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Rebecca Kiekhaefer

Western Michigan University, rebecca.l.kiekhaefer@wmich.edu

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**The Effects of Eutrophication and Salinization on Methane Production in Urban
and Rural Lakes**

Rebecca Kiekhaefer

Dr. Carla Koretsky, Thesis Chair

Dr. Alan Kehew

Denisha Griffey

Davina Wyman

Lee Honors College

Department of Geosciences

Western Michigan University

Kalamazoo, Michigan 49008

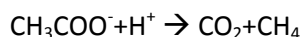
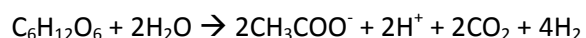
ABSTRACT

Asylum Lake is an urban lake in Kalamazoo, Michigan. The lake is located near the intersection of two major roadways which are heavily salted during the winter. Wintergreen Lake is a rural lake that is on the property of the Kellogg Biological Station in Augusta, Michigan. The lake is surrounded by the Kellogg Bird Sanctuary and is relatively isolated from major roadways. Both lakes are eutrophic, Asylum Lake because of high salinity and lack of turnover (MacLeod, et al., 2011) and Wintergreen Lake because of high nutrient inputs (Threlkeld, 1979). Previous work suggests that road salt deicers can change the physical mixing and redox structure of kettle lakes, resulting in anoxic, redox-stratified hypolimnia. To determine the effects of salinization and eutrophication on methane concentrations in these lakes, water samples were collected on two dates at one meter depth intervals from the surface to the lake bottom (14 meters in Asylum Lake and 5 meters in Wintergreen Lake). *In situ* measurements of temperature, dissolved oxygen, conductivity and pH were taken in the field at 0.5 m depth intervals using a YSI Multiprobe Sonde. Water samples were analyzed for chloride using ion chromatography (IC) and alkalinity, ammonium, iron(II), manganese(II), and sulfide using UV-Vis spectrophotometry (UV-Vis). Methane analyses were conducted at the University of Georgia (UGA) using gas chromatography (GC). The results indicate that Asylum Lake (urban) has more than 10 times the chloride concentration as Wintergreen Lake (rural), as well as significantly higher concentrations of methane at the bottom of the water column.

INTRODUCTION

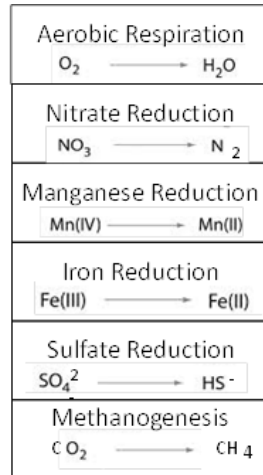
Anthropogenic eutrophication is a condition in a surface water body caused by the addition of excess nutrients due to human influences. This addition spurs the growth of primary producers such as algae (Castro & Freitas, 2011). Examples of nutrient inputs are plant matter (e.g. lawn clippings, leaves), untreated sewage, agricultural runoff and fertilizers. Nutrients such as phosphorous and nitrogen are limiting nutrients, meaning they will be the first nutrients necessary for the survival of organisms in the established ecosystem to be used up because they are found in lesser abundance relative to other required nutrients. With the addition of these limiting nutrients, growth of photosynthetic organisms, i.e. algae and other plants, is accelerated (Castro & Freitas, 2011).

Eutrophication can lead to chemical stratification in lake water columns, because increased primary productivity results in an increase in labile organic matter. The organic matter is initially oxidized through aerobic respiration. However, if dissolved oxygen is not replenished as quickly as it is removed by aerobic respiration, and labile organic matter remains, anaerobic respiration by microbes is the next energetically favored pathway for organic matter degradation (Sposito, 2008). Depletion of oxygen in deep lake waters occurs because of the increase in aerobic respiration resulting from the increase in organic matter, together with the decrease in lake bottom photosynthesis due to a decrease in available sunlight (typically due to large surface algal blooms) and the slow diffusion of oxygen through stagnant waters. Once oxygen is depleted, remaining organic matter is anaerobically oxidized by a series of less energetically favorable terminal electron acceptors such as nitrate, manganese, iron, and sulfate (Sposito, 2008). In denitrification, nitrate is reduced to nitrogen gas and N₂O (a greenhouse gas), and organic matter is oxidized, forming CO₂ and water. If nitrate is depleted, relatively insoluble Mn(IV) and Fe(III) oxides are reductively dissolved, releasing dissolved Mn(II) and Fe(II), together with any metals or ions (e.g. phosphate) bound to the oxide solids. Next, sulfate (SO₄²⁻) and hydrogen sulfate (HSO₄⁻) are reduced, forming gaseous hydrogen sulfide (H₂S) and sulfide (S²⁻). Finally, methanogenesis occurs after all other electron acceptors have been depleted. Methanogenic bacteria use enzymes to breakdown organic matter by reactions such as the following (Thauer, 1998):



