EFFECT OF BIOCHAR AND ACTIVATED CARBON AMENDMENTS ON
GASEOUS MERCURY EMISSIONS OF SOIL AND MERCURY METHYLATION
RATES IN SEDIMENT

by
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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

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ACKNOWLEDGEMENTS

I would like to thank Dr. Cizdziel for overseeing my research, allowing me to work in his lab, and prodding me on with new ideas when I was flustered with failed attempts. I thank my family, friends, and fiancé for supporting me throughout this project. The methylation rate study was a collaborative effort with Derek Bussan, and I thank him for his assistance. Finally, I would like to thank my second and third readers, Dr. Nathan Hammer and Dr. Susan Pedigo. The Sally McDonnell Barksdale Honors College provided funding for this research.
ABSTRACT

EFFECT OF BIOCHAR AND ACTIVATED CARBON AMENDMENTS ON GASEOUS MERCURY EMISSIONS OF SOIL AND MERCURY METHYLATION RATES IN SEDIMENT
(Under the direction of Dr. James Cizdziel)

Mercury is a pervasive global contaminant with a complex biogeochemical cycle. In this biogeochemical cycle, methylmercury (MeHg+) tends to biomagnify and concentrate in fish and seafood consumed by humans. This study examines the effect of sorbent amendments on both the mercury emission from soils and the methylation rates of mercury in sediments, both of which are believed to be major contributors to the global cycle. Biochar and activated carbon were used to treat soils and sediments to explore their effects. It was found that biochar and activated carbon reduced gaseous mercury emission by 25% and 49%, respectively. Methylation rates in the treated sediment effectively decreased by 89% using biochar and by 83% using activated carbon, however this does not take into account potential adsorption of MeHg+ on the amendments or the possibility of the amendments killing the microbes responsible for methylation; therefore, methylation rates could not be said to have unequivocally decreased and may be “best-case scenario” rates. All results from treated sediments were statistically different from the untreated sediment (p-value < 0.001).
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<tr>
<td>DMA</td>
<td>Direct mercury analyzer</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>GC-ICP-MS</td>
<td>Gas chromatography coupled to inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>Hg</td>
<td>Mercury</td>
</tr>
<tr>
<td>Hg&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Elemental mercury</td>
</tr>
<tr>
<td>Hg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Mercuric ion</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>IDMS</td>
<td>Isotope dilution mass spectrometry</td>
</tr>
<tr>
<td>k&lt;sub&gt;d&lt;/sub&gt;</td>
<td>Demethylation rate constant</td>
</tr>
<tr>
<td>k&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Methylation rate constant</td>
</tr>
<tr>
<td>MeHg&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Methylmercury</td>
</tr>
<tr>
<td>SEM</td>
<td>Secondary electron multiplier</td>
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1. Introduction and Background

1.1 Mercury—why do we care?

Mercury (Hg) naturally occurs in the biogeochemical system of the earth, but anthropogenic activities, such as mining, fossil fuel burning, and certain industrial processes have increased the amount of mercury present in the atmospheric, aquatic, and terrestrial systems. Mercury exists in three particularly important forms in its biogeochemical cycle, all of which have impacts on human health: elemental mercury (Hg\(^0\)), gaseous oxidized mercury (Hg\(^{2+}\)), and methylmercury (MeHg\(^+\)). Mercury is a widespread global contaminant that has no known role in biological systems. Furthermore, mercury is a known toxin, and its most prevalent organic form, methylmercury (MeHg\(^+\)) causes multiple problems as a neurotoxin, as it is able to cross the blood-brain barrier.

1.1.1 Sources of mercury

There are both primary and secondary sources of mercury. Primary sources of mercury transfer it from the long-lasting reservoirs of the earth’s crust to the atmosphere where it deposits on land and in oceans. This deposited mercury can be reduced to elemental mercury and then emitted back to the atmosphere. This re-emission of mercury comes from secondary sources, where mercury is exchanged across different surface areas via the atmosphere. The main difference in the two sources is that primary sources add to the total mercury cycling, while secondary sources are the vehicles by which the
global mercury cycle proceeds. Natural primary sources of mercury include mercury emitted from volcanoes, geothermal sources, and topsoil enriched in mercury. The main culprit for increased anthropogenic mercury emissions is coal-fired electricity generation in developing countries, specifically in Asia were almost 40% of global anthropogenic emissions originate. There are other sources of mercury contamination, such as gold mining, in which mercury amalgamation was used to recover gold particles from milled ore in areas such as North Carolina, USA. Total global mercury emissions to the atmosphere range from 6500-8200 Mg yr\(^{-1}\) of which 1900-2900 Mg yr\(^{-1}\) come from primary anthropogenic sources. By analyzing remote lake sediment cores, it has been estimated that present-day mercury deposition is three to five times greater than pre-industrial deposition.

