

DEVELOPMENT OF METHODS FOR DETERMINING DRY DEPOSITION OF
MERCURY USING AN ION-EXCHANGE MEMBRANE: RELATIVE RATES OF
MERCURY DRY DEPOSITION AT SARDIS, ENID, AND GRENADA LAKES

by
Ruiqi Feng

A thesis submitted to the faculty of The University of Mississippi in partial fulfillment of
the requirements of the Sally McDonnell Barksdale Honors College.

Oxford
May 2015

Approved by

Advisor: Dr. James Cizdziel

Reader: Dr. Kristine Willett

Reader: Dr. Nathan Hammer

ACKNOWLEDGEMENTS

I would like to thank my research advisor, Dr. James Cizdziel for his guidance and support during the course of the research process. He's been an exceptional mentor, and I am especially grateful for his patience. I would also like to acknowledge and thank those who have also worked in Dr. Cizdziel's research group for their support. In particular, I would like to thank Jingjing Chen and Derek Bussan for their guidance during the early parts and latter parts of the research, respectively. I appreciate all of the help that they have given me during my research.

I also wish to thank the Sally McDonnell Barksdale Honors College for giving me the opportunity as well as the push to partake in research project during my undergraduate career. In addition, funding provided by the honors college has very helpful in carrying out my research, and I am extremely grateful. I thank my thesis committee members for their time as I complete and defend my thesis.

Finally, I would like to thank my family and friends. Their words of encouragement and their constant support are greatly appreciated.

ABSTRACT

This research focuses on studies developing methods to measure dry deposition of mercury (Hg) using an ion-exchange (IX) membrane to capture gaseous mercury species in the air. Mercury is a toxic heavy metal that is spread globally through the atmosphere. Atmospheric Hg deposits to terrestrial and aquatic ecosystems through wet and dry deposition. While routine methods have been developed to study wet deposition of Hg, measuring dry deposition of Hg is more problematic and often overlooked. In this study, we developed an inexpensive means to deploy a polyethersulfone cation exchange membrane in the field by dangling it within a polycarbonate bottle containing holes in the bottom to allow gas exchange. We tested several different analytical methods to measure the Hg on the membranes including atomic absorption spectrometry, atomic fluorescence spectrometry, and mass spectrometry. After demonstrating that the field method is capable of capturing and retaining airborne Hg on the membrane, we deployed the bottles containing the membranes at Sardis, Enid, and Grenada Lakes, located in north Mississippi. The purpose was to estimate the relative rates of dry deposition of Hg in order to explore differences in the levels of Hg found in fish from these lakes. We hypothesized that point sources near Grenada Lake, including a coal-fired power plant, may result in higher Hg deposition rates, which may be the reason for the higher Hg levels observed in fish from Grenada Lake compared to the other lakes. However, results show that Sardis Lake had the highest dry deposition rates followed by Enid and Grenada Lakes. Thus, the higher levels of Hg in fish from Grenada Lake remain unexplained.

Table of Contents

ACKNOWLEDGEMENTS	ii
ABSTRACT.....	iii
LIST OF FIGURES	v
LIST OF TABLES	vi
LIST OF ABBREVIATIONS	vii
1 INTRODUCTION.....	1
1.1 The Biogeochemical Cycle of Mercury	1
1.2 Measuring Dry Deposition of Mercury	3
1.3 Prior research and purpose of this study.....	4
2 MATERIALS AND METHODS	6
2.1 Sampling Sites	6
2.2 Deploying Cation-Exchange Membranes for Capturing Airborne Mercury.....	9
2.3 Background on the Analytical Instrumentation Used	11
2.4 Analytical Methods	13
2.4.1 Analysis of cation exchange membranes using the DMA	13
2.4.2 Analysis of cation exchange membranes using DMA-ICPMS	13
2.4.3 Analysis of Dry Deposition of Mercury via Leaching of CEM.....	14
2.4.4 Analysis of Dry Deposition of Mercury Using Tekran 2700.....	15
2.4.5 Methods to lower blank levels on the membranes prior to deployment	15
3 RESULTS AND DISCUSSION	16
3.1 Preliminary Experiment.....	16
3.2 Membranes deployed at the lakes and analyzed by the Direct Mercury Analyzer	16
3.3 DMA-ICPMS Analysis of Membranes and time-series experiments	17
3.4 Analysis of Dry Deposition of Mercury by Leaching of Membranes.....	20
3.5 Analysis of Dry Deposition of Mercury with Tekran 2700	21
4 CONCLUSION	23
REFERENCES.....	24
APPENDIX (SUPPLEMENTAL MATERIAL)	27
Experiment designed to lowering the background of membranes prior to deployment ...	27
Preheating the membrane.....	27
Washing CEM with HCl.....	27
Altering Settings on DMA	28
UV-light Exposure	28

LIST OF FIGURES

Figure 1: Conceptual Biogeochemical Cycle of Mercury.	3
Figure 2: Experimental setup on the dams at Sardis, Enid and Grenada Lakes.	6
Figure 3: Sardis, Enid, Grenada lakes and the Red Hills Power Plant in relation to the state of Mississippi and the town of Oxford, MS.	7
Figure 4. Experimental setup for deploying cation-exchange membranes in the field (top) and deployment for early experiments on top of Anderson Hall.....	10
Figure 5: Experimental setup at Sardis Lake	11
Figure 6. Coupling of the DMA and the ICP-MS.....	14
Figure 7: Accumulation of Hg species on CEM with time.....	18
Figure 8: Counts/Second of Grenada Sample.....	19
Figure 9: Counts/Second of the calibration standard.....	19
Figure 10: Dry deposition of Hg by leaching of membranes using ICPMS.....	20
Figure 11: Apparatus for UV light exposure experiment	29
Figure 12: Exposure of CEM to UV Light	31

LIST OF TABLES

Table 1: Mercury levels in fish from north Mississippi Lakes	5
Table 2: Landuse Distribution of Enid Lake and Grenada Lake Watersheds	8
Table 3: Anderson Hall Pilot Study Data.	16
Table 4: Samples from Sardis, Enid, and Grenada Lake (whole membrane analysis)	17
Table 5: Determination of Dry Deposition of Mercury using Tekran 2700	22
Table 5: Cation Exchange Membrane-exposure to UV-light	29
Table 6: Cation Exchange Membrane-Exposure to UV-light.	30

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
CVAFS	Cold Vapor Atomic Fluorescence Spectroscopy
DMA	Direct Mercury Analyzer
EPA	United States Environmental Protection Agency
GEM	Gaseous Elemental Mercury
GOM	Gaseous Oxidized Mercury
ICPMS	Inductively Coupled Plasma Mass Spectrometry
MeHg	Methylmercury (CH ₃ Hg)
PBM	Particle Bound Mercury
PES	Polyethersulfone
IX	Ion Exchange
CEM	Cation Exchange Membrane

1 INTRODUCTION

1.1 The Biogeochemical Cycle of Mercury

Mercury is a pervasive and widespread global contaminant that is dispersed primarily through the atmosphere. Natural sources include volcanic emissions and evasion from vegetation and soil, while anthropogenic sources include coal-fired power plants (CFPPs) and incinerators (Fitzgerald and Clarkson, 1991). Natural sources emit mercury primarily as Hg^0 , also known as gaseous elemental mercury (GEM). GEM plays an important role in the transport and global cycling of mercury. It is slowly converted by photochemical oxidation to Hg (I) and Hg (II), collectively termed gaseous oxidized mercury (GOM), and can stay airborne for months to years (Clarkson et al., 2006). Two of the more common GOM species are HgCl_2 and HgBr_2 . Because of their solubility, the lifespan of GOM in the atmosphere is fairly short, generally lasting between hours and days, depending on atmospheric conditions. Particle bound mercury (PBM) is a third category of atmospheric mercury. Its lifetime also depends on the size of the particle and interaction with moisture, but generally remains airborne for hours to weeks (Huang et al., 2013).

