STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Mercury Speciation via Direct Mercury Analyzer

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

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ABSTRACT

Mercury (Hg) is an environmental pollutant that behaves differently in the environment depending on the chemical species present. Therefore, chemical speciation of mercury has emerged as an important factor controlling mercury behavior and risk in environmental and industrial systems. Methylmercury (MeHg) is one notable species of mercury that is a harmful bio-accumulative toxin for which practical protocols for monitoring and risk assessment are necessary. The presence and quantity of methylmercury and other organomercury species are associated with increased overall mercury risk. A direct mercury analyzer (DMA-80) was used to perform total mercury analysis and chemical speciation of mercury in water samples. The Direct Mercury Analyzer (DMA-80) operates on the principles of thermal decomposition, mercury amalgamation, and atomic absorption detection. The testing focused on development and deployment scenarios to support DOE-EM decision-making and operations in both environmental systems (i.e., with mercury levels in the ng/L range) and in High Level Radioactive Waste (i.e., with mercury levels in the mg/L range). The DMA-80 was a step in measuring total mercury and determining mercury speciation in this project. Experiments were conducted that would quantify total mercury and assess the viability of chemical reduction and amalgamation for separating mercury species in concentration levels typical in both high level "tank" waste and site-specific environmental conditions. Results indicate that the total mercury for the high level "tank" waste was accurate for both inHg and stabilized MeHg. The proof of principle for total mercury in environmental concentration levels and mercury speciation for both was successful. Further testing will be conducted with adjustments made to the packing in the micro columns. Other eluents will also be tested to validate their effectiveness at mercury speciation and total mercury analysis for site specific environmental concentration levels.

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1. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2018, DOE Fellow intern Katherine De La Rosa spent 10 weeks doing a summer internship at Savannah River Site's Aiken County Technology Laboratory under the supervision and guidance of Dr. Brian Looney. The interns' project was initiated on June 4, 2018 and continued through August 8, 2018 with the objective of developing a protocol for utilizing the Direct Mercury Analyzer (DMA-80) for mercury speciation of water samples and monitoring methylmercury (MeHg).

2. INTRODUCTION

Mercury has no known biological role but is present in every living thing and widespread in the environment. It exists in different forms including elemental mercury, inorganic mercury, and methylmercury. Inorganic mercury compounds can occur naturally in the environment. Methylmercury is a highly toxic organic compound and can be very dangerous to humans. At higher doses, it can accumulate in the flesh of the fish and become ingested when these fish are eaten by people, making them ill, (Royal Society of Chemistry, 2018). As mercury enters an aqueous system, it is subject to methylation or demethylation (Figure 1). Methylmercury selectively partitions into biota and biomagnifies through the food chain. Nearly all methylmercury exposures in the U.S. occur through eating fish and shellfish that contain higher levels of methylmercury (United States Environmental Protection Agency, 2018). It is very commonly found in the environment and in humans in trace amounts which will not cause any serious health issues (The Centers for Disease Control and Prevention, 2009).