Increased methanogenesis is potentially problematic, because according to the Environmental Protection Agency (EPA), over 100 years, methane is more than twenty times more efficient in trapping heat in Earth's atmosphere than carbon dioxide. Because the organic matter oxidation pathways occur

sequentially, essentially in order of energetic yield, they result in spatial chemical stratification, as shown in the following diagram:



Salinization is the addition of excess salt to a body of water, primarily due to runoff of road salt deicers. In the United States, 23 million tons of road salt was used in 2005. Road salt is predominantly NaCl, with a small percentage of trace element and other compounds (Novotny et al, 2008). It has been found that runoff from deicer on roads contributes large amounts of salinity to shallow lakes and streams near major roads. This runoff tends to peak during times of snow melt, often in early spring. Chloride levels have been found to reach acute toxicity in some cases, as well as create chemical stratification and prevent seasonal mixing (Novotny et al, 2008; Koretsky et al., 2011). Seasonal mixing in lakes is typically caused by wind currents, which easily mix water of constant density (Wetzel, 2001). However, when there is a density difference in lake strata, mixing requires more energy and is therefore less likely to occur. Density differences in lakes can be caused by thermal and chemical differences. For example, warm water is less dense than cold water and fresh water is less dense than saline water (Wetzel, 2001). In summer and winter seasons, air temperature causes water at the lake surface to be warmer (summer) or colder (winter) than water at depth. In spring and fall, as the air temperature warms (spring) or cools (fall), the water throughout the lake reaches similar temperature, and begins to circulate. This is known as spring or fall turnover, an event when a lake thoroughly mixes after being stratified. The mixing of the water column during these events circulates dissolved oxygen through the entire water column (Wetzel, 2001). When a high salt content is introduced to a lake, the salt increases the density of the fresh water (Novotny et al, 2008). If denser water accumulates at the bottom of the lake, it may prevent overturn events. Therefore, salinization of lakes can potentially lead to lack of

mixing, lack of oxygen at depth, and methanogenesis in the water column, particularly of eutrophic lakes with high inputs of organic matter.

The purpose of this study is to determine the effect of lake salinization, as well as eutrophication, on the production of methane in two kettle lakes, one located in an urban environment and the other in a rural environment. It is hypothesized that lake salinization will result in elevated methane concentrations because salinization will reduce lake physical mixing and create redox-stratified lake column waters, resulting in increased methane production in the water column. To test this hypothesis, samples were collected from two eutrophic lakes, one of which has a large salt input (Asylum Lake) and the other of which does not have a large salt input (Wintergreen Lake). Samples were taken on one date from each lake at the deepest point of the lakes at one meter intervals (water samples) and half meter intervals (*in situ* parameters). It is expected that Asylum Lake will have higher methane production than Wintergreen Lake, particularly in fall and winter, as Wintergreen will turn over and the water will no longer be stratified. In the summer, when both lakes are stratified, it is likely that both lakes will have high methane production due to stratification.

FIELD SITES

Asylum Lake has a surface area of approximately 0.2 square km and a depth at the sample location of about 14 m (the deepest part of the lake; Figure 1). Located in Kalamazoo, MI, the Asylum Lake property was originally used for farming. There are two hydrologically-connected kettle lakes called Asylum Lake and Little Asylum Lake that formed after glaciers retreated at the end of the last ice age. Outwash sediments dominate the subsurface lithology, which consists mainly of loamy sand (USDA SCS). Currently, the area surrounding Asylum Lake is a nature preserve and educational site used by local community members for recreation (primarily hiking) and by WMU geosciences, biological sciences and anthropology students for research and education. Asylum Lake is mainly groundwater fed, with some surface water inflow from runoff. There is a small outflow of surface water from Asylum Lake to Little Asylum Lake. Water flow is west (from the direction of U.S. 131) to east (Sauck & Barcelona, 1992).

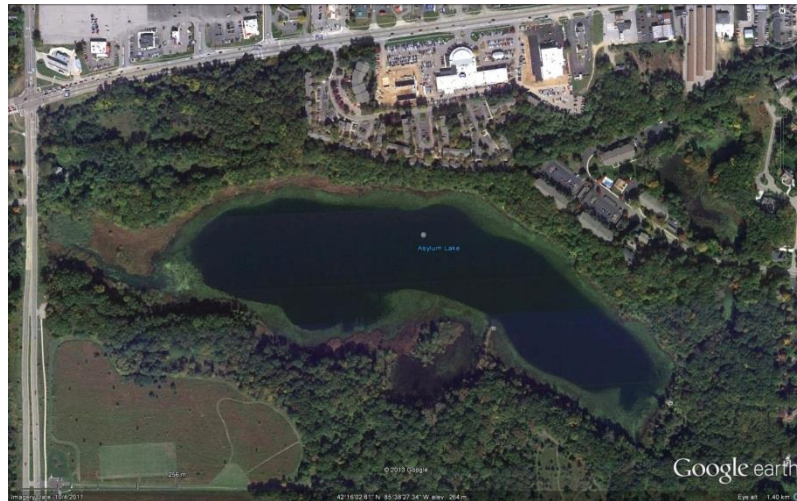


Figure 1. Map showing Asylum Lake sampling site (from Google Earth).

