Spring 5-1-2019

DOM Control of Mercury Methylation in the Water Column of a Meromictic Lake

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A Capstone Project Submitted in Partial Fulfillment of the
Requirements of the Renée Crown University Honors Program at
Syracuse University

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Spring 2019

Honors Capstone Project in Chemical Engineering

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Abstract

The trophic transfer and bioaccumulation of methyl mercury (MeHg) in aquatic ecosystems is a substantial concern, resulting in fish consumption advisories worldwide. Aquatic ecosystems have been identified as the critical environments that breed production of MeHg and low levels of initial accumulation in biota. MeHg production is a microbially-mediated process, occurring primarily at the transition between oxic and anoxic environments. This research aimed to assess the extent to which dissolved organic matter (DOM) affects methylation of mercury in the oligotrophic meromictic lake, Green Lake, in Fayetteville, NY and the warm monomictic lake, Seneca Lake, in Geneva, NY. General physical parameters (pH, temperature, dissolved oxygen, and conductivity) were collected on the field. Additional water column samples were analyzed for sulfide, inorganic anions, dissolved organic carbon, total mercury, MeHg, and DOM. Redox parameters delineated a wide redox transition zone in Green Lake between 18-21 m, while the water column of Seneca Lake remained oxygenated. The highest methylation of mercury, 41-49% (determined by the percent mercury as MeHg), was found at the chemocline of Green Lake. A secondary peak of 33%MeHg was found at the 5 m depth. At these same depths, increases in readily available labile DOM were also found. Substantial methylation and increases in labile DOM were not observed in Seneca Lake. A correlation analysis determined that the changes in labile DOM explained 54% of the changes in the percent MeHg. These findings indicate that high levels of in-situ produced labile DOM stimulated methylation of mercury

Executive Summary

The presence of methylmercury (MeHg), the element's most toxic form, in aquatic ecosystems is detrimental to the organisms within the ecosystems as well as to humans through the process of biomagnification. Elemental mercury is naturally occurring, and can enter aquatic ecosystems through mechanisms of deposition, such as rainwater runoff. When this elemental mercury enters a lake, it has the potential to be methylated, or turned into MeHg.

While methylation has been studied extensively, there are still various aspects about the process that are unclear to researchers. Methylation has been found to be related to sulfur cycling. Aquatic environemnts rich in sulfate (SO_4^{2-}) and devoid of oxygen are habitat for a special class of anaerobic bacteria, called sulfate-reducing bacteria (SRB), which use sulfate in their respiration process. As a side reaction of the metabolism of the SRB, inorganic mercury is converted to MeHg. The unclear portion of this process is to whether the available organic material stilumate or inhibit the production of MeHg.

In this research, I hypothesized that dissolved organic matter (DOM) would have a large impact on Hg methylation. DOM is any matter dissolved in freshwater that originates from the remains of plants or animals, and varies widely, serving many different purposes in a freshwater ecosystem. For this research, I was concerned as to the role of different types of DOM for the methylation of mercury.

I studied the effect of DOM in two different lakes: Green Lake and Seneca Lake. Green Lake is a meromictic lake in Fayetteville, NY. The lake's chemocline occurs between 18 and 21 m, so trends were examined in this region to determine if DOM did impact MeHg production. Using fluorescence spectrometry, high increases in this labile DOM were found to increase in the chemocline at 19 m. In the same region, percent methlation (%MeHg), or the percentage of the

total Hg that is made up of MeHg, also spiked. Correlations were run between the various DOM types and %MeHg, and significant relationships were found with the peaks representing the labile DOM fractions, indicating a partial control of Hg methylation by this type of DOM.

Seneca Lake in Geneva, NY, is a monomictic lake which turns over once annually. Total Hg and MeHg concentrations in the lake were found to be minimal, and decreased as depth increased. There was also no significant trend in labile DOM presence. Paired with an absence of MeHg, this further confirms the likely link between labile DOM and Hg methylation.

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Acknowledgements

I would like to sincerely thank everyone who has helped with the completion of this project. I would especially like to thank those who helped me to run and complete lab tests, including Simone Burns, Reilly Duffy, Nick LoRusso, Geoffrey Millard, Mike Seitz, and Joseph Wasswa. For his dedication to helping me learn how to use lab equipment and achieve the best results possible, I am truly thankful for Mario Montesdeoca. Thank you to Dr. Katie Cadwell for helping me to revise and edit this work. I would like to extend extreme gratitude to Renée Crown for funding a large majority of this project via the Crown Award, as well as the entire Honors staff for their guidance through this process. Finally, this project would not have been possible without the tireless effort of Dr. Svetoslava Todorova, who helped me work to make my research the best that it could be.

Chapter 1

Introduction

Mercury (Hg) occurs naturally in the lithosphere and hydrosphere in its elemental (Hg^0) and ionic (Hg^{2+}) forms but it has increased greatly in these environments due to emissions and releases from anthropogenic activities. These inorganic Hg forms may be transformed to organic, methylated species, such as methylmercury (MeHg). While all forms of Hg are toxic, studies have confirmed that the detrimental ecological and toxicological effects of MeHg are of the greatest concern because MeHg is a neurotoxin, and has the ability to accumulate in biota and humans (Beckers and Rinklebe, 2017).

