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### Investigating the mechanisms driving mercury reduction and emissions in soil

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# **Investigating the mechanisms driving mercury reduction and emissions in soil**

A Thesis Presented in Partial Fulfillment of the Requirements for the Degree of  
Master of Science in Forensic Science

John Jay College of Criminal Justice  
The City University of New York

By

Hamil Patel

May, 2022

# **Investigating the mechanisms driving mercury reduction and emissions in soil**

Hamil Patel

This thesis has been presented to and accepted by the office of Graduate Studies, John Jay College of Criminal Justice in partial fulfillment of the requirements for the degree of Master of Science in Forensic Science.

## **Thesis Committee:**

Thesis Advisor: Dr. Anthony Carpi

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## Abstract

The water-induced emission of mercury from soil has been studied, but a complete understanding of the mechanisms driving mercury reduction and emission in soil has not been reached. The current understanding is an immediate expulsion of soil gaseous mercury upon water treatment and an upward transport of dissolved soil ionic mercury as the water evaporates. We analyzed emissions from several types of samples using various methods to further our understanding on the mechanisms involved. Light-induced emissions from aqueous samples of humic acid (HA) spiked with mercury (II) chloride ( $\text{HgCl}_2$ ) showed that at higher concentrations of HA, less mercury was emitted. Mercury emissions from a soil leachate sample was calculated to be 418.00pg compared to 1,294.45pg emitted from the water treatment of a control soil sample. Lastly, emissions from a frequently watered treatment soil sample reached a consistent amount of mercury emissions that did not increase upon additional water treatments. We believe these findings cannot be explained by published hypotheses. From these data we suspect there are additional factors, like bacterial activity, which could help give a comprehensive explanation to how mercury is reduced and emitted from soil.

# 1. Introduction

## *1.1. Introducing mercury and the mercury cycle*

Mercury is a naturally occurring metal found throughout our environment, in industrial processes, and everyday life. While concentrations vary and small amounts can be found essentially everywhere, efforts to limit human exposure are still very important. Mercury can exist in and transform between several forms such as elemental, ionic salts, and organic species. Its physical and chemical properties give it the “pre-requisites for extensive cycling among environmental compartments” (Schroeder et al., 1989). Each mercury form preferentially exists in different media: air, soil, and water, with varying mobility through the environment. This process of being transformed and transported through the environment is known as the mercury cycle. Sources of mercury in the environment include natural sources, such as volcanos, soil, water, and mineral deposits, and anthropogenic sources such as the burning of fossil fuels, fungicides (U.S. Department of Health and Human Services, 1990), industrial sources such as chlor-alkali plants (Biester, et al., 2002), and the disposal of medical equipment and electronics that contain mercury. While mercury is a natural toxic metal, human activity can, and has, influenced the mercury cycle. Thus, studying the factors that mediate mercury transformation, and mobility between mediums will lead to a better understanding of how we can limit human exposure and adverse health outcomes (Zahir et al., 2005).

The mercury cycle has three broad compartments: atmosphere, land, and water. Elemental mercury ( $\text{Hg}^0$ ) has a significant vapor pressure and is preferentially found in the atmosphere where it easily travels and is a source of long-distance contamination

(Poissant et al., 1998). In the atmosphere, oxidants such as ozone can transform  $\text{Hg}^0$  to more soluble ionic forms such as divalent mercury ( $\text{Hg}^{2+}$ ). And ionic mercury species like  $\text{Hg}^{2+}$  are easily deposited to land and water surfaces (Morel et al., 1998). In bodies of water, sulfur reducing bacteria present in the anoxic sediment layers are known (Compeau & Bartha, 1985) to methylate  $\text{Hg}^{2+}$  into methyl mercury (MeHg) which bioaccumulates in aquatic life, accounting for a large source of human exposure (Davis et al., 1997). Mercury deposited on land can be transported through watersheds into bodies of water, possibly with the aid of organic matter, where humic acid complexation may increase mercury solubility and mobility (Mierle & Ingram, 1991). This process further fuels the creation of MeHg which feeds into the aquatic food-chain and therefore increases the risk of exposure through fish consumption. Reemission back to the atmosphere, from both aquatic and terrestrial environments, is also possible if there is a mechanism for reduction, converting  $\text{Hg}^{2+}$  back to  $\text{Hg}^0$  which can readily volatilize into the atmosphere. While every step in the process is important, the processes that control soil mercury fate are particularly important and require further study as they contribute to both mercury in the air and in aquatic systems.

### *1.2. Mercury Emissions from Soil*

Early researchers were aware of the presence of mercury in the soil and its emissions to the atmosphere, but the exact mechanisms were still being studied. Siegel and Siegel (1988) performed experiments with soils at different temperatures and observed higher mercury emissions from warmer soil samples. They found that plant life may have had a larger influence when soils were below  $21^\circ\text{C}$ , but they concluded that

above 21°C the soil mercury emission behavior could be described by diffusion and vaporization. Similar results in terms of the relationship between soil temperature and emissions of mercury were found by Choi and Holsen (2009) during their field studies. They found areas with significant leaf coverage have lower soil surface temperatures and lower mercury emissions compared to similar soils with less leaf coverage. These results showing a positive correlation between soil surface temperature and mercury emissions were also described by Carpi and Lindberg (1997), and Kim and Lindberg (1995).

Researchers have also investigated other factors that could influence mercury reemissions, like light exposure. When soils are exposed to sunlight, emission of mercury is observed to increase substantially (Carpi & Lindberg, 1997). While the effect of sunlight is difficult to separate from the inherent increase in temperature caused by solar radiation heating up the surface soil, their data showed that sunlight is the dominant factor effecting  $\text{Hg}^0$  emissions – winter  $\text{Hg}^0$  emissions at one site surpassed emissions from the same site during the summer, and a site that was physically shaded and unshaded showed significant differences in emissions despite having similar temperatures (Carpi & Lindberg, 1997).

When looking at specific regions of the electromagnetic spectrum, Moore and Carpi (2005) used filtered light to determine the role of visible light compared to ultraviolet (UV) radiation ( $\lambda = 320 - 380\text{nm}$ ). The visible portion of solar radiation ( $\lambda = 410 - 700\text{nm}$ ) did not significantly increase mercury emissions, but UV radiation was found to have enough energy to play a part in mercury reduction and emissions in soil (Moore & Carpi, 2005). Their research suggests that the higher energy UV radiation might play a large role in reducing  $\text{Hg}^{2+}$  to  $\text{Hg}^0$ , increasing the  $\text{Hg}^0$  present in the soil that

can then drive larger emissions. Furthermore, Moore and Carpi (2005) found by comparing emissions from soils held at 37°C and 47 °C in the dark to soil exposed to light and subsequently heated by the lamps to the same temperatures, the researchers could conclude that UV radiation can, independently from heat, increase mercury emissions. Quinones and Carpi (2011) further found that soil thickness correlated with mercury emissions for samples under 2cm. Samples thicker than 2 cm did not show increased mercury emissions due to the effect of sunlight, as sunlight can only penetrate a soil sample to a certain depth. These data support a light mediated reduction and emissions mechanism in soil.

Research by Choi and Holsen (2009) showed similar results in terms of increased mercury emissions due to sunlight, while focusing more on specific bands of UV radiation. They found that UV-A (365nm) had little effect on mercury from soils, while UV-B (302nm) was particularly efficient at inducing an increase in mercury emissions from soils, and UV-C (254nm) reversed the trend by causing mercury deposition to the soil, possibly due to direct oxidation or via reactions with ozone. Choi and Holsen (2009) measured the moisture content of their soils over the course of their UV radiation experiments; however, due to the variety of variables changing in a given experiment, a specific link between soil moisture content and an effect on mercury emissions could not be made. It was found, however, that water had an influence on mercury emissions from soil. The effect of water on soil mercury emissions had been known at this point (Lindberg et al., 1999; Gillis & Miller, 2000; Song & Van Heyst, 2005) but there was not a consensus in the literature as to the mechanism of this phenomenon.

### *1.3. Humic acids Influence*

The other key factors at play here could be the abiotic chemical mechanisms of mercury reduction. In this regard, humic acids (HA) are of particular interest as they are a ubiquitous group of compounds composed of highly decomposed organic materials (Kerndorff & Schnitzer, 1980; Mierle & Ingram, 1991). More importantly, their ability to transport nutrients and chelate heavy metals in the soil make them especially important in the fate of mercury. According to Allard and Arsenie (1991),  $\text{Hg}^{2+}$  can be quickly reduced by humic substances to  $\text{Hg}^0$  in aquatic systems. In this study, the concentration of humic substances, pH, and concentration of other ions were varied, and the resulting mercury fluxes were measured in aqueous solutions. They showed the addition of humic substances increased the rate of mercury reduction in water compared to a sample with no humic substances. Furthermore, this effect is strongly inhibited when they reduced “the number of available complexation sites by methylation ... indicating an intra molecular process” involving these sites on the humic acid molecule as a site of reduction of  $\text{Hg}^{2+}$  (Allard & Arsenie, 1991). At least in an aqueous environment, this shows that mercury flux is correlated to humic concentrations in water, which plays a role in mercury reduction through being an electron donor to  $\text{Hg}^{2+}$  and a key determinant of emissions from aqueous environments (Jiang, et al., 2015).

Humic acids also have an impact on mercury transport from soil to the aqueous phase. Wang et al. (1997) showed better soil retention of mercury when amended with HA, suggesting HA sequesters mercury in soil, binding it up and making it less able to leach out of the soil. Even when mercury does end up being transported from soil to

water, this sequestration relationship seems to continue as seen in Mierle and Ingram (1991). This study measured the color of runoff and water in nearby waterbodies, and measured mercury concentrations in each. As humic substances are dark compounds, a darker water color was associated with a higher concentration of humics; darker colored, and so higher HA runoff water was associated with higher mercury concentrations (Mierle & Ingram, 1991).