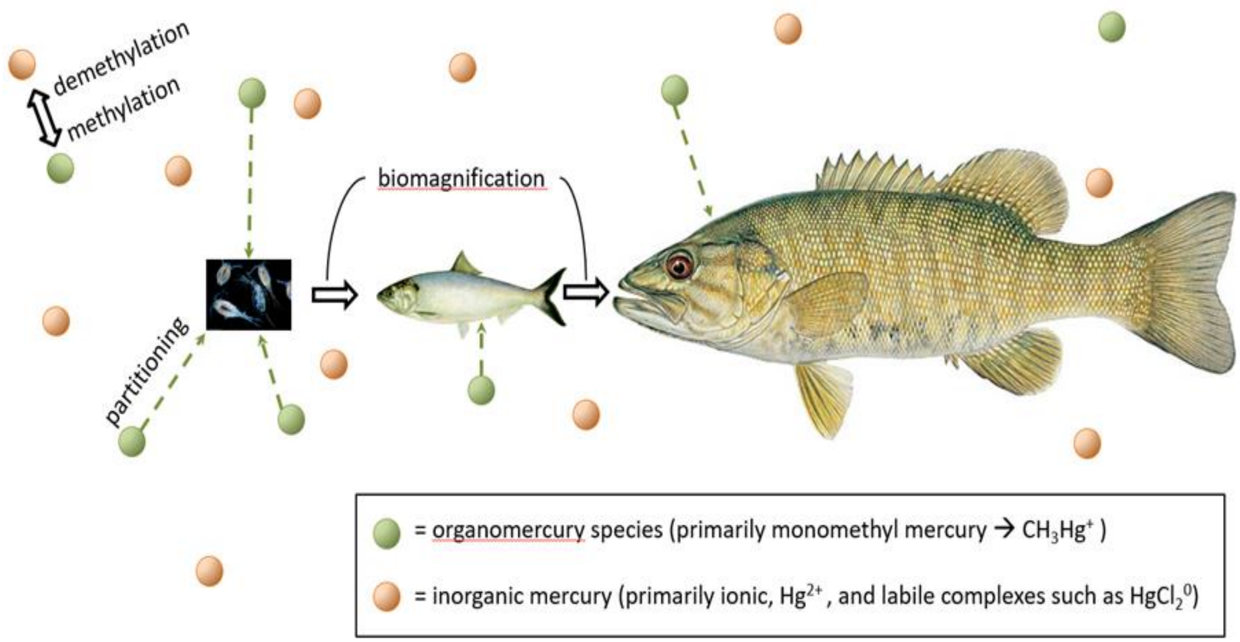

Figure 1: Simplified depiction of the role of mercury speciation in aquatic systems.

Monitoring and understanding mercury speciation are key to effective environmental management. It is particularly important to be able to separate and measure bioaccumulative-toxic species of mercury such as methylmercury. This project involves the development of a protocol for utilizing the Direct Mercury Analyzer (DMA-80) for mercury speciation of water samples and monitoring methylmercury (meHg). The U.S. Department of Energy's (DOE's) Savannah River National Laboratory (SRNL) has developed an alternative analytical paradigm for mercury speciation analysis that is based on a solid phase chemical reduction and amalgamation that traps inorganic and elemental mercury but does not react with organomercury. The method can be applied using a simple-modular microcolumn solid phase extraction (SPE) and solid phase reaction (SPR) protocol. Following the reaction and extraction steps, all sample fractions may be analyzed for total mercury using a simple direct mercury analyzer (an automated system that performs pyrolysis-amalgamation-thermal desorption-spectroscopy).

A Direct Mercury Analyzer (DMA-80) is an automated system that analyzes samples and quantifies the amount of total mercury in each one. There is no sample preparation required which simplifies the analysis. The DMA-80 has a process that allows us to measure the mercury accurately, which includes several steps. The sample is put into a pyrolysis furnace and heated to high temperatures to release the mercury into a flowing carrier gas (air). The gas passes through a catalyst bed which converts all forms of mercury into elemental mercury. The mercury is then concentrated on an amalgamator. After the pyrolysis is complete, the amalgamator is flash heated to release the mercury which is then measured quantitatively in the spectrophotometer (The Milestone DMA-80: Innovation Delivered).