Gaseous mercury moves from the atmosphere to terrestrial and marine ecosystems via dry and wet deposition (Nowak et al., 2014). Wet deposition of mercury refers to transfer of mercury from air to surface via precipitation (e.g., rain, snow, fog). Dry deposition of mercury, referring to deposition to surfaces in the absence of precipitation,

can be similar or even greater in magnitude than wet deposition (Sakata and Marumoto, 2005 and Lindberg et al., 2007). GOM and PBM are removed from the atmosphere via dry deposition at much faster rates than GEM due to their surface/reactive properties (Zhang et al., 2012).

Once in aquatic environments, inorganic mercury can be converted to methylmercury (MeHg) by microorganisms, particularly sulfate reducing bacteria, found in the sediments of both fresh water and salt water systems (Mason et al., 2005). As a result, MeHg can be found in nearly all aquatic species (Clarkson et al., 2006).

Methylmercury is a neurotoxin that biomagnifies up the food chain and is readily absorbed within the gastrointestinal tract. Consumption of fish containing high levels of MeHg is harmful to humans and other wildlife (Costley et al., 2000). Mercury is responsible for most fish consumption advisories in the United States and is considered by the U.S. Environmental Protection Agency to be a high-priority pollutant (Fox et al., 2005). An overview/conceptual model of the biogeochemical cycle of mercury is given in Figure 1.

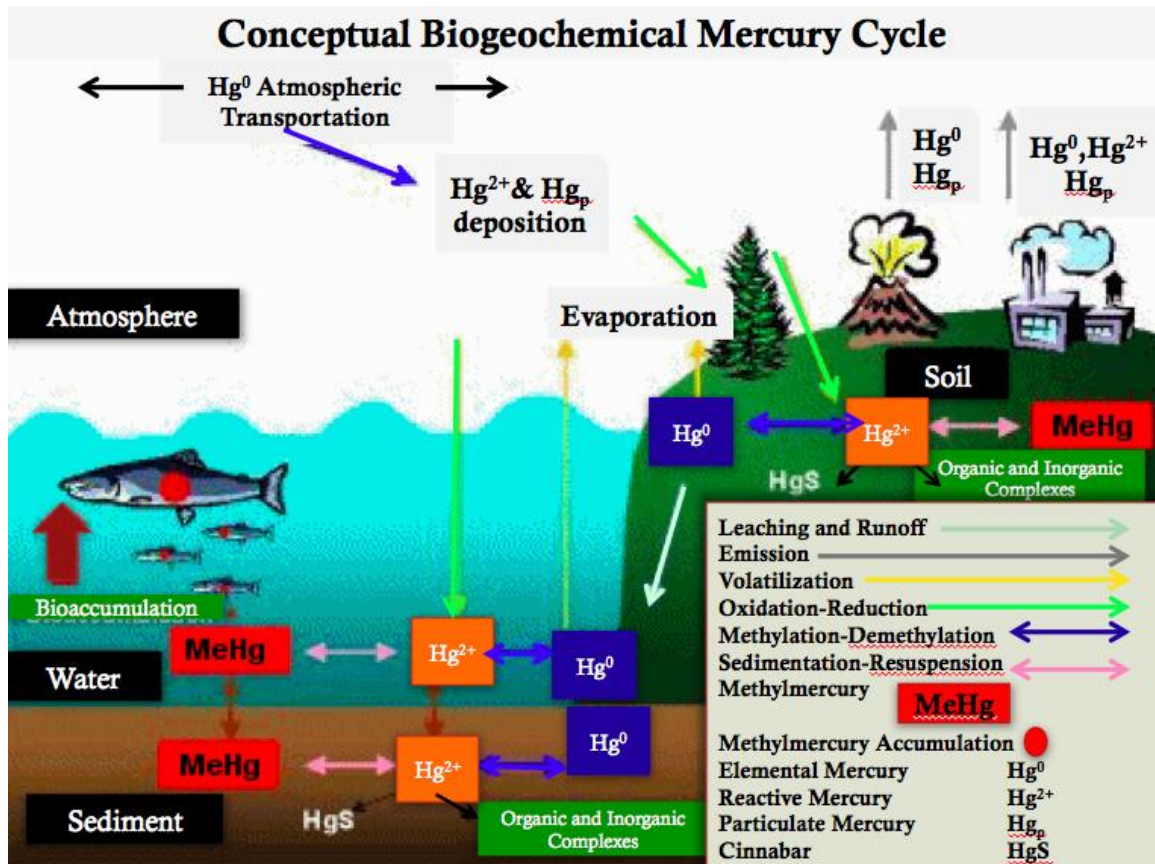


Figure 1: Conceptual Biogeochemical Cycle of Mercury. (Source: Environment Canada, 2013)

1.2 Measuring Dry Deposition of Mercury

Understanding dry deposition of mercury is particularly important because it can be a major contributor of mercury to an ecosystem (Zhang et al., 2011). However, unlike wet deposition of mercury, there are few cost-effective methods of measuring dry deposition of mercury. One approach is the use of surrogate surfaces to capture a portion of atmospheric mercury that comes in contact with the surface. Examples of surrogate surfaces include water surfaces, gold-coated quartz filters, and IX membranes, and often cation-exchange membranes (CEM). Lyman et al. (2005) used a CEM to measure

airborne mercury at sites in Florida and suggested that it was effective at capturing GOM species. The mechanism of GOM retention on the membrane is not fully understood but presumably involves adsorption followed by rapid surface chemistry with other co-collected compounds or membrane functional groups that allows the Hg(II) to eventually chemisorb (E. Prestbo, Tekran Inc., personal communication). Whereas IX membranes by no means represent the heterogeneity of natural surfaces, they nevertheless can be used to estimate and compare the relative rates of Hg dry deposition at different sites.

Another approach to measure dry deposition of mercury is to measure airborne mercury species (GEM, GOM and PBM) using a commercially available automated system from Tekran Corporation. The system determines GEM at ~5 minute intervals, and GOM and PBM at ~ 2-3 hour intervals, reflecting the different levels of these species in the air. However, unlike the IX method, the system is costly and there are logistical challenges (e.g. power requirements, maintenance, etc.) that make it difficult to compare deposition rates at multiple sites.

1.3 Prior research and purpose of this study

Grenada, Enid and Sardis Lakes, located in north Mississippi, are used by the public for recreation, including fishing. The Mississippi Department of Health issued fish consumption advisories for Grenada and Enid Lakes due to high levels of mercury in the fish. Prior research in the Cizdziel group has shown that mercury levels in fish are highest in Grenada Lake, followed by Enid Lake, and then Sardis Lake (Table 1). However, we have been unable to determine the cause(s) for this difference. We hypothesized that point sources near Grenada Lake, including a coal-fired power plant,

may result in higher mercury deposition rates, which, in turn, may be the reason for the higher mercury levels observed in fish from Grenada Lake. To measure dry deposition of atmospheric mercury, one of Dr. Cizdziel's former students (Yi Jiang) tested a polyethersulfone (PES) cation exchange membrane and found that it effectively captured airborne Hg species above blanks (membranes not exposed to air). The purpose of this study was to (1) improve field and laboratory (analytical) methods for estimating dry deposition of mercury using a cation-exchange membrane, and (2) apply the methods to compare dry deposition of mercury at Sardis, Enid, and Grenada Lakes in order to test the above hypothesis.