MeHg production is a microbially-mediated process that is most pronounced in aquatic ecosystems devoid of oxygen and nitrate (Todorova et al. 2009 and 2011, Schaefer et. al, 2011). Although produced from inorganic Hg, MeHg does not always correlate with Hg^{2+} or total Hg because MeHg production varies with geochemical conditions. Availability of labile carbon, reduced conditions, and an optimal sulfate (SO_4^{2-}) to sulfide (HS^-) ratio were found to enhance methylation of Hg^{2+} (Mitchell et. al, 2017, Choi et al., 1994). The ability to produce MeHg was first discovered in sulfate-reducing bacteria (SRB; Compeau and Bartha 1985) and later in iron-reducing bacteria (Flemming et al. 2006), methanogens (Yu et al. 2013), and some synthrophic microorganisms (Pak and Bartha 1998). The recently discovered methylating genes, *hgcA* and *hgcB*, suggest that methylating capability exists among a wider group of microorganisms (Gilmour et al. 2013, Bae et al. 2014, Podar et al. 2014, Podar et al. 2015). Though various

diverse methylating microorganisms have been identified, SRB appear to be the most fervent Hg methylators (King et al. 2001, Bridou et al. 2011, Gilmour et al. 2013).

Natural dissolved organic matter (DOM) is one of the largest sources of biologically available organic carbon and it plays an important role in aquatic ecosystems because it is the main source of energy for microbial metabolism (Lennon and Pfaff, 2005). DOM is comprised of complex and diverse organic compounds ranging from simple biochemicals, complex biopolymers, and degradation products, such as humic substances and black carbon. Amount and composition of DOM varies in aquatic ecosystems based on the source of DOM and the geochemical conditions. DOM is considered allochthonous if it is derived from terrestrial sources (degraded plant material and soil organic matter) and autochthonous if it is derived from aquatic sources (produced by phytoplankton or other organisms). Allochthonous DOM has higher molecular weight, is more aromatic, and consists of more humic-like substances (Toming et al. 2013). Autochthonous DOM consists of low-molecular weight, protein-like substances (Toming et al. 2013)

The different types of organic matter within the total DOM can dictate or aid various biological, chemical, and environmental processes (Hansen et. al, 2016). For years, it has been demonstrated that DOM inhibits MeHg production due to the strong binding affinity of Hg with the sulfur groups in DOM (Graham et al., 2013, Fu et al., 2007, Mazrui et al, 2016). Recently, it has been found that DOM enhances the methylation of Hg^{2+} in aquatic environments under sulfidic and non-sulfidic conditions (Graham et al. 2012, Bravo et al. 2017).

This research examined DOM production and methylation in two specific types of thermally stratified lakes. Based on their mixing pattern, lakes are classified as monomicitic, dimictic, polymicitic, and amictic. Monomictic lakes mix once per year, and can be classified as

warm or cold. A cold monomictic lake is covered with ice for most of the year, but mixes during warm summer temperatures. A warm monomictic lake is stratified most of the year and mixes during cool winter months (Lewis, 1983). Dimictic lakes turn over with traditional temperature changes in the spring and fall, and polymictic lakes turn over multiple times per year due to a variety of temperature gradations (Lewis, 1983). Amicitic lakes are permanently stratified throughout the year. Meromictic lakes are special types of amicitc lakes that maintain stratification due to a checmical gradient.

I utilized the contrasting physical limnology of the meromictic Green Lake in Fayetteville, NY and the warm monomictic Seneca Lake in Geneva, NY to study the biogeochemical interactions between sulfur, Hg and DOM. Both lakes provide a unique environment because of distinctive oxidative and reduced strata formed as a result of strong density stratification. In Seneca Lake, a yearly mixing event after a long period of stratification alters the distribution of dissolved constituents, organic matter composiiton, and the succession of microbial processes. In Green Lake, the permanent density stratification creates three layers – a sufficiently oxidized upper layer (mixolimnion), a permanently anaerobic lower layer, (monimolimnion), and a transitional redox layer between the mixolimnion and the monimolimnion (chemocline) (Hakala 2004, Zerkle et al. 2010). The chemocline of a meromictic lake is permanent and is characterized by steep chemical and density gradients, which is where Hg methylation can be expected to occur. The sulfur cycling in Green Lake has been extensively studied, but no previous studies of Hg and DOM dynamics have been made. To date, there are no known studies of Hg production in the water column of Seneca Lake.

Chapter 2

Methods

Study Site and Sampling

The studies were conducted at Green Lake, Fayetteville, NY (43.0512° N, 75.9659° W), and at Seneca Lake, Geneva, NY (42.6918° N, 76.9202° W).

