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Gas Exchange Of Hg Over Wetlands, Effect Of Biochar And Activated Carbon On Hg Emissions From Soil, And Seasonal Concentrations Of Hg In Rain

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GAS EXCHANGE OF Hg OVER WETLANDS, EFFECT OF BIOCHAR AND ACTIVATED

CARBON ON Hg EMISSIONS FROM SOIL, AND SEASONAL CONCENTRATIONS OF Hg

IN RAIN

A Thesis
presented in partial fulfillment of requirements
for the degree of Master of Science
in the Department of Chemistry and Biochemistry
The University of Mississippi

by

DIVYA NALLAMOTHU

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ABSTRACT

Mercury (Hg) is a global pollutant with human-health and ecological impacts. Gaseous Hg exchange between the atmosphere and aquatic or terrestrial surfaces serves as an important, but not well understood, route for Hg to enter and exit ecosystems. To better understand the role of gaseous Hg exchange in the biogeochemical cycling of Hg, we investigated Hg^0 fluxes over natural wetlands (Sky Lake) and artificial wetlands (UM Field Station) using a dynamic flux chamber and an Hg vapor analyzer based on atomic fluorescence (Chapter 1). We also examined the effect of activated carbon and biochar on Hg emissions from soils for potential remediation purposes (Chapter 2). Finally, we studied the concentration of total-Hg in rain in Oxford, Mississippi, as a function of season and cloud-type (Chapter 3).

Mercury emission fluxes from soils varied diurnally, with higher fluxes during the day, and lower and more stable fluxes during the night. Emission of Hg was correlated ($p<0.05$) with solar radiation for both soil ($r=0.81$) and water ($r=0.95$). Mean ambient levels of total gaseous mercury (TGM) at the Field Station and Sky Lake were 1.57 ± 0.67ng m^{-3} h^{-1} and 1.23 ± 0.58ng m^{-3} h^{-1}, respectively. Mercury emission was generally greater from terrestrial (soil) surfaces compared to aquatic (water) surfaces. For example, the mean flux at the Field Station was 4.5ng m^{-3} h^{-1} over soil versus 2.3ng m^{-3} h^{-1} over water during the same period.

Emission of Hg from soils was greatly reduced when the soil was mixed with biochar or activated carbon at 5% weight. We observed that a 1-2% sorbent-soil ratio appears to be the most

cost-effective approach for potential remediation purposes. While reduction in Hg emissions was size-dependent with the greatest reduction for the finest fraction (<125μm), the larger size-fraction and crude fraction also reduced soil-Hg emissions. For biochar, the mean Hg flux was reduced from 0.70ng m^{-3} h^{-1} to -0.86ng m^{-3} h^{-1} indicating that not only were emissions from the soil decreased but also that Hg in the ambient air was being adsorbed on the biochar. Similarly, activated carbon changed the Hg flux from a net emission to a net deposition. These results show that amending soils with these sorbents can be effective to minimize Hg emissions from contaminated soils.

Concentrations of total-Hg in rain from Oxford, Mississippi were greater ($p<0.05$) in the spring and summer during thunderstorms (38 ± 10pg/g) compared to the fall and winter during non-thunderstorms (6.7 ± 3.9pg/g). This supports the hypothesis that cumulonimbus (thunderstorm) clouds, which reach higher altitudes, are effective at scavenging gaseous oxidized Hg species that accumulate in the upper troposphere.

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I am deeply appreciative of the many individuals who have supported my work and continually encouraged me through the writing of this thesis. Without their time, attention, encouragement, thoughtful feedback, and patience, I would not have been able to see it through.

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This work herein is primarily an extension of that of Yi Jiang and Ryan Sessum, former students of Dr. Cizdziel's group. I am grateful to them for laying the foundation for my study. Indeed, I need to give special thanks to the people in the Cizdziel group, especially Yi Jiang for helping me in setting up the instruments at Field sites and Derek Bussan for his suggestions and help. I also would like to thank Cizdziel group members: Lorlyn Reidy, Oscar Beau Black,

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LIST OF ABBREVIATIONS AND SYMBOLS

Hg	Mercury
TGM	Total Gaseous Mercury
GEM	Gaseous Elemental Mercury
GOM	Gaseous Oxidized Mercury
PBM	Particulate-Bound Mercury
AAS	Atomic Absorption Spectrophotometry
AFS	Atomic Fluorescence Spectrometry
CV	Cold Vapor
DMA	Direct Mercury Analyzer
LOD	Limit of Detection
UM	University of Mississippi
USEPA	United States Environmental Protection Agency
Model 2537A/B	GEM Analyzer
SD	Standard Deviation
LOI	Loss-On-Ignition
DFC	Dynamic Flux Chamber
Tekran 1110	Tekran Automated Dual Switching Unit
Tekran 2505	Mercury Vapor Calibration Unit

CHAPTER ONE

GASEOUS MERCURY EXCHANGE OVER NATURAL AND

CONSTRUCTED WETLANDS IN MISSISSIPPI

ABSTRACT

Mercury (Hg) air-surface gas exchange is an important route of Hg transfer into and out of wetlands, however they're few investigations directly and systematically measuring Hg flux rates in wetlands. In this study, gaseous Hg exchange fluxes were determined over natural wetlands at Sky Lake, located in Mississippi Delta, and over artificial wetlands at the University of Mississippi Field Station. Hg fluxes were measured using a dynamic flux chamber, and environmental variables, including air temperature, solar radiation, humidity, wind speed, and pressure were monitored concurrently. Hg emission fluxes were found to vary diurnally, with higher fluxes during day light, and lower and more stable Hg fluxes during the night. Mean ambient levels of total gaseous mercury were slightly higher at the field station (1.57 ± 0.67 ng·m^{-2}·h^{-1}) compared to remote Sky Lake (1.23 ± 0.58 ng·m^{-2}·h^{-1}). Mercury fluxes from the terrestrial (soil) surface was generally greater than Hg flux from the aquatic (water) surface: at the Field Station, the flux from the soil was 4.52 ± 4.8 ng·m^{-2}·h^{-1} compared to 2.3 ± 1.9 ng·m^{-2}·h^{-1}) for the water; at Sky Lake the Hg flux from the soil was 4.92 ± 2.8 ng·m^{-2}·h^{-1} compared to 0.25 ± 0.49 ng·m^{-2}·h^{-1} for the water. Air-water Hg fluxes were measured at the Field Station in both the winter and summer to compare seasons. Mercury emission rates were higher during the summer (for both the day and night) than the winter suggesting that both temperature and solar radiation are contributing factors to Hg release from wetlands. Overall, Hg fluxes over wetlands are dynamic, changing as dictated by environmental conditions.

INTRODUCTION

Mercury (Hg) is a global pollutant that is primarily dispersed through the atmosphere. In addition to human health concerns, Hg affects the reproductive health of birds and fish.[1] Gaseous elemental mercury (GEM) represents of over 95% of the Hg in the air, has a residence time of 0.5-2 years, and undergoes long distance transport after emission from the sources.[2] Atmospheric Hg has both anthropogenic and natural sources. Unlike point sources of Hg, which have been studied intensively throughout the world, [3, 4, 5] non-point sources of Hg are still relatively under-characterized. Natural non-point sources of Hg include soils and substrates that are geologically enriched in Hg, active geothermal areas, biomass burning (e.g. forest fires), as well as lakes and wetlands;[6] anthropogenic non-point sources include urban surfaces, sewage sludge amended soils, and mine wastes.[7]

To understand the global biogeochemical cycling of Hg in the environment it is necessary to investigate its exchange between the atmosphere and terrestrial and aquatic surfaces. Wetlands are of particular interest because they are rich in biodiversity and serve as shelters, nesting and feeding grounds for birds and fish, but are also considered as hot spots for Hg methylation.[8]

To understand Hg exchange and transformation processes in wetlands, the Hg emission fluxes have been measured over wetlands. A variety of factors have been shown to influence Hg emissions from wetlands. Hg fluxes from natural surfaces (typically reported as ng of Hg emitted or deposited per m^2 per hour) are largely influenced by substrate Hg concentration, sunlight,

temperature, atmospheric turbulence, relative humidity, soil moisture content, and vegetation cover.[9] Another important factor is reduction of oxidized divalent mercury (Hg^{2+}) in soil and aquatic environments to Hg^0, a process that is catalyzed by solar radiation.[10]

The present study focused on Hg gas exchange over natural and artificial wetlands in Mississippi. There are relatively few such studies and none in the mid-south United States. The objectives were to characterize Hg exchange over wetlands (both terrestrial and aquatic surfaces) and to develop insights into the factors controlling Hg fluxes over natural and constructed wetlands in the mid-south United States

MATERIAL AND METHODS

Site description

We investigated Hg air-surface gas exchange at Sky Lake, an oxbow lake located 10 km north of Belzoni Mississippi, during July 2014 (Fig. 1). Baldcypress is a long-lived, deciduous conifer native to the southeastern United States.[11] Sky Lake is believed to have been formed between 7500 and 10,000 BP. [12] The lake presently serves as a functioning backwater ecosystem, with a seasonally inundated, forested fringe up to 0.8 km wide surrounding the lake.[13] The wetland (swamp) undergoes large-scale water level fluctuations that are thought to affect the redox conditions in the sediment resulting in alternating periods of oxic and anoxic conditions. [14] These oscillations in redox conditions may influence the speciation and bio-availability of Hg in the system.

We also measured fluxes over an artificial wetland at the University of Mississippi Field Station during March (winter) and July (summer) of 2014 (Fig. 2). The UM Field Station is a research facility located on a 740-acre site 11 miles northeast of the UM Oxford campus. The Field Station lies within the Eocene Hills of the interior coastal plain of the Southeastern U.S. and is characterized primarily by sandy and sandy-loam soils. The facility includes wetlands and experimental ponds ranging from 0.1 to 2 acres that are fed by springs and small streams. Pond water depth was about 1 meter.

Figure 1. Sky Lake located in the Mississippi Delta a few miles north of Belzoni. Measurements were conducted in the swamp (star).

Figure 2. The University of Mississippi Center for Water and Wetlands Resources (Field Station) and experimental pond #179 where research was conducted.

Mercury flux measurements

Mercury gas exchange over wetlands was measured using a dynamic flux chamber (DFC) (Fig. 3 and 4). There are several methods to estimate air-surface Hg^0 fluxes with the DFC

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having the advantage of being portable, simple to deploy, and not subject to the strict site constraints of other methods. A detailed description of the DFC method has been reported elsewhere.[15, 16, 17] Briefly, a pump draws air from both inside and outside the DFC, through a switching valve (Tekran Model 1115 synchronized multi-port sampler) to a Hg vapor analyzer (Tekran 2537) (Figs. 5 and 6). The analyzer sequentially measures Hg in the air at the DFC inlet and outlet in 10-min intervals providing the necessary data for an Hg flux measurement every 20 min using the formula:

$$F = Q*(Co-Ci)/A$$

Where F is the Hg flux ($ng \cdot m^{-2} \cdot h^{-1}$), Q is the flushing flow rate through the chamber (0.09 $m^3 \cdot h^{-1}$) and controlled by a mass flow controller inside the mercury analyzer, C_o is the air Hg concentration at the outlet ($ng \cdot m^{-3}$) and C_i is the air Hg concentration at the inlet, and A is the footprint area of the chamber (0.036 m^2). The inlet sampling tube was placed at the same height as inlet holes on the flux chamber. The inlet measures the concentration of atmospheric mercury, while the outlet measures either the sum of atmospheric Hg and Hg emitted from the soil within the chamber or the difference between atmospheric Hg and Hg deposited on the soil surface within the chamber. When the outlet concentration is higher than the inlet concentration, Hg is being emitted from the soil; when the outlet concentration is lower than the inlet concentration, Hg is being deposited on the soil. The Tekran analyzer were routinely calibrated using injections of gaseous elemental mercury in ambient air using a Tekran 2505 Mercury Vapor Calibration Unit, replicate injections of known amounts of mercury produced recoveries > 90%.

Figure 3. Experimental setup for measuring Hg flux over wetlands at Sky Lake. Dynamic flux chambers over water and soil can be seen on right.

Figure 4. Experimental setup for measuring mercury flux over wetlands at the UM Field Station.

Figure 5. Mercury Vapor Analyzer (top) and multiport controller and valves (bottom). Used with permission from Tekran Inc.
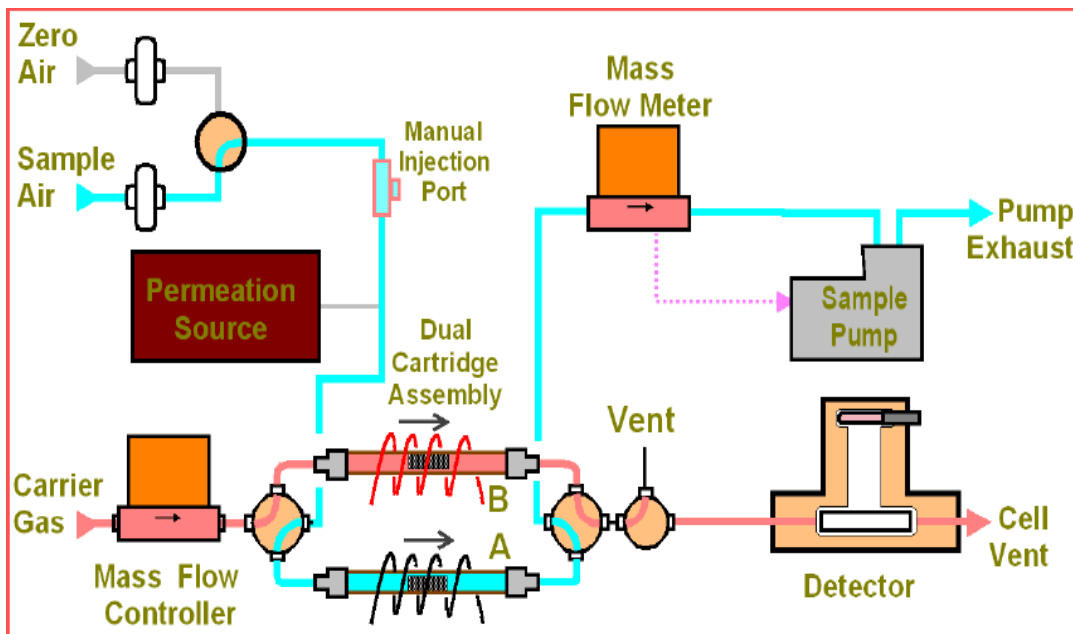
Figure 6. Flow diagram for the 2537 Mercury Vapor Analyzer. Used with permission from Tekran Inc.