Table 1: Mercury levels in fish from north Mississippi Lakes (G. Brown, 2013).

Levels not connected by the same letter are significantly different ($p < 0.05$).

Species	Data / Test	Grenada	Enid	Sardis
Largemouth Bass	Mean:	379	295	229
	Significance:	A	A, B	B
Crappie	Mean:	210	186	143
	Significance:	A	A	B
Channel Catfish	Mean:	377	209	138
	Significance:	A	B	C

2 MATERIALS AND METHODS

2.1 Sampling Sites

Cation-exchange membranes were deployed on the dams at Sardis Lake, Enid Lake, and Grenada Lake in order to compare dry deposition of mercury in the sites (Figures 2 and 3). The membranes were placed inside polycarbonate bottles with holes at the bottom for gas exchange (described below). Sardis Lake has the largest watershed (~3985 km²) followed by Grenada Lake (3406 km²) and Enid Lake (1153 km²). Information on the distribution of land use and land cover for Grenada Lake and Enid Lake watersheds is provided in Table 2. We were unable to determine the land use distribution for Sardis Lake watershed. A large percentage of Grenada and Enid Lake's watershed is used for agriculture.

Both land use as well as point sources of mercury in the vicinity of the lakes may impact mercury in the lakes. The only major point source of mercury in the study area is the Red Hills Power Plant (Figure 3).



Figure 2: Experimental setup on the dams at Sardis, Enid and Grenada Lakes.

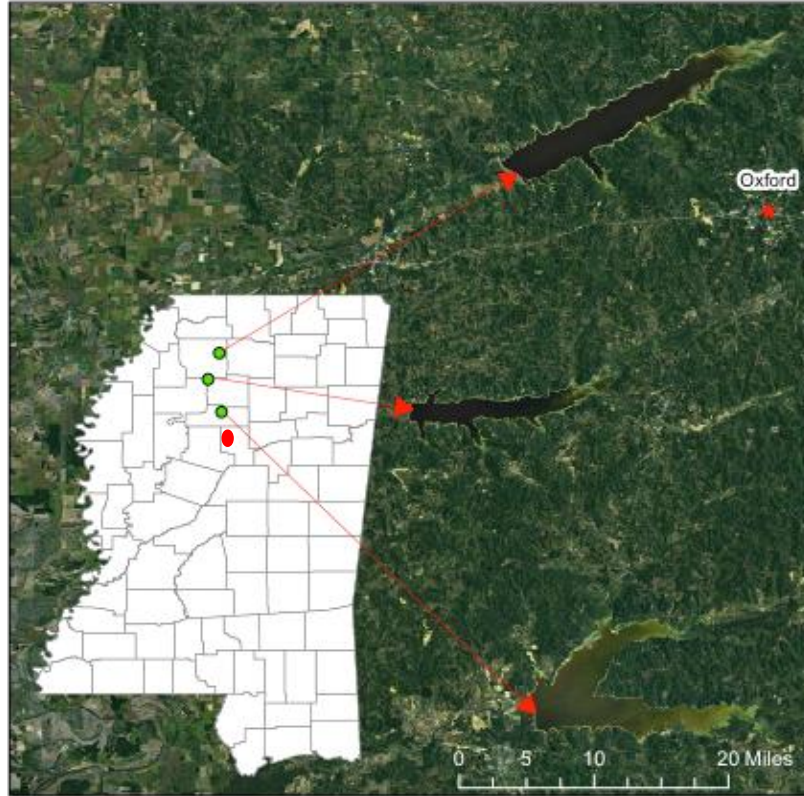


Figure 3: Sardis (top), Enid (center), Grenada (bottom) lakes and the Red Hills Power Plant (red dot) in relation to the state of Mississippi and the town of Oxford, MS.

Lake Watershed		Forest	Agriculture	Urban	Wetland	Water	Disturbed	Total
Enid	Area	143873	160316	4110	16442	12332	73992	411068
	Percent	35%	39%	1%	4%	3%	18%	100%
Grenada	Area	389561	433013	7801	41508	36011	194162	1104800
	Percent	35.5%	39.2%	0.7%	3.76	3.26%	17.6%	100%

Table 2: Landuse Distribution of Enid Lake and Grenada Lake Watersheds(Source: EPA,2000)

2.2 Deploying Cation-Exchange Membranes for Capturing Airborne Mercury

Polyethersulfone (PES) cation-exchange membrane (CEM) was obtained from Pall Corporation. The surface of the flat membrane is hydrophilic and contains an anionic functional groups allowing bidirectional capture (both sides of the membrane). To deploy the membranes at field sites, plastic clips were used to hang 15 cm x 3 cm strips of the CEM inside a two-liter polycarbonate bottle (Figure 4 and 5). To reduce evasion of deposited mercury by high solar radiation, the bottles were painted with opaque, light colored paint. Holes were drilled at the bottom of the bottles to allow for exchange of air, while other bottles remained intact for blank measurements. The bottles (membranes) were exposed to the atmosphere for a period of time (usually for one week or two weeks) to collect Hg-species. Dry Hg deposition rates were calculated as follows.

$$D = [(S - B)/A]/T$$

Where D is the deposition rate in ng / m² h, S is the amount of mercury recovered from the sample, B is the average total mercury recovered from the blanks, A is the surface area of the membrane in m², and T is the deployment time in hours.

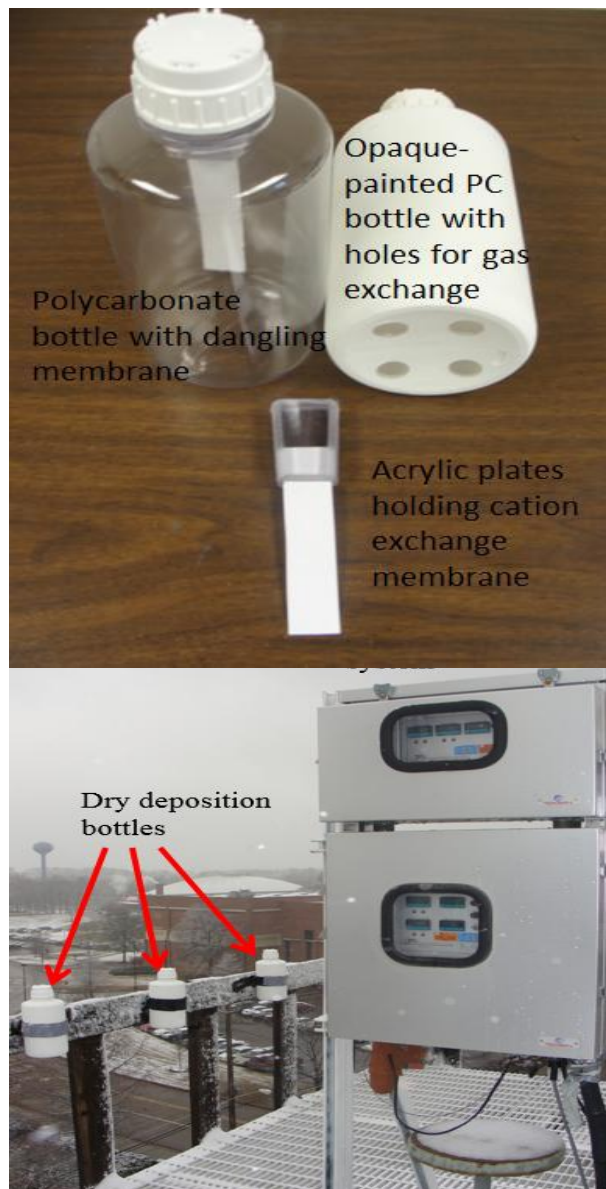


Figure 4. Experimental setup for deploying cation-exchange membranes in the field (top) and deployment for early experiments on top of Anderson Hall (bottom). Acrylic plates were later replaced by plastic clips that wedged into the bottle cap.