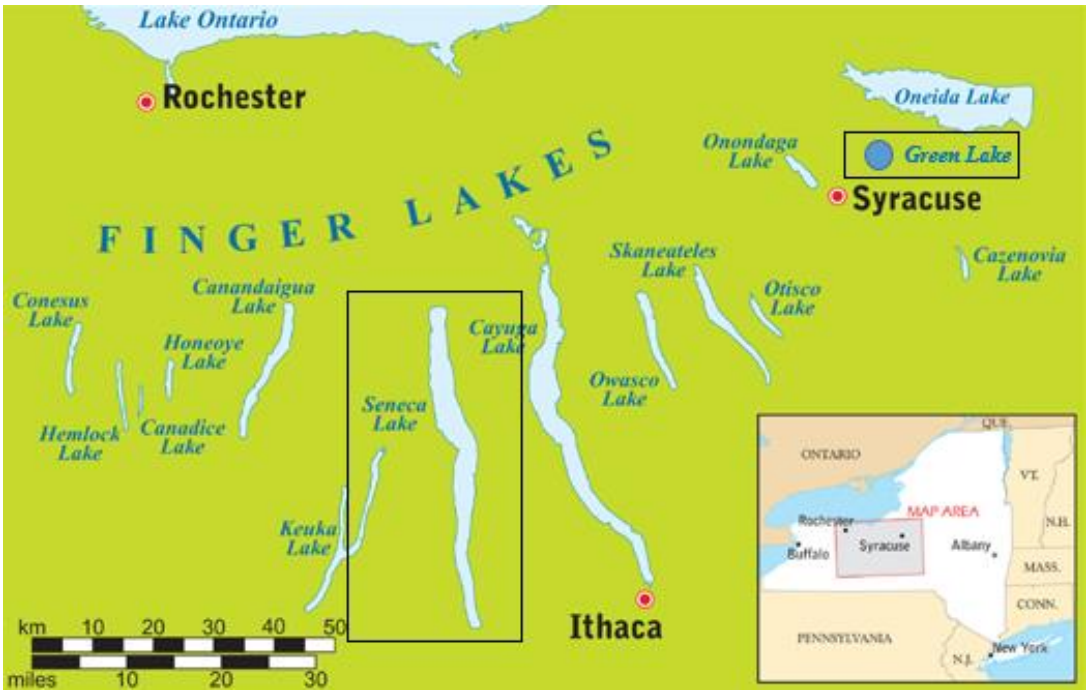

Figure 1. Map of Finger Lakes Region in New York. Green Lake and Seneca Lake are denoted with black boxes.

Green Lake is a glaciated plunge-pool basin. At its deepest location, the lake reaches a depth of about 56 m and has a surface area of 0.3 km^2. Green Lake developed and maintains its meromixes due to saline groundwater inputs (Brunskill and Harris, 1969). The transition between the oxic and anoxic region in this lake is between 18 to 21 m (Brunskill and Harris, 1969, Zerkle

et al., 2009, Havig et al., 2015). Green Lake is highly oligotrophic and its photic zone extends to the chemocline, establishing ideal conditions for the growth of phototrophic bacteria. Purple sulfur bacteria (PSB) are abundant in the water column and at very high density in the chemocline (Meyer et al., 2011).

Seneca Lake is an oligo-mesotrophic lake located in Geneva, New York. It has an average depth of 89 m, with a maximum depth reaching 188 m, and its surface area covers 173 km^2. The lake is warm monomictic. A thermocline typically develops in early May and the lake remains thermally stratified most of the year, mixing from top to bottom only during the winter (Ellis et al., 2004). The thermocline boundary is at around 20 m depth. Despite the strong thermal stratification, lake waters remain well-oxygenated year-round (Halfman, 2016).

Samples of Green Lake were taken on May 31, 2018, in the deepest location of the lake, at a resolution of 5 m and refined to 1 m at the chemocline (Figure 2). Samples of Seneca Lake were taken on September 7, 2018 at a location with a depth of 100 m (Figure 3). Samples were taken every 5 m. Field measurements for pH, temperature, specific conductance, and dissolved oxygen (DO) were taken using a multiparameter YSI sonde (YSI, Inc., Ohio, US). Samples analyzed for Hg were collected in Teflon bottles while utilizing the clean-hand, dirty-hand technique (USEPA, 1996). Additional samples were taken for DOM analysis in 50 mL vials cleaned with acetone before sampling. Samples were preserved on ice and transported to Syracuse University, NY. Green Lake water samples from 18 to 25 m were split, and half of them were filtered through a 0.45 µm Supor® PES membrane (Pall Corporation, NY). All samples for Hg analysis were preserved with 0.5% HCl immediately after returning to the laboratory at Syracuse University.

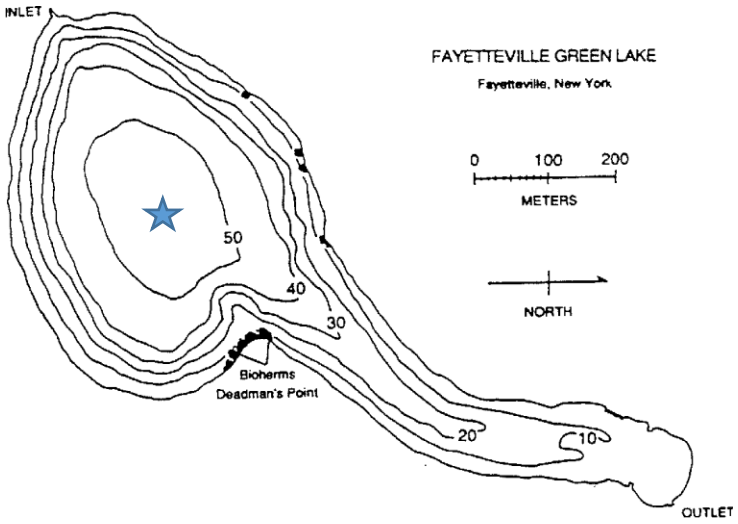

Figure 2. Bathymetric Map of Green Lake. The blue star denotes sampling location.

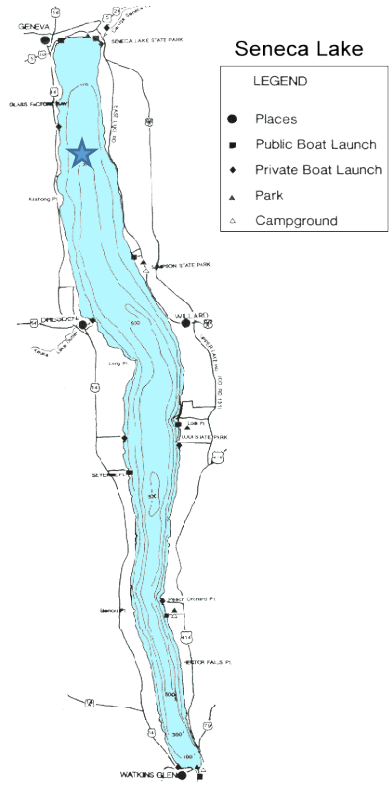

Figure 3. Bathymetric Map of Seneca Lake. The blue star denotes sampling location.