The binding of mercury in soil to HA was further reinforced by Luo et al. (2015) where the effects of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  (gypsum) addition to soil was studied. These types of compounds are commonly deposited from the atmosphere in areas of high air pollution (Larsen et al., 2011). If the ligand binding of mercury to HA is via ionic attraction, this bond should be able to be disassociated. Sulfate ions have a high affinity for  $\text{Hg}^{2+}$  and will compete with organic materials such as humic substances in binding with mercury. Gypsum addition to the soil decreased overall mercury transport, both via emissions into the atmosphere and transport into water. This suggests that the lower mercury fluxes into the atmosphere in the presence of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) could be due to sulfate ions preferentially binding  $\text{Hg}^{2+}$ , making it unable to be reduced and emitted, compared to the organic materials (Luo et al., 2015). Although not specifically focused on humics, Luo et al. (2015) makes a case that a chemical mechanism, especially sulfur-containing ligands, is driving  $\text{Hg}^{2+}$  binding to hinder its mobility from the soil, rather than just physical displacement of soil mercury to the surface. Yamamoto (1995) demonstrated a possible mechanism of oxidation of mercury via the binding of compounds with -SH functional groups in solution, and Luo et al. (2015) showed it could also happen in soils while also proposing a possible remediation method to treat contaminated areas.

In efforts to simplify the complex soil matrix, researchers have used a simplified matrix of sand mixed with different concentrations humic substances. Mauclair et al. (2008) set out to determine whether humics act as electron donors, providing the electrons  $\text{Hg}^{2+}$  needs in order to be reduced to the volatile  $\text{Hg}^0$ , or ligand binding agents which could inhibit the reduction of  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  as proposed by Schuster (1991). By adding increasing amounts of HA to different sand sample (0 – 5%), they showed decreasing  $\text{Hg}^0$  emissions in both light and dark conditions with increasing HA concentration (Mauclair et al., 2008). The added humic substances seemed to strongly bind the mercury, inhibiting reduction and subsequent volatilization. Another explanation is that the dark colored HA could be blocking the light from reaching all the mercury; however, as seen in Quinones and Carpi (2011), sunlight seems to influence emissions of mercury to about 2 cm in soil, which is notably opaquer than sand. In contrast Allard and Arsenie (1991) found that increasing HA in aqueous samples resulted in increasing mercury flux from water, but as that was in aquatic samples, they are not directly comparable to the HA amended sand of Mauclair et al. (2008).

#### *1.4. Water Influences*

Along with its behavior with humic substances, soil mercury also responds by producing gaseous flux upon addition of water (Gustin & Stamenkovic, 2005), and the mechanism behind this is not well understood, (Lindberg et al., 1999; Gillis & Miller, 2000; Song & Van Heyst, 2005; Gustin & Stamenkovic, 2005); a consensus as to the exact mechanisms at play was not confirmed by their research.

Lindberg et al. (1999) measured mercury emissions in desert soils before and after natural and manual rain fall events. An approximate 6-fold increase in emissions were observed between dry samples and samples after the rain event. “Possible causes of the increases in flux include soil gas displacement, desorption of  $\text{Hg}^0$  by water molecules, and desorption of  $\text{Hg}^{2+}$  and subsequent reduction in solution.” Song and Van Heyst (2005) noted a similar increase in mercury flux in response to rain events as Lindberg et al. (1999) while using ~4% - 17% vol/vol, but only measured emissions during the rain event or immediately afterwards. The emissions spike immediately started to decrease after the rain event ended. They explained that this pattern is caused by two different processes where the initial spike is caused by water pushing out the  $\text{Hg}^0$  in the “interstitial soil air space,” and the elevated mercury emissions afterwards is related to the moisture level on the soil’s surface.

Gustin and Stamenkovic (2005) took this work a step further “as the water moves into the soil, [elemental] Hg adsorbed to the soil particles is dissolved into soil gas and [ $\text{Hg}^{2+}$ ] dissolved in the soil water” (p.215). Gaseous mercury over soil samples after watering events was measured, and it was suggested that this phenomenon is driven by the physical process of water displacing or dissolving bound mercury and, as the mercury-containing soil water evaporates, the now mercury-laced solution was proposed to be drawn to the surface where it could be volatilized or reduced (Gustin & Stamenkovic, 2005). While this is a logical conclusion, it only describes a method for transportation of mercury vertically through the soil. Once the mercury (II) chloride ( $\text{HgCl}_2$ ) is at the surface there must be a secondary mechanism to actually reduce it to  $\text{Hg}^0$  that can be emitted in gaseous form. Possibly, this secondary mechanism could be

light-driven, as daytime mercury emissions are far greater than emissions at night in this article; or driven by biological processes, as seen in Fritsche et al. (2008) and will be discussed in the next section; however, as other studies and my own research will find, this phenomenon persists even without a light source.

### *1.5. Biotic Influences*

While we have been looking at soil mercury emissions through the abiotic processes, other researchers have looked at it from a biological angle; however, results are even less clear in these cases. Soil bacteria's ability to oxidize Hg has been shown (Choi & Holsen, 2009), suggesting bacteria have an important role to play in the mercury cycle.

Frescholtz and Gustin (2004) showed evidence against a biological mechanism of action because there was no equivalent rise in CO<sub>2</sub> emissions when Hg emissions rose. This does, however, ignore anaerobic bacteria. Choi and Holsen (2009) fill in the gap by showing that different soil compositions support different types of bacteria. More aerated soils, as the name suggests, are suitable for aerobic bacteria as these soils contain sufficient oxygen for metabolism and tend to have more oxidizing enzymes (Choi & Holsen, 2009). Choi and Holsen (2009) found that aerobic soils tend to have lower Hg emissions and higher deposition rates. Heavy, clay-rich soils have low oxygen and therefore foster anaerobic bacteria which could use mercury reductase to convert ionic mercury to elemental (Schlüter, 2000), and so higher emissions would be expected compared to more aerated soils.

Fritsche et al. (2008) later showed a positive relationship between Hg and CO<sub>2</sub> above soil samples for experimental factors such as increased moisture and temperature. In the same study they found that sterilizing via autoclaving has some effectiveness of reducing both CO<sub>2</sub> and Hg emissions after water additions, furthering the idea that bacteria play a role in soil mercury reduction.

### *1.6. Current Research*

Our lab has a particular interest in clarifying the factors that determine soil mercury's fate in the environment. My research aims to tease apart a few of these variables and help inform future research directions. Several sample types were analyzed, including: aqueous solutions of HA and HgCl<sub>2</sub>, soil leachate samples, and unaltered soil samples that were watered at different intervals. Previous research in our lab showed a strange pattern of enhancement of mercury emissions upon multiple water additions in the dark, seen in Chapter 3, Figure 5. No previous explanation is satisfactory in describing this data. A physical mechanism of Hg<sup>0</sup> movement from the soil, as suggested previously (Gustin & Stamenkovic, 2005; Lindberg et al., 1999), does not explain the increased response we see over the first three water additions for the multiple water addition experiment (Figure 5) as the pool of mercury in the soil should have only gone down and a lower response would be expected.

An avenue for exploration is that water chemically alters some factor in the soil to make Hg<sup>2+</sup> more easily reduced, and this effect increases with water additions. Ciavatta and Grimaldi (1968) showed that HgCl<sub>2</sub> hydrolyzes in presence of water and can form an oxide; however, this oxide will revert back HgCl<sub>2</sub> once the sample is dried. We

hypothesized that after each watering either soil mercury, or compounds in the soil would change in a way (like a hydroxide formation in response to water) to make the mercury more easily reducible, and thus result in higher emissions upon subsequent water additions. Another explanation might be that mercury adhered to soil particle surfaces could be, with the addition of water, redistributed (Gustin & Stamenkovic, 2005) onto organic molecules like HAs (Mierle & Ingram, 1991, Wang et al., 1997). Ligands on HAs could have intramolecular interactions (Mauclair et al., 2008), leading to electrons being donated to reduce  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  (Allard & Arsenie, 1991). If this transport and subsequent reduction is facilitated and controlled by the presence of water, this could be a possible mechanism to explain this seemingly potentiation of mercury emissions on subsequent water additions.

Focusing on the interaction between mercury and humic acid, by measuring mercury emissions from solutions of  $\text{HgCl}_2$  and HA, we see its effect on mercury reduction without the complex matrix of soil complicating the equation. As we see those multiple factors such as temperature, light, organic matter, bacteria, and water have a role to play we also need to consider the interaction between these variables. As light intensity increases the temperature will follow. As organic matter and water increase so does microbial activity. The research in this thesis attempts to tease apart some of these variables to further fill in a more complete picture of the mechanisms controlling soil mercury's fate in the environment.

Both soil and aqueous samples of humic acid amended with a precise amount of  $\text{HgCl}_2$  were held in various conditions as we measured gaseous emissions of elemental mercury leaving the Teflon lined chambers that held each sample. We measured

emissions from humic acid samples while illuminating them with simulated solar radiation. Mercury emissions were integrated over time to get the total mercury emissions for each concentration of humic acid. We analyzed leachate samples using a similar methodology and compared the results with a soil sample under the same conditions. Another way we researched soil mercury emissions is by varying the amount and time between water additions. In this frequently watered soil sample, the amount of water was adjusted to only return the soil water content (SWC) to its initial value at the start of the experiment and this was performed before the samples were completely dry. This was then compared to soil that was allowed to dry completely before reintroducing water. Across these various experiments we aim to further understand how mercury transport can be attributed to a complex mix of differing mechanisms.

Soil mercury emissions are important to the mercury cycle and may contribute to contamination concerns and human exposure (Selin, 2009). It is vital to understand the factors that influence the transportation and transformation of mercury in our environment to inform policies to limit damage to ecosystems and reduce our exposure to mercury.