We measured Hg fluxes from both water-air and soil-air during the same period of time (Figs. 3 and 4). In that scenario, port one was used to sample ambient Hg in the air, port two for soil-air flux, and port three for water-air flux. While only one port is "sampled" (measured) at a time using a flow rate of 7.5 L min^{-1}, the ports (lines) not sampled were continuously flushed at 0.1 L min^{-1} using independent digital flow controllers. The system was checked for contamination using a Tekran 1100 Zero Air Generator, and fluxes were only measured when the system was considered free of contamination (i.e. no detectable Hg levels). Concentrations of gaseous Hg were measured using a Tekran 2537A mercury analyzer (Tekran Inc., Toronto, Canada). The analyzer operates two independent sampling paths and was set to preconcentrate atmospheric Hg onto gold-coated quartz traps during five-minute time periods, resulting in time resolutions of 10 min (average measurement of the two gold traps).

Prior to the field measurements, all tubing, fittings and the chamber cover were rinsed with D.I. water and methanol. The mercury flux measurement system was tested before measuring soil samples to ensure that the concentration difference between inlet and outlet was less than 5% when placed on a clean impermeable Teflon sheet. The system blank was tested before flux measurements were made by using a Teflon sheet, served as the bottom surface for the DFC. The blank results were negligible (mean=0.08 ng$\cdot$m$^{-2}\cdot$h^{-1}) for the study period, so the flux results are reported without correction for the chamber blanks. The detection limits for the mercury analyzer was 0.1 ng$\cdot$m^{-3}.

Meteorological and solar radiation measurements

Meteorological conditions, including ambient air temperature, wind speed, wind direction, relative humidity, pressure and precipitation, were measured using Vaisala WXT 520 automatic weather station located near the flux chamber (Fig. 4, left). Solar radiation was

measured by using Li-1400 data logger. Data logging for both systems were programmed to

record data at 5-minute intervals to match the analysis interval of the mercury vapor analyzer.

RESULTS AND DISCUSSION

Concentrations of Hg in the ambient air and soil at the study sites

Mean total gaseous mercury (TGM) concentrations in the ambient air were slightly higher at the Field Station (1.57 ± 0.67 ng·m^{-2}·h^{-1}) compared to Sky Lake (1.23 ± 0.59 ng·m^{-2}·h^{-1}), but the difference was not statistically significant (Table 1). These TGM levels are generally consistent with background levels for the northern hemisphere, which is believed to be ~1.2 ng·m^{-3}. [18]

Table 1. Total gaseous mercury concentrations (TGM) in the ambient air at Sky Lake and University of Mississippi Field Station

Site	TGM Concentration (ng m^{-3})		
	Range	Median	Mean $\pm$ SD
UM FS	0.62 - 3.32	1.39	1.57 ± 0.67
Sky Lake	0.62 - 4.50	1.09	1.23 ± 0.59

Mercury fluxes over wetland soil and water

Summary statistics for Hg exchange fluxes over wetlands is given in Table 2. For soil-air exchange, there were similar levels of Hg emissions from both the natural and artificial wetlands: mean Hg soil/air flux from the Field Station was 4.52 ± 4.8 ng·m^{-2}·h^{-1} (range 0.84 - 15.50 ng·m^{-2}·h^{-1}), while the emission at Sky Lake was 4.92 ± 2.8 ng·m^{-2}·h^{-1} (range 1.74 -13.1 ng·m^{-2}·h^{-1}). At the Field Station there were 55 data points for the soil/air flux, of which 50 were net emissions

and 5 were net depositions. Similarly at Sky Lake there were 54 data points for the soil/air flux, of which all were net emissions.

For Hg water-air exchange, the mean flux from the Field Station (2.3 ± 1.9 ng·m^{-2}·h^{1}) was higher than Sky Lake (0.25 ± 0.49 ng·m^{-2}·h^{1}). The lower flux and higher variability at Sky Lake may be due to the wetland/forest canopy limiting and fluctuating the intensity of solar radiation reaching the water surface; whereas the Field Station pond is out in the open (Fig. 8). At the Field Station there were 55 data points for the water-air flux, of which total 54 were net emissions and 1 was a deposition. Similarly at Sky Lake there are 54 data points for the water-air flux, of which 37 were net emissions and 16 were deposition. We also found that Hg deposition was greater during the winter compared to the summer (see seasonal differences below).[19]

In all the cases Hg flux from terrestrial (soil) surfaces was generally greater than from aquatic (water) surfaces (Fig.7). It is noted that concentrations of Hg in the soil are significantly higher than the water (ppb vs. sub-ppb levels). There also appears to be a lag in the water response to sunlight, though more experiments are needed to confirm this. This is not surprising given the significantly different characteristics of the surfaces and the properties of each media.
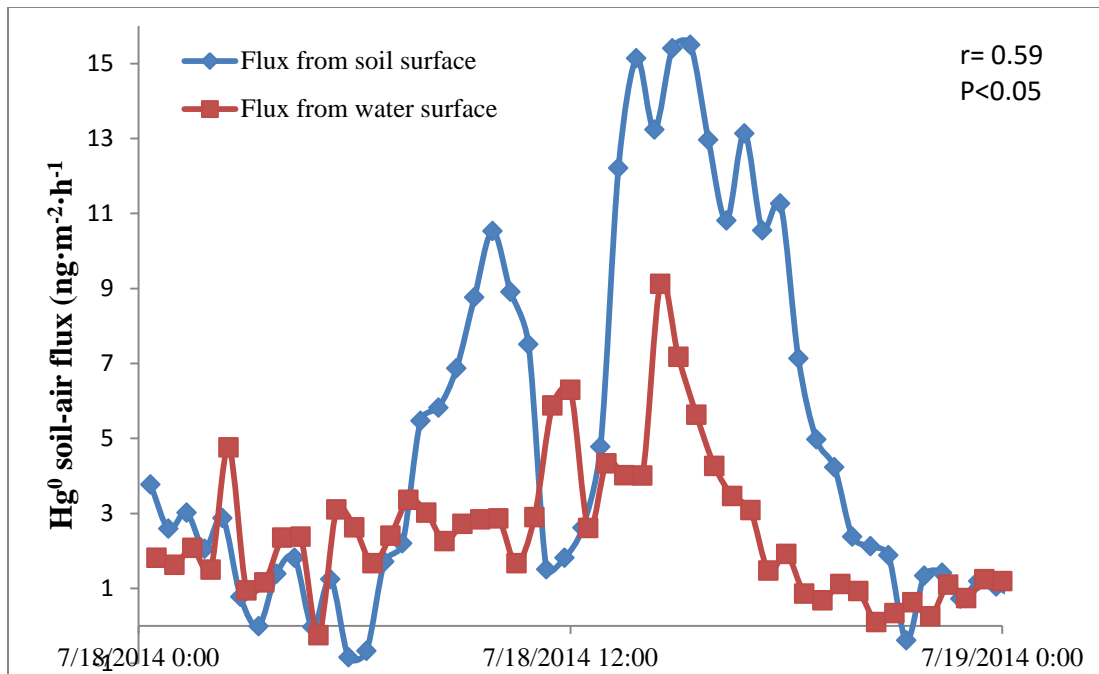
Figure 7. Hg flux from soil surface is more than water surface

Table 2. Summary statistics for soil-air and water-air Hg fluxes at the UM Field Station and Sky Lake. NA=Not Available

Site / Season	Sampling period	Hg flux soil/air (ng.m^{-2}.h^{-1})			n Emission (Deposition)	Hg flux water/air (ng.m^{-2}.h^{-1})			n Emission (Deposition)
		Range	Median	Mean ± SD		Range	Median	Mean ± SD	
Field Station / Summer	18-19 July 2014	(-0.84)-15.5	2.20	4.52 ± 4.8	50(5)	(-0.25)-9.12	1.82	2.3 ± 1.9	54(1)
Field Station / Winter	15-18Feb 2014	NA	NA	NA	NA	(-2.87)-2.58	0.12	0.12 ± 0.71	125(73)
Sky Lake / Summer	22-23 July 2014	1.74-13.11	4.10	4.92 ± 2.8	54(0)	(-0.87)-11.8	0.26	0.25 ± 0.49	37(16)

Table 3. Diurnal pattern for soil-air and water-air Hg fluxes at the UM Field Station and Sky Lake

Site / Season	Time	Hg flux air/soil (ng.m^{-2}.h^{-1})			Hg flux air/water (ng.m^{-2}.h^{-1})		
		Range	Median	Mean ± SD	Range	Median	Mean ± SD
Field Station / Summer	Day	1.51-15.5	8.13	8.27 ± 4.58	1.48-9.12	3.02	3.66 ± 1.88
	Night	(-0.84)-3.80	0.87	1.0 ± 1.15	(-0.25)-4.76	1.09	1.24 ± 1.08
Field Station / Winter	Day	NA	NA	NA	(-2.87)-2.58	0.11	0.11 ± 1.02
	Night	NA	NA	NA	(-0.66)-1.17	0.12	0.13 ± 0.25
Sky Lake / Summer	Day	2.28-13.11	5.74	6.34 ± 3.0	0.23-1.31	0.55	0.60 ± 0.3
	Night	1.74-5.26	2.81	3.13 ± 1.0	0.17-0.52	0.28	0.31 ± 1.0
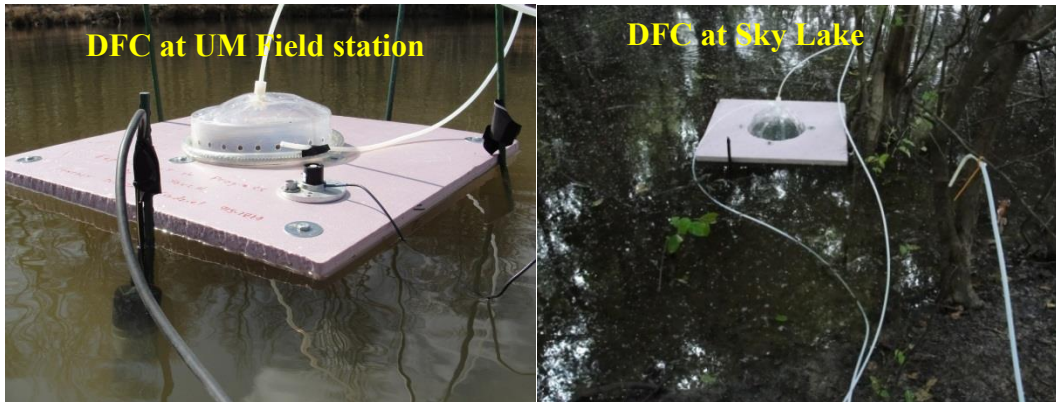
Figure 8. Experimental setup for water-air Hg flux measurements at the Field Station (left) and Sky Lake (right). Note that the dynamic flux chamber at Sky Lake is shaded due to the surrounded by foliage.

Influence of environmental factors on mercury fluxes

The greatest Hg fluxes were observed at maximum solar radiation (Fig. 9), suggesting that thermal and/or photochemical reactions are contributing to the enhanced emissions for both soil-air and water-air interfaces. Relationships between Hg fluxes and four main meteorological parameters (solar radiation, temperature, wind speed, and pressure) are plotted in Figures 10-13 and Pearson correlation coefficients given in Table 4. The strong correlation between Hg emission and solar radiation (r=0.95, p<0.05), suggests that solar radiation is a primary factor controlling Hg emissions from wetlands. Others have found photo-induced dissolved gaseous Hg correlates with incident radiation. [20] Another factor that promotes reduction of metals like Hg^{+2} in natural waters is dissolved organic carbon (DOC).[21] DOC can serve to absorb light and transfer energy to an electron acceptor, and thus enhance Hg emission in natural waters containing high levels of DOC. [22, 23] Given the high biological productivity in the swamp at Sky Lake, one would expect to find higher levels of DOC in its water compared to the Field Station

ponds. Unfortunately, the flux data from Sky Lake was highly variable, perhaps due to the forest canopy limiting radiation reaching the water surface as previously discussed, so we were unable to test this hypothesis.

Solar radiation can also enhance Hg emission by indirectly increasing the overall temperature of the soil and water. [24] The solubility and saturation potential of Hg^0 is dependent on temperature, as well as pressure and water salinity.[21] We found a significant correlation between Hg flux and temperature for soil (r=0.67, p<0.05) but not for water, suggesting that the water-air Hg exchange is driven more by photo-reduction than thermal effects. When a temperature effect dominates the evasion is thermodynamically controlled by the enthalpy of volatilization.