### 1.1.2 Biogeochemical cycle of mercury

Mercury is dispersed globally through the atmosphere via methods mentioned above. Approximately 95% of the total mercury in the atmosphere is in the elemental state. It very slowly (residence time of months) oxidizes to the Hg\(^{2+}\) state, and most of this occurs in fog and cloud droplets at the solid-liquid interface with ozone being the main oxidant. This long residence time of the mercury in the atmosphere lends to its ability to travel long distances from its source before deposition. Wet precipitation of dissolved Hg\(^{2+}\) is the main way in which the mercury returns to the earth’s surface. It can also adsorb onto aerosols, such as soot, which occurs chiefly over land where aerosols are more abundant, and this promotes deposition. This deposited Hg\(^{2+}\) can be reduced to
Hg\textsuperscript{0} by microorganisms and re-emitted to the atmosphere via secondary emission, or it could be converted to MeHg\textsuperscript{+} by other microorganisms (Figure 1).

While iron-reducing bacteria can methylate mercury, sulfate-reducing bacteria are largely responsible for the methylation of Hg\textsuperscript{2+}.\textsuperscript{4} Since sulfate-reducing bacteria tend to reside in anoxic environments, such as sediment, much methylation occurs in wetlands.\textsuperscript{8} Phytoplankton concentrate mercury from their environment and serve as a primary access point for mercury into the aquatic food web.\textsuperscript{9} The methylmercury then biomagnifies all the way up the food chain, reaching peak concentrations in large predatory fish such as tuna and swordfish.\textsuperscript{4} This biomagnification is a concern for populations of humans that rely on fish for a major component of their diet.

Figure 1: Biogeochemical cycling of mercury\textsuperscript{10}
1.1.3 Health effects of mercury

Elemental mercury does not pose much of a health risk to humans unless inhaled. There is very little absorption of elemental mercury in the gastrointestinal tract, and absorption of elemental mercury through contact with the skin is insignificant. However, about 80% of inhaled mercury enters the bloodstream directly from the lungs. Mercury can take from weeks to months to leave the body, so accumulation can result from mid- to long-term exposure.\textsuperscript{11} Most people have very little exposure to elemental mercury, so there aren’t any widespread health concerns for mercury poisoning through elemental mercury.\textsuperscript{12}

Methylmercury is the main route of exposure to mercury for humans. This exposure comes from our diet, especially in coastal areas where consumption of fish is greater. Methylmercury is able to cross the blood-brain barrier and the placental barrier by complexing with the thiol group on the amino acid cysteine.\textsuperscript{13} Methylmercury’s toxicity mainly stems from its interactions with a class of enzymes containing selenium, termed selenoenzymes. These enzymes reverse oxidative damage to the brain and many endocrine organs. The binding of mercury to the selenium in these enzymes irreversibly inhibits them and increases the oxidative stress on the body. Increased dietary intake of selenium has been shown to reverse some of the more acute symptoms of methylmercury toxicity, which include distal sensory disturbances, auditory disturbances, tremors, ataxia, dysarthria, constriction of visual fields, and tremors.\textsuperscript{14} The effects can be more severe in cases of prenatal exposure as methylmercury inhibits the development of the brain.\textsuperscript{14} Exposure to increased amounts of mercury during pregnancy is associated with lower infant cognition.\textsuperscript{15}
1.2 Biochar and activated carbon

Biochar is defined as a carbon-rich, porous, fine-grained substance produced by thermally decomposing biomass under low oxygen concentrations and temperatures between 300-1000°C.\textsuperscript{16} Activated carbon is composed of defective graphene layers, which are formed by selective gasification of carbon atoms via thermal activation or treatment with phosphoric acid for chemical activation. The activated carbon is filled with pores (or holes) greatly increasing surface area and intensifying van der Waals forces as a result (Figure 2). The resulting van der Waals forces give the activated carbon the ability to adsorb molecules onto its surface and within the pores.\textsuperscript{17} The major difference between activated carbon and biochar is that activated carbon has undergone treatment specifically to increase its porosity.