Analytical Methods

To detect major anions in the water samples, Ion Chromatography with Chemical Suppression of Eluent Conductivity was used (APHA 1992). Samples were injected into a stream of hydroxide eluent and passed through a series of ion exchangers. Anions were detected using an Ionpac AS 18 high-capacity, hydroxide-selective, anion-exchange column. Duplicate samples, continuous calibration verification (CCV), continuous calibration blanks (CCB), and spiked samples were run with every batch of 20 samples to ensure quality assurance and quality control (QA/QC). All CCV values were within the acceptable QA/QC range of ±10% recovery, with values ranging from 98.4% to 101.8%. CCBs were all below the detectable limit.

Since SRB play a large role in methylation, samples were tested for sulfide using the methylene blue method (HACH Company, 2018). For each sample, 0.5 mL of ferric chloride and dimethyl-p-phenylenediamine were added, and if sulfide was present, the sample reacted with the reagents and produced methylene blue. The amount of sulfide in each sample was detected using a spectrophotometer (HACH Company, Loveland, OH).

Samples were filtered after collection for DOM and dissolved organic carbon (DOC) analysis. For DOM analysis, samples were run through an Aqualog CCD Detector (Horiba Instruments Inc., Japan) to observe fluorescence and absorbance spectra. For DOC analysis, the Persulfate UV Oxidation Method was used (APHA 2000). Samples reacted with sodium persulfate and oxidized via UV light to CO_2 through a Phoenix 8000 machine (Teledyne Tekmar, Mason, OH). All CCV values were within the acceptable QA/QC range of ±10% recovery, with values ranging from 96.0% and 106.6%. CCBs were all below the detectable limit.

Total Hg analysis was performed using automated oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS) (Tekran 2600, Tekran, Toronto,

ON). Samples were oxidized with BrCl, and reduced with NH_2OH:HCl and $SnCl_2$ solutions following USEPA Method 1631 (USEPA, 2002). Spiked samples were introduced for every batch of ten samples. Quality control samples were within the acceptable range of ±15% recovery. CCV values ranged from 89.4% recovery to 105.8% recovery. The method detection limit and external verification samples ranged from 100% to 110% and from 86% to 110%, respectively.

MeHg analysis was performed using the modified USEPA Method 1630 (USEPA 1998). Samples were adjusted to a pH of 4.3-4.6 with citrate buffer and ethylated with sodium tetraethyl borate to form methylethyl Hg. The methylethyl Hg formed from this reaction was purged to a tenax trap with N_2 gas, converted to elemental Hg, and detected in a Cold Vapor Atomic Fluorescence Spectrometer. All quality control samples were within the acceptable range, with CCV values between 83.3% and 107.6%. Blanks were below the detectable limit.

Chapter 3

Results and Discussion

Physical Characteristics of Green Lake

Physical parameters delineated a stratified lake with a steep oxycline between 15 and 20 m (Figure 4A), consistent with previous studies on the lake (Brunskill and Harris, 1969, Zerkle et al., 2009, Havig et al. 2015). The temperature decreased from 22°C in the mixolimnion to 7.7°C in the monimolimnion. A chemocline peak in temperature was observed at 19-20 m depth, which Culver and Brunskill (1969) suggested is a result of light energy accumulation at the dense bacterial layer. Culver and Brunskill (1969) estimated that the amount of light transmission they measured in the fall can increase the temperature in the chemocline with 0.3°C. I observed an increase of 0.7°C, but it should be noted that this study was conducted in May when the amount of solar radiation is much higher.

The DO concentrations remained around 8.4 mg/L (100 % saturation) up to 10 m, peaked at the 10 m depth (11 mg/L or about 99% saturation), and then sharply decreased to below 2 mg/L (the detection limit of the probe) below 20 m depth. The positive heterograde at 10 m (increased DO below the surface) might be a combined result of photosynthetic activity just above the thermocline and the increased solubility of oxygen at low temepratures (Figure 4A).

Both pH and conductivity remained constant in the mixolimnion, with conductivity ranging from 1481 to 1778 µs/cm and a pH ranging from 7.73 to 7.98 (Figure 4B). Approaching the chemocline, at a depth of 18-21 m, conductivity steadily increased to 4087 µs/cm in the monimolimnion, while pH decreased to 6.97. The observed increase of specific conductance is

associated with increase of dissolved salt ions coming from groundwater sources (Takahashi et al. 1968, Brunskill and Harris 1969). The decrease in pH is most probably a result of the anaerobic microbial metabolism.