Mercury emission flux was also correlated with pressure (r=0.91, p<0.05), and to a lesser extent wind speed (r=0.34, p>0.05). Both can affect the dynamics of the Hg exchange at interfaces. As noted, the fluxes at Sky Lake were more variable, presumably because of the foliage resulted in solar radiation which intermittently hit the surface of the water. Thus, the correlation between Hg flux and meteorological variables for Sky Lake were generally weaker than for the Field Station (Table 4).

Typical water quality parameters (conductivity, dissolved oxygen, oxidizing-reducing potential, and water temperature) varied only slightly over the time Hg flux measurements were conducted (Fig. 14). Thus, there was little correlation between the two suggesting that these factors are not controlling gaseous Hg exchange between the air-water interfaces.
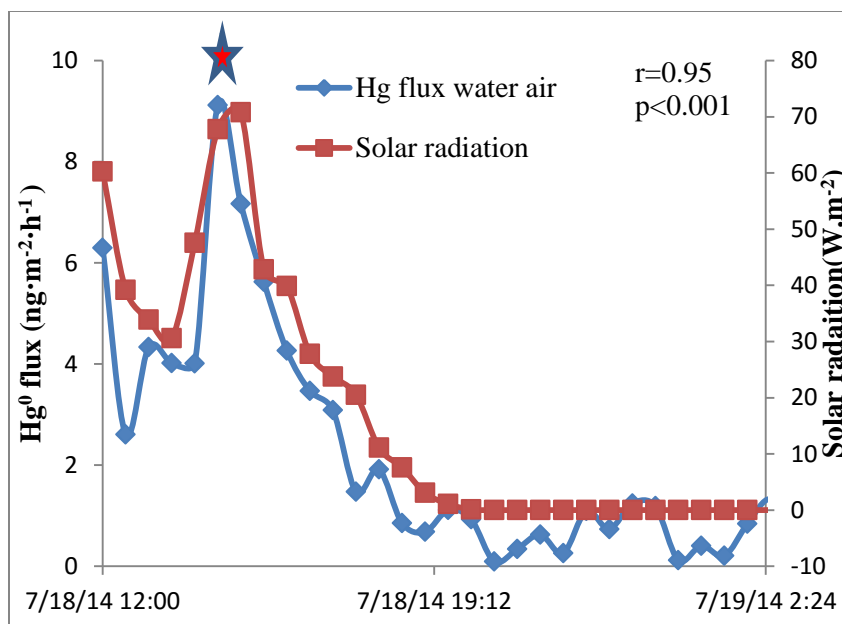
Figure 9. Mercury emissions were highly correlated with solar radiation, with the greatest flux at maximum solar radiation (star). Data shown for Field Station air-water exchange.

Table 4. Pearson correlation for Hg flux with meteorological parameters at the Field Station and Sky Lake. Red indicates r values with p<0.05.

Site	Surface	Temperature	Pressure	Wind Speed	Solar radiation
Field Station Summer	Soil	0.67	0.91	0.13	0.81
	Water	0.12	0.38	0.34	0.95
Field Station Winter	Water	0.04	-0.80	0.10	0.38
Sky Lake	Soil	0.58	0.52	0.05	0.36
	Water	0.31	0.22	0.07	0.07
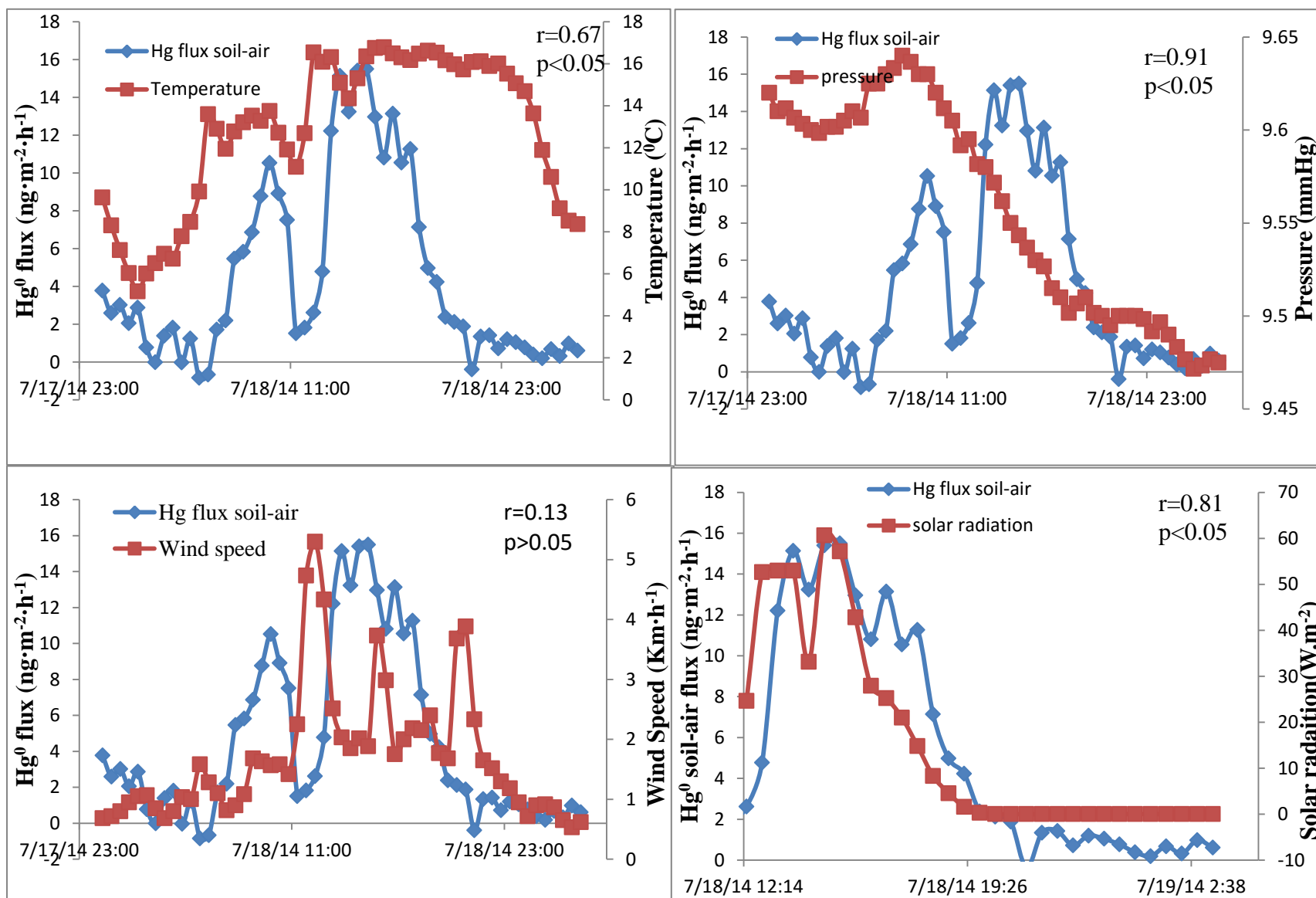
Figure 10. Relationships between soil-air Hg flux and air temperature (top left), pressure (top right), wind speed (bottom left) and solar radiation (bottom right) at the UM Field Station.
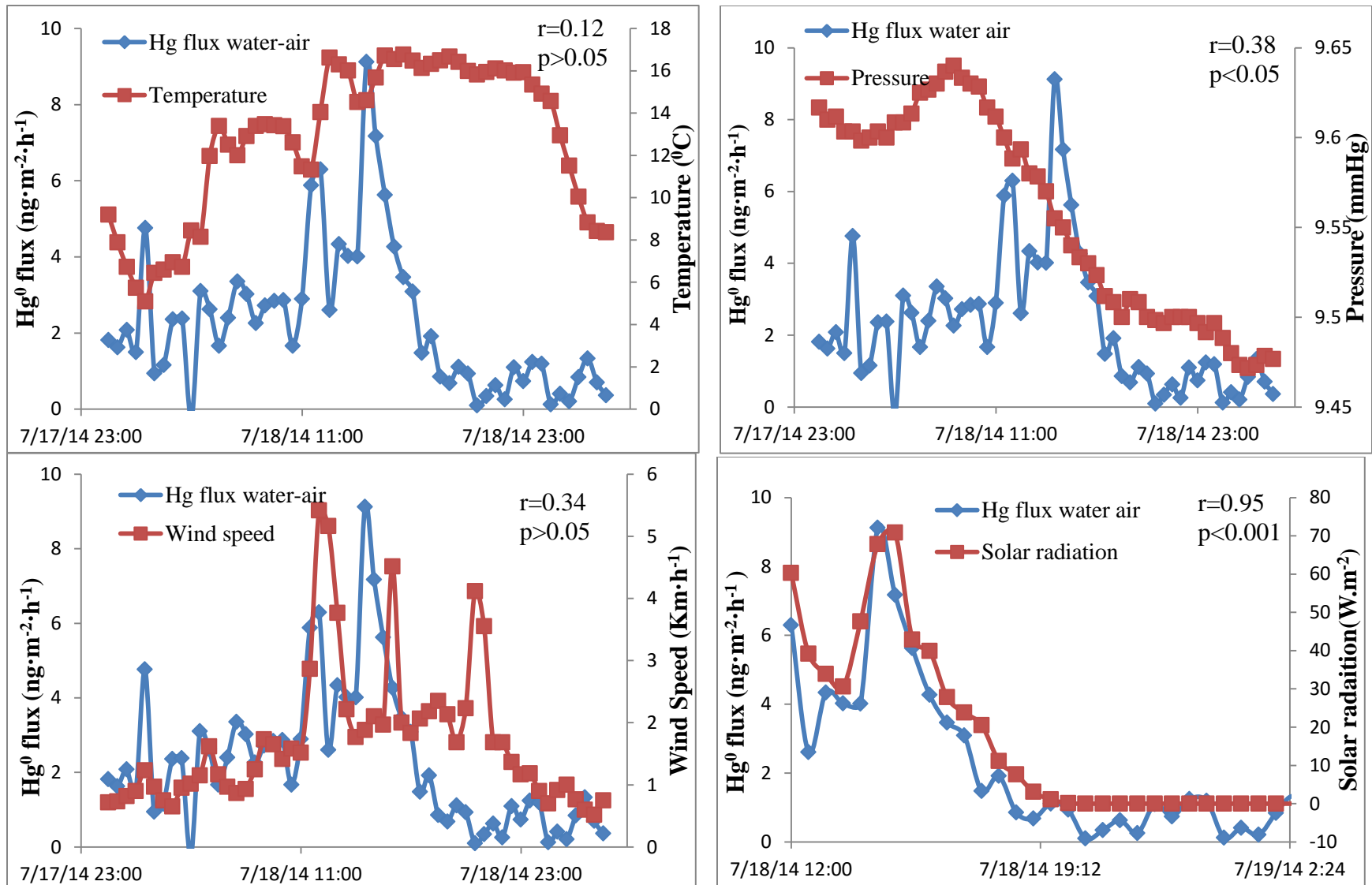
Figure 11. Relationships between water-air Hg flux and air temperature (top left), pressure (top right), wind speed (bottom left) and solar radiation (bottom right) at the UM Field Station in summer.
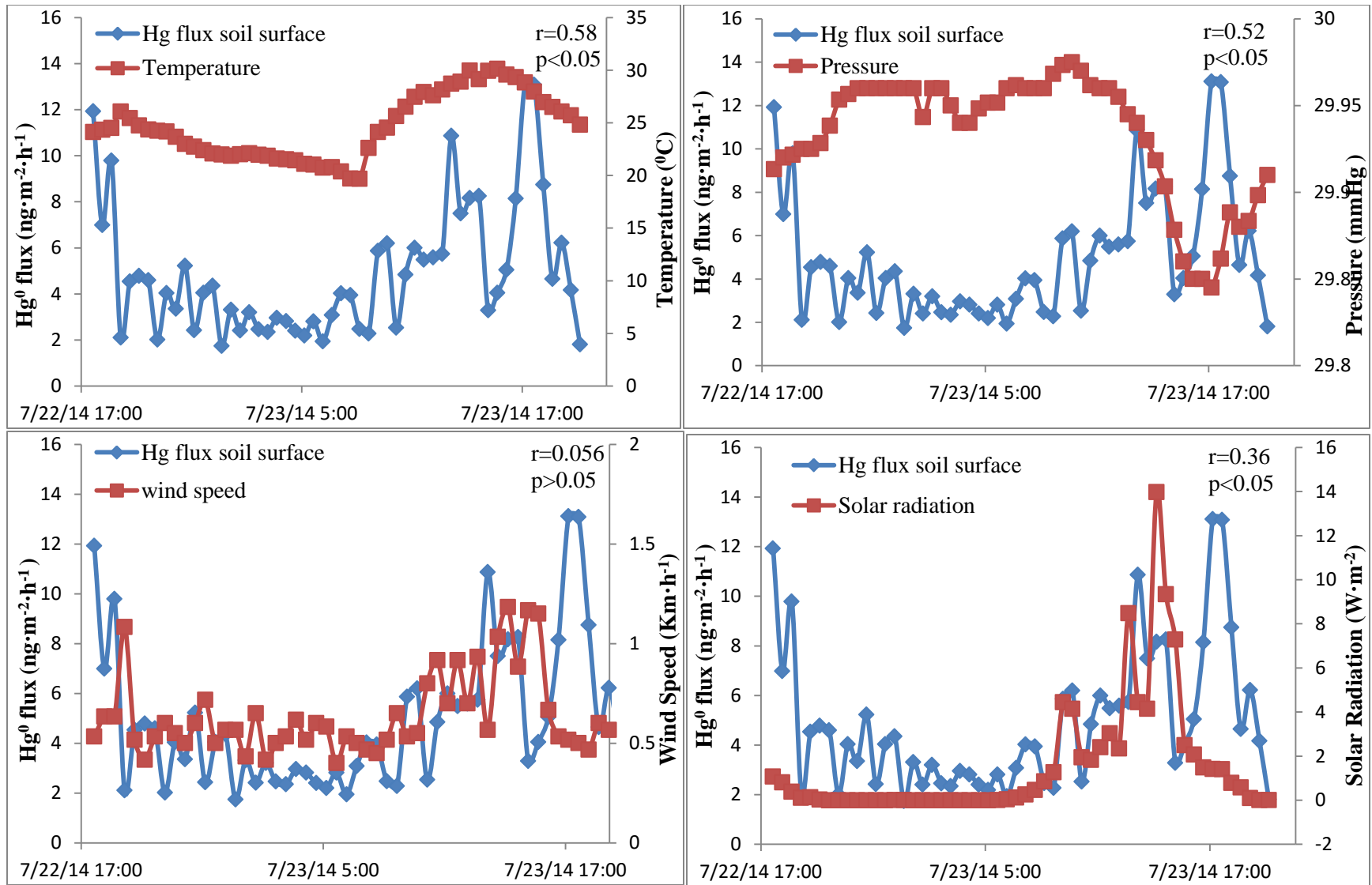
Figure 12. Relationships between soil-air Hg flux and air temperature (top left), pressure (top right), wind speed (bottom left) and solar radiation (bottom right) at Sky Lake in summer.
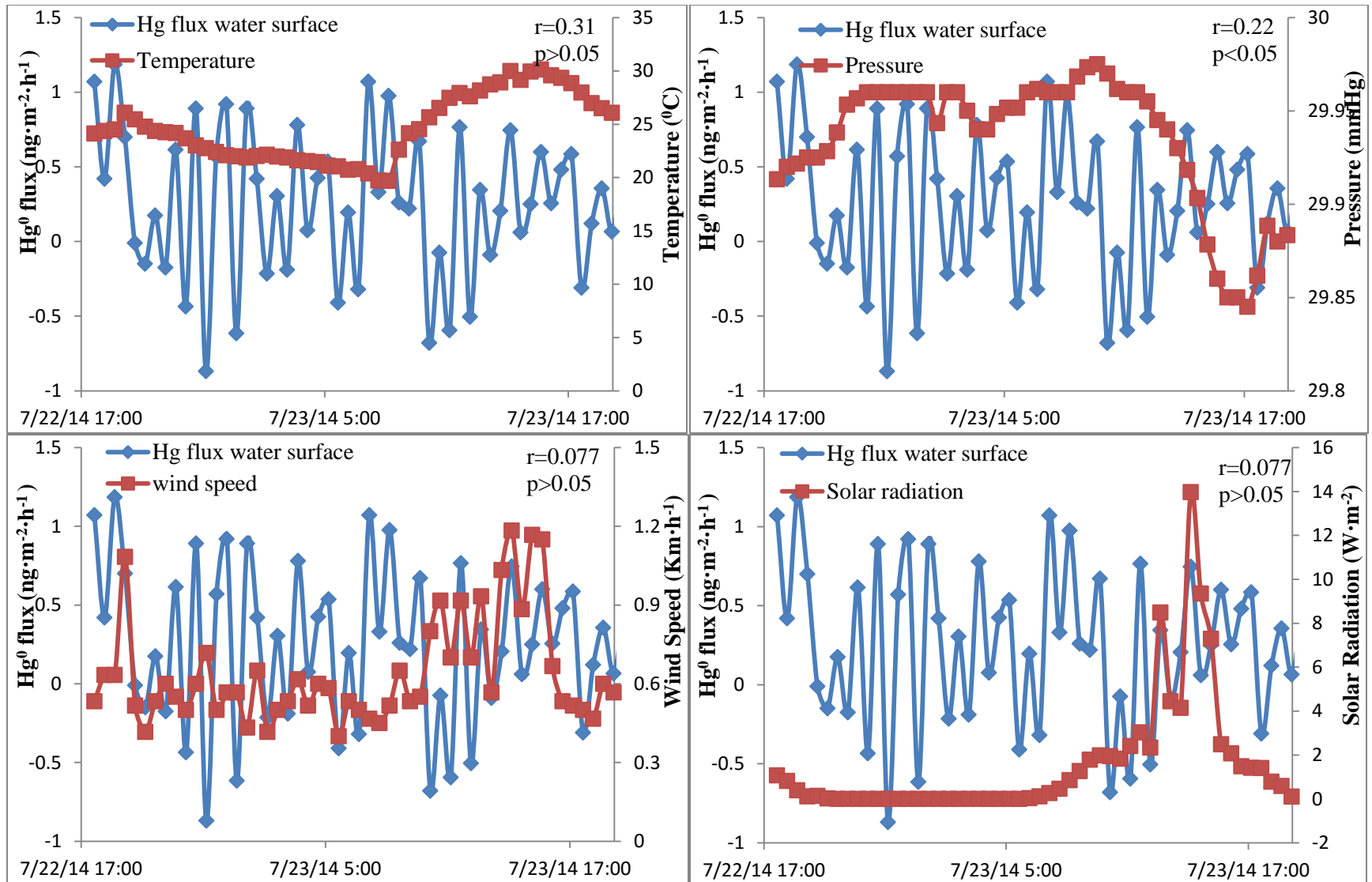
Figure 13. Relationships between water-air Hg flux and air temperature (top left), pressure (top right), wind speed (bottom left) and solar radiation (bottom right) at Sky Lake in summer.
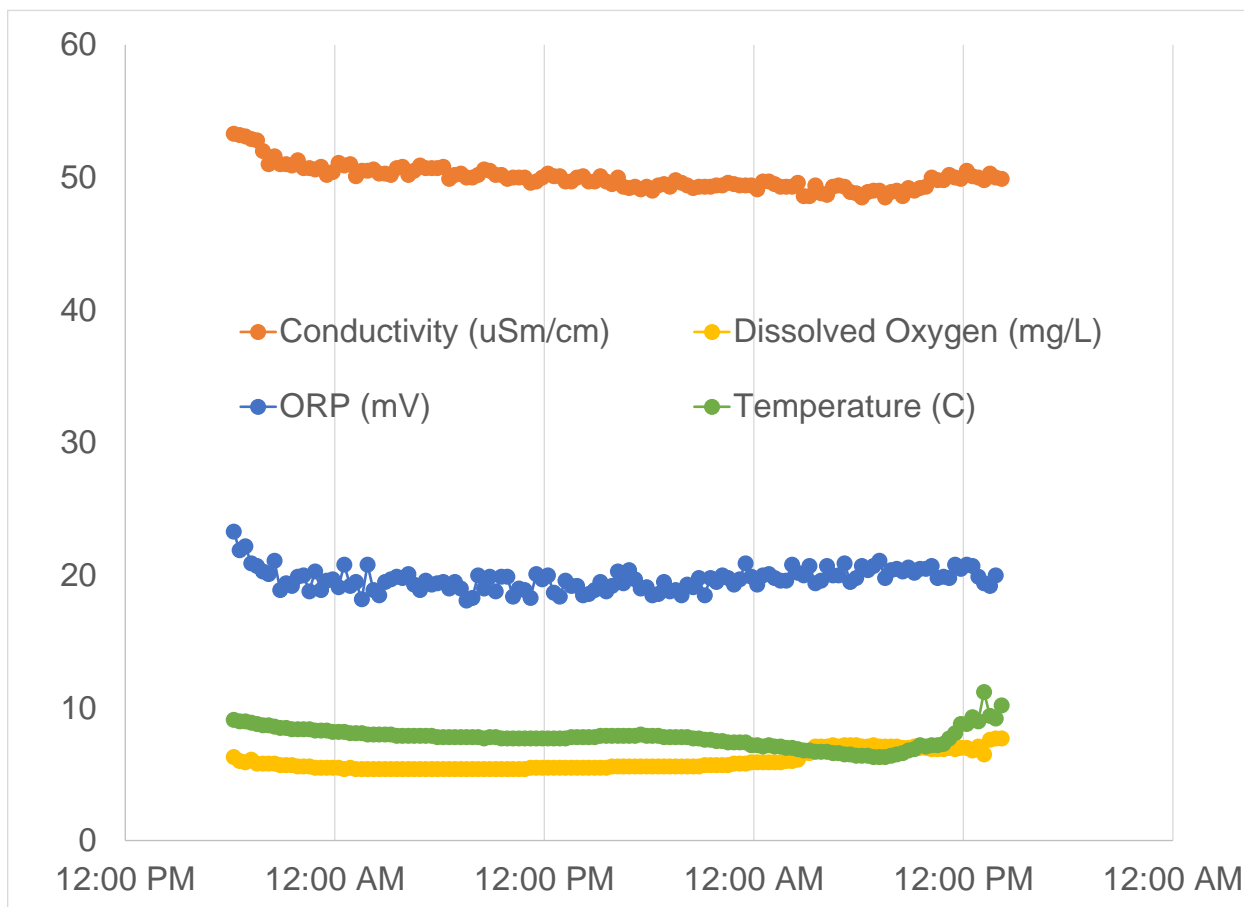
Figure 14. Variation in typical water quality parameters collected concurrently with Hg fluxes during the winter of 2014 at the UM Field Station.