Wintergreen Lake has a surface area of approximately 0.16 square km and a depth at the sample location of about 5 m (Figure 2). Located in Augusta, MI, Wintergreen Lake is part of the Kellogg Biological Station and is within the Kellogg Bird Sanctuary. As a result, excess nutrients are introduced to the lake from the presence of birds (Threlkeld, 1979). These excess nutrients have caused Wintergreen Lake to become eutrophic, and this lake has been recognized as eutrophic for nearly 40 years (Sarnelle & Wilson, 2005). Wintergreen Lake is surface water fed, and is classified as a drainage kettle lake (Crowley, 1971). In the 1960's, the lake was clearly dimictic (Crowley, 1971). As at Asylum Lake, outwash sediments dominate the subsurface lithology, which consists of a sandy loam (USDA SCS).



Figure 2. Map showing location of sample site at Wintergreen Lake (from Google Earth).

METHODS

A YSI Multiprobe Sonde was used to measure dissolved oxygen (DO), pH, temperature, and conductivity *in situ* at each lake at approximately 0.5 m vertical intervals in the deepest part of the lake, which was accessed by canoe or rowboat. At each lake, samples were collected at 1 m intervals from the surface to depth using a vertical point water sampler. Replicate samples were taken for quality control at each depth. Field blanks of ultrapure ($>18\text{M}\Omega$) water were also used for quality control. 25 mL samples were collected at each depth and filtered using 0.2 μm syringe filters on the boat. Two replicates were preserved by acidification with a drop of concentrated nitric acid and two were kept unacidified. 600 μL samples for sulfide analyses were preserved in 600 μL of a Zn acetate trap solution for subsequent analyses using the methylene blue method (Koretsky et al., 2011). Samples were taken at Asylum Lake on 18 November and 8 December and at Wintergreen Lake on 17 November of 2012.

Water samples for methane analyses were collected directly from the vertical point water sampler first because these samples are very sensitive to oxygen. These samples were collected with tubing connected from the water sampler to a 140 mL plastic syringe, which was rinsed with water from the sampler and then filled to overflowing with an extra two syringe volumes to minimize any mixing with air in the syringe. Next, a total of 60 mL was injected from the filled syringe into a 60 mL serum bottle containing a pellet of NaOH. The bottles were filled slowly from the bottom up to minimize turbulence. The serum bottles were then capped with rubber stoppers using a needle in the stopper to allow excess water to expel from the vial to make room for the stopper. The stoppers had been previously boiled in a 1 M NaOH solution. After collection, samples were taken back to the lab, where 15 mL of helium was injected into each sample with a 20 mL syringe and needle through the stopper, while 15 mL of water was displaced by the helium into a second 20 mL syringe and needle also through the stopper. This process was conducted with the sample vial upside down. After the helium injection each sample was shaken and stored upside down prior to methane analysis by GC at the University of Georgia (Figure 3). For the GC analysis, gaseous samples were injected into the GC FID using a glass 1000 μL syringe. The sampling and analysis processes were repeated with two bottles each of ultrapure water and a saturated NaCl brine as a quality control for each sample date.

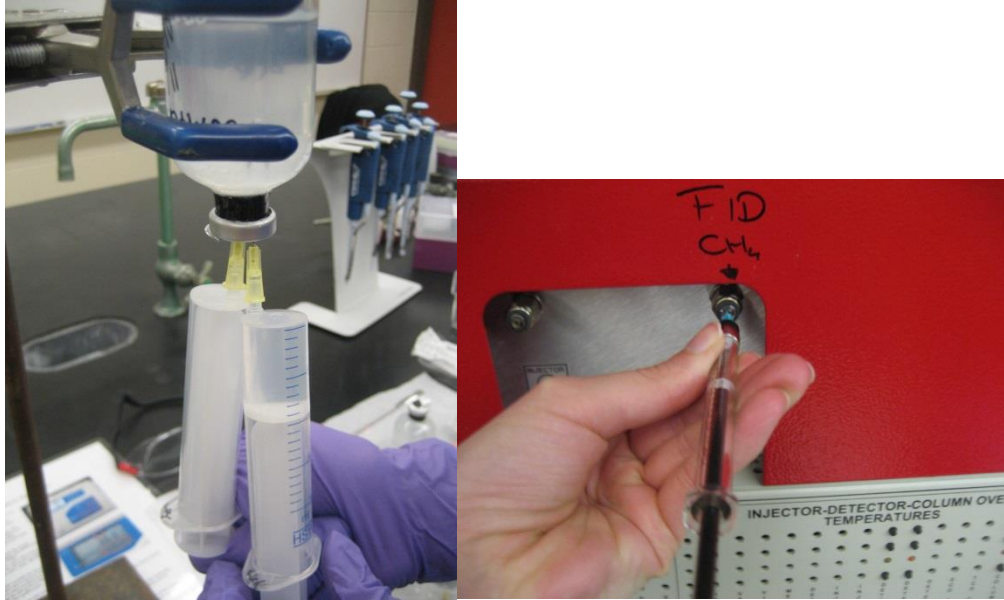


Figure 3. (A) Injection of helium into serum bottles with water samples for methane analyses. (B) Methane analyses using gas chromatography.