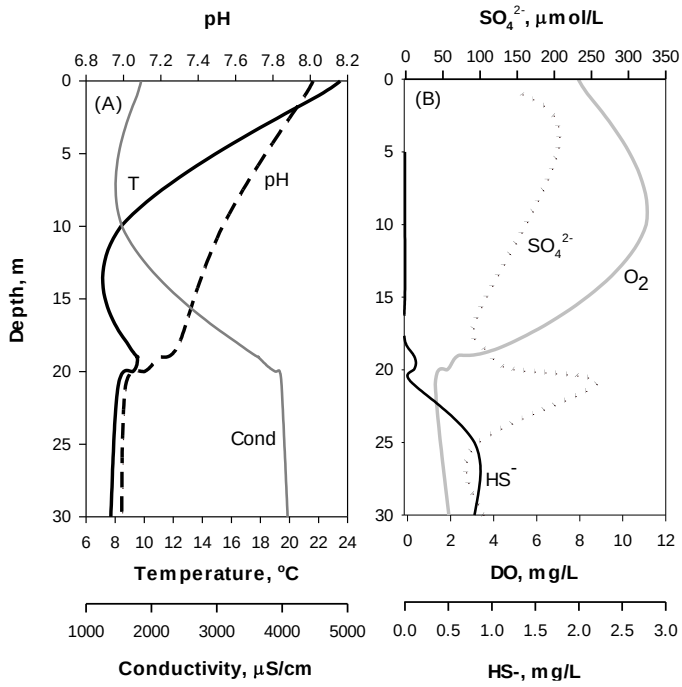

Figure 4. Vertical distribution of (A) Conductivity (grey line), temperature (black line) and pH (dashed line) and (B) Dissolved O_2 (grey line), SO_4^{2-} (dotted line), and HS^- (black line). The shaded region delineates the chemocline.

Chemical and Optical Characteristics of Green Lake

Sulfate and sulfide in the water column were measured to delineate the zone of sulfate reduction. Sulfate and sulfide are used as indicators for microbially-mediated sulfate reduction. During their metabolism, SRB use sulfate to produce sulfide. Sulfate remained between 0.203 and 0.156 mM in the monimolmnion. It fluctuated in the chemocline (Figure 4, shaded region)

and reached a local minimum at 18 m depth followed by a local maximum at 20 m depth. Sulfide concentrations were undetectable in the mixolimnion but quickly increased to 0.8 mg/L just below the chemocline.

Vertical distribution of Hg species showed distinctive profiles with peaks in the chemocline (Figure 5A). Total Hg concentrations were uniformly low in the mixolimnion, gradually increased below 15 m to reach a peak of at 3.92 ng/L at 19- 20 m depth, and then remained at ~ 1.7 ng/L in the monimolimnion. Similarly, MeHg remained below 0.008 ng/L in the monimolimnion and peaked at the 20 m depth (0.66 ng/L). The concentrations of Total Hg and MeHg in the mixolimnion of Green Lake are lower than the concentrations observed in other pristine lakes (Dennis et al., 2004, Eckley and Hintelmann, 2006). I attribute this to the ultra-oligotrophic state of the lake and the deep photic zone, which established ideal conditions for photodemethylation. Photodemethylation occurs in the photochemically active layers in lakes (Klapstein and O'Driscoll, 2018), which for Green Lake is the whole mixolimnion.

To assess the depths with highest potential for methylation, I calculated the %MeHg (the amount of total Hg as MeHg), which has been used as an indicator for methylation efficiency (Fleck et al. 2016). The %MeHg was between 1% and 8% in the mixolimnion, reached 49% at 19 m depth, and then was between 3% and 23% in the monimolimnion. The %MeHg in Green Lake are unusually high given that in most freshwater lakes the %MeHg in the water column is < 1-3% (Nguyen et al. 2005, Ullrich et al. 2001, Gray et al. 2014), whereas the maximum observed in this lake was 49%. Elevated %MeHg (20-70%) has been reported in the anaerobic water column of only a few pristine lakes (Watras et al. 1995, Eckley and Hintelmann 2006). The %MeHg in chemocline of Green Lake is comparable with values most often observed in

contaminated aquatic sediments, anaerobic hypolimnia of contaminated eutrophic lakes, and wetlands (Marvin-DiPasquale et al. 2003, Todorova et al. 2009, Gilmour et al. 2018).

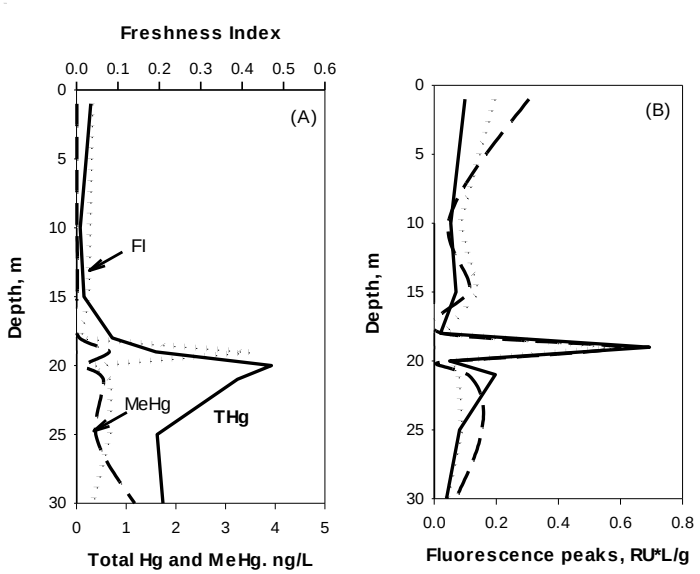

Figure 5. (A) Vertical distribution of Total Hg (black line), methyl Hg (dashed line), and DOM Freshness Index (dotted line). (B) Vertical profiles of Fluorescent DOM peaks B (black line), T (dotted line), and M (dashed line). The shaded region delineates the chemocline where purple sulfur bacteria are present.