## 2. Methods and Materials

### *2.1. Humic acid samples*

Humic acid (HA) samples were prepared by adding humic acid sodium salt (60 %-Alfa Aesar, Ward Hill, MA) and a solution of mercury (II) chloride ( $\text{HgCl}_2$ ) to reverse-osmosis (RO) water. All samples contained the same volume (4.5mL), and concentration of  $\text{HgCl}_2$  at 0.1144 ppm. This was prepared by diluting a mother solution of concentrated  $\text{HgCl}_2$  (~19.8 ppm), generated by dissolving  $\text{HgCl}_{2(s)}$  (Sigma-Aldrich) in

RO water. The  $\text{HgCl}_2$  mother solution was kept sealed in the dark at room temperature, with the current concentration determined using a Direct Mercury Analyzer (DMA-80, Milestone) immediately prior to preparation of humic acid containing  $\text{HgCl}_2$  solutions, as discussed in the Instrumentation and calculations section below. HA was dissolved from a solid, humic acid sodium salt, with enough RO water to create the appropriate dilutions between 0.01 and 0.50 % w/w. Serial dilution was used when a balance could not accurately measure smaller amount of HA for the 0.01 and 0.02% w/w HA samples.

Humic acid containing  $\text{HgCl}_2$  solution was pipetted as 9 x 500  $\mu\text{L}$  droplets onto a clean Teflon lined tray in a 3 x 3 grid array, using a graph paper template with appropriate measurement markings under the Teflon sheet to ensure consistent droplet spacings between trials. Teflon, or PTFE, is extensively used throughout this study because it is non-reactive to a wide array of compounds, including mercury and its various species and is translucent and stable under ultraviolet radiation (Ferry et al., 1996).

Prepared samples were irradiated with simulated solar radiation from a solar simulator type lamp system (Sun 2000, Abet technologies). Mercury measurements from the air leaving the chambers were recorded using the Tekran 2537X. Sample temperature was controlled using a cooling plate attached to a recirculating heating/cooling device containing ethylene glycol (Thermo Fisher Scientific RTE 7). The temperature was set to 14°C to offset the influx of heat by the solar simulators, and surface temperatures measured with an infrared thermometer, (Fisher Scientific, Pittsburgh, Pennsylvania) to ensure a sample surface temperature of 25°C.

## *2.2. Soil Samples*

Soil samples for this study were collected from a residential area in Connecticut, stored in zip top bags, and kept at 2 °C when not in use. Soil was spread in a thin layer on a large plastic lab tray to air dry in a dark room under a laminar flow hood for at least three days. Air dried soil was then sifted to remove larger debris and mixed to homogenize. Air dried homogenized soil was stored in an amber glass bottle and stored at -20°C prior to use in experiments.

For an experimental run, 64.2g of soil was weighed onto a 0.002 inch thick Teflon sheet lined metal tray in a uniform layer of 10.6 cm diameter and 2.0 cm thickness. A Teflon lined paper collar was used to confine the soil to the desired area, and a new collar was used for each sample. A small portion of each sample was withheld, and total mercury content measured by the Direct Mercury Analyzer (DMA-80) to ensure soil samples from different collection batches had similar concentrations of mercury.

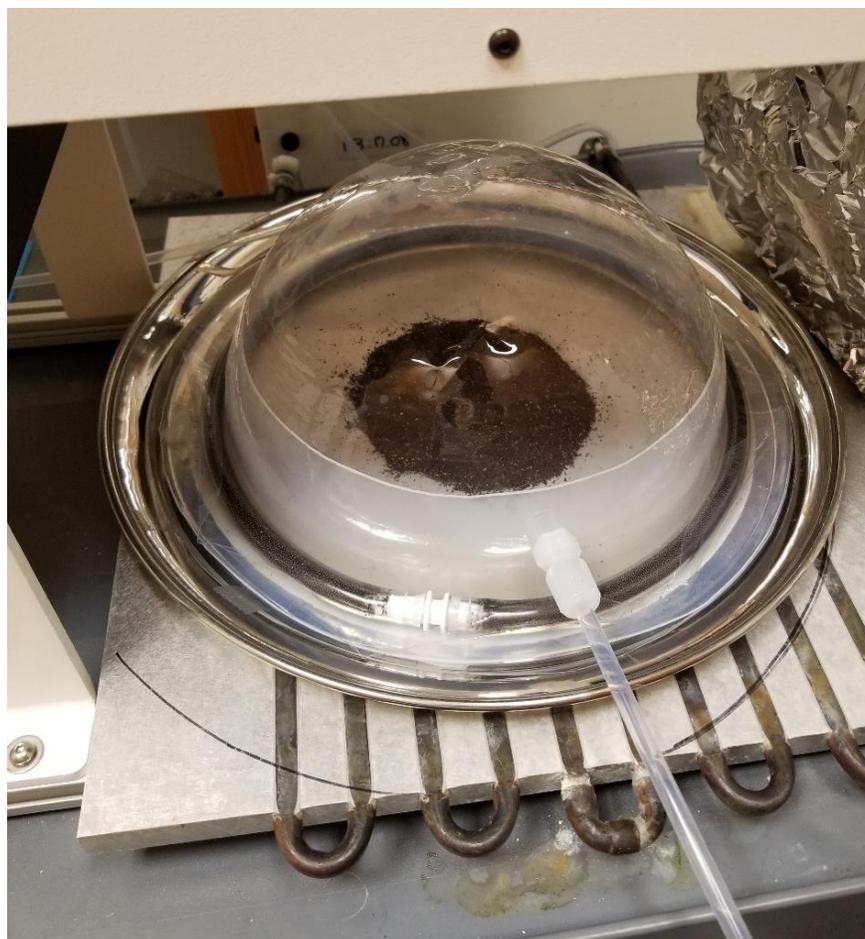


Figure 1. Experimental set-up showing a soil sample in a dynamic flux chamber, John Jay College, New York (own photo).

Prepared samples were placed under a semi-spherical Teflon dynamic flux chamber. Chambers were based on those used by Kim and Lindberg (1995) and are a modification of those used later by Carpi and Lindberg (1998), and Carpi et al., (2007). Briefly, the flux chamber is a dome of 24.2 cm diameter and ~2.4 L internal volume. Chambers consist of a thin Teflon film over a thicker Teflon ring. A weighted ring was placed around the base of the chamber and acted to prevent the introduction of room air into the chamber, (see in Figure 1). Air was introduced to the chamber through Teflon tubing ( $\frac{3}{8}$ " inner diameter,  $\frac{1}{2}$ " outer diameter) from a zero air generator (Tekran, Zero Air

Generator, Model 1100), which produced mercury-free air (mercury  $< 0.1\text{ng/m}^3$ ). Having a steady, clean source of air allowed for greater precision, and eliminates environmental factors like ozone and ambient mercury background levels from influencing our measurements. Soil sample temperature was controlled using a cooling plate attached to a recirculating heating/cooling device (Thermo Fisher Scientific RTE 7) set at  $25^\circ\text{C}$  in dark conditions, and  $14^\circ\text{C}$  when irradiated with a Sun 2000 solar simulators (Abet technologies, Milford, Connecticut). Mercury analysis was performed using a Tekran 2537X as discussed in the Instrumentation section below.

### *2.3. Soil water addition*

For water addition experiments, reverse osmosis (RO) water was applied to the prepared soil sample while the Tekran 2537X was not actively sampling the air under the chamber. The sample was removed from the chamber, and the desired mass of water was added, as determined by a Mettler Toledo balance (Mettler Toledo, XS800TL). A spray bottle was used to apply the water to the surface of the soil taking care to evenly cover and minimize disturbing the soil surface. Once wet, the sample was replaced into the chamber at 30 seconds prior to the beginning of the sampling cycle for that chamber. Every water addition was performed in the same manner.

### *2.4. Leachate samples*

Leachate samples were prepared by mixing RO water and soil at a 2:1 ratio in a clean Pyrex bowl. This slurry was mixed for 60 seconds every 5 minutes for a total of one

hour, and then vacuum filtered through a fritted glass filter to separate the leachate from solids. A 64.2 g portion of leachate was immediately poured into a 90 mm polystyrene petri dish and placed under a flux chamber. Total mercury concentrations in the leachate were determined using a Tekran 2600; see methods below.

### *2.5. Instrumentation: Tekran 2537X*

The Tekran 2537X is a cold vapor atomic fluorescence spectrometer (CVAFS) that we used to determine mercury flux from samples by measuring concentration of elemental mercury in the air and using known measurements to calculate flux. Air is pulled in from the flux chambers into the instrument where it passes through a gold coated sand trap. Mercury vapor forms an amalgam with the gold trapping it in place. After the sampling time the instrument switches to the other chamber as it heats up the gold trap, decomposing the amalgam and releasing the mercury back in vapor form. Argon gas is used to carry the gaseous mercury into a spectrometer where it absorbs ultraviolet light produced by a bulb and fluoresces at several wavelengths. Fluorescence is measured at 253.7nm and is used to calculate mercury concentrations. The instrument performs daily automatic calibrations. Several hours of zero mercury measurements were left between samples or experimental variables to prevent one sample or variable to influence readings on the next sample.

The instrument provides a concentration in air ( $\text{ng}/\text{m}^3$ ) and fluxes ( $\text{ng}/\text{m}^2/\text{h}$ ) were calculated using the steady state equation:

$$F = (C_0 - C_i) Q / A$$

where  $F$  is steady state flux ( $\text{ng}/\text{m}^2/\text{h}$ ),  $C_0$  and  $C_i$  are mercury concentrations ( $\text{ng}/\text{m}^3$ ) in air at outlet and inlet respectively,  $Q$  is the flushing flow rate ( $\text{m}^3/\text{h}$ ), and  $A$  is the surface area ( $\text{m}^2$ ) of the sample (Kim & Lindberg, 1995). After flux measurements were determined, they were recorded and graphed with respect to time. Summations of flux measurements over a specific time-period, and after unit conversion, can be used with to determine mass of mercury emissions in response to an experimental variable like light exposure of water addition as discussed previously.