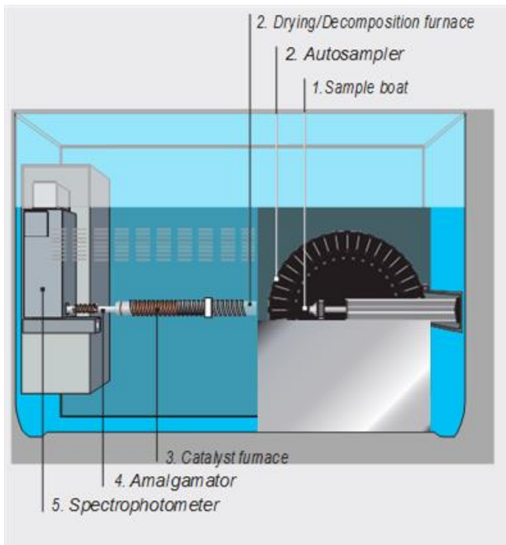

Figure 2: Milestone DMA-80 "How It Works" diagram

Previous SRNL research examined mercury speciation by reactive diffusive gradient in thin film (rDGT) samplers that incorporated the reduction and amalgamation reactions. Chemical speciation of mercury has emerged as the most important factor controlling mercury behavior and risk in environmental and industrial systems. The presence and quantity of methylmercury and other organomercury species are associated with increased overall mercury risk. The aim of this project is to advance the understanding of the performance of the direct mercury analyzer (DMA-80) under a range of DOE relevant water chemistry conditions to quantify total mercury and analyze typical DOE high level liquid "tank" waste samples using nonradioactive simulants. Innovative sorbents will also be tested to extend the range of the direct mercury analyzer to environmental concentration levels while performing scoping tests to demonstrate proof of principle for the chemical reduction amalgamation modular micro columns for mercury speciation. This involves the examination of various micro column configurations, documentation of the speciation performance for typical DOE high level liquid "tank" waste samples using nonradioactive simulants, and performance of tests to examine possible extension of the speciation paradigm to environmental concentration levels. The goal is to develop and deploy practical methods for monitoring mercury speciation to support DOE EM decision-making and operations. The need applies to mercury in both environmental systems and in High Level Radioactive Waste.

3. RESEARCH DESCRIPTION

DMA- 80

The Direct Mercury Analyzer, also known as, the DMA-80 operates on the principles of thermal decomposition, mercury amalgamation, and atomic absorption detection. There is no sample preparation required. The sample simply needs to be weighed and loaded onto the carousel. Each sample takes about 5-8 minutes to analyze. The DMA-80 is good for many reasons. Up to 40 samples can be loaded onto the carousel and left for analysis. There is no need to wait as the auto-sampler allows each sample to be analyzed in sequential order until all have been processed. The DMA-80 can analyze solids, liquids, and gases, achieves a detection limit as low as 0.001 ng of mercury and can measure up to 30.000 ng of mercury.

Sample boats are loaded onto the instrument auto-sampler, dried and then thermally decomposed in an oxygen-rich stream. Mercury is then released and flows through the catalyst, while every other substance that interferes is eliminated. The mercury is trapped by the gold amalgamation, and everything else get flushed out. The amalgamation furnace is heated and releases the mercury which is then carried into measuring cells (Cell 0, 1, 2) and recorded quantitatively. This DMA-80 was used in this project for speciation in water samples and quantifying total mercury.

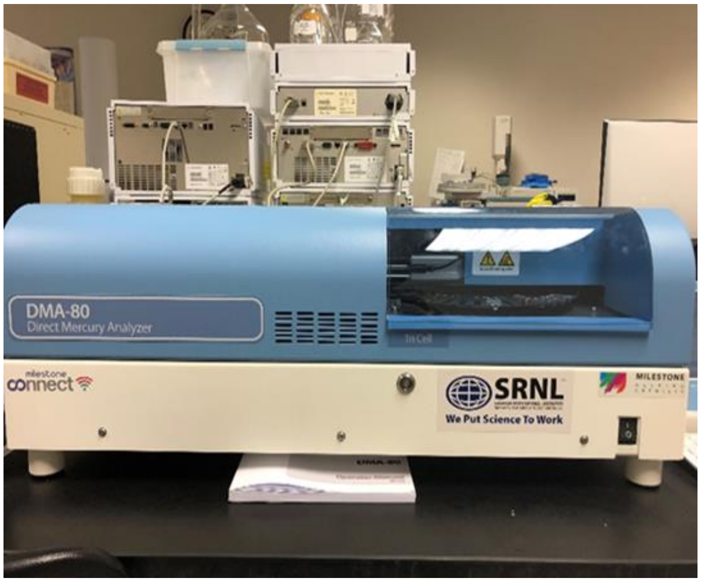

Figure 3: Direct Mercury Analyzer

Preparation of Standards and Eluents

For calibration and total mercury analysis, various inorganic mercury (inHg) and methyl mercury (meHg) stock solutions were prepared with concentrations (as Hg) ranging from 1 ng/mL up to 10000 ng/mL from certified standards (High Purity Standards ***, and Brooks Rand ***). For the speciation studies standards for InHg and MeHg of 10 ng/mL (as Hg), were prepared using

100 ng/mL stock solutions. An eluent solution (for rinsing microcolumns) was prepared in 200 mL batches by mixing 5.8 g of NaCl and 200 mL of deionized (DI) water.