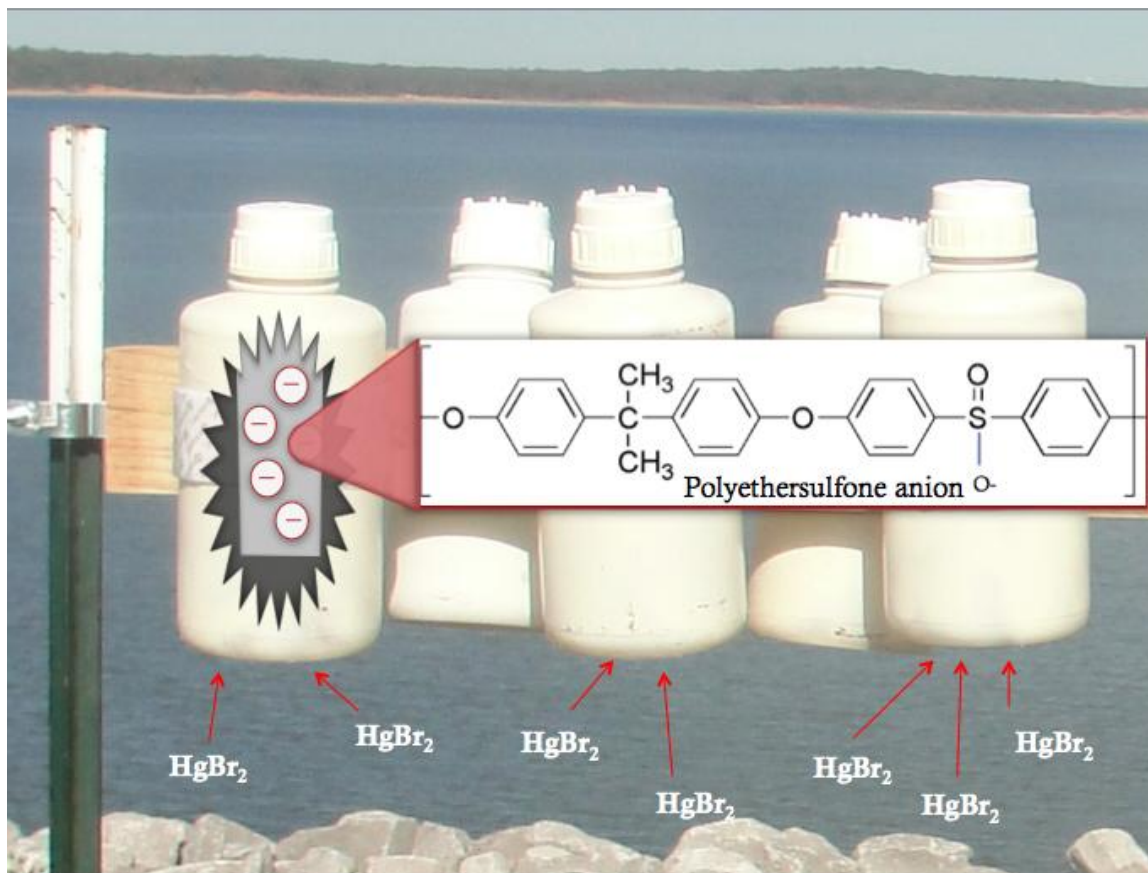


Figure 5: Experimental setup at Sardis Lake. Membranes strips hang inside bottles that have holes in the bottom to allow gas exchange.

2.3 Background on the Analytical Instrumentation Used

Mercury adsorbed on the membrane was analyzed using atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS) and mass spectrometry (MS). For AAS, a Direct Mercury Analyzer (DMA) was used (Milestone, Inc.). The DMA is one of the most commonly used instruments for determining mercury in samples. The instrument doesn't require sample treatment. The sample is sealed inside the instrument and combusted as oxygen flows over the sample and as the temperature is raised. Oxygen carries the combusted gases and Hg through a catalyst where Hg species are converted to elemental mercury vapor (Hg^0) and where chemicals interfering with the

experiment are trapped. Elemental mercury vapor is then carried to a tube containing gold-coated sand and forms an amalgam with gold. The trap is heated, and mercury is then carried in a pulse through a single beam spectrometer. Mercury concentration is then calculated using the Beer-Lambert Law by the absorbance measured at 253.7nm.

The AFS instrument used was a Tekran 2600. Compared to AAS, AFS is more sensitive and has lower detection limits because it has a lower background signal. Unlike the AAS instrument, the Tekran 2600 has dual gold traps. The gold traps are heated to evolve the trapped mercury, which is then carried by a stream of ultra-high purity argon into the fluorescence cell. The mercury is excited with a mercury lamp and fluorescence is detected off-axis with a photomultiplier tube. Both the DMA and Tekran 2600 use the unique properties of mercury (high vapor pressure, tendency to form an amalgam with gold) to measure mercury.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was also used a method to determine mercury. One of the advantages that the ICP-MS over other instruments is that it can be used to determine isotopes of Hg. The argon ICP is used as the ionization source. Ions from the plasma enter into the mass spectrometer through a two-stage interface. Ions and plasma gas pass through the sampler core, where the plasma is centered, into a vacuum-pumped region. Most of the argon gas is pumped away from the region, and the remaining ions pass through the skimmer cone into the mass spectrometer. Ion lenses are used to introduce the ions into the mass spectrometer where the ions are counted and an intensity versus m/z ratio plot can be generated. The mass spectra are relatively simple and elements can be easily identified from the mass and isotope ratios.

2.4 Analytical Methods

2.4.1 Analysis of cation exchange membranes using the DMA

The cation exchange membranes were deployed at Sardis Lake, Enid Lake, and Grenada Lake, with nine bottles deployed at each location. Cation exchange membranes (15x3cm) were suspended in each bottle using a plastic clip. After two weeks, three samples and a blank were collected from each location for analysis. Samples were placed directly into the DMA for analysis. Some membranes were sub-divided to obtain replicate measurements.

2.4.2 Analysis of cation exchange membranes using DMA-ICPMS

Because of low signals from the DMA, we coupled the DMA to the ICPMS to achieve greater sensitivity. In addition, to lower background concentrations, we deployed blanks in the field that were sealed in a Ziploc bag. The bags containing the blank membranes were then placed into polycarbonate bottles. The sample membranes were deployed in the same manner as before. Membranes were collected and analyzed by DMA-ICPMS coupling. An entire sample membrane was inserted into the DMA for analysis. Mercury from the DMA analysis of the membranes travels to the ICP-MS (Figure. 6). Prior to analysis, a calibration curve was made by injecting known amounts of Hg^0 into the DMA oxygen carrier gas through a tee-junction outfitted with a septa.