All protein-like fraction of the DOM (peaks B, T, and M) followed similar vertical distributions in the water column of Green Lake, with increases in the chemocline, as well as at the 5m depth (Figure 5B). The peaks had very low specific fluorescence in the mixolimnion and monimolimnion. However, noteworthy peaks were detected at 19 m depth. The humic-like DOM peaks (A and C) had similar vertical distributions with low specific fluorescence in the mixolimnion and monimolimnion, but with peaks in the chemocline at 20 m. I also examined the vertical distribution of the DOM Freshness Index (FI), which had the highest concentration at 19 m depth at 0.417, while it remained between 0.028 and 0.079 for the rest of the water column.

Physical Characteristics of Seneca Lake

Vertical profiles of physical parameters for Seneca Lake demonstrated that the lake was thermally stratified (Figure 6A). Temperature decreased quickly from 25°C at the surface to 12.5°C at 20 m, then more gradually until it reached ~5.0°C at 45 m, and remained stable at ~ 4.0°C below 80 m depth. The thermocline extended between 10 am and 20 m, which is consistent with previous studies on the lake (Halfman, 2016). The vertical profile of pH followed a similar concave distribution. The maximum pH occurred in the top 5 meters (pH=9.5) before gradually decreasing to 8.5 at 20 m depth. Below the thermocline, pH remained between 8.3 and 8.4. Specific conductance increased from the surface at 644 μs/cm to 696 μs/cm at a 46 m depth, where it remained stable at this conductivity until reaching the 107 m depth. The decreased conductivity at the epilimnion is most probably a result of hydraulic inputs to the lake during the stratified period, which dilute the solute concentrations coming via groundwater inputs.

DO was present at measurable concentrations throughout the water column (Figure 6B). The DO in the epilimnion was at ~ 7 mg/L or about 83% of saturation. The hypolimnion was more enriched in oxygen due to the lower temperatures and maintained concentrations of 8.6- 8.8 mg/L, which correspond to 70-76% of saturation. The minimum DO of 6 mg/L (~ 60 % saturation) occurred at ~ 15 m depth, which corroborate with other studies on the lake that found minimum DO to be between 5 and 7 mg/L (Halfman, 2016). The large hypolimnetic volume and the oligo-mesotrophic conditions in Seneca Lake prevented the complete depletion of DO in the lower parts of the lake at the end of summer, a phenomenon which is usually observed in temperate lakes in Upstate New York (Halfman, 2016, Todorova et al., 2009).

Sulfate concentration showed negligible variability in the water column. Concentrations were somewhat lower at the surface (357 μmol/L), stabilizing around 372 μmol/L below 45 m

depth. Sulfide was not detected throughtout the water column. The lack of measurable decrease in SO_4^{2-} concentrations and concomitant production of HS^- indicate that microbial sulfate-reduction was absent at Seneca Lake.

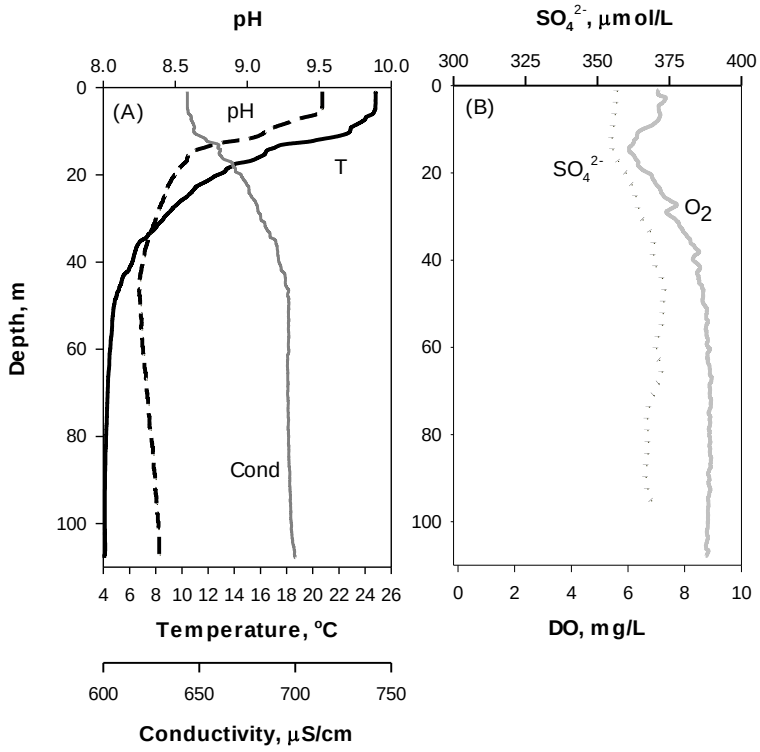

Figure 6. Vertical distribution of (A) Conductivity (grey line), temperature (black line) and pH (dashed line) and (B) Dissolved O_2 (black line) and SO_4^{2-} (dotted line) in Seneca Lake.

Chemical and Optical Characteristics of Seneca Lake

Total Hg concentrations exhibited very small variability in the watercolumn (Figure 7A). Concentration were between 0.19 and 0.32 ng/L in the epilimnion and below 0.2 ng/L in the hypolimnion, with the exception of a single peak of 0.58 ng/L at 30 m, which does not appear related to any other physical or chemical changes in the water column. The elevated THg concentrations in the epilimnion compared to the hypolimnion reflect atmospheric inputs which are diluted in the hypolimnion during winter mixing.