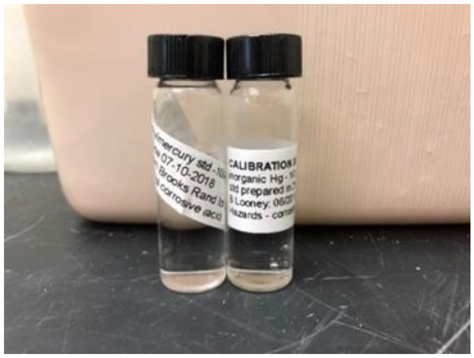

Figure 4: InHg and MeHg standards (100 ng/mL)

Figure 5: NaCl standard (0.5 M)

Total Mercury for High Level Liquid “Tank” Waste

To test total mercury for high level liquid “tank” waste sample boats were loaded by pipette directly from the 100 ng/mL mercury stock solutions. Quartz boats were loaded for all liquid samples. Each boat was loaded with 100 to 200 µL of InHg or MeHg stock solution using a calibrated pipette. Triplicates of all samples were made and placed for analysis on the DMA. A number of runs were completed – some using liquid samples and some with an added stabilizer to minimize sample loss while waiting on the autosampler carousel. The anticipated result was 100 ng/L (i.e., 10 to 20 ng in the sample). For the MeHg, a stabilizer consisting of 0.02 g of Si-Thiol had to be added to avoid evaporation of the MeHg.

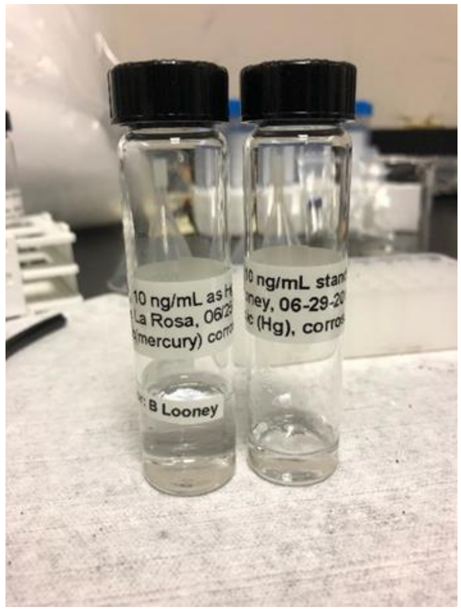

Figure 6: InHg and MeHg standards (10 ng/mL)

Total Mercury for Environmental Concentration Levels, Micro Columns

To test for total mercury at environmental concentration levels, two sets of experiments were performed, one via micro columns and the other via sorption and filtration. Volumes of 50 ng/L of InHg and 50 ng/L of MeHg were diluted in 200 mL of DI water, respectively, for each set of micro columns prepared. Micro columns were prepared in triplicate sets, one set with carbon, another with Si-Thiol, and a third with mixed constituents. Each micro column was capped with a ceramic end at the bottom and quartz wool at the top. In Figure 8 you can see a line of columns filled with copper, Si-Thiol, and carbon respectively. These columns were placed on a vacuum box with a funnel and then flushed with a sample of 50 ng/L of InHg or MeHg in 200 mL of DI water. In Figure 7, there is a carbon micro column attached to the vacuum box in the process of being flushed with the sample made for environmental concentration levels in a funnel.

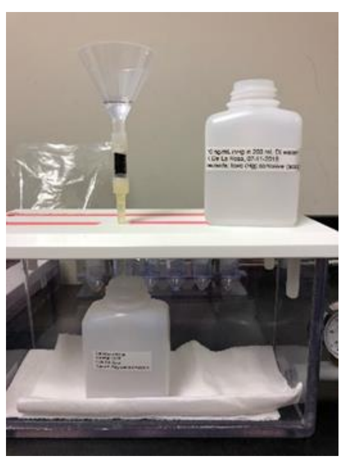

Figure 7: Vacuum Pump with Carbon Micro Column Set

Figure 8: Micro Columns Samples of Carbon, Si-Thiol, and Copper

The Mixed columns contained an even mixture of Carbon, Si-Thiol, and Copper, which we prepared in weigh boats, as seen in Figure 9, and then mixed into the columns using a spatula. These were placed on a vacuum box with a funnel and then flushed with 50 ng/L of Hg in 200 mL DI water. They were then placed on the DMA to be analyzed (Figure 10).