Seasonal differences for Hg fluxes

Air-water Hg fluxes at the Field Station was higher during the summer compared to the winter (Fig. 15). Indeed, both day and night emission rates were higher during the summer (Table 3) suggesting that both temperature and solar radiation are contributing factors for Hg gas exchange in wetlands. In warm season, the Hg fluxes over wetland water-air ranged from (-0.25)-9.12 ng·m^{-2}·h^{-1} and the predominant flux of was emission, averaging 2.3 ± 1.9 ng·m^{-2}·h^{-1}. The flux diminished in the winter season with an average of 0.12 ± 0.71ng·m^{-2}·h^{-1}. In summer, Hg fluxes over wetland were strongly correlated solar radiation (r=0.95, p<0.05), and pressure

(r=0.91, p<0.05). In contrast, fluxes in winter were only correlated with solar radiation (r=0.38, p<0.05) (Table 4).
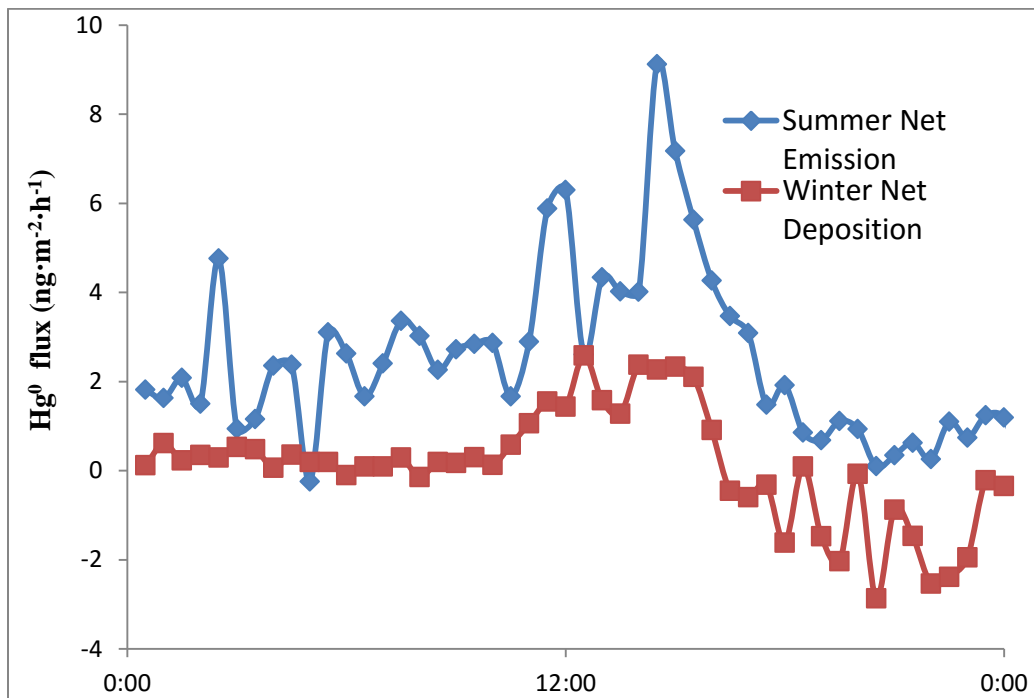
Figure 15. Seasonal differences for mercury fluxes at Field Station

CONCLUSIONS

Gaseous Hg exchange fluxes were measured using a dynamic flux chamber over wetlands at Sky Lake and the University of Mississippi Field Station. Solar flux was strongly correlated with Hg emission, with higher fluxes during daylight and lower and more stable Hg fluxes during the night. Mean ambient levels of total gaseous mercury was slightly higher at the Field Station compared to remote Sky Lake, but both were within the range considered normal for natural background. Hg flux from terrestrial (soil) surfaces was generally greater than from aquatic (water) surfaces. At Sky Lake the Hg flux from the soil was 4.92 ± 2.8 ng$\cdot$m$^{-2}\cdot$h^{-1} and from the water 0.25 ± 0.49 ng$\cdot$m$^{-2}\cdot$h^{-1}. Hg fluxes were higher during the summer compared to the winter. Overall, Hg fluxes over wetlands are dynamic, changing as dictated by environmental conditions.

