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Predictive Model of Ocean Sediment Binding

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ABSTRACT

This project explored the relationship between sediment size, sediment composition and the concentration of mercury. The samples were taken from Narragansett Bay in Rhode Island. Knowledge and understanding of the binding ability of heavy metals, specifically mercury, will help to improve remediation efforts in the future. Analysis of elemental composition was conducted using the Elementar Analyzer and much troubleshooting of the instrument was necessary. End result of the project was the ability to work successfully with an advisor, as well as the ability to troubleshoot, operate and maintain the instrument.

INTRODUCTION

Mercury pollution is prevalent in the Narragansett Bay due to the Brayton Power Point which is located on 306 acres of land at the head of the bay. Brayton Point is New England's largest fossil-fueled generating facility, burning about 40,000 tons of coal every three days, resulting in 741 pounds of mercury pollution in 2009 (Carini, 2011). The pollution gets into the atmosphere and accumulates in clouds as water condenses. When the clouds finally break, as either water or snow, the pollution is carried down as well. The pollution then gets onto the soil and into the ground water and eventually into the ocean where it settles to the bottom. The mercury gets into the fish and shellfish that people eat, and then gets incorporated into our bodies. Even the mercury that settles at the bottom eventually gets back into the water column when the bay gets dredged. Mercury pollution is still being put into the bay every day, and

possibly by understanding the mechanisms behind its binding abilities, future remediation can be improved.

This project was intended to explore and analyze the distribution of mercury in Narragansett Bay Rhode Island, in hopes for a better understanding of how the metal binds. We postulated that sediment size would have an effect on binding abilities, more specifically that smaller granule sizes would have more metals bound to them.

METHOD

Sediment samples were taken from fifteen different locations in Narragansett Bay. These samples were dried and sieved through two different sizes, 850 and 230. Mercury analysis was intended to be conducted with the Direct Mercury Analyzer DMA-80, and that process will be explained further on. In addition to looking at the mercury content of the samples, we also wanted to analyze the general composition of the sediment, more specifically the carbon, sulfur, hydrogen, nitrogen and oxygen by using the Elementar Analyzer (in the section to follow). Due to complications with the previous instruments we turned to Microwave Digestion for an analysis of the general heavy metals in the samples.

ELEMENTAR ANALYSIS

The Elementar Analysis instrument was planned to be our main form of analysis and experimentation, but we ran into the problem of it not working properly, which became a big issue that we needed to address and take care of. In the beginning I was not very knowledgeable

about the instrument or how it worked, but I learned quite quickly. The purpose of the instrument was to analyze the content of carbon, sulfur, hydrogen, nitrogen, and oxygen from samples, because these elements are the most common in nature. The basic premise of the instrument is that solid (or liquid) samples are decomposed at high temperatures to sublime (or vaporize) into the gas form. The gas sample is then cleaned and separated into the different components (carbon, nitrogen, hydrogen, sulfur and oxygen) and it is determined, with accuracy up to 0.1%, the percent composition of those components. Knowing the composition of the samples would be important later on during the analysis of the results because different concentrations of different elements could have an impact on the binding ability of the samples. For example, high sulfur concentrations in samples lead to higher binding abilities. Knowing this information would allow us to look at all the possible reasons behind the binding ability of the samples.

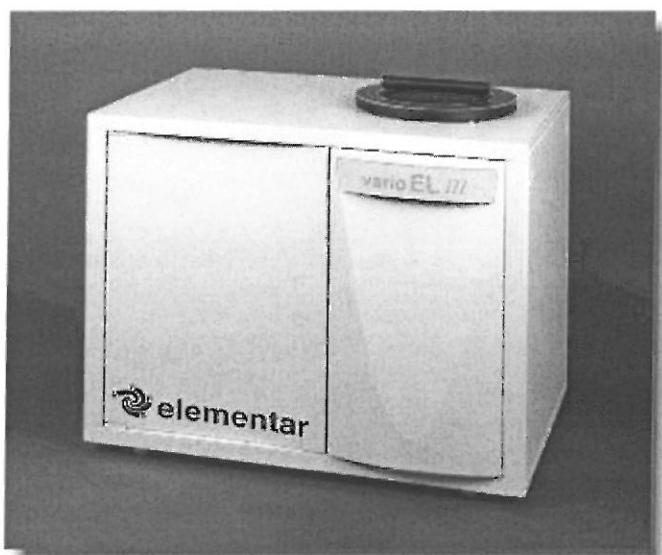


Figure 1. Image of the Elementar instrument in the Roger Williams University laboratory.