![Activated carbon under an electron microscope](image)

**Figure 2: Activated carbon under an electron microscope\textsuperscript{18}**

1.3 Previous studies using biochar and activated carbon for contaminated soil and sediment remediation

Both activated carbon and biochar have been used to amend soils \textit{in situ} by reducing the bioavailability and/or mobility of contaminants.\textsuperscript{19} Biochars and activated carbons have also been compared with respect to their sorption capacity, and it was found that while sorption capacities for organic compounds and inorganic mercury tended to be
1-2 orders of magnitude higher for activated carbons, similar sorption capacities were observed for MeHg\(^+\).\(^{20}\) A study by Gilmour\(^ {21}\) showed that sorbent amendments such as activated carbon and biochar can reduce Hg and MeHg\(^+\) concentrations and uptake by biological organisms such as earthworms. From this, it could be inferred that the same amendments could reduce the availability of mercury for biotic uptake where it could be converted to methylmercury.

1.4 Isotope dilution mass spectrometry

In depth discussion of IDMS can be found elsewhere.\(^ {22}\) Briefly, the method of isotope dilution includes mixing a sample with an artificial spike, enriched in a minor isotope of the analyte of interest, and measuring the isotopic ratios of the mixture using a mass spectrometer. These isotopic ratios, the mass of the sample, the mass of the spike, and the known concentration of the spike can be used to calculate the concentration of the analyte in the sample.\(^ {22}\) This is the best method of internal standardization, as the isotope of an analyte is as chemically similar to the analyte as can be achieved without using the analyte itself.

1.5 Methylation rate equations

The equation for the rate of methylation of mercury is as follows:

\[
\frac{d[\text{CH}_3^{200}\text{Hg}^+]}{dt} = k_m[200\text{Hg}^{2+}] - k_d[\text{CH}_3^{200}\text{Hg}^+] \tag{1}
\]

where \(k_m\) is the rate constant for methylation and \(k_d\) is the rate constant for demethylation. If the concentration of \(200\text{Hg}^{2+}\) is made to be much greater than that of \(\text{CH}_3^{200}\text{Hg}^+\), Equation 1 can be reduced to:
\[
\frac{d[\text{CH}_3^{200}\text{Hg}^+]}{dt} = k_m[200\text{Hg}^{2+}]
\] (2)

Upon integrating Equation 2, the following equation results:

\[
[\text{CH}_3^{200}\text{Hg}^+] = k_m[200\text{Hg}^{2+}]t
\] (3)

Solving Equation 3 for \( k_m \) yields the equation used for determining the methylation rate constant:

\[
k_m = \frac{[\text{CH}_3^{200}\text{Hg}^+]}{[200\text{Hg}^{2+}]t}
\] (4)

1.6 Purpose and hypotheses

The purpose of the study described herein was to explore whether biochar and activated carbon could reduce gaseous mercury emissions in soil and methylation rates in sediment. There are no known studies involving the monitoring of gaseous mercury emissions from biochar and activated carbon amended soils or for determining the effects of the amendments on methylation rate in natural sediments. It was hypothesized that both the biochar and activated carbon would reduce gaseous mercury emissions, with the activated carbon being more effective as predicted in previous research.²⁰ It was also hypothesized that the amended sediment samples would have lower rates of methylation than the unamended sample, but slightly higher methylation rates than the autoclaved samples, in which all of the microorganisms believed to contribute to methylation have been killed.
2. Experimental

2.1 Direct Mercury Analyzer

The Milestone DMA-80 was used in this experiment to determine the mercury emissions from soil and to determine the total mercury in the sediment (Figure 3). Direct mercury analyzers have been described in detail elsewhere. Briefly, samples are weighed into nickel boats that are placed in an autosampler. These boats are inserted into the combustion tube, where the sample is thermally decomposed with oxygen as the carrier gas. The gaseous products pass through a heated Mn₃O₄/CaO-based catalyst to complete oxidation and trap potentially interfering compounds. The elemental mercury and other products from decomposition are carried to a gold-coated sand trap. There, the Hg⁰ forms an amalgam with gold while other products are removed from the system. Later in the sequence, the trap is rapidly heated to send a pulse of elemental mercury vapor into a single beam spectrophotometer. The mercury concentration is calculated based on the absorbance at 253.7 nm and the weight of the sample.
2.2 Inductively coupled plasma mass spectrometry