In each methane sample collected, the relative size of any air bubbles within the vial prior to helium injection was noted. These air bubbles could dilute the methane samples and contribute oxygen, resulting in underestimates of the methane concentrations. The size of each bubble was rated from non-existent (1) to largest volume (5), as shown in Table 1 (and Appendix I). The difference in bubble size between replicate samples was compared to the difference in methane concentration.

Table 1. Bubbles observed in replicate samples.

Sample	Bubble Size	Methane Concentration (μM)	Bubble Size	
W 3A	1	1.66	1	none
W 3B	2	1.68	2	o
A 4A Nov	2	1.55	3	O
A 4B Nov	2	1.59	4	O
A 6A Nov	5	1.72	5	O
A 6B Nov	2	1.74		
A 13A Nov	4	132		
A 13B Nov	2	209		

No significant correlation was found between the size of the air bubble in the sample prior to helium injection and the analyzed methane concentration. As shown in Table 1 and Appendix I, an increase, decrease or no change in bubble size between samples corresponded to an increase in methane concentration found in those samples.

Alkalinity, ammonium, manganese (II), and sulfide were measured using the bromophenol blue, hypochlorite, formaldoxime, and methylene blue methods, respectively, with a UV-Vis spectrophotometer. Iron (II) was measured using the acidified samples by the ferrozine method with a UV-Vis spectrophotometer. Ion chromatography (IC) was used to analyze chloride levels in the samples. Analyses of samples using UV-Vis and IC were conducted by Denisha Griffey and Davina Wyman.

RESULTS AND DISCUSSION

The temperature throughout the water column in Wintergreen Lake is nearly constant, which suggests that the water column is well mixed, although the lake could still be chemically-stratified and not thermally-stratified. In November, the temperature in Asylum Lake decreases very slowly with depth in the upper 12 m, and decreases more rapidly below 11.5 m depth (Figure 4A). In December, the temperature in Asylum Lake was essentially constant with depth. Similarly, the dissolved oxygen in Asylum Lake in November decreases slowly from the surface to a depth of around 11 m, below which there is a sudden drop in DO, and below 11.5 m there is no detectable dissolved oxygen (Figure 4B). In December, the decrease in dissolved oxygen was more gradual and there was detectable oxygen present to a depth of 14 m. Dissolved oxygen in Wintergreen Lake decreases slightly with increasing depth, but Wintergreen Lake does not become anoxic as Asylum Lake does. This is likely due to the fact that Wintergreen Lake is dimictic, thus it experiences turnover in fall and spring of each year. This allows substantial mixing within the water column and allows dissolved oxygen to remain high at the bottom. Wintergreen Lake is also very shallow compared to Asylum Lake, so wind currents travelling over the surface of Wintergreen Lake will likely cause more mixing in the full water column compared to the much deeper Asylum Lake. The differences in the profiles for Asylum Lake between November and December are likely due to the seasonal decrease in temperature at the surface.