MeHg concentrations were between 0.01 and 0.017 ng/L in the epilimnion but remained below detection limit in the hypolimnion (Figure 7A). The highest %MeHg of 8.8% was at the surface. Most DOM peaks had uniform specific fluorescence throughout the water column except for Peak A wich showed increases at 10 m and 50 m depth (Figure 7B). This closely follows the trend of MeHg production, remaining largely stable around 0.6, without much deviation except for a decrease to 0.5 at the 5 m depth. The FI, which is typically associated with recently-produced DOM was between 0.65 and 0.73, except at 5 m depth where it was 0.38.

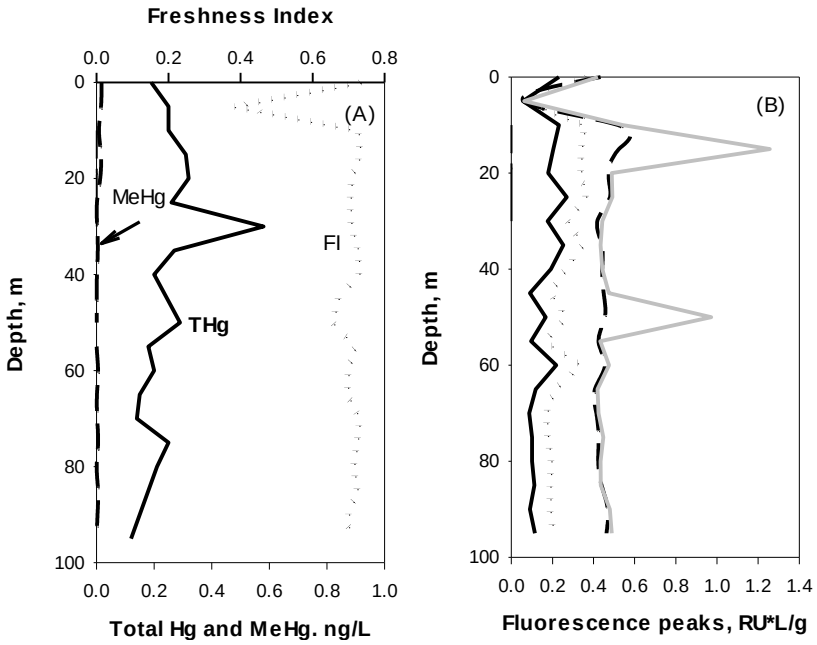

Figure 7. Vertical distribution of (A) Total Hg (grey line), methyl Hg (black line), and DOM Freshness Index (dotted line) in Seneca Lake. (B) Fluorescent DOM peaks B (black line), T (dotted line), M (dashed line) and C (grey line) for Seneca Lake.

DOM Control of MeHg Production

Green Lake and Seneca Lake have juxtaposing physical and limnological characteristics. Green Lake remains thermally and chemically stratified during the whole year, which results in complete depletion of DO below 20 m, formation of a sulfate-reduction zone, and enhanced production of MeHg in the chemocline. In contrast, Seneca Lake is thermally stratified most of the year, but stays oxygenated without a clear sulfate-reducing zone or substantial increase in MeHg.

The protein-like components of DOM did not appear to enahce accumulation of MeHg in the aerobic zones (Figures 5 and 7) but had pronounced effect on MeHg production under sulfidic conditions. The highest %MeHg in the chemocline of Green Lake (19 m depth, 49%) was most highly associated with the bioavailable fraction of the DOM (Figure 8), with occured within the zone of sulfate reduction. Both the protein-like components of DOM and FI are considered to represent the freshly-produced organic material (autochthonous DOM), which is considered the labile, bioavailable fraction of DOM (Fellman et al., 2010, Hansen et al., 2016). The humic-like peaks A, E and N, which were highly correlated with %MeHg in Seneca Lake (Figure 9), are thought to be of allochthonous origin, mainly as a result of the breakdown of the externally-supplied organic material in the water (Fellman et al. 2010, Hansen et al. 2016). The association of MeHg with terrestrial DOM in Seneca Lake demonstrates that MeHg was most probably delivered from the watershed and not produced in the lake.

The methylation of Hg in aquatic environments has been primarily attributed to the activity of SRB. My findings confirm that net MeHg production is enhanced in sulfidic environments by the presence of readily-available DOM. However, labile DOM is not linked to substantial MeHg formation under aerobic conditions. This finding is critically important in understanding the mechanisms governing the methylation of Hg.