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CHAPTER TWO

EFFECT OF BIOCHAR AND ACTIVATED CARBON

AMENDMENTS ON GASEOUS MERCURY EMISSIONS FROM

SOIL

ABSTRACT

Mercury (Hg) emission from soil is believed to be a major contributor to the Hg global cycle. In prior work by the Cizdziel research group, it was found that both activated carbon and biochar reduced Hg emissions from soils. However, that initial study was small-scale (grams) and yielded limited data with no flux measurements. In current study we scaled-up the experiment (kg quantities) and measured Hg fluxes using a dynamic flux chamber coupled to a continuous mercury vapor analyzer. We found that both activated carbon and biochar reduce emissions to near zero when mixed with soil at ~5% by weight. We observed that a 1-2% sorbent-soil ratio appears to be the most cost-effective approach for potential remediation purposes. While reduction in Hg emissions was size-dependent with the greatest reduction for the finest fraction (<125 μm), the larger size-fraction and crude fraction also reduced soil-Hg emissions. We also found that "capping" soil with sorbent-amended soil was effective at decreasing Hg emissions from the soil below. Overall, based on these results we suggest that field studies are warranted. In addition, other types of biochar (besides pinewood biochar) and activated carbon chemically-impregnated with I, Cl or S to enhance Hg capture could be examined.

INTRODUCTION

Mercury (Hg) occurs naturally in the environment but anthropogenic activities, such as mining, fossil fuel burning, and certain industrial processes have increased the amount of Hg present in the atmospheric, aquatic, and terrestrial systems. Three species of Hg play a particularly important role in the environment: elemental mercury (Hg^0), gaseous oxidized mercury (Hg^{2+}), and methylmercury ($MeHg^+$). Among natural sources, soils have been implicated as major contributor of Hg^0 to the atmosphere .[1] Mercury can be deposited to- and emitted from- terrestrial surfaces. Evasion of Hg from soils appears to be driven by multiple factors, such as solar radiation, soil temperature, soil moisture content, and wind speed. Emissions from soils typically exhibit daily variability and can be quite high in areas of enriched substrates. [2, 3]To minimize risk to humans and wildlife, emissions from Hg-contaminated soils needs to be controlled. One promising approach is amending soils with sorbents, such as activated carbon or biochar. Biochar is attractive as a potential remediation material because it is becoming more readily available (and less costly) as biomass fuels are explored as a component of renewable energy.

Activated carbon and biochar

Activated carbon and biochar are both carbon-rich porous, fine-grained substances. The sorbents are typically used for removing organic contaminants from drinking waters, a process that is thought to be accomplished by weak van der walls forces. [4] Biochar is formed from burning biomass in the absence of oxygen (pyrolysis) which forms charred organic matter. The low oxygen environment is what prevents combustion. The typical temperatures used to produce biochar are between 300-1000°C. Activated carbon is a term that is applied to a wide range of amorphous carbonanceous materials. Common materials to form activated carbon are nutshells, peat, wood, coal, and petroleum coke. The carbonization of the raw materials is typically at temperatures below 800°C an in inert atmosphere. The material is then activated through chemical or thermal means. Activation by chemical treatments provide an opportunity to have a more uniform surface that which can be obtained by thermal activation.[5,6] 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 (Fig. 16). The resulting van der Waals forces give the activated carbon the ability to adsorb molecules onto its surface and within the pores.[4]The major difference between activated carbon and biochar is that activated carbon has undergone treatment specifically to increase its porosity.
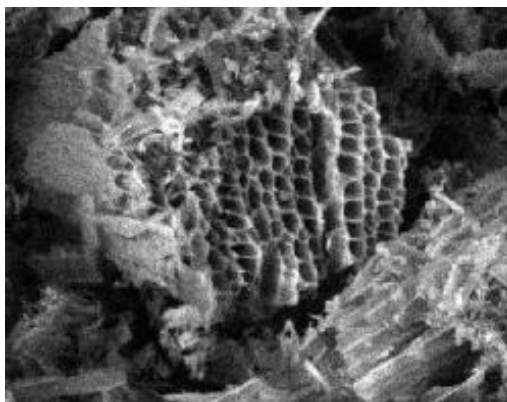
Figure 16. Activated carbon under an electron microscope.[7]

Activated carbon and biochar for remediation of contaminated soil

Activated carbon and biochar have high sorption properties and have been previously used as an *in situ* amendment for reducing pesticide residues in crops by reducing the bioavailability and/or mobility of contaminants.[8] Biochars and activated carbons have 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 $MeHg^+$.[9] A study by Gilmour[10] showed that sorbent amendments such as activated carbon and biochar can reduce Hg and $MeHg^+$ concentrations and uptake by biological organisms such as earthworms.

In prior work we found biochar decreased the gaseous Hg emissions from soil by an average of 25%, and activated carbon by 49%.[11] This difference between the two most likely attributed to higher porosity of the activated carbon due to its being thermally or chemically treated. In that initial work conducted by an undergraduate in the Cizdziel lab, three Teflon vials containing <10 g of unamended soil, amended soil, and an empty (blank) vial were fit into a hot block at 80.0°C (Fig. 17). Ultra-high purity nitrogen gas was passed through a gold Hg 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 Hg picked up by the carrier gas. The three gold traps were

analyzed using the DMA. Whereas the results were promising, the approach was produced

limited data and the experiment was run at temperatures generally not considered

environmentally relevant.

In the present work, we scaled up the work we scaled-up the experiment (kg quantities)

and measured Hg fluxes at room temperature using a dynamic flux chamber coupled to a

continuous mercury vapor analyzer. This was considered the next step to study the effects of

sorbents on Hg release fluxes from soils prior to conducting logistically challenging and

expensive field experiments.
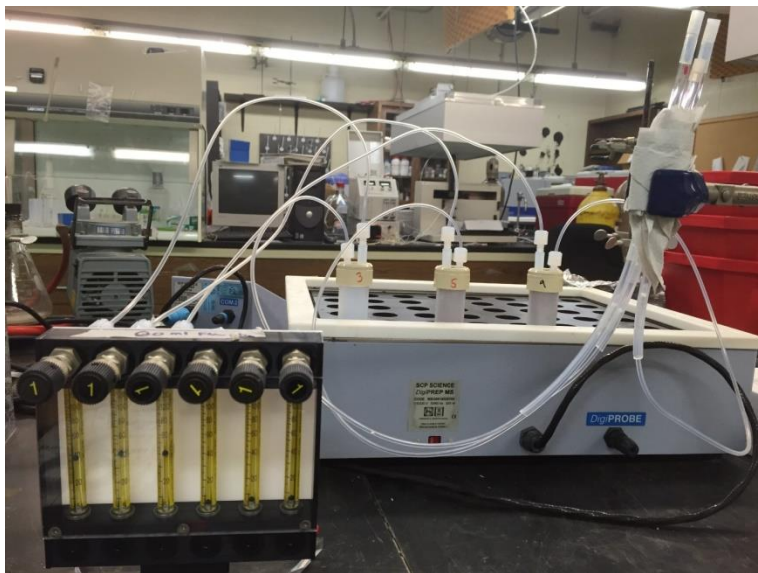
Figure 17. Initial experimental setup for pilot study.[11]

MATERIAL AND METHODS

Activated carbon and biochar, and soil 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. For biochar we used the crude material (as received) as well as biochar that was ground with a mortar and pestle and sieved. The particles in the range of 500-1000 μm and <125 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, super active collected from cotton fields in Oxford, MS.

Table 5. Particle size distribution of crude biochar used in this study

Size fraction (μm)	Weight (%)
>1000	36.4
500-1000	31.8
250-500	23.8
125-250	5.1
<125	3.0

Direct Mercury Analyzer

Total-Hg in the soil was measured using a direct mercury analyzer (DMA-80; Milestone,

Inc.) (Fig.18). Direct mercury analyzers have been described in detail elsewhere.[12] 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 Mn_3O_4/CaO-based catalyst to complete

oxidation and trap potentially interfering compounds. The elemental Hg and other products from

decomposition are carried to a gold-coated sand trap. There, the Hg^0 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 Hg vapor into a single beam spectrophotometer. The Hg

concentration is calculated based on the absorbance at 253.7 nm and the weight of the sample.
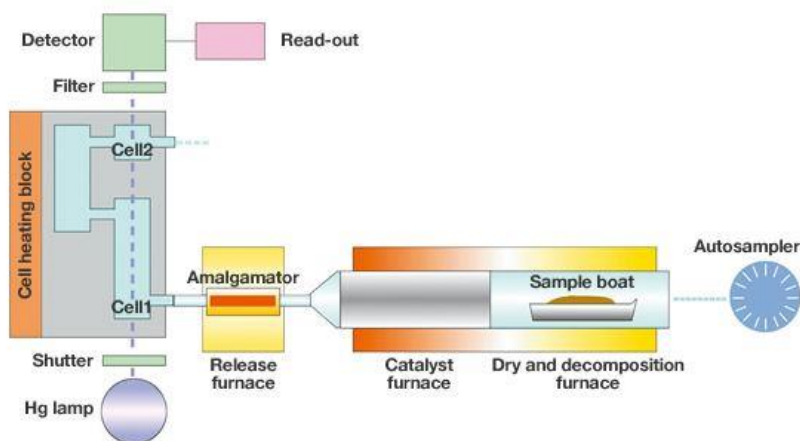
Figure 18. Schematic of direct mercury analyzer used in this study[12]

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Table 6. Direct Mercury Analyzer parameters

DMA Parameters	
DMA gas flow	200 mL min^{-1}
Drying	200 °C
Drying	60 (s)
Decomp	650 °C
Purge	60 (s)
Amalgam	12 (s)
Record	45 (s)

Mercury flux measurements

Mercury flux measurements were carried out using a Teflon dynamic flux chamber (DFC) as described previously described in Chapter 1. Briefly, a pump draws air (7.5 L min^{-1}) through teflon tubing: one connected to DFC 1 situated over unamended soil, another to DFC 2 situated over amended soil, and a third external to the DFCs in ambient air. The tubes are connected to a synchronized multiport sampler (Tekran 1115)which directs flows to the continuous Hg vapor analyzer (Tekran 2537).

About 50 grams of sorbent (activated carbon and biochar) was mixed with ~950 g of soil (yielding a 5% sorbent-soil mixture, dry weight basis), placed into aluminum trays, and covered with a DFC (Figs. 19 and 20). In addition, experiments were conducted with sorbents that were sieved <125 μm) to test the effect of surface area. Each experiment was run over ~24 hours, with a flux measurement generated every 20 minutes.
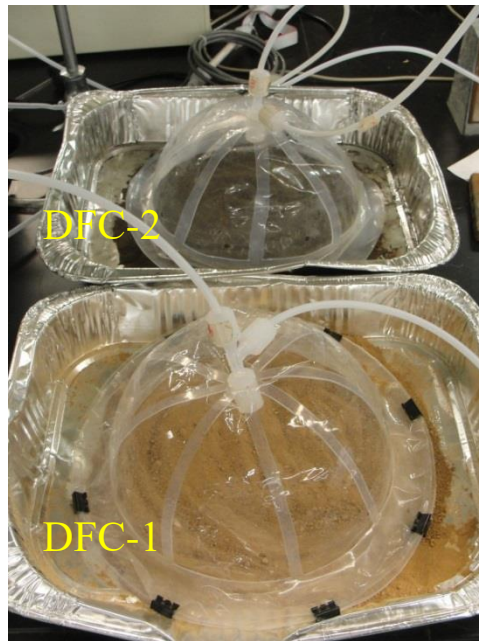
Figure 19. Amended soil (top) and unamended soil (bottom) in each tray with two DFC's continuously measuring Hg release flux from the soils.
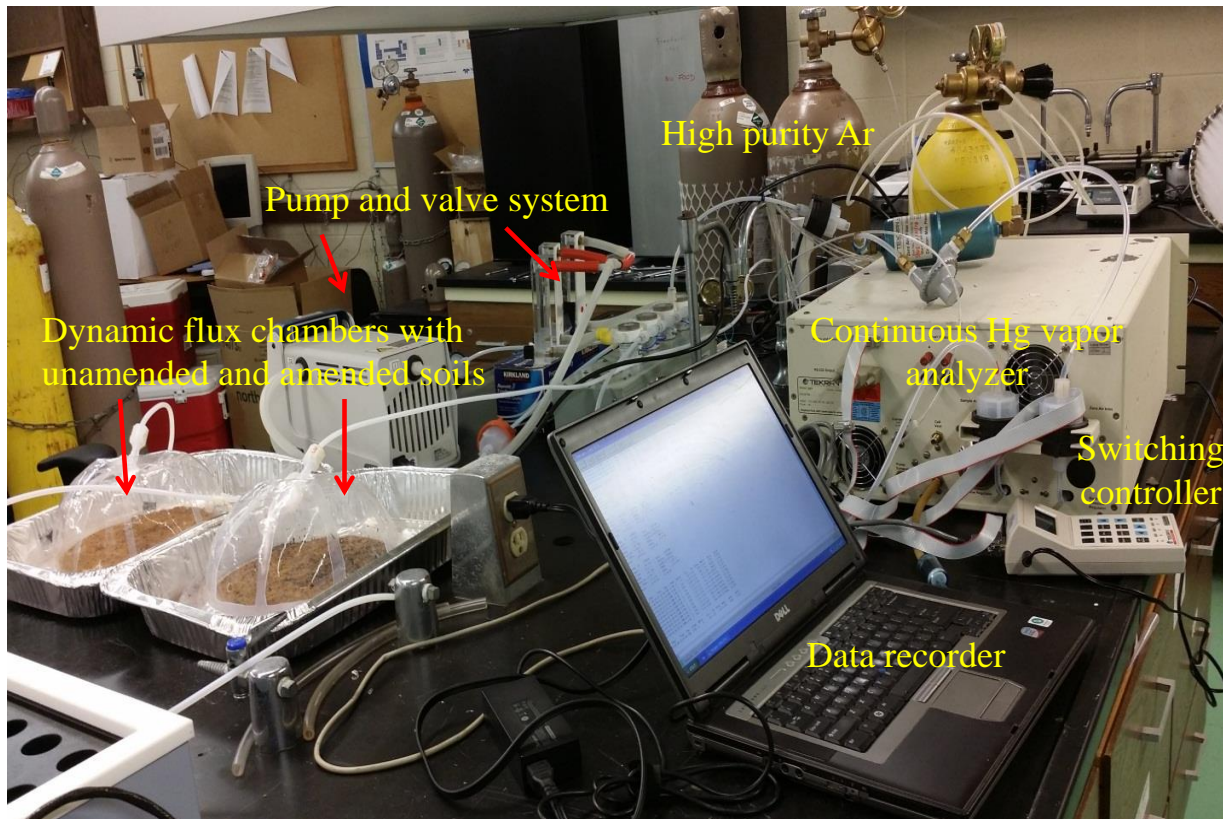
Figure 20. Experimental setup for measuring Hg fluxes over soils amended with sorbents.