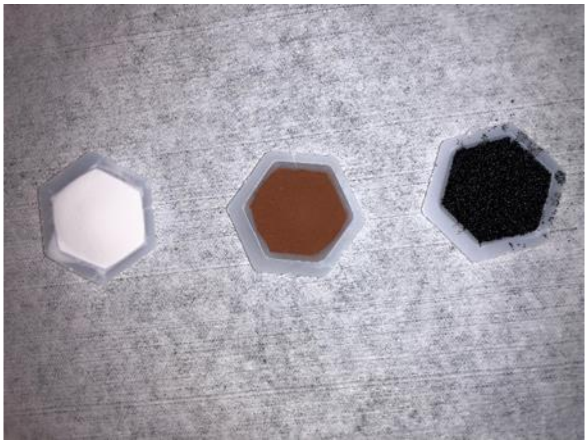

Figure 9: Weigh boats with carbon, Si-Thiol, and copper used for mixed micro columns

Figure 10: Micro columns on DMA auto sampler carousel

Total Mercury for Environmental Concentration Levels, (Filtration)

For filtration, a sample of 50 ng/L of Hg was created in 200 mL DI water with 0.5 g Si-Thiol. The samples were left for two days to allow the mercury to sorb onto the Si-Thiol. A filter container was used on a vacuum pump and the filter was then folded and placed on a nickel boat and analyzed on the DMA.

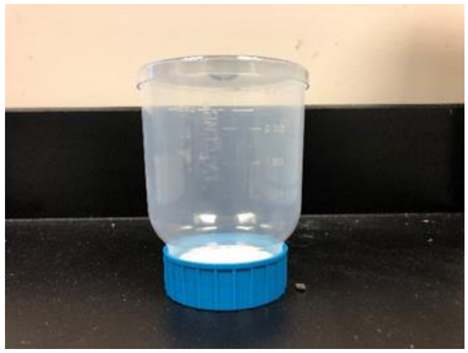

Figure 11: Filter with container attached

Mercury Speciation via Micro Columns for High Concentration

For mercury speciation in high concentration micro columns were used with different levels of copper. There were 4 sets of triplicates with 0.1 g Cu, 0.3 g Cu, 0.5 g Cu, and a blank with no copper for both InHg and MeHg. Each micro column was capped with a ceramic end at the bottom and then quartz wool at the top. At the bottom of the column, 0.1 g of 140-270 glass beads were added to help with the flow of InHg or MeHg in the micro column. These were placed on a vacuum box with a funnel on top and flushed with 1 mL DI water, 1 mL 10 ng/L of InHg or 10 ng/L MeHg, and 12 mL of NaCl. They were then analyzed on the DMA. The expectation was to see the speciation between InHg and MeHg showing 10 ng/L for InHg and 0 ng/L for MeHg.

Figure 12: Blank, 0.1 g, 0.3 g, and 0.5 g copper columns

Mercury Speciation via Micro Columns for Environmental Concentration Levels

For mercury speciation at environmental concentration levels, triplicates were made of micro columns filled with nothing but 0.1 g of 140-270 glass beads, and another set with 140-270 glass beads and 0.5 g of Cu. A sample consisting of 50 ng/L of Hg in 200 mL DI water was prepared and then flushed through the micro columns on the vacuum box with a funnel. They were then analyzed on the DMA. The experimental result expected is to observe the speciation between InHg and MeHg, with 10 ng/L for InHg and 0 ng/L for MeHg. This will be proof that this mercury speciation method was successful.

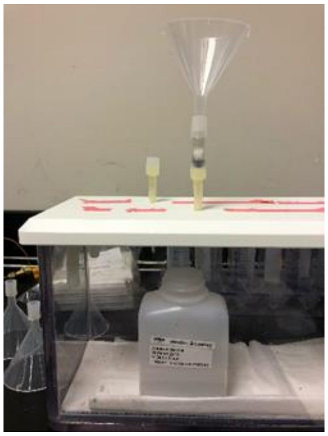

Figure 13: Copper column (0.5 g) on vacuum box

4. RESULTS AND ANALYSIS

Reagents Tested for Experiment

A series of reagents were tested for the experiment, including a variation of different silica sands, Si-Thiol, copper, and glass beads. This was tested to measure the blank concentrations in each set of reagents (in units of ng/g). As seen in Figure 14, glass beads measured the smallest amount of mercury. This was used to pack the bottom of the micro columns. The Si-Thiol and copper were also used in various experiments performed for this project. Overall, we notice that they all have a low concentration of mercury which could affect the use of it in environmental concentration levels.