A programmable controller (Tekran 1115 Controller) with a 4-port valve system (Tekran 1115 Valve) was used to allow a pair of samples to be analyzed from two flux chambers concurrently on the same instrument. The instrumental sampling time was 5 minutes, and each chamber outlet was sampled twice in succession before switching to the other sample. While a sample was not being actively analyzed the line still had the same volume of mercury-free air moving through it to prevent stagnation or buildup of mercury vapor.

## *2.6. Solar simulators and Jaz Spectroradiometer*

To replicate sunlight, we used pairs of Sun 2000 solar simulators (Abet technologies, Milford, Connecticut), with appropriate filters to supply consistent and uniform radiation to a 35 x 35 cm square. To ensure consistency between trials, measurements were taken across the visible, UVA, and UVB spectra using a Jazz Spectral Analyzer (Ocean Optics, Dunedin, Florida). The average across 5 readings taken throughout the experiment between samples are seen in Table 1, below.

Table 1. Sun 2000 solar simulator output power measured for each range of radiation shown as an average of 5 measurements using Jaz Spectroradiometer

Radiation category	Wavelength range (nm)	Average Power (W/m <sup>2</sup> )	Standard deviation
Visible	390-700	104	2.62
UVA	315-400	15.6	0.88
UVB	280-315	1.40	0.04

Prior to using, the Sun 2000 it was allowed to warm up and stabilize for at least 30 min with the shutters closed. This ensures consistency in the output of visible, UVA, and UVB radiation throughout the experiment. The shutters were opened, which exposed the samples to irradiation, at the same time as the Tekran 2537X started collecting from the desired sample.

### *2.7. Instrumentation: Direct Mercury Analyzer*

A portion of each soil sample was taken, and the total mercury content was measured using a Direct Mercury Analyzer (DMA-80). Analysis started by filling nickel boats with  $0.30\text{g} \pm 0.05\text{g}$ , done in triplicate. The nickel boats were cleaned in a muffle furnace for two hours, allowed to cool and stored in that furnace. The DMA-80 was run with no boats, and with empty boats prior to experimental analysis to both further clean out mercury that may have accumulated in the instrument or boats over time and to the verify cleaning procedure was effective in eliminating mercury on the boats. Nickel boats with peaks heights above 0.005 absorbance were subjected to repeated cleaning steps in the DMA-80 as needed. Quartz boats were used for liquid samples and were cleaned with

RO water and run empty and analyzed until, as with nickel boats, under 0.005 abs mercury readings were achieved.

The DMA-80 heats these boats to dry the sample, then decomposes them at 700°C to volatilize all the mercury in a sample. The gaseous mercury is carried to a gold trap where it amalgamates. Another heating cycle releases the mercury in a more concentrated vapor to then be analyzed through atomic absorption. Measurements for each sample, obtained in parts per million (ppm), were recorded and new samples were obtained if samples did not have similar total mercury contents.

### *2.8. Instrumentation: Tekran 2600*

We used a Tekran 2600 (Tekran inc., Canada) to measure the total mercury contents of the leachate samples and the  $\text{HgCl}_2$  mother solution. This instrument, like the Tekran 2537X, is based on CVAFS; however, it is designed to analyze mercury in liquid samples. First 1mL of leachate was diluted with 23.785mL RO water and is treated with 125  $\mu\text{L}$  bromine monochloride ( $\text{BrCl}$ ) to oxidize different mercury ions in solution into  $\text{Hg}^{2+}$ . Then 30  $\mu\text{L}$  hydroxylamine hydrochloride ( $\text{HAHCl}$ ) was added to eliminate excess  $\text{BrCl}$  which could otherwise damage the instrument. The final step was to add 60  $\mu\text{L}$  stannous chloride ( $\text{SnCl}_2$ ) which reduced all the  $\text{Hg}^{2+}$  to elemental mercury ( $\text{Hg}^0$ ) in solution and seal the vials with open top caps containing a Teflon lined septum. The volatile  $\text{Hg}^0$  was then forced into the headspace of the instrument vials by introducing an inert gas, argon, into the bottom of the vial. The headspace of the vial was sampled, and the gas was drawn into the instrument and passed over a gold coated sand trap, similar to

the process that occurs in the Tekran 2537X and DMA-80 discussed above with the distinction that the Tekran 2600 used a second stage gold trap to further concentrate the mercury before it heads to the detector. All samples were analyzed in triplicate, and their averages concentrations recorded.

Reagent blanks were used to correct for any contamination of reagents. A calibration curve was made prior to analyzing leachate samples with five standards, with at least two higher and two lower than the leachate sample. A stock solution of 1000 ppm mercury (II) nitrate ( $\text{Hg}(\text{NO}_3)_2$  Fisher Scientific), stored at  $2^\circ\text{C}$ , was diluted to the appropriate calibration standards concentrations and treated with the same reagents as discussed above.

### 3. Results

#### *3.1. Humic Acid*

Figures 2 and 3 show results from a series of experiments in which various concentrations of humic acid were added to a sand substrate and then treated with 0.1144ppm of  $\text{HgCl}_2$ . Each sample had the same amount of  $\text{HgCl}_2$  with varying HA concentrations ranging from 0 to 0.5%. The amount of mercury measured in each cycle was summed over the course of the experiment to show the accumulated or running total mercury emitted over time in the figures. A zoomed graph shows more clearly the distinction between lower concentration humic acid samples (Figure 3). With increasing HA concentrations, the total amount of Hg released decreases. As time proceeds, all samples reach a static level, denoting no more mercury is being emitted by the sample.

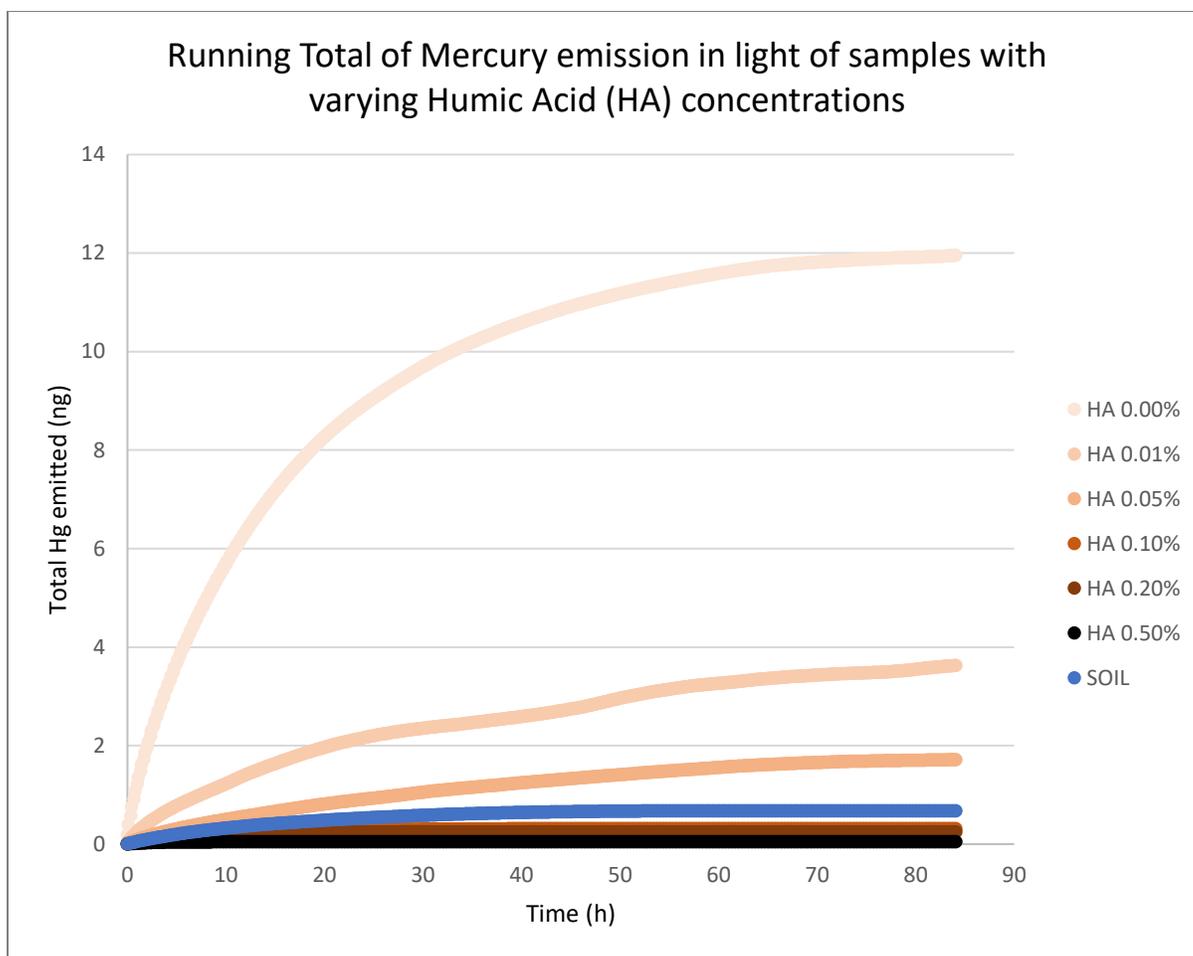


Figure 2. The sum of mercury (ng) emitted from samples containing either 0.00, 0.01, 0.05, 0.10, 0.20, or 0.50% (w/w) humic acid in water during exposure to simulated solar radiation (Abet Solar Simulator, 400-700nm = 100w/m<sup>2</sup>, 315-400nm = 14.1w/m<sup>2</sup>, 280-315nm = 1.50w/m<sup>2</sup>). Increasing humic acid (HA) concentration of a sample is shown as increasingly darker orange lines from 0.00% in the lightest shade to 0.50% in the darkest shade. An untreated soil sample is shown as a comparison in blue.