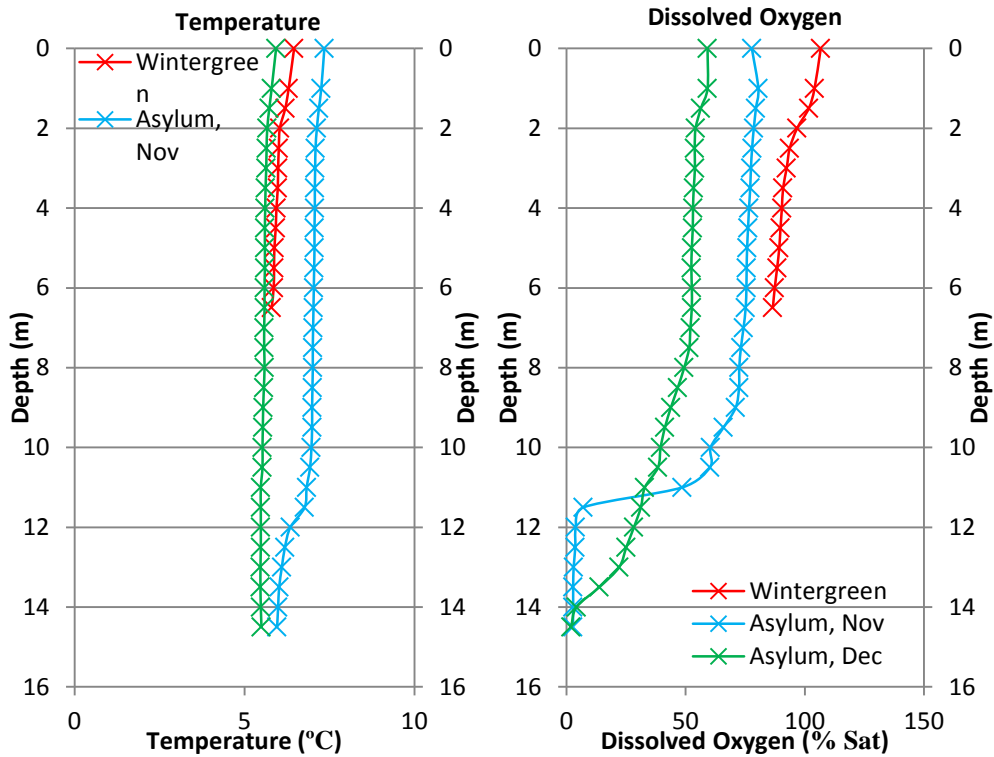


Figure 4. (A) Temperature and (B) dissolved oxygen profiles measured at Wintergreen Lake (17 November, 2012) and at Asylum Lake (18 November and 8 December, 2012).

Asylum Lake shows very different trends in temperature and dissolved oxygen in the summer months, as shown in Figure 5 (data from Koretsky et al, 2011). The temperature profiles in May and July reflect the warmer air temperature near the surface, but decline rapidly with depth, reaching similar temperatures at depth to those measured in this study in November and December. The difference in temperature between the surface and bottom of Asylum Lake in the summer indicates that the lake is not fully physically-mixed during this season. The trend in dissolved oxygen in Asylum Lake in summer shows mixing at the surface, which is indicated by constant dissolved oxygen saturation in the upper 2 m of the water column. The increase in dissolved oxygen at a depth of 4 m, particularly in July, is likely due to active photosynthesis of aquatic vegetation (algae). Below a depth of 6 m in the summer profiles, there is a sudden depletion of oxygen in the water column, leading to redox-stratification of the water column (Koretsky et al, 2011). Data collected in July 2010 (Koretsky et al, 2011) show an increase in manganese (II) and ammonium concentrations from 6 m to 10 m (ammonium) and 8 m to 11 m (manganese). The manganese concentrations decrease slightly from 11 m to the bottom of the water column. Iron (II) concentrations were at or near the concentration found in the blank, thus iron (II) was

not present in significant concentrations in Asylum Lake in July 2010 (Koretsky et al, 2011). This data indicates that Asylum Lake is redox-stratified in the summer months. In the November and December of 2012, manganese (II), iron (II), ammonium, and sulfide were not found in significant concentrations. All of these dissolved chemical species are removed from the water column by reaction with dissolved oxygen. Thus, it appears that Asylum Lake does mix in the fall, at least partially, delivering oxygen to the bottom of the lake, which reacts with these reduced species and limits redox-stratification. As the lake mixes, it is expected that the methane concentration at the bottom will decrease because methane is also removed from the water by reaction with oxygen.

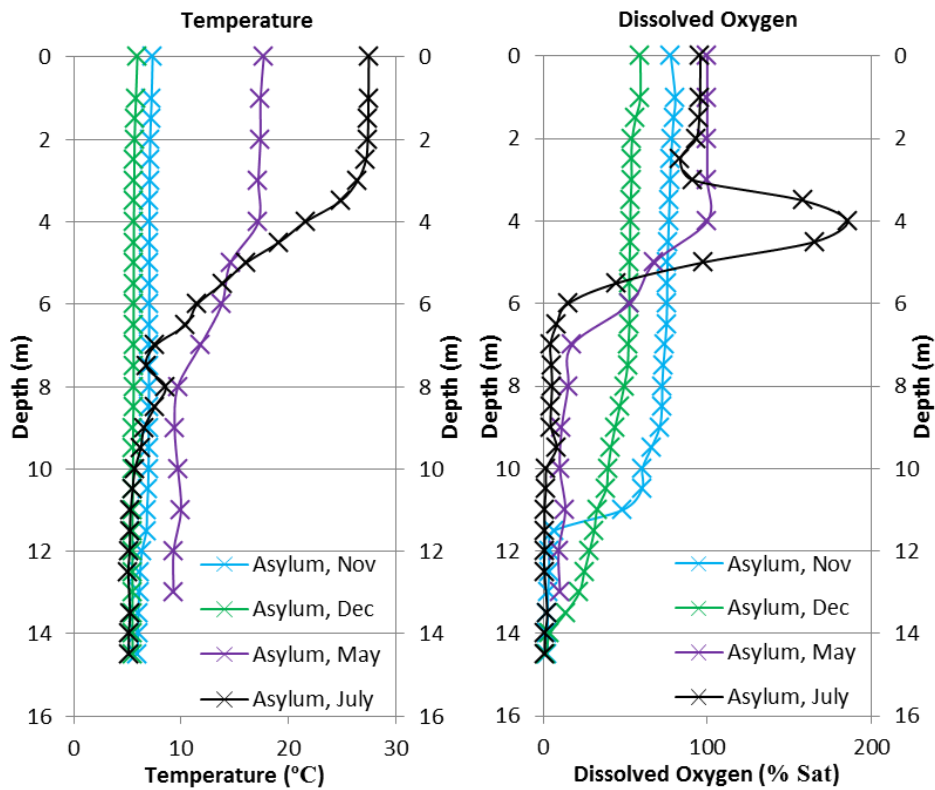


Figure 5. (A) Temperature and (B) dissolved oxygen profiles measured at Asylum Lake on 18 November and 8 December, 2012 (this study) compared to data measured on 17 May and 13 July, 2010 by Koretsky et al. (2011).