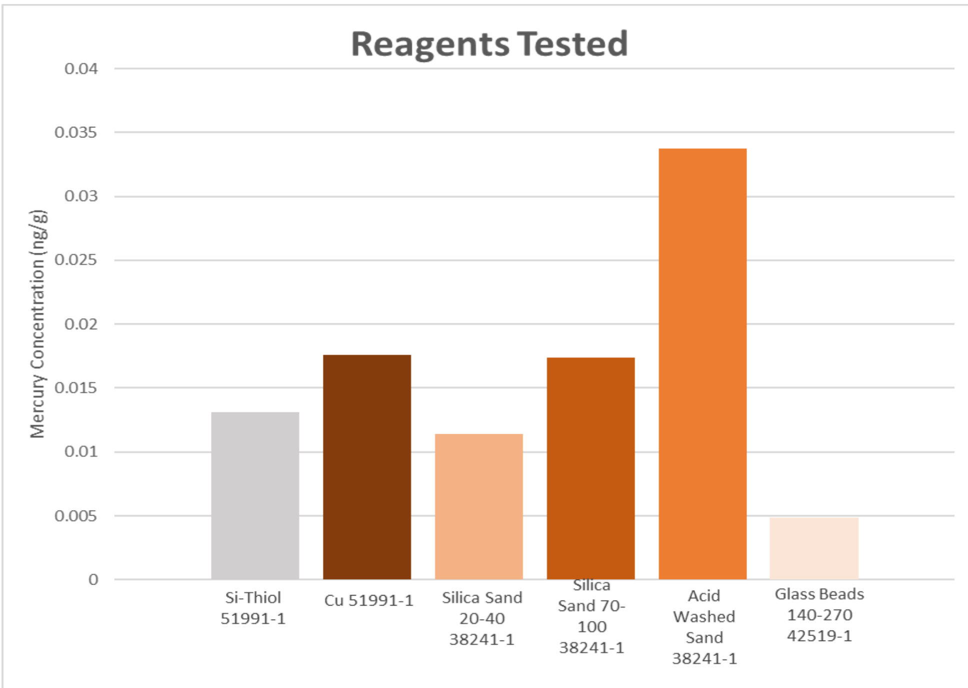

Figure 14: Reagents tested

Total Mercury: High Level Liquid "Tank" Waste Samples

Tests for total mercury at high concentrations were successfully validated (Figure 15). The InHg retained a mercury fraction of almost 1, while MeHg only retained good mercury fraction results due to the Si-Thiol that was added to stabilize it. As seen in Figure 16, without the Si-Thiol, the MeHg, overtime, would decrease in the amount of mercury retained. When Si-Thiol was added, the MeHg was retained even after left standing for 7 hours on the carousel.

Figure 15: Mercury standards for validation of high concentration Hg samples

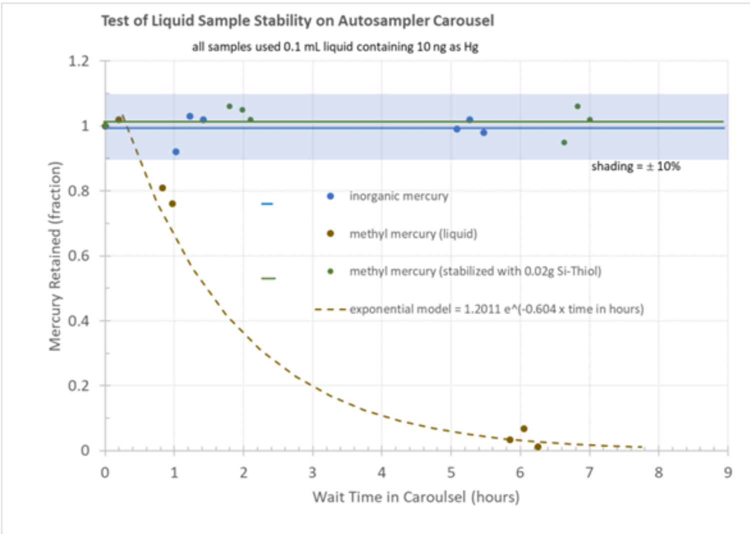

Figure 16: Test of liquid sample stability on auto sampler carousel

Total Mercury: Environmental Concentration Levels

This study was successful in "Proof of Principle" for calculating total mercury at environmental concentration levels. Figure 17 shows that the first method of using micro columns was successful in retaining the 10ng/L of MeHg with the mixed columns (105%) and Si-Thiol (110%), while carbon (55%) was not as successful. InHg had 90%-95% sorption with the mixed columns. Mixed columns (90%-95%) had the best results compared to the carbon (50% retained) or Si-Thiol (75%) micro columns.