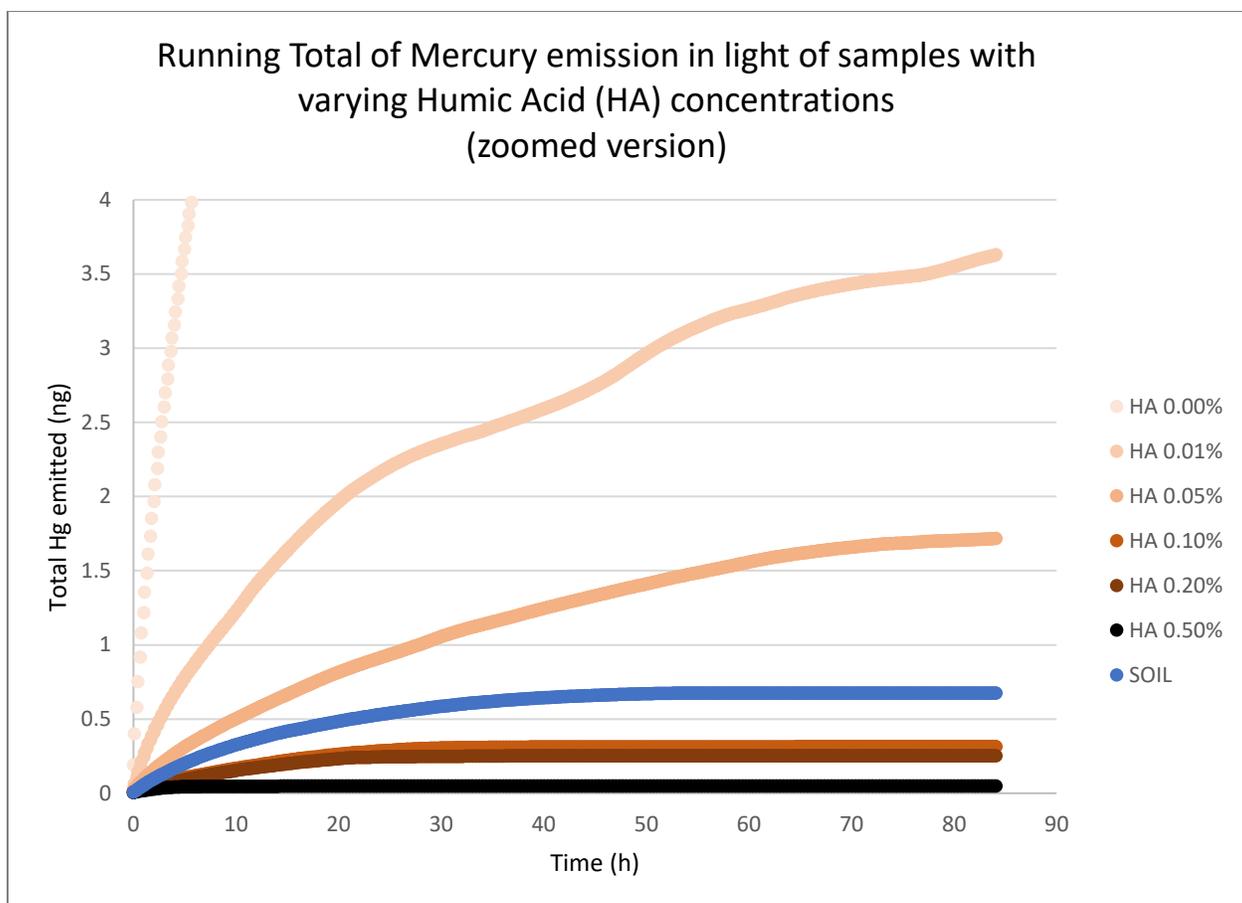


Figure 3. This is a zoomed version of Figure 2. Samples with higher HA are assigned darker shades of orange.

As HA concentration increase in the samples, the total amount of mercury released decreases with larger differences seen between the smaller concentrations of HA. Sample HA 0.00% with no humic acid and HA 0.01% with a 0.01% solution of humic acid showed the largest emissions in Figure 2. In a zoomed in version of this graph, Figure 2, the remaining samples are shown in progressively darker shades of orange as the concentration of humics increase in each sample. These samples demonstrate a decreasing trend in mercury emissions as the concentration of humics increases. With increased HA concentration, the amount of mercury emitted incrementally decreases. While our soil sample, in blue (Figure 2), has a different amount

of mercury (0.2029ppm) than our humic acid samples (0.1144ppm), it is interesting to note that the soil sample can be seen to fit in between the 0.05% and 0.1% HA samples with respect to mercury emissions.

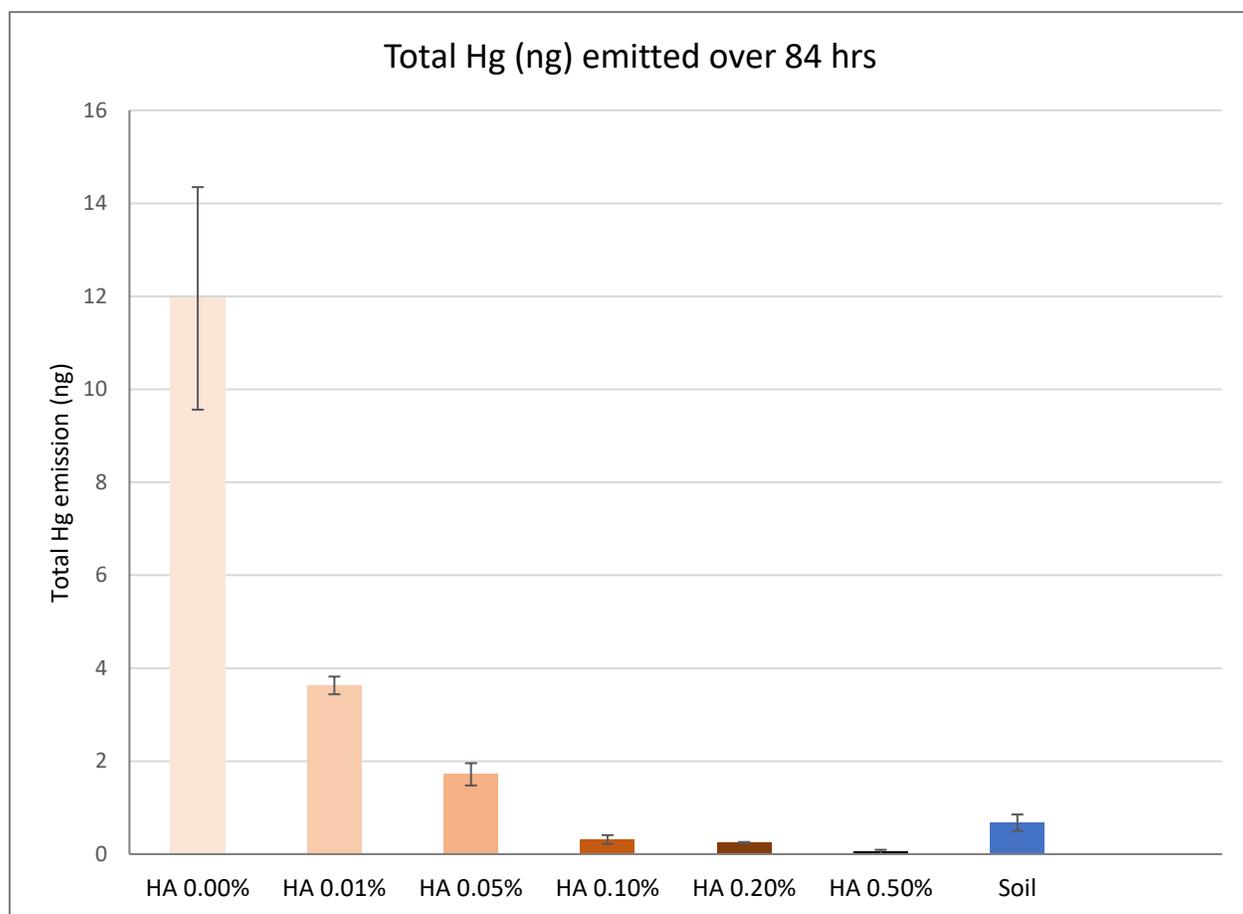


Figure 4. Total measured Hg emitted from samples with varying concentrations of humic acid exposed to light over 84hrs. Mass calculations were made during light exposure for 84hrs after initial light exposure.

### *3.2. Long term soil emissions with water*

A long-term experiment was conducted by a previous research assistant in the lab, Richard Khusial. This was performed by adding 20% w/w RO water (58g) eight separate

times to a soil sample of 290 g over 1100 hrs. Results seen in Figure 5 show that over multiple water additions, mercury emissions from the soil sample increase over the first four water additions but then start to decline for the following four water additions. Research in our lab has shown this pattern before and concluded that there must be something in the soil to explain this phenomenon. Experiments in this thesis with HA (Figures 2 – 4) and soil leachate (Figures 6 and Figure 8) were conducted to isolate variables in soil to try to reveal the underlying mechanism.