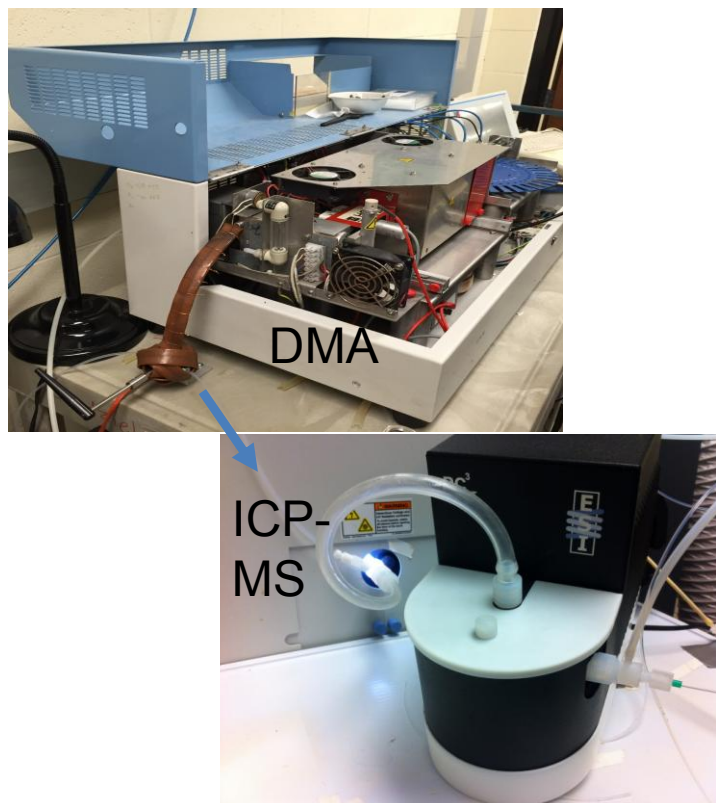


Figure 6. Photo showing the coupling of the DMA and the ICP-MS

2.4.3 Analysis of Dry Deposition of Mercury via Leaching of CEM

Another set of samples was deployed in the same manner as before: samples were suspended in the polycarbonate bottles with plastic clips for bidirectional capture of gaseous oxidized mercury species. To lower blank concentrations, the blanks were sealed into Ziploc bags and placed in polycarbonate containers. This set of samples analyzed by leaching the cation-exchange membranes. Membranes were placed in 15 mL tubes and leached with 10 mL of 1% HCl and 0.2M BrCl solutions. The analyte was then analyzed directly by ICP-MS.

2.4.4 Analysis of Dry Deposition of Mercury Using Tekran 2700

A final set of membranes was analyzed by the Tekran 2700. The membranes were deployed in the same locations as before. This time the blanks were placed into a glass vial and capped. The vial was then placed into a Ziploc bag and put into a polycarbonate bottle. The samples were deployed in the same manner as before. The membranes were placed in glass vials and leached using a bromine monochloride solution. The oxidized mercury from the membranes was reduced to elemental mercury by using SnCl_2 . The vials were then capped tightly and Hg was sparged from the vial through a needle into the CVAFS-based instrument.

2.4.5 Methods to lower blank levels on the membranes prior to deployment

Several methods were tried to lower blank concentrations on the CEM prior to deployment, including heating in an oven, heating in the DMA in an oxygen environment, heating in the DMA in an argon environment, HCl washing, and exposure to UV light. Each was unsuccessful or inconsistent. To be thorough, these results are summarized in the appendix (supplemental material).

3 RESULTS AND DISCUSSION

3.1 Preliminary Experiment

Prior to deploying the membranes at the lakes, we tested the experimental setup on top of Anderson Hall. Two membranes (one blank and one exposed to air) were placed in polycarbonate bottles and deployed on top of Anderson Hall. Two weeks after deployment the samples were collected and analyzed using the DMA. The results showed that mercury concentration on the air-exposed membrane was well-above mercury on the blank membrane (Table 3). While the amount of Hg was clearly above the blank level, it was later found that the peak was above the calibration curve and thus the determined amount and concentration of Hg may not be accurate. Nevertheless, this preliminary study encouraged us to continue and deploy the membranes at the lakes.

Table 3: Anderson Hall Pilot Study Data.

	Hg (ng)	Conc. ($\mu\text{g}/\text{kg}$)	Deposition Rate ($\text{ng} / \text{m}^2 \text{hr}$)
Blank membrane	9.2	50.1	6.1
Air-exposed membrane	115*	504*	76*

***Values for air-exposed membrane were above the highest standard and thus are only estimates and should be viewed with caution.**

3.2 Membranes deployed at the lakes and analyzed by the Direct Mercury Analyzer

At the lakes, individual strips of CEM (15 cm x 3 cm) were cut and placed into bottles (one per bottle) and the bottles left out for a 2 week period. The samples were

retrieved and analyzed by the DMA. At the lab, we sub-divided the individual membrane strips and placed them in the DMA. However, the smaller sections yielded inconsistent results, perhaps due to the smaller absolute concentrations of Hg. However, when analyzing the entire membrane results improved (Table 4). Interestingly, regardless of the size of the membrane, a general spatial trend emerged, with Sardis Lake samples yielding the highest concentration of Hg per membrane area, Grenada the lowest, and Enid somewhere in between. This is opposite of what we initially hypothesized and will be discussed later.

Table 4: Samples from Sardis, Enid, and Grenada Lake (whole membrane analysis)

Sample	Hg (ng)	Deposition Rate (ng / m² hr)
Sardis	118	78
Enid	51	33
Grenada	11	7

3.3 DMA-ICPMS Analysis of Membranes and time-series experiments

Because the DMA absorption values (signals) were so low, we decided to try a more sensitive measurement technique. Unfortunately, our CVAFS system was not working properly so we used the ICP-MS. To simplify the analysis, we coupled the DMA directly to the ICP-MS as described earlier. The DMA-ICPMS results showed the same trend seen by the DMA-alone: Sardis > Enid > Grenada.

We also tested accumulation of mercury in membranes deployed for different lengths of time. The results also showed the accumulation of Hg-species on the membranes increases with time deployed, but not in a linear fashion (Figure 7).

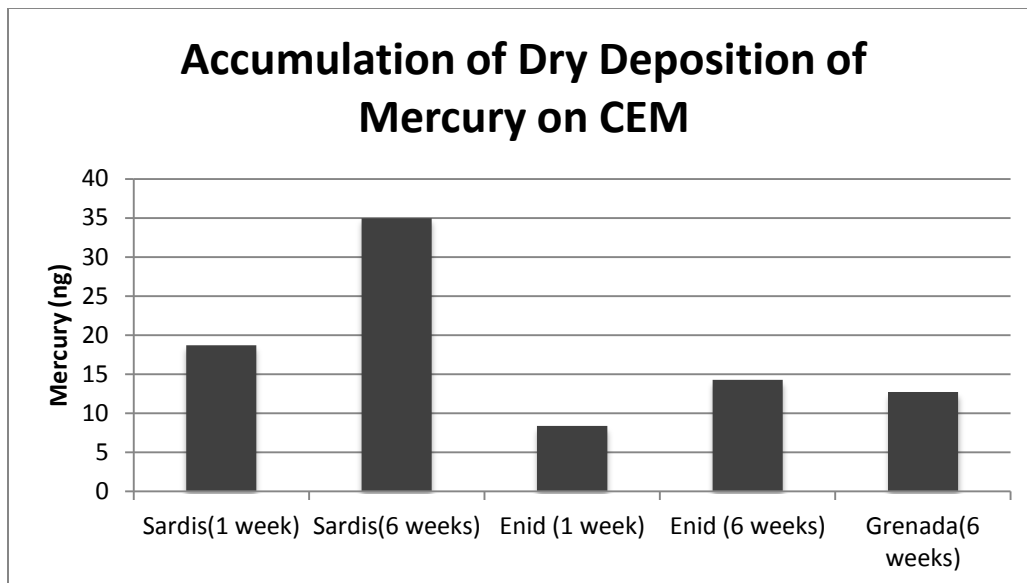


Figure 7: Accumulation of Hg species on CEM with time. No sample was collected for Grenada 1 week.