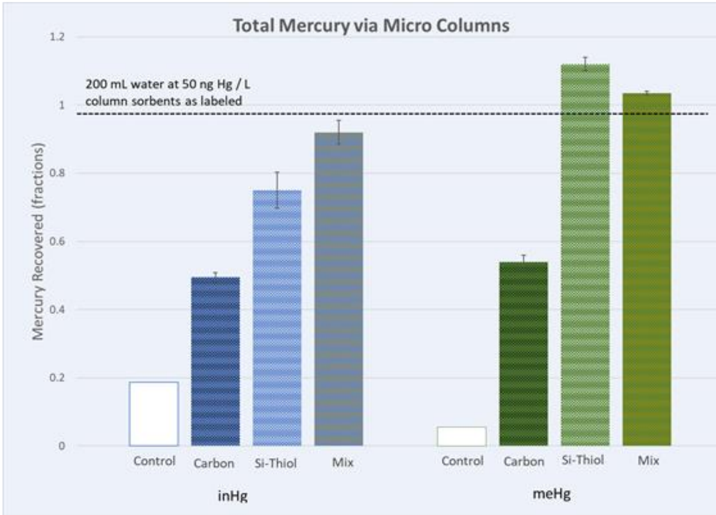

Figure 17: Total mercury via micro columns for environmental concentration levels

Figure 18 shows how the second method of sorption and filtration was also successful in "Proof of Principle." InHg had 90% mercury retention, while MeHg had 100% mercury retained. Results from both methods indicate the study methodology is, but may need improvement with respect to the packing of the micro columns. Measurements derived from the mixed columns will assist in research of alternatives.

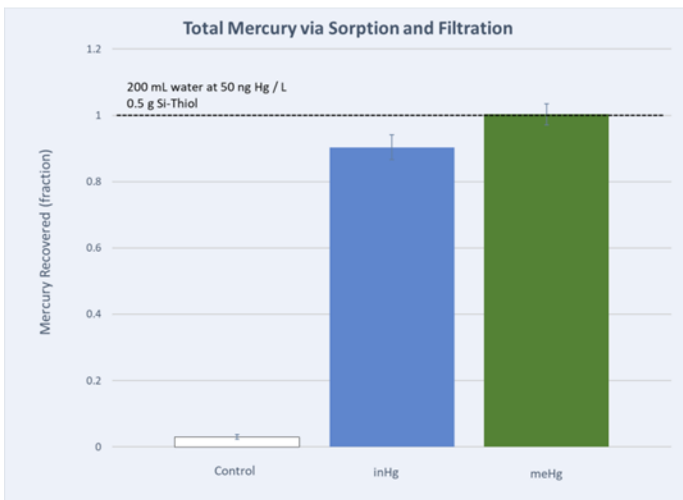

Figure 18: Total mercury via sorption and filtration for environmental concentration levels

Mercury Speciation: High Level Liquid "Tank" Waste Samples

The mercury speciation tests were able to conquer our "Proof of Principle" by showing a trend of retaining the InHg and extracting the MeHg. The point of the speciation tests was to separate the inorganic from the methyl mercury. The study with high concentration was successful in showing this trend but the method needs improvement. Figure 19 shows that for 0.5 g Cu, there is 85% InHg retention and almost 20% MeHg retained.