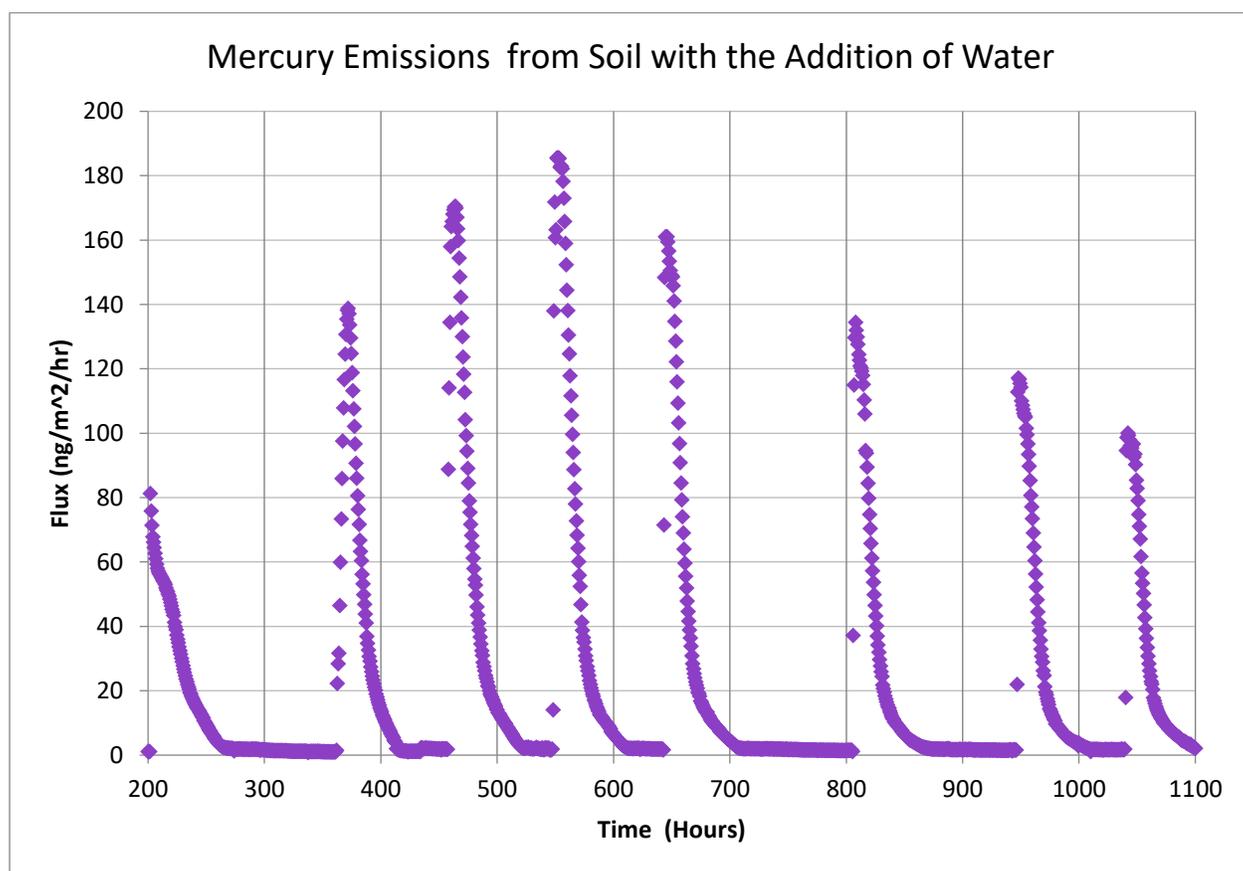


Figure 5. Soil was watered at 20% w/w several times while allowing it to dry before subsequent water addition. Mercury emissions were continuously being measured and spikes in emissions are seen to follow water treatments, and the water dries. Graph created by Richard Khusial.

### 3.3. Leachate

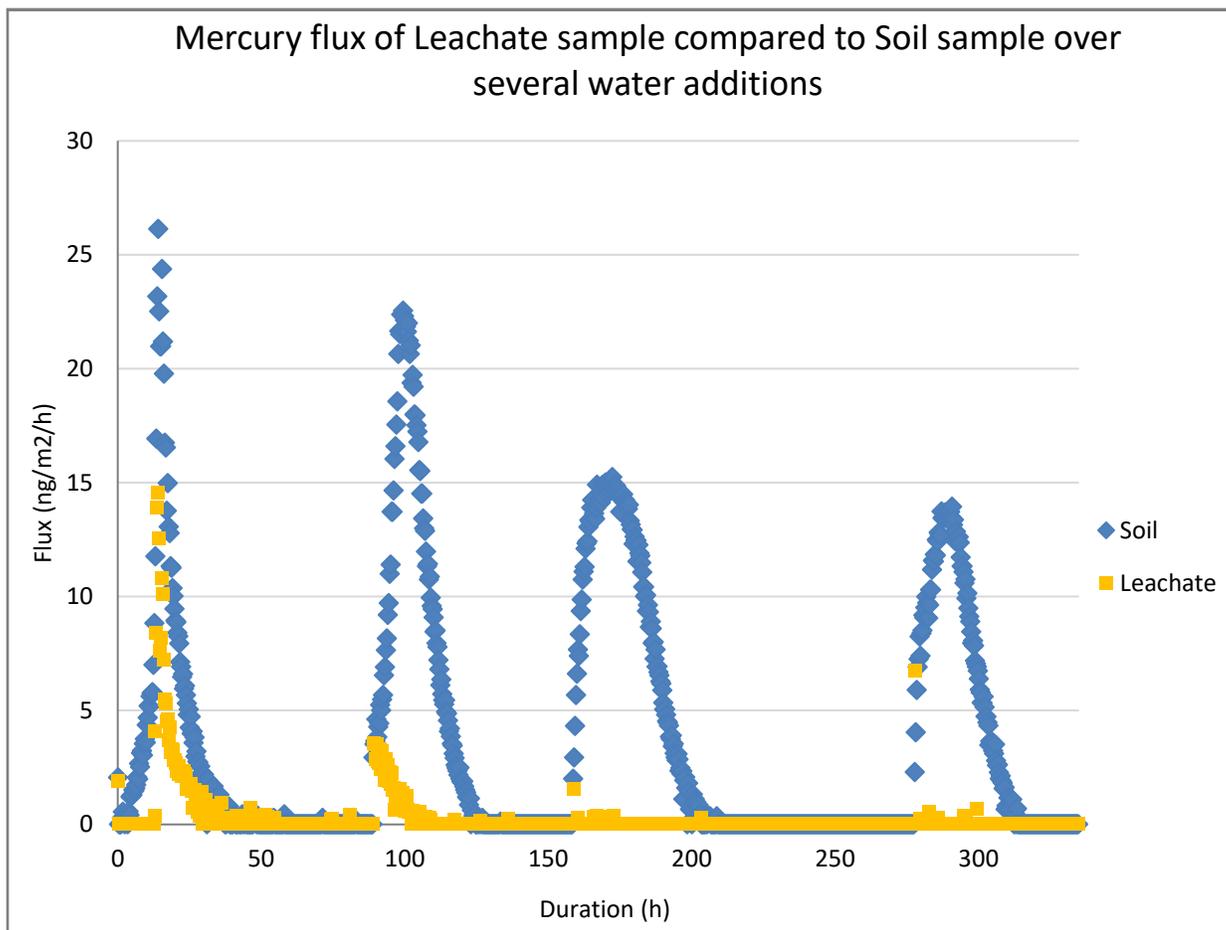


Figure 6. Comparing Hg flux ( $\text{ng}/\text{m}^2/\text{h}$ ) due to water addition (25g RO water) between a sample of (64.2g) soil, shown in blue, and 25g of soil leachate, shown in yellow, over several water additions in the dark.

In order to test whether the soluble component of the soil system caused the mercury emissions noted, we extracted leachate from a sample of soil as described in the Methods chapter. The leachate sample, in yellow, was compared to our control sample of soil, in blue, in Figure 6. On each water addition, after the initial wet phase a peak in mercury emissions was measured. While the soil sample continues to show large, smooth peaks after watering multiple times, the leachate sample shows a sharp response followed by a rapid decrease in mercury emissions in Figure 6. The first mercury flux peak of a

leachate sample accounts for 418.00pg of Hg while 1294.45pg was emitted from the soil with the same amount of water, seen in the first water addition in Figure 7. Upon rehydrating, the soil sample shows a characteristic pattern of increase in total mercury flux for the first three water additions before starting to decrease (Figure 6). The leachate sample, in contrast, only showed decreasing emissions upon water additions, suggesting that the component of soil that caused the spike in Hg emissions following water addition is not limited to the soluble fraction.