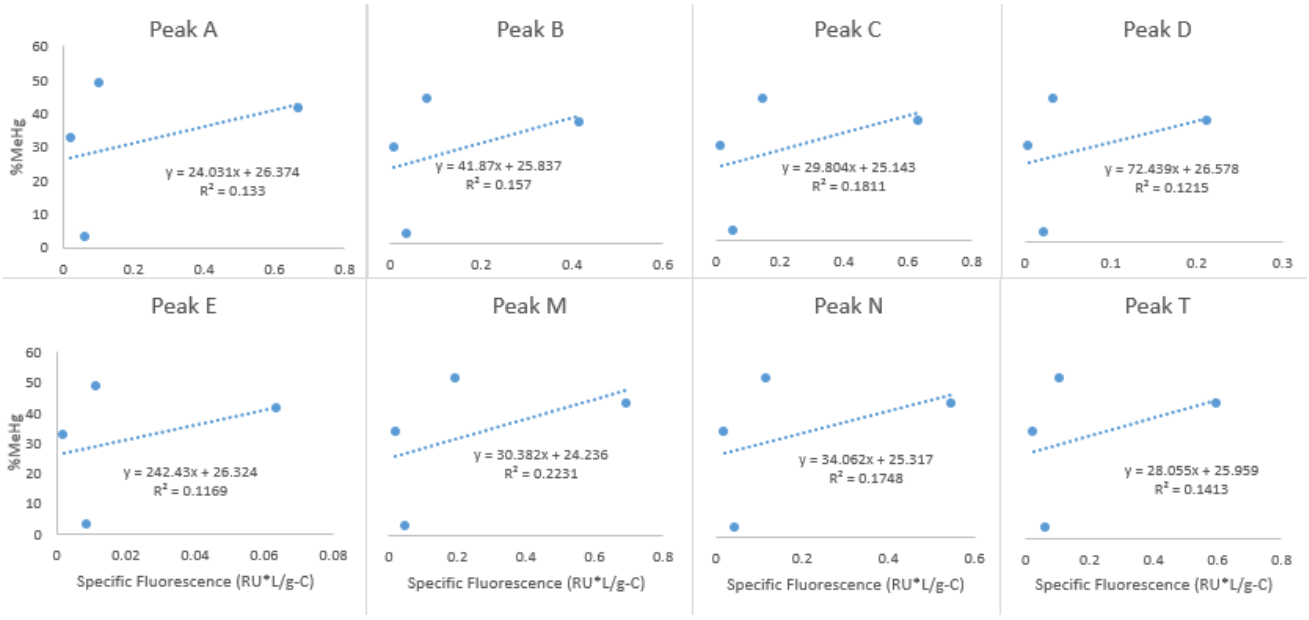

Figure 8. Correlations between %MeHg and DOM specific fluorescence between 18 and 21 m in Green Lake

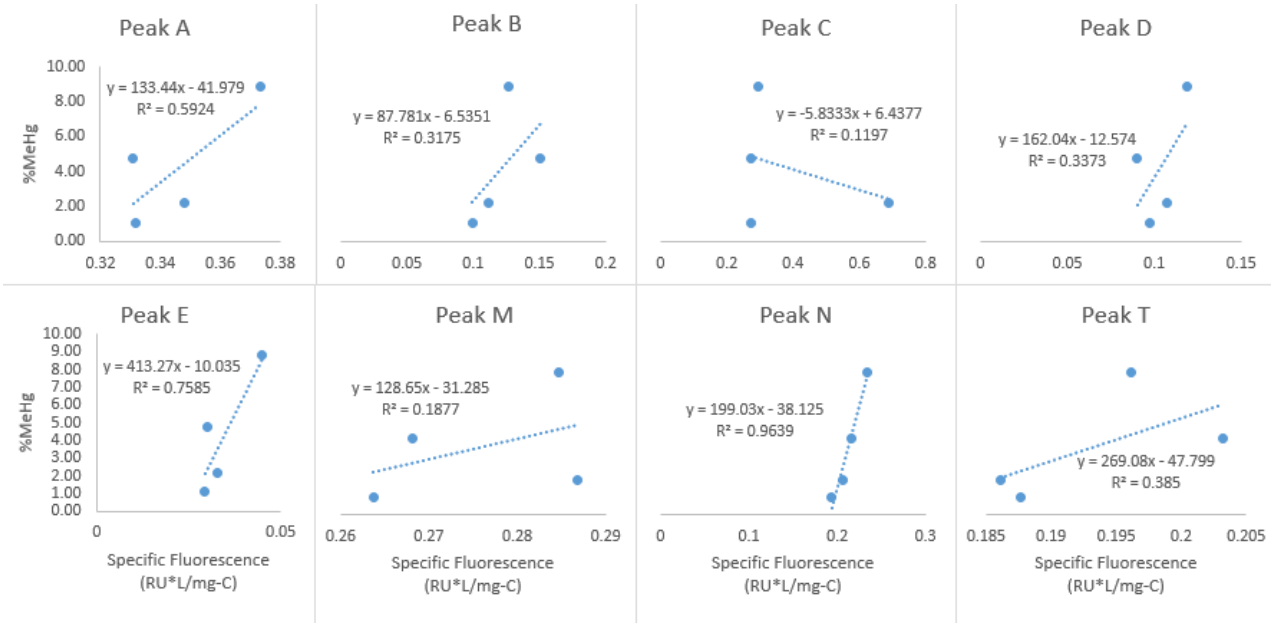

Figure 9. Correlations between %MeHg and DOM fluorescence between 10 and 25 m in Seneca Lake

Chapter 4

Conclusions

This is the first study which examines the biogeochemical interactions of Hg and DOM in a meromictic lake. In the chemocline of Green Lake, both total Hg and MeHg increased and nearly half of the total Hg was in the form of MeHg. The presence of specific types of freshly-produced DOM appeared to enhance the production of MeHg. This is not the case in the monomictic Seneca Lake where both total Hg and MeHg remained low. The highest potential for Hg methylation - 8.82% - was detected at the surface of the lake, which is insignificant compared to 50% in the chemocline of Green Lake. DOM peaks in Seneca Lake also did not correlate with the small amount of MeHg production, likely due to the insignificant amount of both methylated Hg and DOM present in the well-oxygenated lake. Lack of both DOM and MeHg in Seneca Lake further confirm a link between labile DOM and Hg methylation. Correlations run between %MeHg in the chemocline of Green Lake and labile DOM peaks shows that certain types of this DOM account for at least 10-25% of the significant methylation in the meromictic lake. Similar correlations run in the thermocline of Seneca Lake also show significance of DOM presence on methylation despite lack of significant DOM and Hg methylation trends in the lake.

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