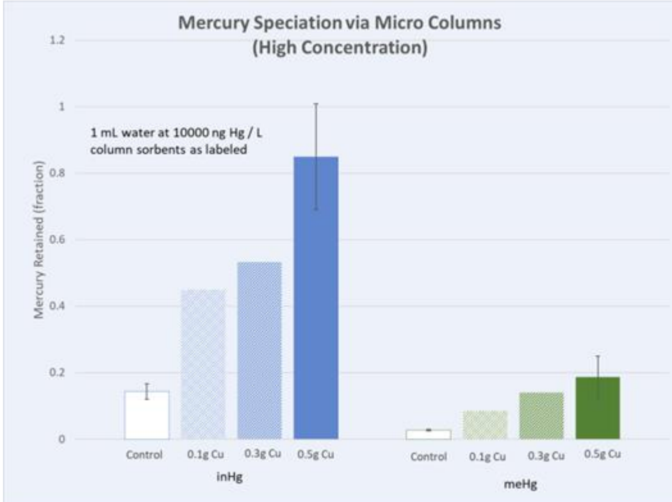

Figure 19: Mercury speciation via micro columns for high concentration

Mercury Speciation: Environmental Concentration Levels

For environmental concentration levels, mercury speciation was also successfully shown; however there were poorer results than that of the high concentration levels for InHg and better results for MeHg. Experiments resulted in 65% InHg retention and around 5% MeHg retained.

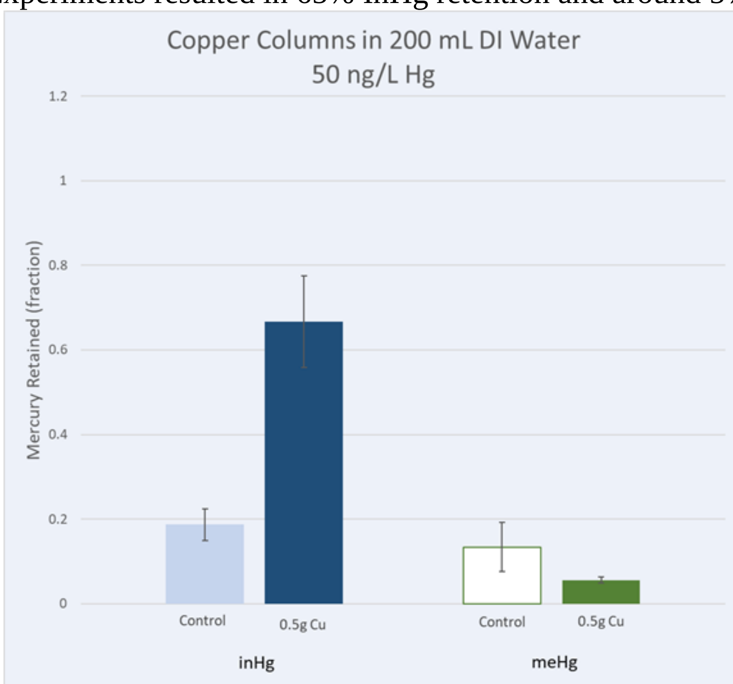

Figure 20: Mercury speciation via copper columns for environmental concentration levels

For both tests on mercury speciation, it was found that the trend is good enough for proof of principle but can be validated if the goal of retaining 100% of InHg and 0% of MeHg is attained. This can be achieved if the packing of the copper columns were perfected to help retain all the InHg. Testing different eluents, other than NaCl should also be pursued, in an attempt to remove all the MeHg.

5. CONCLUSION

The purpose of this study was to understand the performance of the direct mercury analyzer (DMA-80) to quantify total mercury under a range of water chemistry conditions that are relevant to DOE. Tests were also performed to demonstrate proof of principle for mercury speciation. This was accomplished by running different experiments that would validate the performance of the direct mercury analyzer to quantify total mercury. The proof of principle for mercury speciation was also successfully demonstrated.

The results for total mercury at high concentrations came out at almost perfect numbers for both InHg and stabilized MeHg. While total mercury had promising results, it was concluded that the total mercury at high concentrations was validated, while for environmental concentration levels needs more tests. With respect to mercury speciation, the packing materials for the micro columns need to be improved to help sorb all the InHg. A different eluent needs to be used to help flush out all of the MeHg that is sticking onto any copper or Si-Thiol.

6. FUTURE WORK

Future work on this study will include reviewing different packing methods for the micro columns to improve flow characteristics and the capture of InHg and desorption of MeHg. This includes different amounts of copper or experimenting with other reductants and amalgamators (e.g., gold).

This will also be used to improve the total mercury results for InHg. Experiments with other eluents will also be initiated for mercury speciation. NaCl has worked well to extract the MeHg, however a stronger reagent is needed to improve the extraction.

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