The Thermo Fisher Element XR ICP-MS was used to determine both total mercury and methylmercury in the study on methylation rates in sediments (Figure 4). ICP-MS instruments have been described in detail elsewhere. Briefly, the sample is introduced into an argon plasma and ionized. The ions are differentiated according to their mass to charge (m/z) ratio by a mass analyzer. The ICP-MS used is a double focusing instrument which utilizes a magnetic sector first for directional focusing followed by an electric sector for energy focusing of the ion beam. The ions are detected by a secondary electron multiplier (SEM) detector for lower concentrations (ppq to ppm) or a Faraday detector for higher concentrations.

![Figure 4: Schematic of ICP-MS](image)

2.3 DMA-ICP-MS coupling

To analyze total Hg in sediments, the DMA was coupled to the ICP-MS. This method has not been reported in the literature, so a paper was submitted and accepted for publication detailing the setup. A teflon tube was inserted into the outlet of the DMA analysis cell and wrapped in a heat coil to prevent condensation. This tube was connected to a valve directing the carrier gas either to vent or to the ICP-MS. The major
obstacle to overcome was the use of different gases by each instrument. This was solved by the use of the valves shown in Figure 5. Oxygen was used in the DMA for the combustion process, but before the Hg was purged from the amalgamator, the carrier gas was switched to argon. The second valve was then set to direct the carrier gas to the ICP-MS instead of venting, and the ICP-MS data acquisition was begun. The valves were reset after data acquisition completed.

![Figure 5: DMA-ICP-MS interface and valve positions (shown in ICP-MS analysis mode)](image)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Valve 1</th>
<th>Valve 2</th>
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</thead>
<tbody>
<tr>
<td>Dry/Ash (O₂ to vent)</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Purge 1 (Ar to vent)</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Analyze (Ar to ICPMS)</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Purge 2 (Ar to vent)</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Reset to dry/ash</td>
<td></td>
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</tr>
</tbody>
</table>

2.4 GC-ICP-MS

To determine the amount of methylmercury in the sediments, GC-ICP-MS was utilized. The GC column from a Tekran 2700 Methylmercury Analyzer was used. The effluent from the atomic fluorescence cell (post-GC) of the MeHg⁺ analyzer was coupled to the ICP-MS such that the separated compounds entered the ICP-MS at different times (Figure 6). Before analysis, the solution was ethylated such that all mercury compounds would become volatilized. Hg⁰ is volatile in itself; the mercuric ion would become diethyl mercury; and methyl mercury would become methyl ethyl mercury. The solution was purged using argon gas, and the mercury compounds were collected on a Tenax trap.
The compounds were desorbed via heating the Tenax trap, and carried to the GC column. In the GC column, the molecules with the larger alkyl groups would take longer to pass through than the molecules with smaller or no alkyl groups because of greater interactions with the column. Using standards and spikes, it was confirmed that the correct peaks were being used.

![GC-ICP-MS schematic](image)

**Figure 6: GC-ICP-MS schematic**

2.5 **Biochar, activated carbon, and soils used in this study**

Activated carbon prepared from coconut shells (Sargent-Welch, 8-12 mesh) and pinewood biochar gasified at ~830°C obtained from Mississippi State University were used as amendments in this experiment. The amendments were ground with a mortar and pestle and sieved. The particles in the 250-500 µm range were used. To drive off surface-bound mercury and to lower background, both amendments were also “heat cleaned” in a vacuum oven at 170°C and -675 mbar gauge pressure for 24 hours and stored in plastic bags prior to use. The soil used in this study is classified as a fine-
loamy, mixed, superactive, mesic Typic Hapludoll from Iowa. The soil had been previously characterized as having a mercury concentration of 24.74 ppb.