In this region, alkalinity is typically controlled by carbonate species due to the dissolution of carbonate-rich rock in the subsurface. Alkalinity concentrations in Wintergreen Lake follow a slight decreasing trend with increasing depth (Figure 6A). In contrast, alkalinity concentrations in Asylum Lake increase gradually with depth. Alkalinity is also contributed by anaerobic respiration, which releases

bicarbonate into aqueous solution as organic matter degrades and by the dissolution of carbonate particulates. The concomitant increase in alkalinity with a decrease in dissolved oxygen suggests that organic matter is degraded anaerobically at depth in Asylum Lake in December, and especially in November.

pH in Wintergreen Lake is nearly constant with depth, which is consistent with the availability of dissolved oxygen which likely allows aerobic respiration to persist throughout the lake water column. The pH in Asylum Lake in November is nearly constant in the upper 11 m, below which it decreases suddenly at the same depth that the decrease in temperature and dissolved oxygen was observed. Oxidation of reduced species such as Fe(II), Mn(II) and sulfide by oxygen results in decreasing pH, suggesting that oxygen mixed into the deeper waters of Asylum Lake is removed as it reacts with these reduced species. In December, the decrease in pH in the bottom 2 m did not occur, likely due to the persistence of oxygen in the water column.

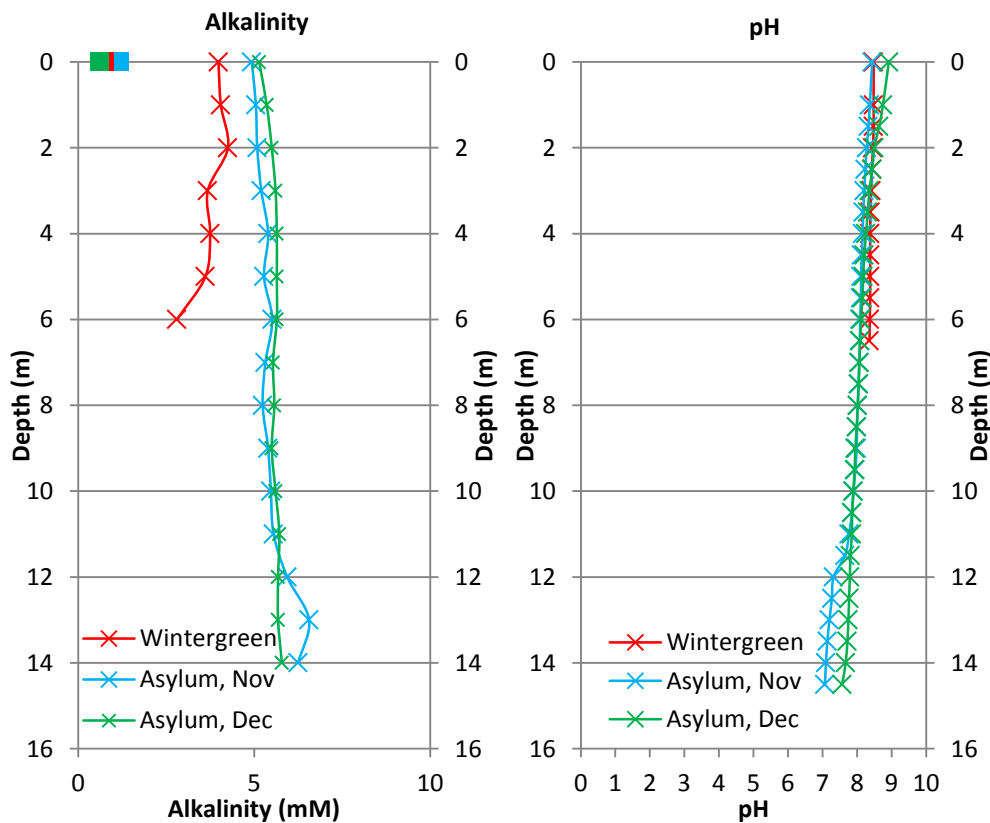


Figure 6. (A) Alkalinity and (B) pH measured at Wintergreen Lake (17 November, 2012) and Asylum Lake (18 November and 8 December 2012). Squares indicate analyses of field blanks.

Chloride concentrations are over 10 times greater in Asylum Lake than in Wintergreen Lake (Figure 7A). In both lakes, the concentrations of chloride are nearly constant with depth. This is in agreement with previous work which shows that Asylum Lake has a large input of salinity due to run off of road salt from nearby heavy traffic routes (MacLeod et al, 2011; Koretsky et al., 2011). In contrast, Wintergreen Lake is surrounded by dirt roads, foot paths, and forest and is not expected to have a significant input of salt. In November, the chloride concentrations in Asylum Lake were slightly higher than in December.