Due to the instrument not working properly many steps had to be taken before the instrument could actually be used. Because I was not familiar with the instrument in the beginning, the first few steps for me just involved asking my advisor several times a week if the instrument was fixed yet; he was first looking at it himself trying to troubleshoot, but when he couldn't find the problem he needed to call the manufacturer to get their help. A couple times he let me assist him in some basic troubleshooting techniques, like running a leak test. Where the instrument is connected to helium and oxygen tanks and it was necessary to make sure that the gases entered the instrument at the proper pressures, and that the gases were not leaking out of any of the connecting tubes inside of the instrument. But after the leak test offered no sources of error, my advisor decided it was time to call the company. After several weeks of questioning "is it ready yet" he finally told me that the company had a look and they did what they could, but still the instrument was not operating correctly, so this time we decided to have another look at it.

We conducted another leak test and discovered that the gases were not at the proper pressure inside of the instrument, and in fact there was barely any pressure at all. We checked and rechecked all of the connector pieces and all of the tubes and we finally caught a break. When we opened the compartment that contained the combustion and reduction tubes, we discovered that the combustion tube had a large crack from the bottom to about a third of a way up the foot long tube. It was obvious that the tube needed to be replaced, so we consulted the operation manual about how to do it, and we began searching the lab for the proper materials. After we gathered the materials, my advisor put me in charge of replacing the tube. I was a little

nervous but gladly accepted the challenge. I consulted the manual and carefully layered the new materials into the new tube. I filled the tube with layers of quartz wool, corundum balls, separating tubes, aluminum wool, and silver wool. When using the different wools I had to employ special care and caution because they needed to be flattened to fit properly, and small particulates would get in the air that could have been inhaled. Therefore, these preparations took place under the hood in the laboratory. When the tube was filled my advisor approved of my work and we inserted the tube back into the instrument. Although changing the combustion tube did not completely fix the instrument, it was still valuable experience that I gained.