RESULTS AND DISCUSSION

We first investigated the effect of activated carbon and crude biochar on Hg emissions from soil before evaluating parameters that impact those Hg release fluxes. Mercury concentration in the soil used in this study was 21ng/g and loss-on-ignition (an estimate of organic matter) was 1.1%. We found significant reductions in Hg emissions from soil amended with 5% (wt/wt, dry weight basis) for both activated carbon and crude biochar over a 24-hour period (Fig. 20). There was essentially a 100% decrease in Hg emissions from the amended soils, with the flux changing from net emission to net deposition of Hg. The observed reduction in Hg release fluxes is likely attributed to a combination of physisorption and chemisorption, with the later increasing in importance with temperature. [13] Because biochar is less expensive than activated carbon, we chose to use it for subsequent investigations into parameters impacting Hg fluxes from sorbent-amended soils.
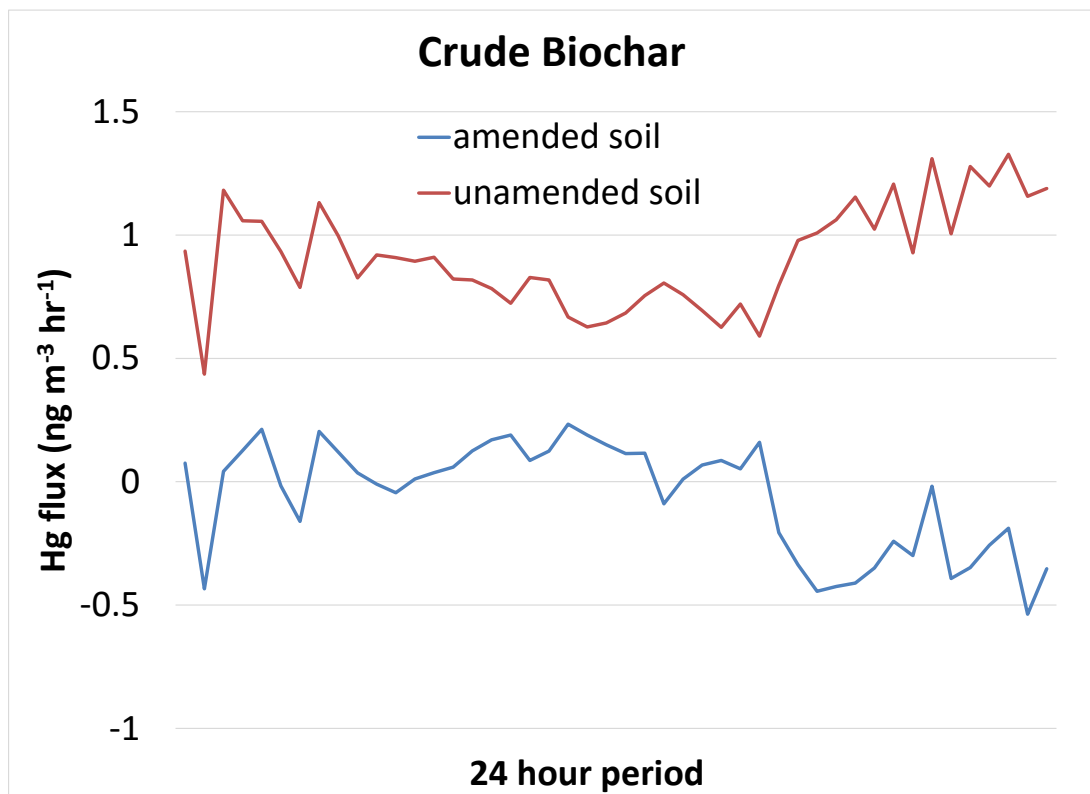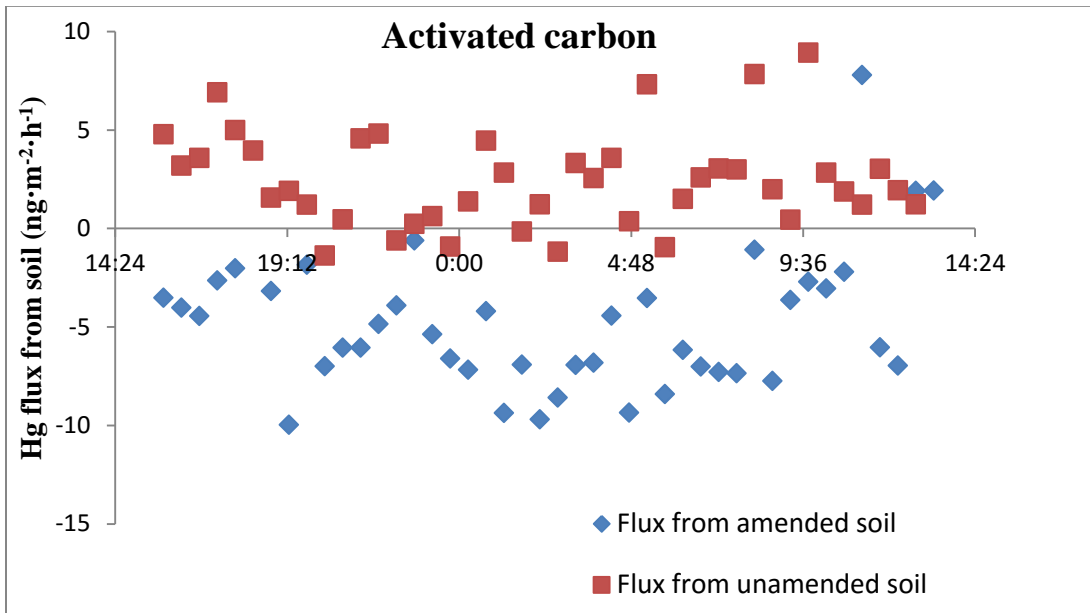
Figure 21. Mercury fluxes from unamended soil and the same soil amended with 5% (wt/wt) activated carbon (top) and crude biochar (bottom).

Effect of different size fractions of biochar on Hg emissions

Particle size distribution (and the corresponding change in surface area per unit mass) can have profound impact sorption properties. Here we studied the impact of biochar particle size on Hg emissions, focusing on size fractions between 500-1000 μm and <125 μm. While both size fractions deceased emissions, the finest fraction (<125 μm) showed the greatest reduction in soil-Hg emissions (Table 7 and Fig. 22). However, the results also show that all biochar in all sizes were equally effective at reducing Hg flux emissions (changing a net emission to a net deposition), suggesting that crushing and sieving of biochar to attain lower size fractions may not be necessary at the 5% sorbent-soil ratio.

Table 7. Effect of different size fractions of biochar on Hg emissions

| Size fraction | Hg Flux (ng· m^{-2}· h^{-1}) | | | Number of data points |
	Range	Median	Mean ± SD	
<125μm	(-1.62) - 0.04	-0.55	-0.56 ± 0.49	46
>500μm	(-0.73) - 0.01	-0.25	-0.29 ± 0.27	44
Unamended soil	(-0.43) - 0.44	0.12	0.14 ± 0.19	44
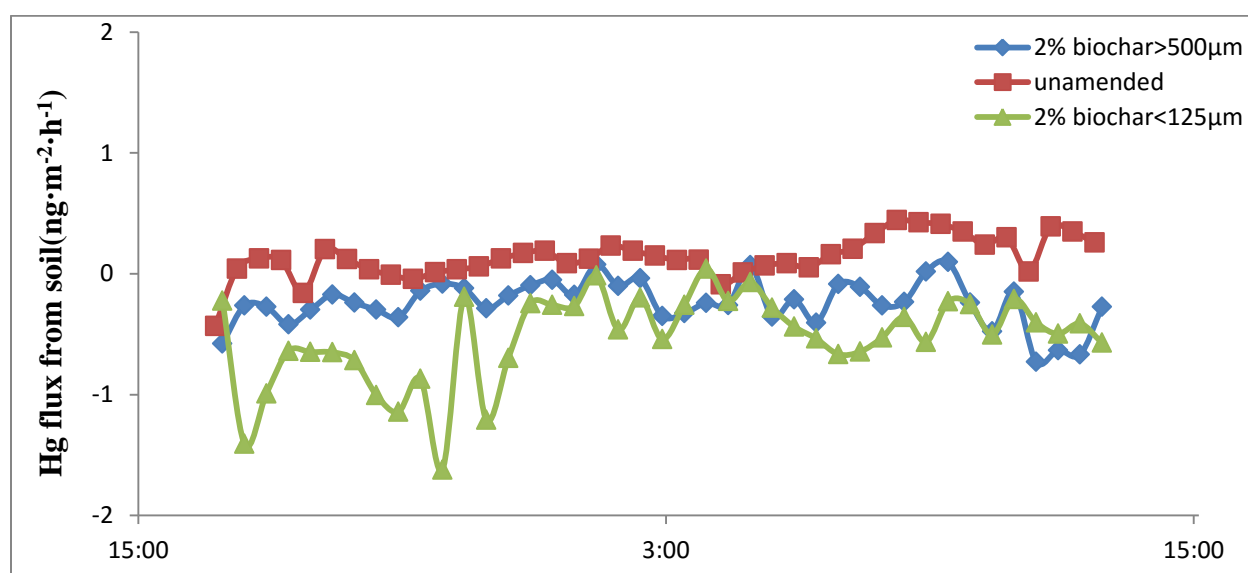
Figure 22. Hg flux from soils amended with different size fractions of biochar

Effect of soil-sorbent ratio

Soil mixed with 0.5% sorbent was not effective at lowering Hg emissions, however soil mixed at 1% and 2% was effective (Table 8 and Fig. 23). Unamended soil went from net Hg emission to net Hg deposition when mixed with 1%, 2% and 5% biochar. Hg flux for soil dropped from 0.16 ± 0.23 ng·m^{-2}·h^{-1} to -0.42 ± 0.18 ng·m^{-2}·h^{-1}, -0.56 ± 0.49 ng·m^{-2}·h^{-1}, and -0.81 ± 0.20 ng·m^{-2}·h^{-1} when mixed with biochar at 1%, 2% and 5% (dry wt), respectively. Thus, a 1%-2% sorbent-soil ratio appears to be the most cost-effective approach for remediation.