2.6 Gaseous mercury emissions from soil: initial trials

Various experiments were tried before settling on the method detailed in section 2.7. Headspace analysis of the soil was attempted while heating the vial in a hot block, but this idea was abandoned because the levels of Hg in the headspace were too low for reliable (accurate and reproducible) results. Next, samples were run on the DMA, which would have been advantageous because the autosampler would increase sample throughput. The samples were heated to 180°C for five minutes while passing gas over them. However, the biochar tended to combust when oxygen gas was used (which is normally used in the DMA for the pyrolysis step), so argon gas was used, instead. Unfortunately, only half a gram of soil could fit in the nickel boats used by the DMA, and the program would not allow heating for more than five minutes. These two factors were the most probable contributors to the unreproducible results obtained by this method.

2.7 Sorbent effects on gaseous mercury emissions from soil

Prior to analysis, gold traps were cleaned of mercury by heating to 950°C with ultra-high purity argon gas passed through them at 80 mL/min. About 6 grams of soil was weighed to nearest 0.1 mg into a 60 mL Teflon vial. Into another vial, ~ 6 grams of soil and ~ 0.3 grams of biochar were weighed to nearest 0.1 mg to make the sample 5% amendment by weight. Both vials were covered with parafilm and vigorously shaken for about a minute. A third empty Teflon vial was used as a blank. These three vials were
snugly fitted into a hot block, which was set at 80.0°C. Ultra-high purity nitrogen gas was passed through a gold mercury scrubber and then over each soil sample at 40 mL/min. The gas was then carried to a gold coated quartz trap, which collected any gaseous mercury picked up by the carrier gas (Figure 7).

![Image](image.jpg)

**Figure 7: Experimental setup for gaseous mercury emissions**

This setup was allowed to run for 19-24 hours, after which the three gold traps were analyzed using the DMA. If the traps were not analyzed immediately, they were stored with Teflon plugs until analysis, usually within the next day. The gold coated quartz pieces were carefully removed and placed in a nickel sample boat to be analyzed on the DMA, the parameters of which are shown in Table 1. The gold coated quartz pieces were carefully placed back into the trap, and the cycle was repeated. The next run was then set up using clean Teflon vials and the cleaned gold traps.
Table 1: DMA Parameters

<table>
<thead>
<tr>
<th>DMA Parameters</th>
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<tr>
<td>DMA gas flow</td>
<td>200 mL min(^{-1})</td>
</tr>
<tr>
<td>Drying</td>
<td>200 °C</td>
</tr>
<tr>
<td>Drying</td>
<td>60 (s)</td>
</tr>
<tr>
<td>Decomp</td>
<td>650 °C</td>
</tr>
<tr>
<td>Purge</td>
<td>60 (s)</td>
</tr>
<tr>
<td>Amalgam</td>
<td>12 (s)</td>
</tr>
<tr>
<td>Record</td>
<td>45 (s)</td>
</tr>
</tbody>
</table>

2.8 Sorbent effects on mercury methylation rates in sediments

Sediment and the water used to make the Me\(^{199}\)Hg\(^+\) and \(^{200}\)Hg\(^{2+}\) spikes were obtained from a pond at the Whirlpool Trails in Oxford, MS (Figures 8 and 9). Sediment was obtained from the top two inches of the pond bottom and homogenized in the lab via mixing with gloved hands.
Figure 9: Wetlands at Whirlpool Trails from which samples were obtained

About 90 g of sediment was weighed into amber jars, and 5% by dry weight amendment was added to the amended samples. The samples were grouped into four categories: (1) no amendments, (2) autoclaved, (3) biochar amendment, and (4) activated carbon amendment. All samples were spiked with Me$^{199}$Hg$^+$ and 200Hg$^{2+}$ containing 10-100% of the ambient levels of MeHg$^+$ and Hg$^{2+}$ in the sample. All samples were homogenized by mixing with a plastic spatula after the amendment (if any) and spike were added. All samples except those to be autoclaved were placed into a vacuum oven (Figure 10), which was subsequently evacuated, replacing the air with nitrogen gas to make an inert environment. The oven was set to 25°C. The autoclaved samples were covered with aluminum foil, autoclaved for 20 minutes, allowed to rest for 24 hours, then autoclaved again and placed with the rest of the samples in the vacuum oven. The samples were allowed to incubate in the inert environment at 25°C for two weeks. The samples were then placed in a freezer at -80 °C for a day. Afterwards, the samples were lyophilized at 0°C and 0.420 mBar absolute pressure with a collector temperature of -54°C for seven days. The samples were stored in a freezer until analysis.
2.8.1 Total mercury analysis

The samples were first analyzed for total mercury using the DMA-ICP-MS. Sample (~0.02 g) and $^{201}\text{Hg}^{2+}$ spike (~0.01 g, 465.6 ppb) were weighed to the nearest 0.1 mg in a nickel sample boat. The spike was added immediately before the sample was placed in the DMA to be analyzed via isotope dilution mass spectrometry.