For another set of samples, we monitored two isotopes of mercury. Strangely, the $^{202}\text{Hg}/^{201}\text{Hg}$ isotope ratio did not match natural abundances. The natural abundance of ^{202}Hg is 29.86% and ^{201}Hg is 13.18%(Webelements). However, the ratio appears to be opposite in the data collected (Figure 8). Either the isotope data was collected under the wrong mass value or there was an isobaric interference for the lighter isotope stemming from the sample membranes (matrix effect) that was contributing to its signal. The later may be the case because Hg^0 calibration injections yielded the expected ratio (Figure 9). While data for ^{202}Hg appears unaffected, this phenomenon still deserves attention and could be considered for future work. Also, occasionally during DMA analysis of the membrane there was a popping sound indicating small explosions as the membrane combusted, which could be a safety issue. Thus, we tried yet another approach for measuring Hg on the CEMs: leaching.

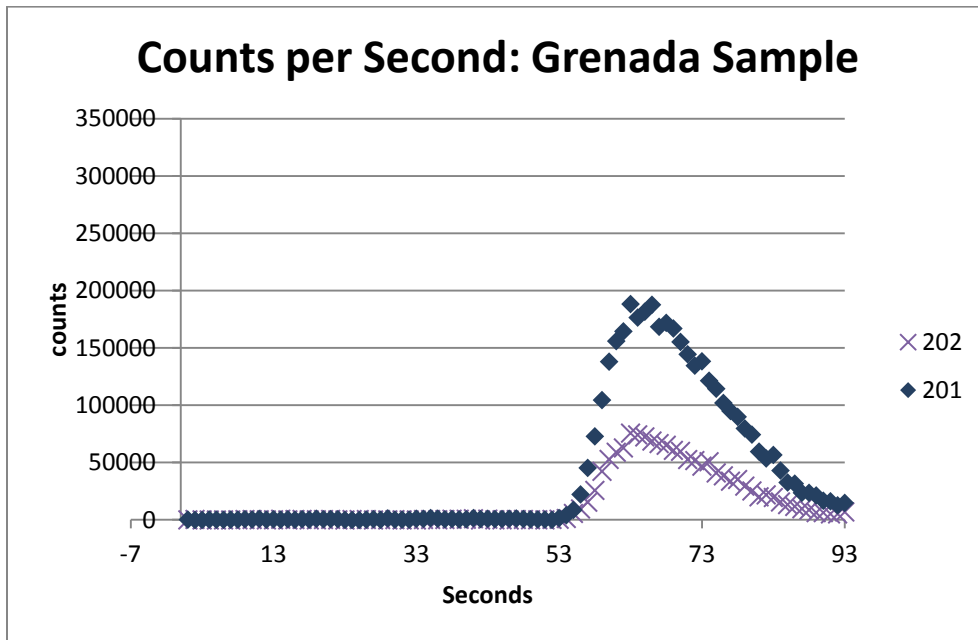


Figure 8: Counts/Second of Grenada Sample shows that there is more ²⁰¹Hg than ²⁰²Hg.

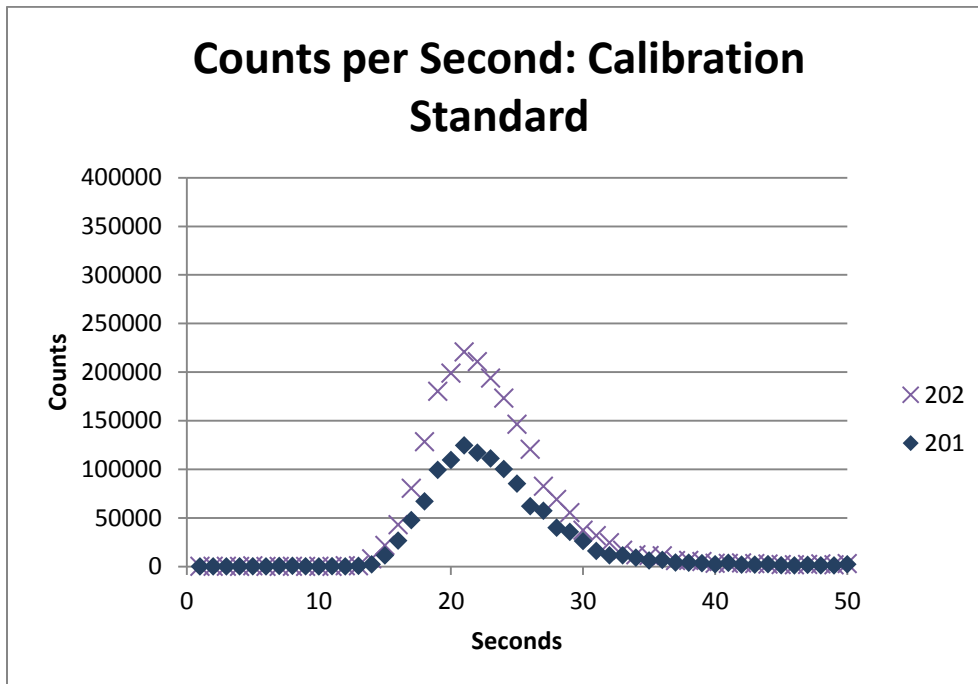


Figure 9: Counts/Second of the calibration standard shows that there is more ²⁰²Hg than ²⁰¹Hg, which agrees with the natural occurrence of mercury isotopes.

3.4 Analysis of Dry Deposition of Mercury by Leaching of Membranes

Field-deployed membranes were leached with a solution of 0.1M BrCl which serves as an oxidizing agent and stabilizes Hg(II) in solution. The results from ICP-MS analysis of the leachates showed the same trend as that of analysis with the DMA: Sardis Lake > Enid Lake > Grenada Lake. However, the uncertainty with the data was sufficiently large, and the differences were not statistically different ($p > 0.05$). Developing ways to lower blank concentrations in the solutions may improve the method and should be considered in future work.

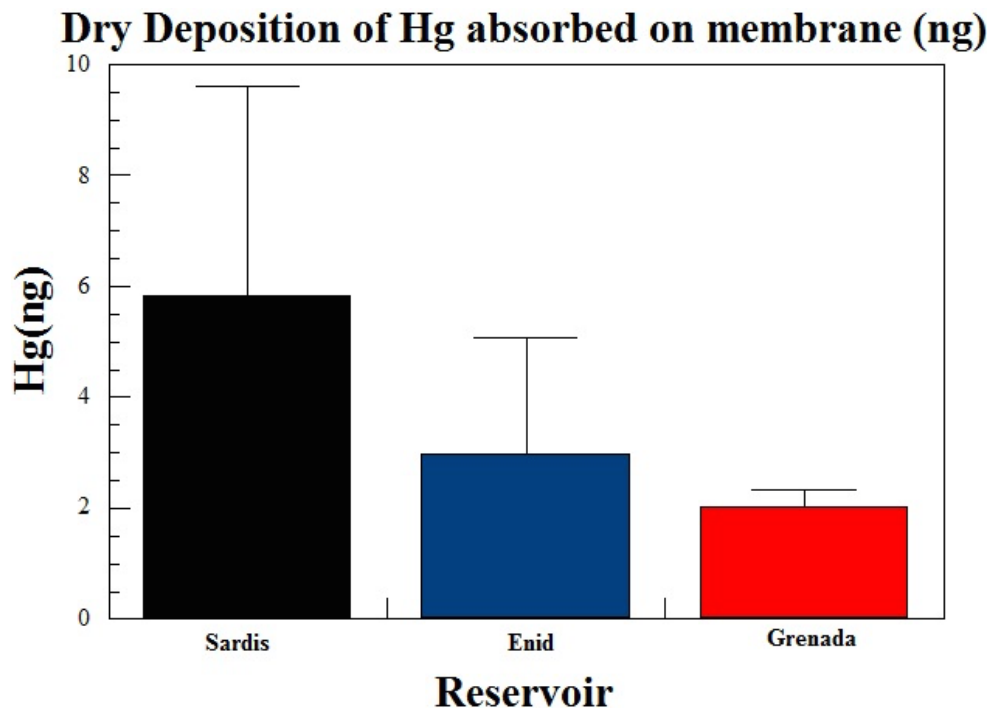


Figure 10: Dry deposition of Hg by leaching of membranes using ICPMS. The differences among the lakes for mercury concentration weren't statistically different. A t-test was run, showing that the p-value was 0.216.