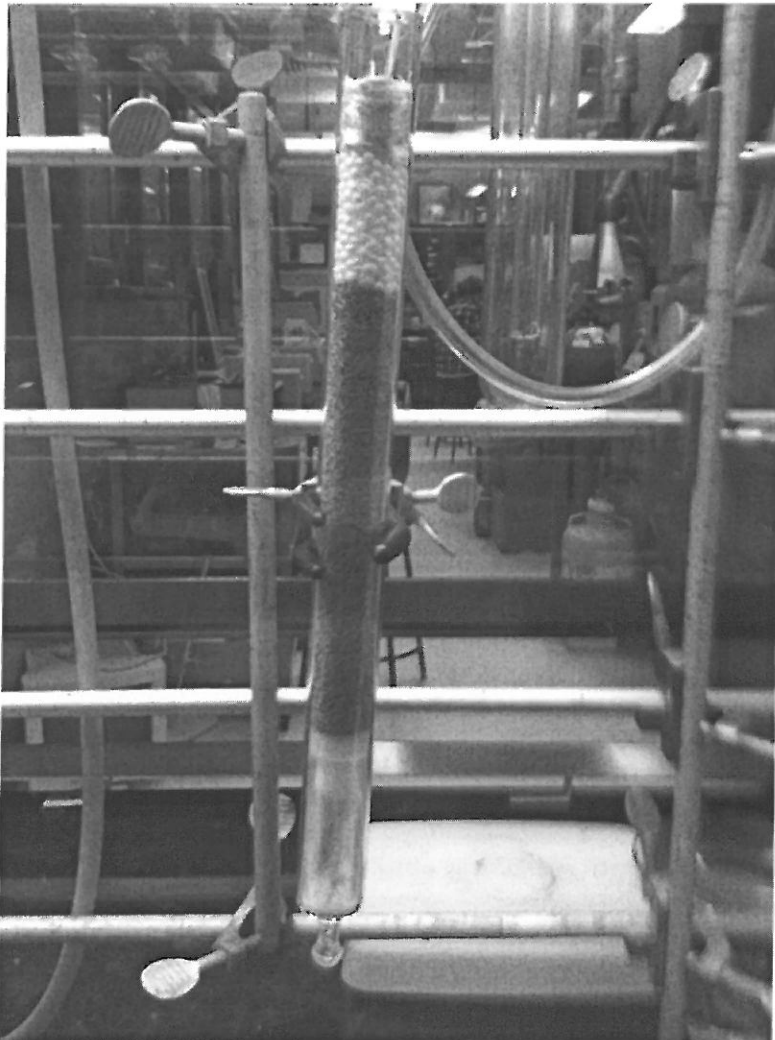


Figure 2. Image of the reduction tube of the Elementar Analyzer after being refilled with new materials.

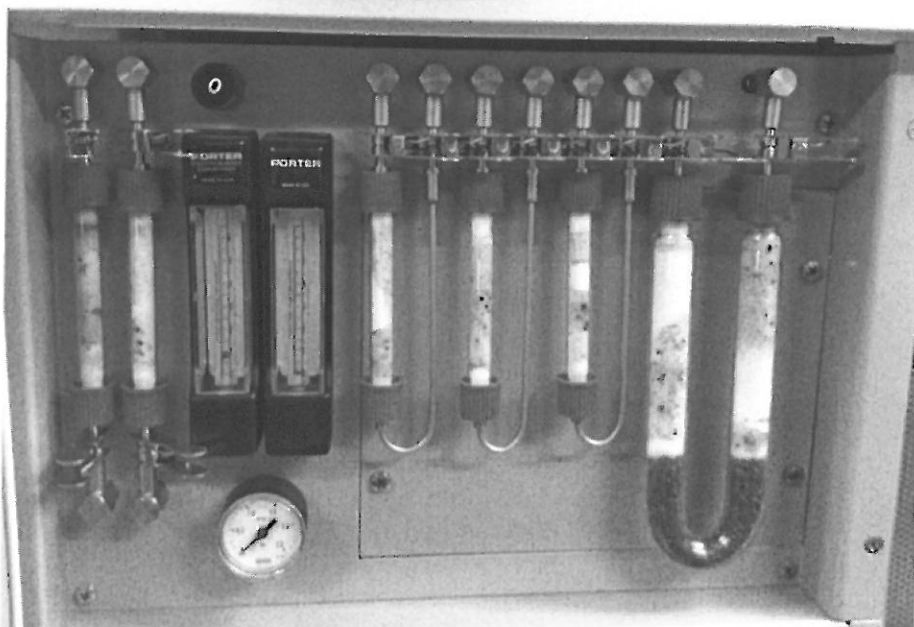


Figure 3. Image of the drying tubes of the Elementar before being replaced



Figure 4. Image of the drying tubes of the Elementar after being replaced

After replacing the combustion tube we thought it would be a good idea to also replace the reduction tube. This process was very similar to replacing the combustion tube; layers of quartz wool, separation tube, silver wool, and also copper filings (see Figure 2). We also thought it would be a good idea to replace the drying tubes. There are five small drying tubes, each element (carbon, hydrogen, sulfur, nitrogen, and oxygen), has their own corresponding tube to dry the samples before analysis. Each drying tube needed to be removed individually, the contents disposed into the solid waste, and wiped down with a Kimwipe. Into the drying tube went a small cotton filter, followed by Sicapent and another small cotton filter. Sicapant, or phosphorus pentoxide, is a drying agent that is great for fast-flowing gases, it also contains an indicator so the user can tell when replacing is necessary. Figure 3 shows the drying tubes before they were replaced, and Figure 4 shows the drying tubes after they were all replaced. It can be seen that the contents of the tubes before changing were blue-green, indicating that the Sicapent was holding water.

