near the lake shore because of their high potential for nutrient loading.

◆ Spreading awareness about the factors that affect the water quality of the lake is a good way to protect the lake water.

8. References

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