Methane concentrations in Wintergreen Lake were comparable to the methane concentration of the blank throughout the entire water column. Asylum Lake also had methane concentrations near the methane concentration of the blank in the upper 10 m (Figure 7B). However, methane levels increase to an average of 50 μM in December and 120 μM in November in the lower 3 m of Asylum Lake. The higher methane concentrations in November most likely result from the lack of oxygen, which is more depleted in November than December. This indicates that some mixing does occur in Asylum Lake, allowing restoration of dissolved oxygen in the deepest portion of the water column.

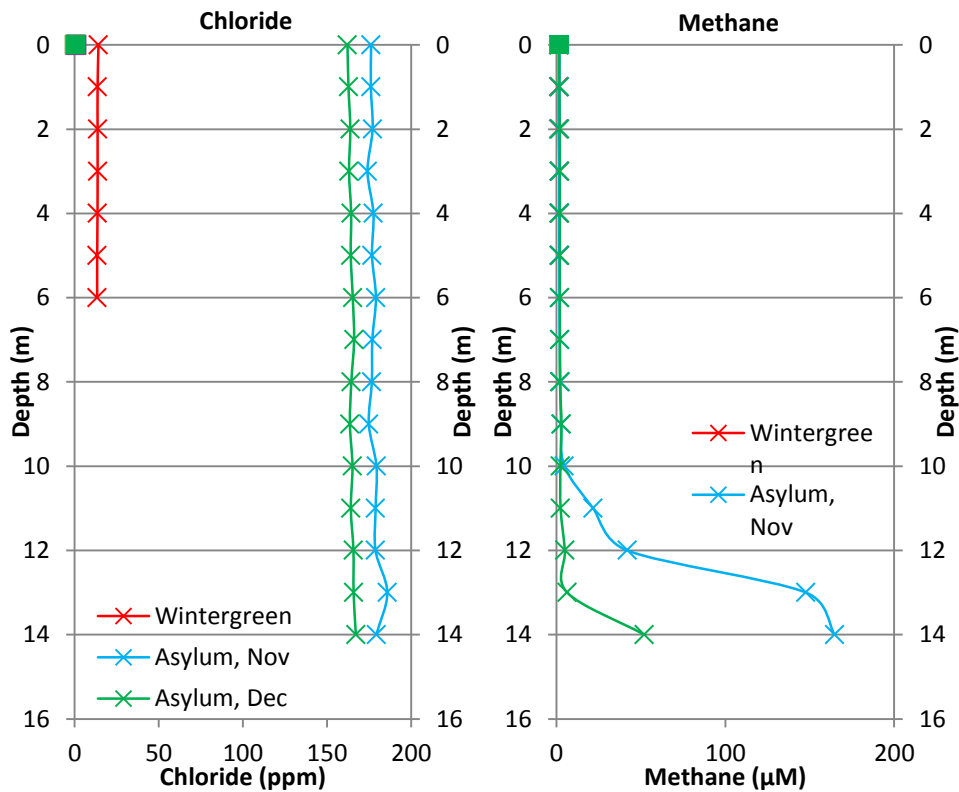


Figure 7. (A) Chloride and (B) methane profiles at Wintergreen Lake (17 November, 2012) and Asylum Lake (18 November and 8 December, 2012). Squares indicate field blanks.

The increase in methane at the bottom of the lakes is likely due to the lack of oxygen in the hypolimnion. Methane producing bacteria require anoxic conditions, whereas methane oxidizing bacteria require oxygen to thrive (Pielou 1998). Previous work indicates that surface methane concentrations in small lakes in both North America and Eurasia, particularly Wisconsin and Finland, average between 0.2 and 2 μM (Bastviken et al, 2004; Juutinen et al, 2009). Just above the lake bottom sediments, methane concentrations in Asylum Lake increased to an average of 150 μM in November and 50 μM in December. The methane concentrations throughout Wintergreen Lake are comparable to the average surface water concentrations reported for North America and Eurasia, which is likely due to the shallow depth of the lake and the thorough mixing of oxygen throughout the water column. In 1971, a study of methane concentrations in Wintergreen Lake was conducted over several months. The data showed peak methane concentrations in late summer, which decreased through September. There was no data collected after September, but the concentration of methane averaged less than 5 μM at the end of the study (Strayer & Tiedje, 1978). If the methane concentrations continued to decrease, it is likely they were present at similar concentrations in November 1971 as found in November 2012. In contrast, at Asylum Lake in December, methane concentrations just above the sediments were found to be 52 μM , over double the average found in previous studies in Finland. In November, the concentration and vertical extent of elevated dissolved methane was much greater, with a concentration of 42 μM at a depth of 12 m, which increased to 165 μM at 14 m. Based on the previous work at Wintergreen Lake and the change in methane concentrations observed in Asylum Lake between the two sample dates, it is expected that the methane concentrations at the bottom of these lakes will decrease in the fall and winter and increase in the spring and summer. In previous work, it was estimated that 40% of methane produced in lakes such as Wintergreen Lake and Asylum Lake is released into the atmosphere (Strayer & Tiedje, 1978). With a mean depth of around 1 m containing elevated methane concentrations (100 μM) and a surface area of 0.2 km (Sauck & Barcelona, 1992), Asylum Lake could theoretically release 120 kg of methane into the atmosphere per year. Furthermore, prior studies suggest that much more methane is released to the atmosphere via ebullition (bubbles) compared to release of methane through passive diffusion of dissolved methane (Strayer & Tiedje, 1978). Only dissolved methane was measured in this study, suggesting that much more methane might be released from these lakes. Based on the limited data collected in this study, generalizations about the seasonal chemistry and mixing of these lakes cannot be drawn, however, it appears that Asylum Lake could be a significant source of methane to the atmosphere.