After these replacements I began being able to weigh out samples to use in the instrument. This required carefully measuring out small quantities of sediment (5 micrograms) into tin boats. These boats then had to be delicately folded into a 'patty-cake' and loaded into the carousel with diligent notes and labeling being made in the lab notebook. In addition to the samples, boats of the calibrated standards (sulfanilic acid) had to be included for every run. For each sample, a second replicated one was also included to ensure our accuracy. By having the replicates we were able to compare the results of each and compare to make sure that the instrument was working properly and giving constant results, which it was.

MERCURY ANALYSIS

For the analysis of the mercury content we intended to utilize the Direct Mercury Analyzer DMA-80 instrument in the lab, but the instrument was broken and in the process of being fixed. The instrument would have been a simple way to analyze the mercury content of the samples due to the innovative technology of Milestone (the company that manufactures the instrument). The instrument requires no sample preparation, but gives results in about 5 minutes that can detect down to a limit of about 0.0015 ng of mercury. The samples are loaded onto the sample boats onto the carousel where a pneumatic arm injects the sample, and boat into a furnace for drying and decomposition. The decomposed sample is then carried, with air, to the catalyst bed (B), where interferences are removed and all species of mercury are reduced to elemental mercury. Next, the sample is carried to the gold amalgamator (C) and it then is heated and travels through a single beam atomic absorption spectrometer (D). Although we were not able to utilize the Mercury Analyzer, hopefully when another student steps into the project next year they will have the opportunity to do so.

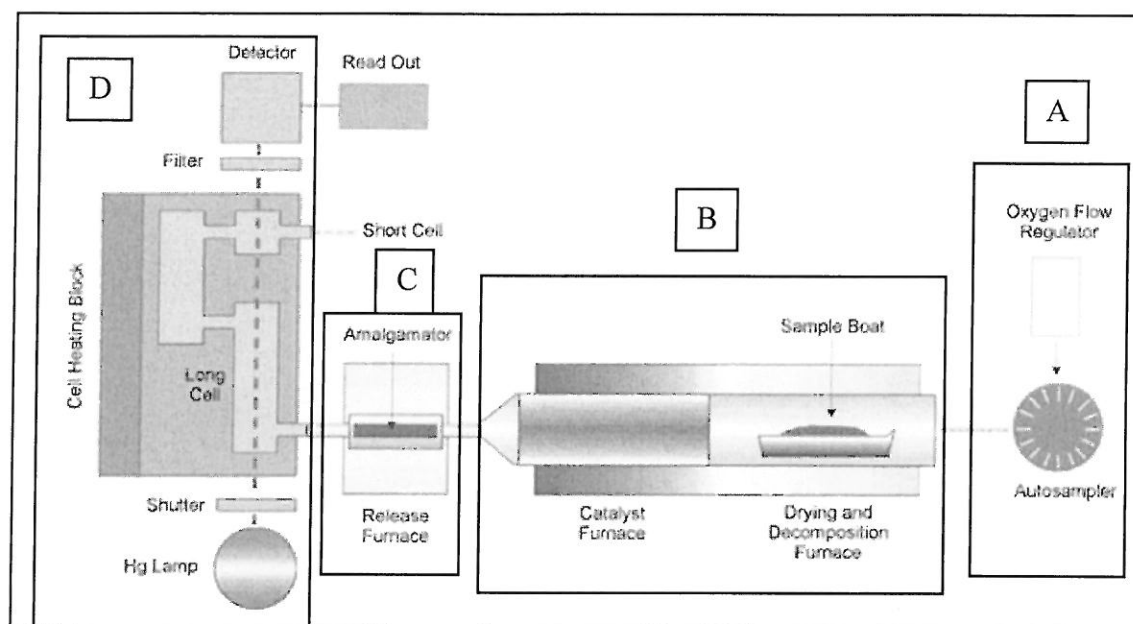


Figure 4. Visual representation of the internal process of the DMA-80 Mercury Analyzer. Section A shows where the samples and the oxygen enter. Section B shows the catalyst bed and where the samples are dried. Section C is the gold amalgamator, and section D is the single beam atomic absorption spectrometer.