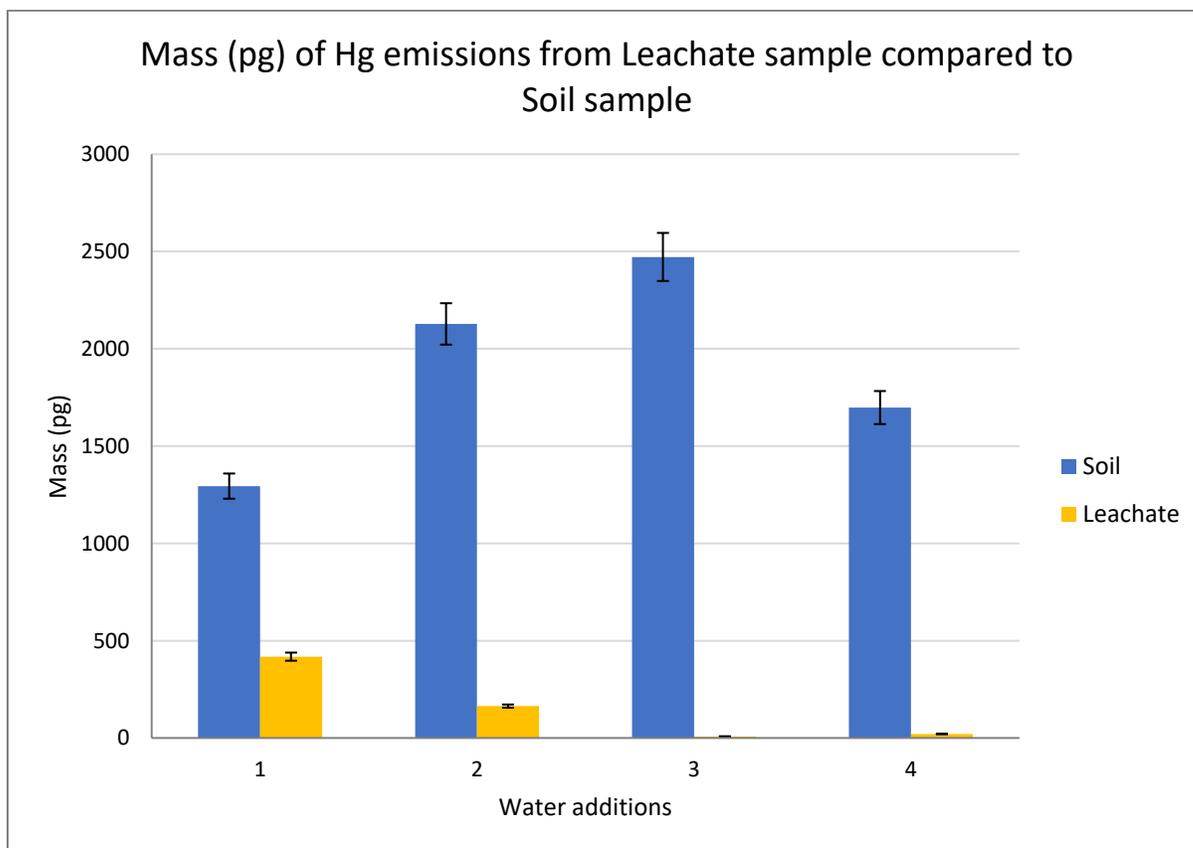


Figure 7. Total emission of Hg (pg) following water addition in a sample of soil, shown in blue, and 25g of soil leachate, shown in yellow, over several water additions in the dark. Mercury emissions were converted into mass and summed over 50 hours after water each water addition. Soil peaks show a typical increasing pattern over the first three water additions and leveling off in the subsequent peak, like we have seen in previous experiments, see Figure 5. The leachate shows emissions the first peak but decreased to near zero after the second peak.

### *3.4. Frequent water additions*

Previous data in our lab showed that soil samples demonstrate a characteristic pattern when watered, allowed to dry, and then watered again (see data by Richard Khusial on Figure 5). While the mechanism is not fully understood as to explain these observations, we wanted to answer the question of whether this is partially due to the cycle of being wet and letting dry completely before watering again, or if a soil sample can be restimulated with water before it fully dries and while it still holds a measurable water content. To analyze this question, a soil sample was rehydrated back to its initial 30% SWC by adding the same amount of water by weight that was lost every several hours. By only rehydrating back to the initial SWC it allows us to re-water the sample without oversaturating it and prevent the samples from overflowing.

In Figure 8, the control sample shown in red was only watered to 30% SWC after it has fully air-dried from its previous water addition. The sample in blue, “Frequently Watered”, was watered again with the mass of water that we measured it had lost to that point, see Figure 9. At time 21hrs the sample measured 13.7g lighter than it was when watered to 30% SWC so 13.7g of RO water was added in the same method. This brings the sample back to 30% SWC. A similar procedure was performed at 27 hours where 8.9g water was added. Both samples were watered again after they had dried out as seen at 163 hours.

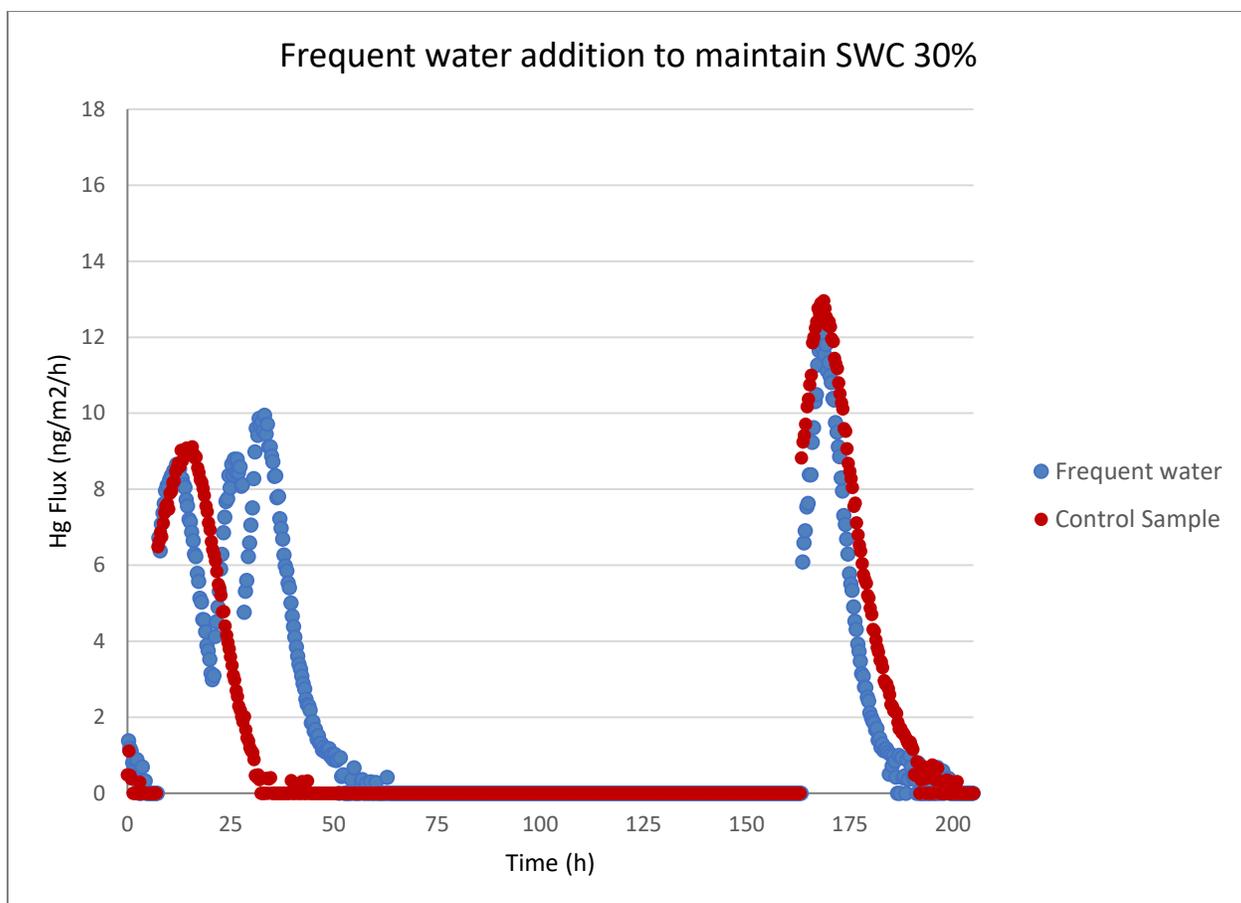


Figure 8. Two identical soil samples, 64.2g, watered in the dark on different schedules. The control sample, shown in red, was a soil sample watered only after it has completely dried in air, at 0% soil water content by weight (SWC w/w). The frequent water addition sample, shown in blue, was watered after flux measurements started to decrease but before it dried completely.

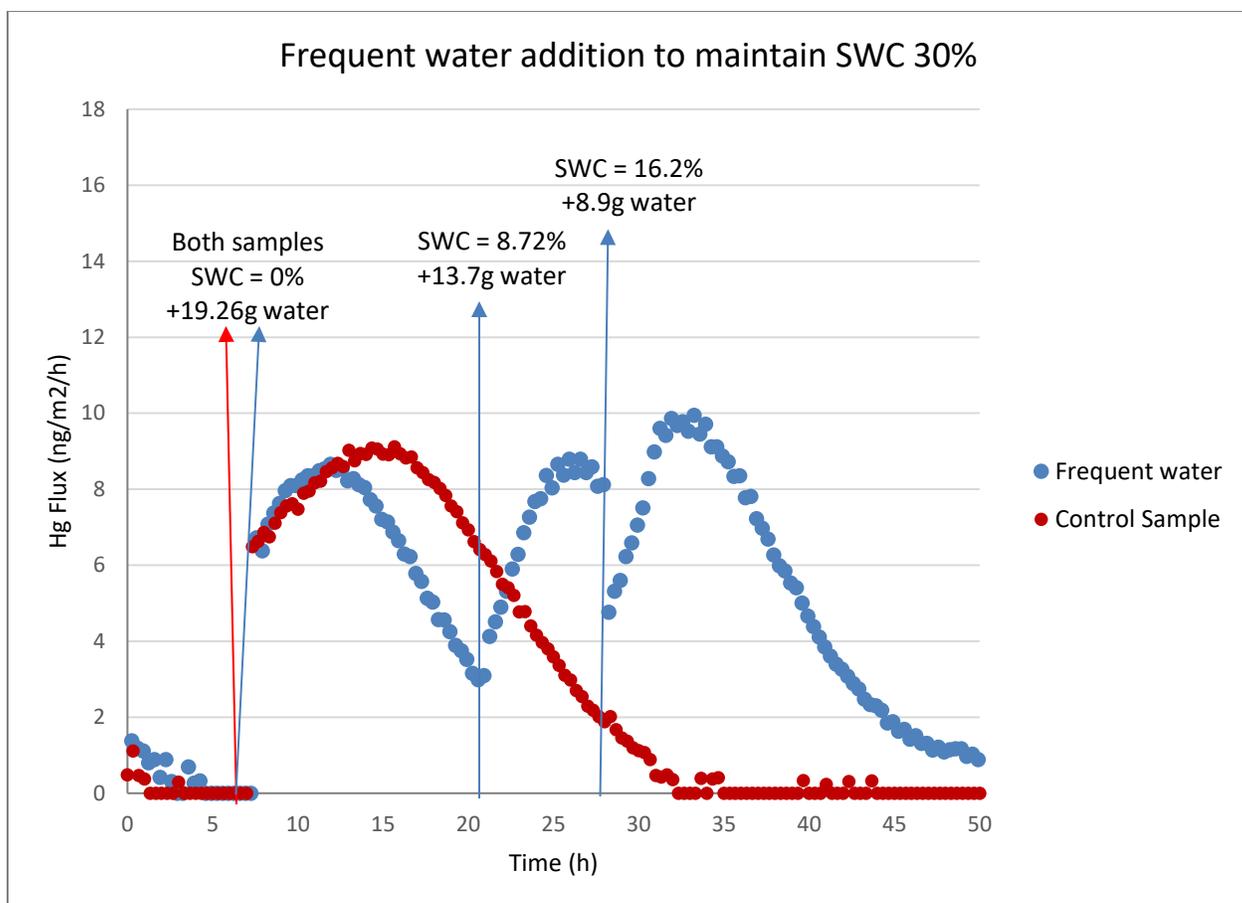


Figure 9. Zoomed in graph of Figure 8. Two identical soil samples watered in the dark at different times. Regular water additions, shown in red, was a soil sample watered only after it had completely dried in air, at 0% SWC (w/w). Frequent water addition sample, shown in blue, was watered after flux measurements peaked but before it dried completely. The amount of water added (g), and soil's SWC (%) before watering is shown above time of watering in boxes.