CONCLUSIONS

The data collected in this study cannot conclusively refute the hypothesis that lake salinization will result in elevated methane concentrations. While there are higher salinity and methane concentrations in Asylum Lake as compared to Wintergreen Lake, this could be the result of other factors, such as the significant difference in the depth of these two lakes. The high methane concentrations at the bottom of Asylum Lake indicate that the lake is redox-stratified, as methane would not persist in oxic waters. The salinization in Asylum Lake could have created or exacerbated the stratification of the lake column waters, due to the higher density of saline water. The data collected in this study agrees well with data previously collected in both lakes. Although reduced species including Fe(II), Mn(II) and sulfide were below detection limits, dissolved oxygen and methane data suggests that Asylum Lake remains partially redox-stratified in late fall (November), which might have been expected based on previous data indicating that significant redox stratification occurs in the summer months. The summer redox stratification likely results in the elevated methane concentrations still found at depth in Asylum Lake in the fall. The persistence of dissolved oxygen at depth in Asylum Lake in December indicates that Asylum Lake at least partially mixes during late fall. In contrast, Wintergreen Lake appears to mix fully, in agreement with results of prior studies. It is probable that the high salinity in Asylum Lake allows the persistence of high methane concentrations in late fall season, which does not occur in Wintergreen Lake. However, the depth difference between the two lakes is too large to conclude definitively that elevated salinity is the cause of the persistent methane at depth in Asylum Lake. Future analysis of these lakes, and other kettle lakes, in the summer and winter seasons are required to determine the influence of salinity on mixing and seasonal methane accumulation in salinized urban lakes.

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Appendix I: Methane Concentration and Relative Bubble Size for All Samples

Bubble Size

1	none
2	o
3	o
4	O
5	O

Sample	Bubble Size	Methane Concentration (μM)
W DI no need	3	1.39
W NaCl A	2	1.43
W OA	4	1.39
W OB	4	1.39
W 1A	2	1.39
W 1B	1	1.39
W 2A	1	1.39
W 2B	1	1.39
W 3A	1	1.66
W 3B	2	1.68
W 4A	3	1.63
W 4B	2	1.60
W 5A	4	1.92
W 5B	1	1.66
W DI need	3	1.39
W NaCl B	3	1.39
Asylum 11/18:		
DI A	2	1.52
NaCl A	2	1.39
0A	3	1.78
0B	3	1.65
1A	2	1.74
1B	5	1.54
2A	3	1.62
2B	3	1.64
3A	1	1.64
3B	4	1.66
4A	2	1.55
4B	2	1.59

5A	1	1.68
5B	3	1.64
6A	5	1.72
6B	2	1.74
7A	3	1.81
7B	2	1.96
8A	2	2.09
8B	2	2.46
9A	1	2.68
9B	3	2.64
10A	3	4.76
10B	2	4.56
11A	2	19.70
11B	3	23.64
12A	5	41.00
12B	2	42.70
13A	4	104.01
13B	2	146.21
14A	4	147.85
14B	5	152.04
DIB	4	1.39
NaCl B	2	1.39
14A	4	193.79
14A	4	125.29
14A	4	204.51
14B	5	204.51
13A	4	131.66
13B	2	208.98
Asylum 12/18:		
DI A	3	1.39
NaCl A	didn't check	1.45
0A	didn't check	1.39
0B	2	1.93
1A	2	1.39
1B	3	1.98
2A	3	1.92
2B	4	1.93
3A	2	1.96
3B	3	1.95

4A	3	1.94
4B	2	1.96
5A	3	1.95
5B	5	1.96
6A	3	1.96
6B	3	1.97
7A	4	1.98
7B	5	2.00
8A	5	1.99
8B	5	2.00
9A	3	
9B	3	2.91
10A	2	2.27
10B	4	2.31
11A	2	2.41
11B	3	2.41
12A	5	5.00
12B	5	4.87
13A	didn't check	6.42
13B	3	6.30
14A	didn't check	50.39
14B	2	53.66
DIB	didn't check	1.92
NaCl B	4	1.80

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