MICROWAVE DIGESTION

We turned to microwave digestion as an alternative method to investigate the heavy metals present in the sediment samples, specifically cadmium, lead and chrome. The instrument



Figure 5. Image of the Microwave Digestion instrument in the Roger Williams University laboratory.

works by digesting the sample in acid (nitric acid for our experiment) at high temperatures in order to release the metals from complex matrices. Samples of 5 micrograms were weighed out and put into the plastic capsules for the microwave digestion. Also into the capsules went an aliquot of nitric acid. When placing the capsules into the tubes we had to be very careful in our process and note taking. Because of the nature of the instrument, digestion, anything that would be written on the capsules for labeling purposes would be gone when we took the capsules out of the instrument after running, therefore we had to be very meticulous in labeling and making note of which capsule was on top, in the middle, and on the bottom, and we had to make sure that the capsules stayed in those locations. Once the three capsules were safely inside the tube, it was filled with 11.8 mL of nanopure water and sealed shut. The tubes were then loaded into the carousel inside the instrument and the parameters for heating were set. First the temperature probe needed to be put in place and checked to make sure that it would register a change in temperature, this was done simply by holding the probe in your hand while watching the screen to make sure the instrument noticed the change in temperature from room to body temperature.

Next the temperature limits were set: take 10 minutes to heat to 125 degrees Celsius, and then stay at that temperature for 15 minutes, and finally take 30 minutes to cool back to room temperature. The instrument was left alone to run its course and after the cycles were finished we returned to retrieve the samples.

When removing the capsules from the tubes we again had to be careful to make sure they remained in the correct order, so before removing the capsules we made sure to get organized: gathering and laying out our equipment, labeling tubes and recording values in our notebook.

For each capsule, two volumetric tubes were needed. The tubes were labeled with the location and sieve number of the corresponding capsule, and one for each set was labeled with a 'D,' for



Figure 6. Image showing the 54 sample tubes prepared to be sent to URI for further analysis using ICP-MS.

dilution. Into all six tubes went an aliquot of 11.8mL of nanopure water. Next the microwave digestion tube was opened, the waste water gently poured into a waste container, and the capsules were removed and placed in order on the lab bench. From each capsule 1 microliter of digested sample was extracted. This microliter was injected into the corresponding tube and shaken up to allow for proper mixing. Next 1 microliter was extracted from that tube and injected into the corresponding tube labeled 'D,' thus creating the diluted sample. This process

was carried out for each of the capsules in each of the tubes. In total there were 9 microwave digestion tubes, 27 capsules, 27 sample tubes and 27 diluted sample tubes.

The sample tubes were then sent to the University of Rhode Island for further analysis. URI has the technology for the next step of analysis, ICP (inductively coupled plasma) mass spectrometry. This mass spectroscopy is capable of detecting metals in concentrations as low as parts per trillion. The instrument ionizes the samples with inductively coupled plasma, and then followed by mass spectrometer to separate and identify the ions present. Inductively coupled plasma is a source of plasma in which the energy is supplied by electric currents that are produced by electromagnetic induction. Atomic absorption mass spectroscopy is a more common form of analysis that could have been conducted in the laboratory at Roger Williams University, but ICP-MS is faster, more sensitive, and more precise. ICP-MS also allows for the scanning of all elements simultaneously, whereas atomic absorption spectroscopy does not allow for that. The use of ICP-MS is very prevalent in the environmental science field for uses with water and soil testing.

OUTCOMES

Due to the complications with the instruments that were needed for this research project we were not able to produce a table of data that resulted from the research. But I did learn a lot of valuable information. I learned about patience and persistence, specifically when it came to working with my advisor. Because of my persistence and commitment to working on the project he put me in charge of important tasks that otherwise I don't think I would have been able to

work on. Additionally I learned a lot about the Elementar Analyzer Instrument in the lab. By the end I was able to operate, maintain, and trouble shoot the instrument, which are skills that not many students walk away from their undergraduate careers knowing. I got to take a look inside and replace parts that would improve the quality of results for any future users of the instrument.

REFERENCES

Carini, Frank. "Brayton Point Ranked 4th in Mercury." *Brayton Point Ranked 4th in*

Mercury Pollution. Eco RI News, Jan. 2011. Web. 17 May 2012.

<<http://www.ecori.org/pollution-contamination/2011/1/26/brayton-point-ranked-4th-in-mercury-pollution.html>>.