3.5 Analysis of Dry Deposition of Mercury with Tekran 2700

Because our CVAFS was not working properly, we tried to measure Hg in the leachates using the Tekran 2700, which is a MeHg analyzer but uses a CVAFS cell (after pyrolysis of the MeHg). However, the field blanks had relatively high mercury levels compared to the air-exposed membranes (Table 5). This may have resulted from the conditions under which the membranes were deployed. During this time there were particularly high amounts of precipitation (rain, snow, etc.) and some of the bottles were turned such that some water may have come in contact with the membranes. The polyethersulfone cation exchange membranes are hydrophilic, and moisture may have affected the membrane's ability to trap or retain oxidized mercury on its surface. However, the blank membranes in this case were placed into fairly airtight vials, sealed in a Ziploc bag, and then placed into a polycarbonate bottle. The relatively high mercury content shown by the blanks may have resulted from the fact that the blanks were not washed clean of Hg.

Table 5: Determination of Dry Deposition of Mercury using Tekran 2700

Sample name	Peak area	Calculated mercury (pg)
Blank Reagent	402	16.6
Sardis 3	304	14.3
Sardis 2	367	15.7
Sardis Blank	3850	95.2
Grenada Blank	6226	149.3
Grenada 1	308	14.4
Grenada 2	614	21.4
Grenada 3	441	17.4
Enid Blank	3869	95.6
Enid 1	308	14.4
Enid 2	614	21.4
Enid 3	441	17.4

4 CONCLUSION

The spread of mercury through the atmosphere, its deposition to aquatic systems, and subsequent conversion to methylmercury is the subject of intensive study. In Mississippi there are a number of mercury-related fish consumption advisories, including for Grenada and Enid Lakes. Because dry deposition of mercury is a major contributor of mercury to ecosystems, finding easy and reliable methods to measure it is of great interest. This experiment focused on developing and testing of such a method using a cation exchange resin. Several methods including AAS, AFS, and mass spectrometry were tried and the merits of each are discussed herein. Regardless of the approach, a trend emerged for airborne Hg species with Sardis Lake > Enid Lake > Grenada Lake. However, the reason for the higher levels of mercury in fish in Grenada Lake compared to the other two lakes remains unexplained. Future work should focus on refining the methods described herein to improve blank and uncertainty levels.

REFERENCES

- Brown Jr., Garry.(2013). Studies of Mercury in Water, Sediment, and Fish in Mississippi: Concentrations, Speciation, Cycling, and Isotopic Composition.PhD dissertation, University of Mississippi. Oxford: UMI. (Publication No. 3595505)
- Clarkson, Thomas W., and Laszlo Magos. "The Toxicology Of Mercury And Its Chemical Compounds." *Critical Reviews In Toxicology* 36.8 (2006): 609-662. *Environment Complete*. Web. 5 Jan.2015.
- Costley, Claire T, "Determination Of Mercury In Environmental And Biological Samples Using Pyrolysis Atomic Absorption Spectrometry With Gold Amalgamation." *Analytica Chimica Acta* 405.(2000): 179-183. *ScienceDirect*. Web. 5 Jan. 2015.
- Fitzgerald, William F., and Thomas W. Clarkson. "Mercury and Monomethylmercury: Present and Future Concerns." *Environmental Health Perspectives* 1991: 159. *JSTOR Journals*. Web. 2 Jan. 2015.
- Fox, B.S., K.J. Mason, and F.C. Mcelroy. "Determination of Total Mercury in Crude Oil by Combustion Cold Vapor Atomic Absorption Spectrometry (CVAAS)." *Journal of ASTM International* 2 (2005): 196-206. Print.
- Huang, Jiaoyan, Matthieu B. Miller, Peter Weiss-Penzias, and Mae Sexauer Gustin. "Comparison of Gaseous Oxidized Hg Measured by KCl-Coated Denuders, and

- Nylon and Cation Exchange Membranes." *Environmental Science & Technology* 47.13 (2013): 7307-316. Print.
- Lindberg, S., R. Bullock, R. Ebinghaus, D. Engstrom, X. Feng, W. Fitzgerald, N. Pirrone, E. Prestbo, and C. Seigneur. "A Synthesis Of Progress And Uncertainties In Attributing The Sources Of Mercury In Deposition." *AMBIO: A Journal of the Human Environment* 36 (2007): 19-32. Print.
- Lyman, Seth N., Mae S. Gustin, and Eric M. Prestbo. "A Passive Sampler for Ambient Gaseous Oxidized Mercury Concentrations." *Atmospheric Environment* 44 (2010): 246-52. Print.
- Mason, Robert P., Michael L. Abbott, R. A. Bodaly, O. Russell Bullock, Jr. Jr., Charles T. Driscoll, David Evers, Steven E. Lindberg, Michael Murray, and Edward B. Swain. "Monitoring the Response to Changing Mercury Deposition." *Environmental Science & Technology* (2005): 14A-22A. Print.
- "Mercury and the Environment." *Government of Canada, Environment Canada*. 9 July 2013. Web. 30 Mar. 2015. <<https://www.ec.gc.ca/mercure-mercury/default.asp?lang=En&n=67E16201-1>>.
- "Mercury: Isotope Data." *Webelements*. Web. 24 Apr. 2015. <<http://www.webelements.com/mercury/isotopes.html>>.
- Nowak, Bartosz, Katarzyna Korszun-Kłak, and Urzula Zielonka. "Long-Term Measurements of Atmospheric Mercury Species (TGM, TPM) and Hg Deposition in the Silesian Region, Poland – Concept of the Mercury Deposition Coefficient." *Archives of Environmental Protection* 40.3 (2014): 43-60. Print.

Sakata, M., Marumoto, K. (2004). Dry deposition fluxes and deposition velocities of trace metals in the Tokyo Metropolitan area measured with a water surface sampler. *Environmental Science & Technology*, 38. Pp. 2190–2197.

Zhang, Xiaotong, Zia Siddiqi, Xinjie Song, Khakhathi L. Mandiwana, Muhammad Yousaf, and Julia Lu. "Atmospheric Dry and Wet Deposition of Mercury in Toronto." *Atmospheric Environment* 50 (2011): 60-65. Print.

Zhang, L., P. Blanchard, D. Johnson, A. Dastoor, A. Ryzhkov, C.j. Lin, K. Vijayaraghavan, D. Gay, T.m. Holsen, J. Huang, J.a. Graydon, V.I. St. Louis, M.s. Castro, E.k. Miller, F. Marsik, J. Lu, L. Poissant, M. Pilote, and K.m. Zhang. "Assessment of Modeled Mercury Dry Deposition over the Great Lakes Region." *Environmental Pollution* (2012): 272-83. Print.