2.8.2 Determination of methylmercury by GC-ICP-MS

The acetate buffer and 1% sodium tetraethyl borate used in this procedure were prepared according to EPA Method 1630. Distillation equipment was cleaned with deionized water, followed by distilling 14% HCl in the apparatus, followed by another rinse and flush with deionized water. The equipment was allowed to dry in a laminar flow hood.
Sediment (0.5 g) was added to a 60 mL Teflon distillation vial, and spiked with 0.05 g of Me$^{201}$Hg$^+$. For accuracy, only 0.1 g of estuarine sediment (ERM-CC580) certified reference material was used. Deionized water (25 g), 20% KCl (0.5 mL), and 50% H$_2$SO$_4$ (1 mL) were added to the sample vial. The vials were heated at 120°C in a hot block with ultra-high purity nitrogen gas bubbling through the sample solution at ~40 mL/min (Figure 12). Distillation was allowed to proceed until the receiving vial contained 20-25 mL of distillate. Some distillation lines were wrapped in aluminum foil to discourage distillate buildup in the line, which slowed the already lengthy process. After distillation, 0.5 g of distillate (0.1 g if ERM-CC580 certified reference material) was weighed into a brown amber vial. Next, 225 µL acetate buffer was pipetted into the vial, and deionized water was added for a total solution weight of 30 g. Sodium tetraethyl borate (1%, 30 µL) was added and the vial was quickly capped with a septum cap and shaken. The vials were transferred to the autosampler of the methylmercury analyzer. The outlet of the methylmercury analyzer was coupled to the ICP-MS using a Teflon tube to allow IDMS measurements.
Figure 11: Methylmercury distillation setup

Figure 12: Coupling of the GC column from a MeHg\(^+\) analyzer to the ICP-MS
3. Results and Discussion

3.1 Sorbent effects on gaseous mercury emissions from soil

Biochar decreased the gaseous mercury emissions from soils by an average of 25% (Figure 13). In run 2, the amended vial was not homogenized for as long as the other runs, which may have contributed to the small difference observed in its unamended and amended soils.

![Figure 13: Mercury emissions from unamended and biochar amended soils](image)

Activated carbon decreased gaseous mercury emissions from soils by 49% (Figure 14), which is almost double the effectiveness of biochar. This is what was predicted in the
paper by Gilmour\textsuperscript{21} and is most likely attributed to the much higher porosity of the activated carbon due to its being thermally or chemically activated.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure14.png}
\caption{Mercury emissions from unamended and activated carbon amended soils}
\end{figure}

In future studies, it may be interesting to see the differences resulting from using various temperatures for the hot block. Higher readings would be expected for higher temperatures, which could help determine if there are meaningful differences in using different amendments. Also, studies could be done to see if certain types of biochar or activated carbon are better amendments, since this study only used pinewood biochar and one brand of activated carbon. Further studies could be done with various particle sizes to see if a smaller particle size (greater surface area per unit mass) would reduce emissions further. Since mercury emissions from soils are a major contributor to atmospheric mercury levels, this research has implications for treating all soils, but more
specifically areas that may have been contaminated by mercury via industrial processes or spillage.

Further work can also be done under more realistic conditions using a setup similar to that used by Dr. Yi Jiang, who previously studied mercury flux in Dr. Cizdziel’s lab during his doctoral research. Using this setup, activation energies for increasing mercury flux could be obtained. Assuming a pseudo-first order reaction, these would be obtained using the Arrhenius equation:

$$\ln(F) = \ln(A) - \frac{E_a}{RT}$$  \hspace{1cm} (5)

where $F$ is mercury flux, $R$ is the gas constant ($1.9872 \text{ cal·K}^{-1}$), $T$ is the soil temperature in Kelvin, $A$ is a pre-exponential factor (a frequency factor representing the number of times mercury atoms gain enough energy to be thermally desorbed), and $E_a$ is the activation energy. This would give information about the effects of temperature and photoreduction on the amended and unamended soils for further investigations into the effectiveness of the amendments.