Table 8. Hg flux for soil amended with biochar at different sorbent ratios

Biochar-soil ratio	Hg Flux (ng· m^{-2}· h^{-1})			Number of data points
	Range	Median	Mean ± SD	
Unamended soil	(-0.62) - 0.67	0.15	0.16 ± 0.23	46
0.50%	(-0.21) - 0.66	0.23	0.22 ± 0.17	56
1%	(-1.01) - 0.00	-0.40	-0.42 ± 0.18	52
2%	(-1.62)- 0.04	-0.55	-0.56 ± 0.49	46
5%	(-1.16) - (-0.4)	-0.79	-0.81 ± 0.20	44
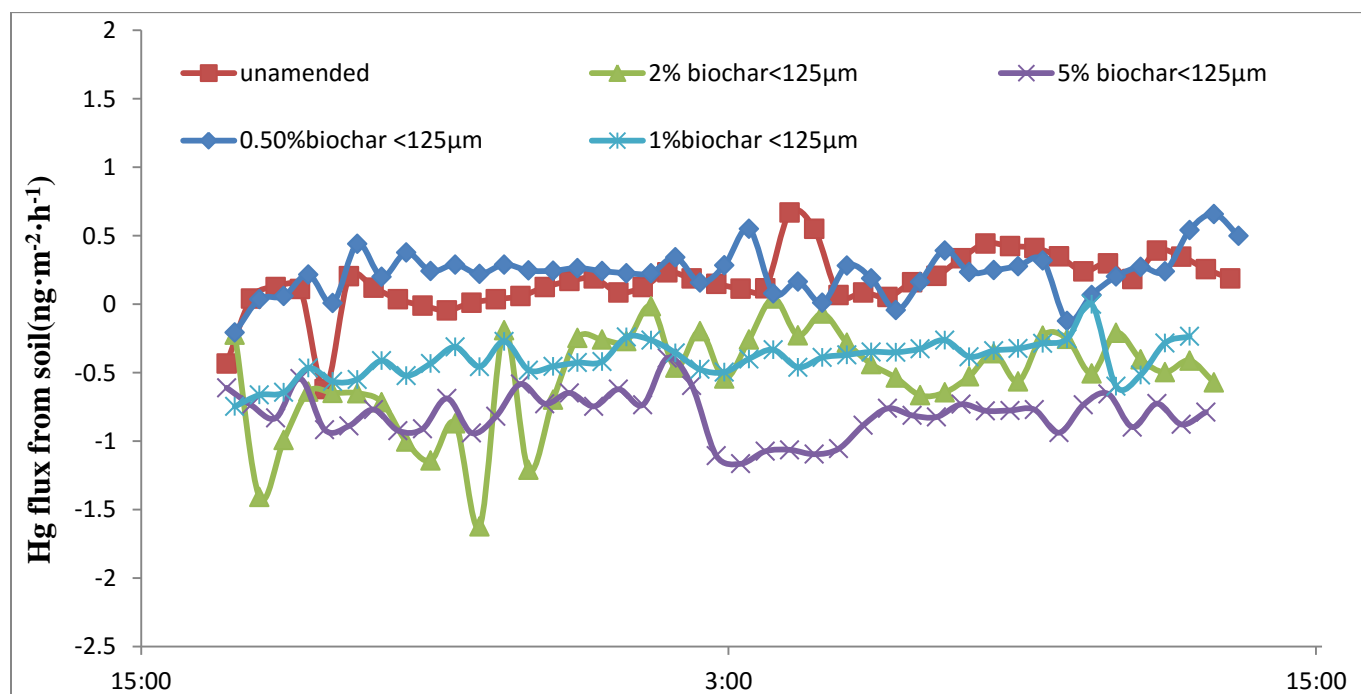
Figure 23. Hg flux from soils amended with different weight % of biochar

Does the reduction in Hg emissions decrease with time?

We measured the Hg flux from soil freshly amended with biochar, which as expected decreased the Hg flux. We then re-analyzed that same soil sample three month later (Table 9 and Fig. 24). The freshly amended soil had a mean deposition of -0.81 ± 0.20 ng·m^{-2}·h^{-1} and after three months the flux had not changed much (-0.96 ± 0.43 ng·m^{-2}·h^{-1}), suggesting the treatment continued to be effective over this time-frame. However, the impact of natural weathering needs to be addressed as this experiment was conducted in the lab.

Table 9. Effect of time on Hg emissions from soil amended with 5% biochar

Test	Hg Flux (ng· m^{-2}· h^{-1})			Number of data points
	Range	Median	Mean ± SD	
Unamended soil	(-1.90) - 2.73	0.50	0.70 ± 0.81	46
Amended soil	(-1.16.) - 0.40	-0.79	-0.81 ± 0.20	44
Amended soil rerun 3 months later	(-1.71.) - 0.22	-0.92	-0.96 ± 0.43	58
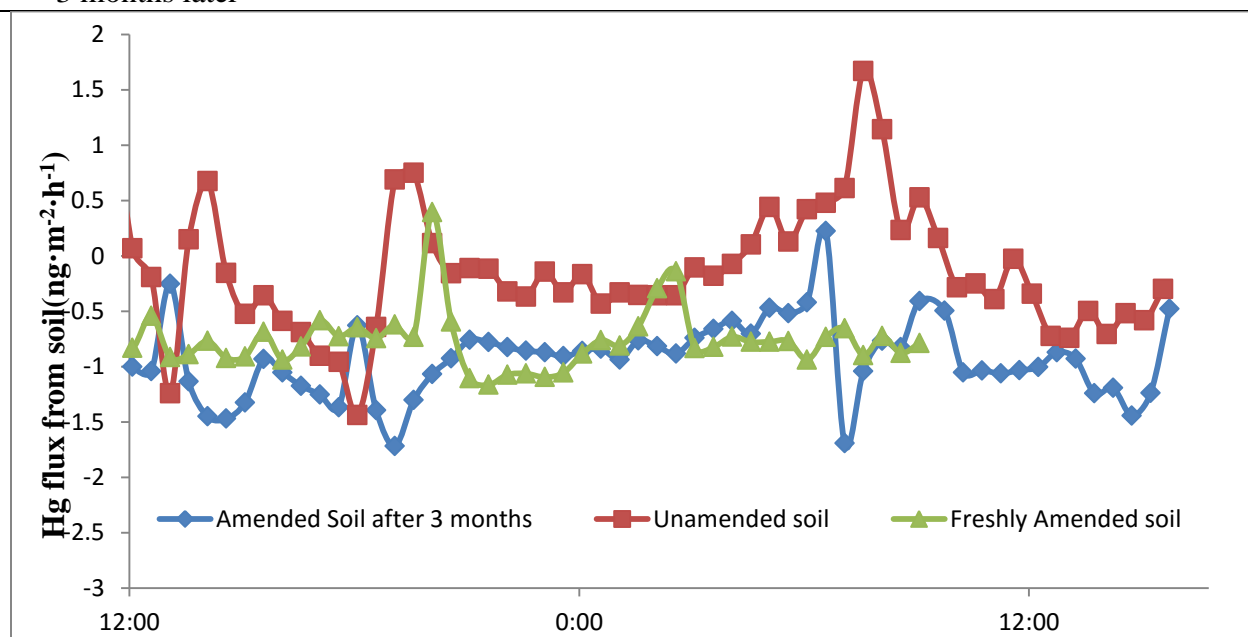
Figure 24. Hg emissions from soil freshly amended with biochar and the same material three months later, as well as unamended soil.

Does a layer of sorbent-amended soil reduce Hg emissions from underneath?

To determine whether a 1-2 cm top-layer of biochar-amended soil over unamended soil (capping) is effective at reducing emissions from the soil beneath, we measured the Hg flux from unamended soil, freshly amended soil, and the freshly amended soil placed over unamended soil (Table 10 and Fig. 25). We found that emissions from the "capped" soil were significantly decreased compared to the unamended soil, suggesting that even a small layer of sorbent amended soil may be effective at decreasing gaseous Hg emissions from contaminated soil.

Table 10. Hg flux from biochar amended soils with and without unamended soil underneath

Soil type	Hg Flux (ng·m-2·h-1)			Number of data points
	Range	Median	Mean ± SD	
A	(-1.16) – (-0.40)	-0.79	-0.81 ± 0.20	49
B	(-3.03) -(-0.36)	-1.37	-1.40 ± 0.49	48
C	(-0.44) - 0.54	0.06	0.02 ± 0.24	44

A = 5% biochar amended soil alone;
B = 5% biochar amended soil placed over unamended soil
C = unamended soil
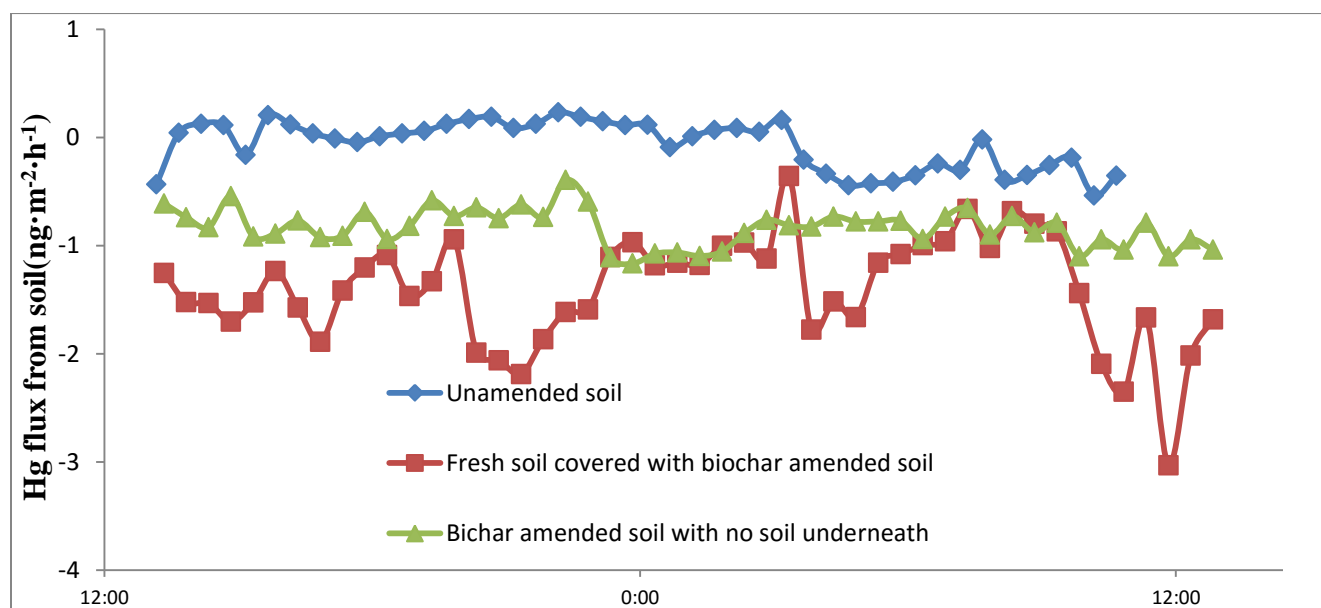
Figure 25. Hg flux from biochar-amended soil with and without fresh soil underneath.

CONCLUSIONS

Hg emissions from soils are a major contributor to atmospheric Hg levels. We tested the effect of activated carbon and biochar on Hg emissions from soil under laboratory conditions as a first step toward field studies of potential sorbent-remediation of highly contaminated soils. We observed a decrease in Hg emissions from the amended soil of essentially 100%, changing from net emission to net deposition of Hg. We observed that a 1-2% sorbent-soil ratio appears to be the most cost-effective approach for potential remediation purposes. While reduction in Hg emissions was size-dependent with the greatest reduction for the finest fraction (<125 μm), the larger size-fraction and crude fraction also reduced soil-Hg emissions. We also found that "capping" soil with sorbent-amended soil was effective at decreasing Hg emissions from the soil below. Overall, based on these results we suggest that field studies are warranted. In addition, other types of biochar (besides pinewood biochar) and activated carbon chemically-impregnated with I, Cl or S to enhance Hg capture could be examined.

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CHAPTER THREE

CONCENTRATION OF MERCURY IN WET DEPOSITION IN

OXFORD, MS AS A FUNCTION OF SEASON AND CLOUD-TYPE

ABSTRACT

The dominant pathway for new mercury (Hg) input into ecosystems is atmospheric deposition. In this study we examined the concentration of total-Hg in rain in Oxford, Mississippi as a function of season and cloud-type. Concentrations averaged 38 ± 10 ng/L in the spring and summer during thunderstorms (cumulonimbus clouds) and 6.7 ± 3.9 ng/L during non-thunderstorms (nimbostratus clouds). This agrees with the hypothesis that convective clouds (cumulonimbus) are more effective at scavenging gaseous oxidized mercury species that accumulate in the upper troposphere than rain clouds that occur are lower in altitude. The mean wet deposition rate of Hg was 19.7 $\mu g \cdot m^{-2}$, with the highest rate in April and lowest in February. The mean rate agrees with estimates from the National Atmospheric Deposition Program's Mercury Deposition Network. The data from this study will be used in an ongoing Hg mass-balance study of a nearby Hg-impacted reservoir (Enid Lake).

INTRODUCTION

The dominant pathway for new mercury (Hg) input into ecosystems is atmospheric deposition.[1] Atmospheric Hg deposition is critical in understanding the cycling of Hg, global Hg mass balance estimates, and Hg sources.[2,3] Both wet and dry deposition are important processes for the movement of Hg from the atmosphere to land and water surfaces. Wet deposition is associated with precipitation events (e.g. rain, snow), whereas dry deposition is Hg deposition in the absence of precipitation.[2] A number of researchers have estimated that direct wet deposition accounts for between 50 and 90% of the mercury entering surface waters.[4,5,6,7]

Wet deposition of Hg ranges from more than 25 $\mu g \cdot m^{-2}$ yr. in south Florida to less than 3 $\mu g \cdot m^{-2}$ yr. in northern California, and is highest in the southeast United States (Fig. 26). In addition, the average Hg concentration in rain is about two times higher in summer than in winter, and the average deposition is more than three times greater in summer than in winter. A leading hypothesis is that thunderstorms (cumulonimbus) are more effective at scavenging gaseous oxidized mercury species that accumulate in the upper troposphere compared to nimbostratus clouds.[8] Convective clouds, such as cumulonimbus, can reach upwards of 10 km (Fig. 27 & 28), whereas stratiform clouds only reach ~4 km in height. Thus, the high levels of Hg wet deposition in the southeast US may not be associated with local sources. Information on Hg in rain in the mid-south US is much more limited.

One of the most critical measurements needed to understand the biogeochemical cycle of Hg and to verify atmospheric models is the rate of Hg wet deposition. Deposited Hg can readily

be converted to methyl-Hg by microorganisms in the aquatic environment. Atmospheric deposition is considered a major source of Hg to lakes in the mid-south region.