APPENDIX (SUPPLEMENTAL MATERIAL)

Experiment designed to lowering the background of membranes prior to deployment

Experiments were done to see if the mercury content in the cation exchange membrane could be lowered, thus establishing lower blank concentrations for the experiment.

Preheating the membrane

An experiment was done to see if heating the membranes could drive off some of the mercury on the membrane. The membranes were heated for about an hour at 100 degrees Celsius and were then analyzed and compared to the results from blanks that were not preheated. The results from this experiment were inconsistent. Some of the membranes that were heated had less mercury than the blanks that were not heated and some had more mercury. Preheating the membrane was abandoned.

Washing CEM with HCl

Another experiment was done to see if washing the cation exchange membrane with hydrochloric acid could get rid of some of the mercury on the membrane. For the experiment, a blank membrane that had not been washed with HCl was analyzed, and a second membrane washed with HCl, dried in a 50 mL glass tube, and was also analyzed. The results showed that membrane washed with HCl had higher mercury content, possibly reflecting Hg in the HCl wash solution.

Altering Settings on DMA

The membrane was run through the DMA at low temperatures to drive off any retained Hg in an effort to lower blank levels. The decomposition time was changed to 0 seconds and the drying time was decreased to 60 seconds and the drying temperature was lowered to 50°C. The results showed that this approach was effective to lower the Hg on the membrane however if the membrane was put too close to the hot catalyst it became charred. The membranes were also tested with argon gas running through the DMA instead of oxygen. In the experiment with argon, all the previous conditions from the oxygen-run DMA experiment (decomposition time, dry time, etc) were kept. The membrane was tested with argon gas running through the DMA instead of oxygen because it was believed that argon would prevent the combustion with the membrane. The membrane also had lower amounts of mercury each time it ran through the DMA when using argon. Occasionally the membranes analyzed with argon gas also showed some evidence of combustion suggesting that some oxygen was getting into the system.

UV-light Exposure

A UV-lamp was used to determine if gaseous elemental could be driven off by UV-light exposure. The experiment also tested whether the cation exchange membrane could also adsorb mercury vapor. For the experiment, the cation exchange membrane was suspended in a tube containing a drop of liquid mercury for about 90 minutes. After exposure to liquid mercury, the membrane was exposed to UV-light for an hour. In the experiment, three membranes were tested. Membrane 1 served as a blank, and membrane 2 was exposed to liquid mercury vapor. Membrane two was then split into

two sections with one piece being analyzed right after being exposed to mercury vapor and another being exposed to UV-light for an hour. The results concluded that the cation exchange membrane was capable of absorbing mercury. Although it was thought that exposure to UV-light would drive off gaseous elemental mercury, the results show that the mercury content on the membrane actually increased after exposure to UV-light.

Table 5: Cation Exchange Membrane-exposure to UV-light

	Hg(ng)
Blank membrane	0.82
Hg exposed membrane	52.4
UV light exposed membrane	214

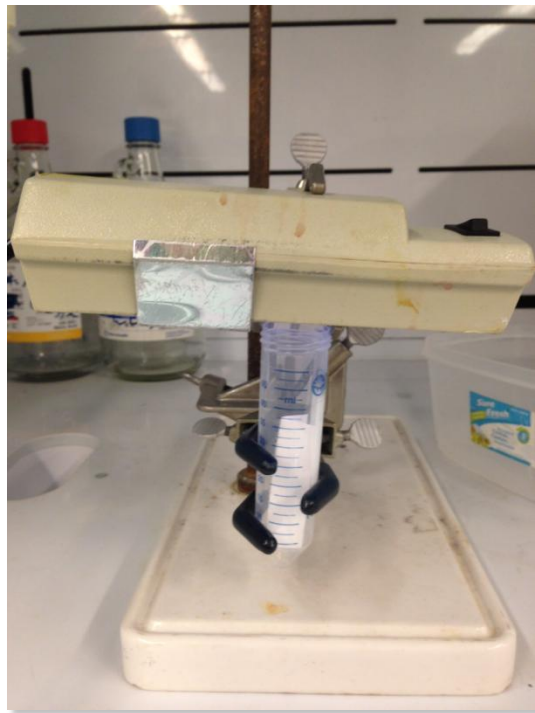


Figure 11: Apparatus for UV light exposure experiment

The experiment with UV-light was done again to confirm the results of the first UV-light experiment. During the second time that the experiment was performed, more membranes were used to get more accurate and reliable data. In the second experiment with UV-light, one membrane was used as a blank, and three were exposed to gaseous elemental mercury vapor. Like the previous experiment, the membranes were exposed to mercury vapor for about an hour. After an hour, the membranes are collected and cut in half lengthwise. One group was analyzed right away while the second was then exposed to UV-light. In the second experiment, the placement of the UV-lamp differed. Unlike the first experiment where the lamp was placed above the folded membrane, the second experiment had the UV-lamp parallel to the membrane and each side of the membrane was exposed to UV light for an hour. The results from the second experiment agreed with the results of the first experiment: exposure to UV-light actually increased the amount of mercury on the membranes.

Table 6: Cation Exchange Membrane-Exposure to UV-light

Sample	Concentration (ng/g)
Blank (no UV exposure)	178
Membrane 1(no UV exposure)	196
Membrane 2 (no UV exposure)	449
Membrane 3 (no UV exposure)	225
Blank (UV exposure)	223
Membrane 1 (UV exposure)	260
Membrane 2 (UV exposure)	402
Membrane 3 (UV exposure)	570
Blank (UV exposure)	223

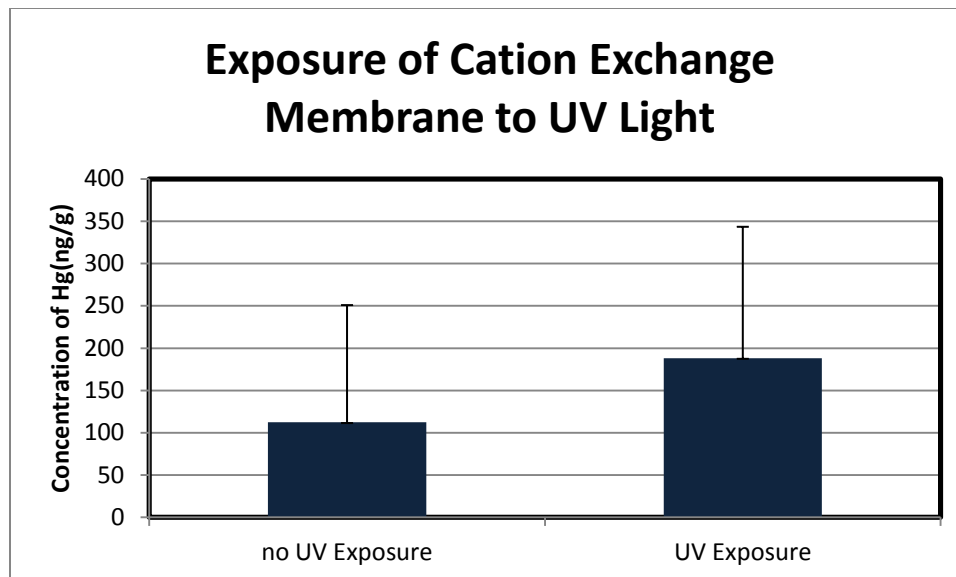


Figure 12: Exposure of CEM to UV Light