Figure 15: Proposed setup for larger scale testing
3.2 Methylation rates in sediments

An example chromatogram for the determination of total mercury in the sediment using the DMA-ICP-MS coupling is shown in Figure 16. The sample run in this figure is of natural isotopic abundances, as the peak heights are correlated with the relative natural abundances of each isotope.

![Example chromatograph from DMA-ICP-MS](image)

**Figure 16: Example chromatograph from DMA-ICP-MS**

The results from the methylation rate study are presented in Figure 17. For precision calculations, four samples were run per category with two coming from the same incubation jar. It is interesting that the biochar amendment was almost as effective as autoclaving the samples. Autoclaving, of course, kills the microorganisms that are instrumental in methylating the mercury via biological processes. All methylation rates
for treated sediments were statistically different from the methylation rate of the untreated sediment (p-value < 0.001).

An interesting consequence of using the sorbents to reduce the methylation rate is that it cannot be known for certain that the actual methylation rate was decreased given the current methodology of the procedure. It is known that the amount of available methylmercury is decreased, but it is possible that the methylmercury adsorbed to the biochar after methylation. Published research has shown both biochar and activated carbon to be effective for binding MeHg\(^+\).\textsuperscript{20} For this reason, the results for the amendments in Figure 16 may not reflect the actual methylation rates because it is not known how much Hg\(^{2+}\) or MeHg\(^+\) adsorbed to the amendment. It could also be possible that the addition of the biochar or activated carbon killed the microbes responsible for methylation, which would also account for their reduced methylation rates.
Figure 18 is a better representation of the results of the experiment as it shows the amount of methylmercury that was able to be recovered from the reaction mixture. Biochar reduced the amount of available methylmercury by 89% while activated carbon reduced the amount of methylmercury by 83%. All treated sediments were statistically different from the untreated sediment (p-value < 0.001). Table 2 summarizes the data obtained.

![Graph showing methylmercury recovery for each treatment](image)

**Figure 18: Methylmercury recovered for each treatment**
*(Error bars represent one standard deviation.)*

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Total $^{200}\text{Hg}$ (nmol/g)</th>
<th>$\text{Me}^{200}\text{Hg}^+$ Available (nmol/g)</th>
<th>$% \text{ Me}^{200}\text{Hg}$</th>
<th>$k_m$(day)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.186</td>
<td>0.00922</td>
<td>4.97</td>
<td>3.86E-03</td>
</tr>
<tr>
<td>Autoclaved</td>
<td>0.159</td>
<td>0.00068</td>
<td>0.43</td>
<td>3.08E-04</td>
</tr>
<tr>
<td>Biochar</td>
<td>0.161</td>
<td>0.00102</td>
<td>0.63</td>
<td>4.59E-04</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>0.152</td>
<td>0.00156</td>
<td>1.03</td>
<td>7.43E-04</td>
</tr>
</tbody>
</table>

**Table 2: Methylation rate study: data summary**
Further studies should focus on potentially extracting the adsorbed mercury and methylmercury from the biochar by some process and analyzing the soil for reduced amounts of living microbes after addition of amendment so that it can be unequivocally stated that the methylation rate was decreased by the addition of the amendment.
4. Conclusions

For soil under the experimental conditions, biochar was shown to reduce gaseous mercury emissions by 25%, while activated carbon reduced emissions by 49%. For sediments, biochar reduced the amount of available methylmercury by 89% while activated carbon reduced available methylmercury by 83%. These promising results deserve further attention, specifically pertaining to the use of different amendments and different particle sizes for the reduction of gaseous mercury emissions and in determining if the methylation rate actually decreased by potentially desorbing the mercury and methylmercury from the biochar and analyzing amended soils to be sure that the amendment is not killing the microbes responsible for methylation.
16. (a) Mesa, A. C.; Spokas, K., Impacts of biochar (black carbon) additions on the sorption and efficacy of herbicides. INTECH Open Access Publisher: 2011; (b)