In the present study, rain was collected in Oxford, Mississippi over the course of two years and analyzed for total-Hg. The purpose was to: 1) determine the atmospheric wet deposition rate to the region to aid in mass balance studies of local reservoirs which have fish consumption advisories due to high levels of Hg, and 2) to test the hypothesis that thunderstorms produce rain with higher levels of Hg than non-thunderstorms.
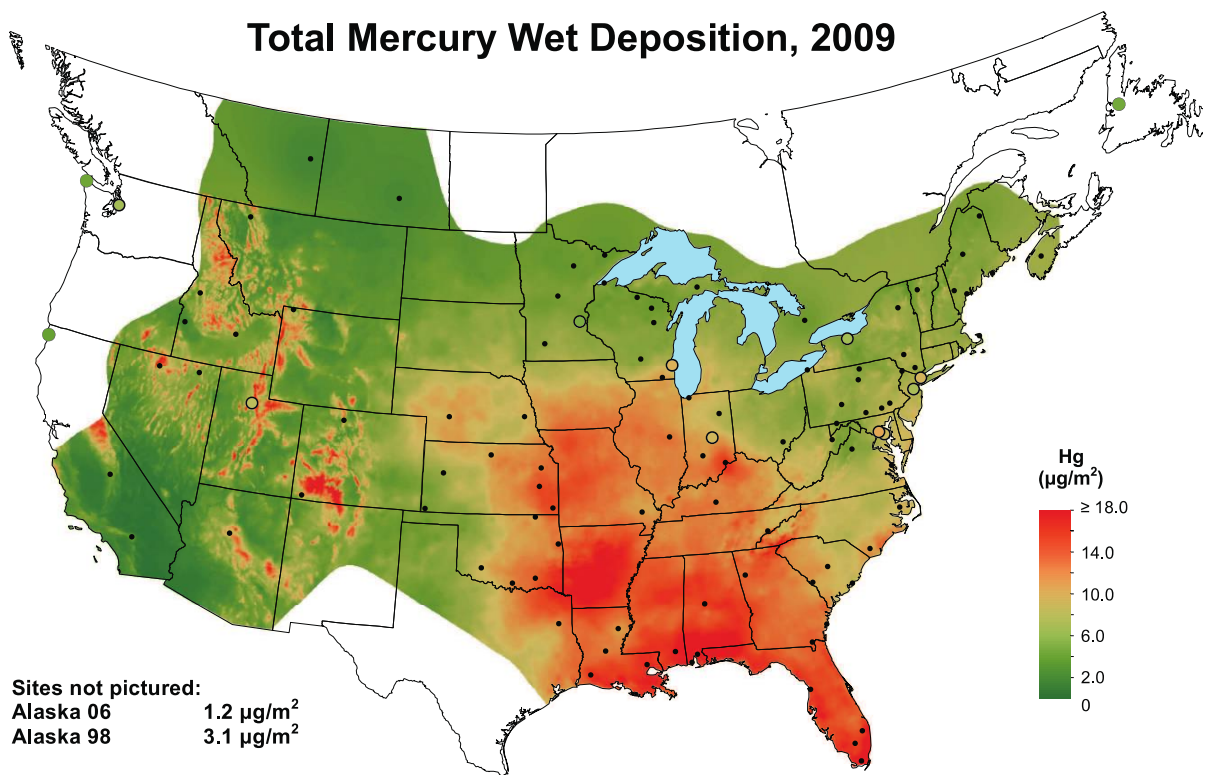
Figure 26. Total mercury wet deposition in the United States in 2009. [9]

Figure 27. Cumulonimbus cloud, taken from the International Space Station.[10]

Figure 28. Aerial view of thunderstom clouds .[10]

MATERIAL AND METHODS

Sample collection and preservation

Precipitation (rain) was collected outside the Department of Chemistry and Biochemistry at the University of Mississippi (34° 21' 57" N, 89° 31' 31" W) using acid washed 2 liter polycarbonate bottles (Nalgene®) with a 11-in diameter low-density polyethylene funnel. The setup was secured on a ring stand and placed on the site for collection (Fig. 29). The first ~100ml of rainwater was discarded. This served to further clean out the bottles and condition the bottles before collection. Once collected, samples were transferred to 50ml polyethylene tubes and preserved to 0.4% HCl using 12N HCl.


Figure 29. Rainwater collection apparatus outside of Coulter Hall on the University of Mississippi campus.

Determination of total-Hg

Rain samples were analyzed following EPA method 1631 "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (CVAFS)". [11] In short, bromine monochloride (BrCl) was used as an oxidizing agent to convert all Hg species in the samples to Hg^{+2}. The sample is reduced with hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) to destroy free halogens, followed by stannous chloride ($SnCl_2$) to reduce Hg^{2+} to Hg^0 for subsequent detection by CVAFS. Because of instrumental problems, samples from April-July 2015 were analyzed by Brooks Rand Lab using the same procedure. Data presented herein are the mean of duplicate measurements with the relative percent difference <20%.

RESULTS AND DISCUSSION

The concentrations of total-Hg in the rainwater ranged from 4.1-51.4 ng/L y^{-1} (Fig. 30). Concentrations were highest during the spring and summer (April-August; 38 ± 10) and lowest during the fall and winter (September-March; 6.7 ± 3.9 ng/L). This trend is consistent with studies in the southeast US. [12] As discussed earlier, one of the factors that impact the concentrations of Hg in rainfall is the type of cloud that generates the precipitation. Large convective summer thunderstorms (cumulonimbis clouds) routinely occurring in the southeast (and mid-south) US during the spring and summer reach relatively high levels in the atmosphere and scavenge a pool of gaseous oxidized mercury in the upper troposphere. [13, 14] The mean wet deposition rate of Hg was 19.7 $\mu g \cdot m^{-2}$, with the highest rate in April and lowest in February (Fig. 31). Wet deposition was normalized using a weighted average based on 65% likelihood of rain from thunderstorms during the warm season versus 18% during the cold season (WeatherSpark/NOAA). This is comparable to the wet deposition rate from National Atmospheric Deposition Program models (NADP, Atmospheric Mercury Network, 2009). The data from this study will be used in an ongoing Hg mass-balance study of a nearby Hg-impacted reservoir (Enid Lake).
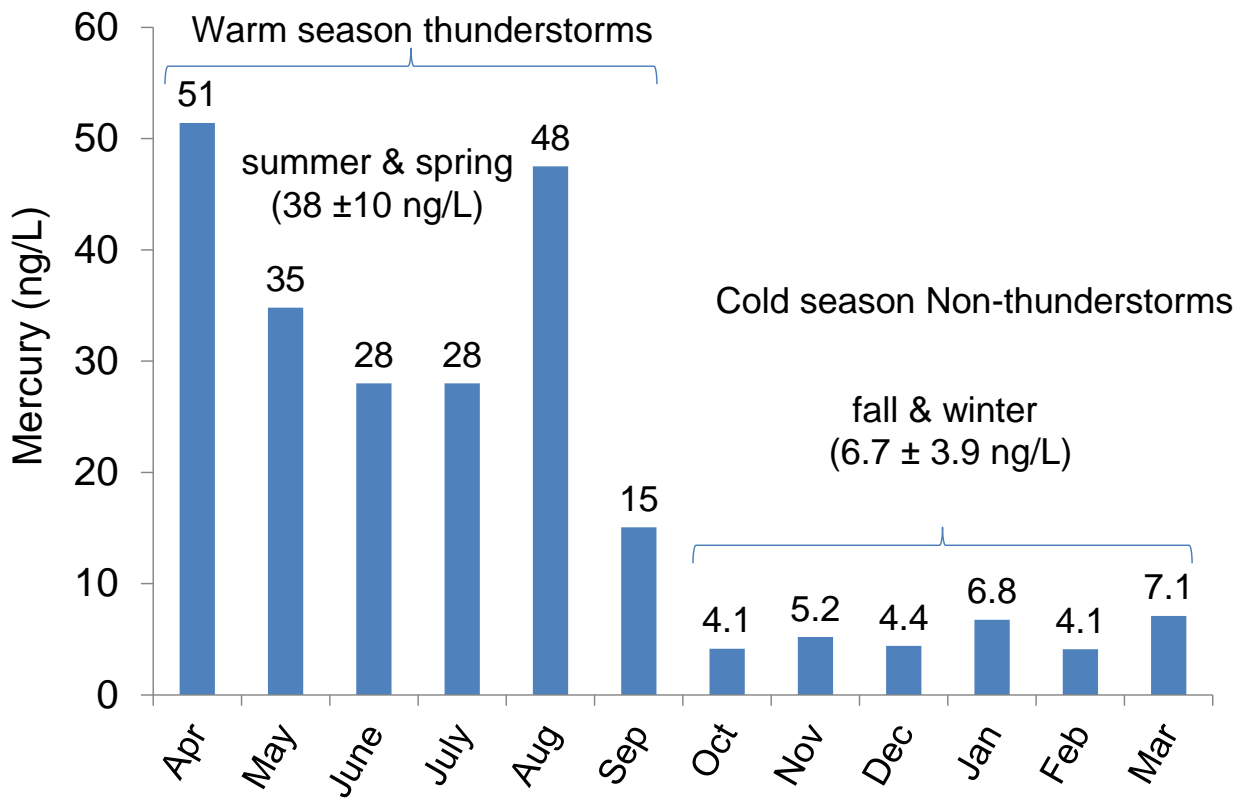
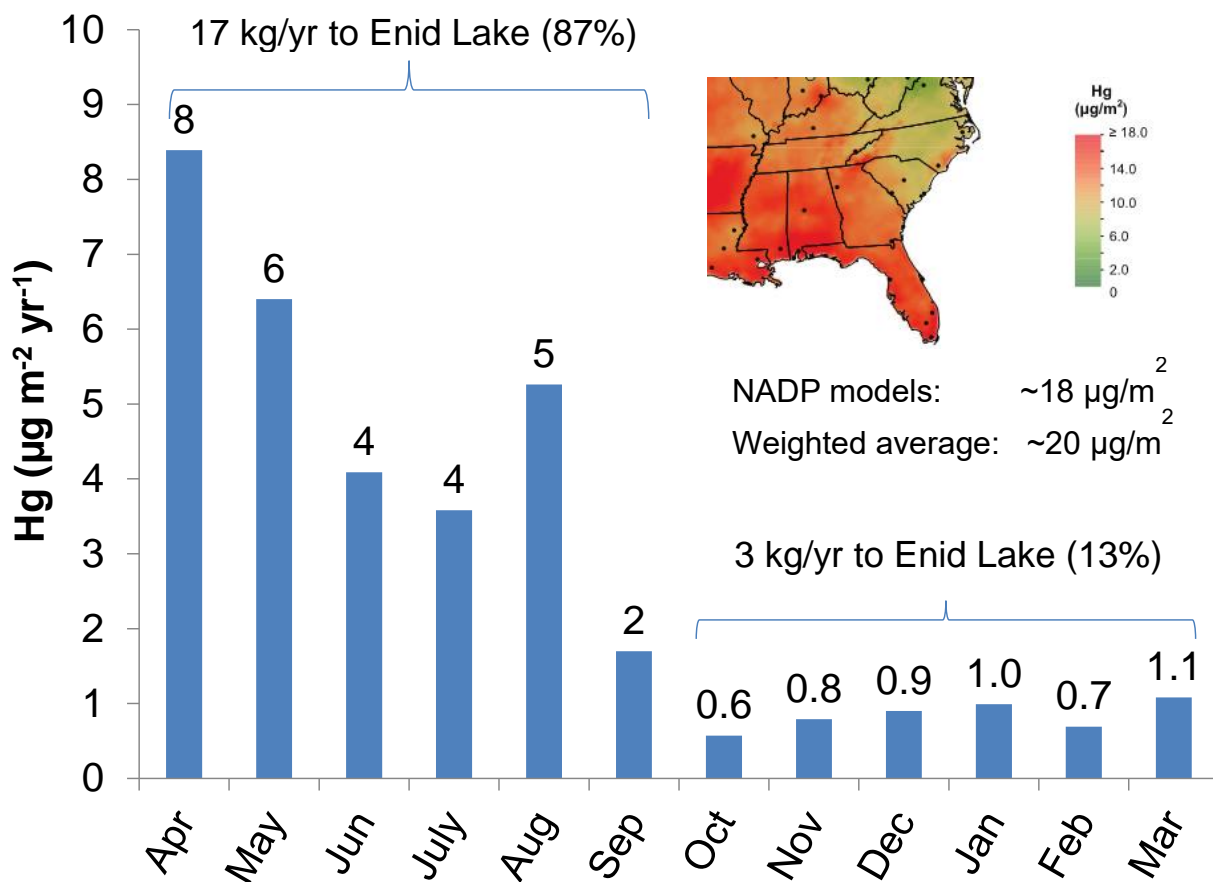**Figure 30. Total-Hg concentrations in rain in Oxford, MS during 2013-15.**

Figure 31. Raw wet deposition rate based on Hg concentrations shown in Figure 30. See text for explanation of normalized data.

CONCLUSIONS

Concentrations of total-Hg in the rain were statistically higher ($p<0.05$) in the spring and summer during thunderstorms (38 ± 10 ng/L) compared to the fall and winter during non-thunderstorms (6.7 ± 3.9 ng/L). This supports the hypothesis that thunderstorms (cumulonimbus clouds) generate rain with higher Hg levels than non-thunderstorm clouds because they reach higher altitude and scavenge gaseous oxidized Hg species that can accumulate in the upper troposphere. The mean wet deposition rate of Hg was 19.7 $\mu g \cdot m^{-2}$, with the highest rate in April and lowest in February.

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