The experimental sample, seen in blue (Figure 9), shows an immediate increase in mercury emissions after it was rehydrated at 21 hrs. while it still had a SWC of 8.72%.

Additional observations, in Figure 9, were made at 27 hrs. when the experimental (Frequent water) sample showed an immediate decrease in the following measurement in mercury emissions after being rehydrated. This sample then showed increased emissions until hour 35. Later, both samples were allowed to air dry fully before rehydrated back to

30% SWC at 163 hours seen in Figure 8. Both samples showed similar mercury emissions at 163 hrs. (Figure 8).

## 4. Discussion

### *4.1. General discussion*

The interactions between different species of mercury and soil components are complex, and the explanations in the literature as to the mechanism of mercury emitted from soil does not fully cover its behavior, as our observations show. The present experiments look at the mercury emission phenomenon in a wide array of ways. With a narrow focus on HA, one component of many that makes up soil, we can observe the drastic inhibition of mercury photoreduction with increasing concentrations of HA (Figures 2 – 4). As more compounds are pulled into question in the leachate experiments, we observe a wider view of this phenomenon (Figures 6 and 7). And finally, analyzing natural soil samples with varying our water addition methods, we can understand the complexity of the mechanisms at play (Figures 8 and 9). With these data, my research helps further complete the proposed explanations to better align with our observations.

### *4.2. Humic Acids*

Humic acids (HA) are a group of organic molecules made from decomposing organic matter. Different soils will have differing amounts of these molecules which may tell us something about how they behave in terms of mercury emissions.

Humic acids are shown (Figure 2) to reduce the photoreduction of  $\text{HgCl}_2$  in solution. The addition of any amount of humic acid to a  $\text{HgCl}_2$  (aq) sample drastically reduces mercury emissions under simulated sunlight. With increasing amounts of HA in the sample, the measured emissions of mercury were increasingly hindered, see Figures 2 – 4. In this experiment, samples with higher concentrations of HA showed a suppression of mercury being photo-reduced and emitted as measured in the air leaving the flux chambers. Total mercury emitted over the 84 hours of the experiment, can be seen in Figure 4, where the quick decline of total mercury emitted with increasing HA is clear.

The largest difference between two HA samples was observed between the HA 0.01% and HA 0.05% samples, in Figure 3. But the largest difference overall is between our control, HA 0.00% with no humic acid added, and HA 0.01%. This response seems strongest towards the dilute end of the spectrum, indicating the mercury emissions process is sensitive to any amount of HA in the soil matrix, compared to the more concentrated end where the mercury emissions from HA 0.10% and HA 0.20% was almost indistinguishable. One explanation for this phenomenon could be that HA is binding up mercury in the sample tightly enough to hinder its ability to be photoreduced by the simulated light source. As observed in Wang et al. (1997), increased levels of HA in soil can lead to a higher retention of mercury within the soil as water passes through the soil column, lowering mercury transport to bodies of water. The proposed idea that HA is binding up Hg ions in a HA-Hg complex, stabilizing it, and lowering the amount of mercury in solution. Mierle and Ingram (1991) also showed that the prominent form of mercury in runoff water were these HA-Hg complexes. There is clear evidence that HA-Hg complexes can drive the fate of mercury in the environment.

With the various functional groups on HA, a wide range of ions can be bound up in these complexes, and the strength of these bond varies. From Kerndorff and Schnitzer (1980) we know “order of sorption [on HA] was ...  $\text{Hg} = \text{Fe} = \text{Pb} = \text{Al} = \text{Cr} = \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni} > \text{Co} > \text{Mn}$ ”. Their explanation of “competition for active sites such as  $\text{CO}_2\text{H}$  and phenolic OH groups” supports this idea but the connection between this binding and inhibition of photoreduction has not been made. The  $\text{Hg}^{2+}$  ions seem to be the metal ion most readily attracted into this complex formation, and thus the Hg-HA complex is more stable in this form than other ions. This complex formation, preferentially geared towards Hg, could be the mechanism inhibiting mercury’s photoreduction in the presence of HA.

By setting up our experiments to show mercury emissions from a sample composed of just  $\text{HgCl}_2$ , water, and HA, we looked specifically at HA’s role in mercury reduction and emission without the complex mixture of compounds and particles in natural soils. HA’s behavior is complex and can vary depending on if it is in soil or water, and what ions are present (Allard & Arsenie, 1991; Mierle & Ingram, 1991; Wang et al., 1997). For that reason, HA’s effect on mercury emissions, as seen in these data, does not yield a straightforward explanation in terms of mechanisms of action.

An explanation for the decreased mercury photoreduction in the presence of HA was due to the dark color of these HA complexes physically blocking solar radiation from reaching the mercury, as we know HAs play a large role in determining the color of runoff water (Wang et al., 1997) and that UV radiation plays a role in mercury reduction and emissions from soil (Carpi & Lindberg, 1997). Future experiments could be performed with a compound that similarly blocks some of the light, like HA, but is otherwise chemically inert to Hg or HA. HA is a dark brown-black in its solid form and

each dilution is predictably shaded to correlate with their concentration, with darker samples having higher concentrations HA. While this does not explain why the relationship between concentration and total mercury emissions are not linear, this could be one part of the overall mechanism.

#### *4.3. Leachate*

There are far more compounds that can influence mercury reduction and emission from soil than just HA. While the humic acid experiments used a simple system to view the reduction mechanism of mercury in soil, it leaves out the numerous other compounds found in soil. By soaking the soil sample in water for several hours and filtering off the solids we analyzed how the soluble portions of a soil influenced mercury emissions. In a broader sense we wanted to determine how much impact the water-soluble components of soil had on the overall mercury emissions in soil. While some humic acids are soluble, this also includes many other compounds found in natural soil. These components of the soil, found in the leachate, can be shown to account for a portion of soil emissions. While we did not analyze the exact components of this leachate, it is fair to conclude that a portion of DOM available in the soil was extracted, along with a portion of the naturally occurring mercury.

Roughly one-third of the mercury emissions seen in our soil sample, 1,294pg in Figure 6, was seen in the leachate sample, 418.0 pg. This could mean that at least one-third of the mercury being emitted from a wet soil sample could be attributed to the sole presence of water or other interactions in solution. All parts of the soil sample were in

contact with water, and the leachate sample was made with the same amount of soil to maximize the comparability between these two samples. As suggested in Mierle and Ingram (1991) and Wang et al. (1997), humic substances in the soil may have a large role to play in the mobility of soil mercury.

Ravichandran (2004) and Xia et al. (1999) show that sulfate groups facilitate Hg-DOM complex formation in aquatic environments. Mercury's affinity to sulfate groups on DOM could further explain the stability of Hg in the presence of sulfate-containing organic compounds in the leachate and how at least 418.0pg of mercury was extracted simply by mixing soil in water as the Hg-HA complex is dissolved and separates from the solid soil portion. This can be seen in the first peak of the leachate sample as this portion of mercury is released by photoreduction and the measurement is seen in Figure 6. Further watering the soil sample produced increasingly large peaks over the first three water additions followed by a decrease, which is to be expected based on past research, but further waterings of the leachate showed only minor emissions of mercury. We suspect after several water treatments either the mercury in the leachate sample had depleted as a result of emissions or had formed Hg-DOM complexes that hindered emissions.

#### *4.4. Frequent water addition*

The observation of mercury emissions from soil in response to water addition has been known for a long time. Gustin and Stamenkovic (2005) proposed that there is displacement of elemental mercury in soil air space, and an upward flow of dissolved

mercury ions to the soil's surface while it dries as an explanation to this phenomenon. While this could explain part of our observation, it does not propose an actual mechanism for mercury reduction and needs additional amendments to fully describe mercury emissions with multiple water additions.

In the frequent water addition experiment, it was shown that a soil sample with some water content can still be further stimulated by additional water to emit more mercury (Figure 9). After each additional water addition, hour 21 and hour 27, the additional water was shown to reactivate the mercury emission process. The first water addition was when the sample was relatively dry, 8.72% SWC, which resulted in the sample to immediately give off more mercury per hour. The second water addition was when the sample was relatively more wet, at 16.2% SWC, which caused the sample to initially decrease in mercury emissions but gradually increasing afterwards.

In the frequent water addition experiment, with additional water being added each time, the amount of soil being wet stays roughly constant. If this is the case, we would not expect large changes in water penetration of the sample. So, the redistribution hypothesis proposed by Gustin and Stamenkovic (2005) fails to explain why frequent addition of water to maintain the soil's water level continues to stimulate emissions, since one would expect that as mercury in the soil is eliminated by emission into the air, subsequent water addition would show similar or smaller mercury flux. From what we can see in our own soil samples and data, there seems to be a separate process leading to these observations. As seen in Figure 5, there seems to be a pattern of increasing mercury emissions in response to the first several water additions, and then the response decreases. The explanation proposed in Gustin and Stamenkovic (2005) doesn't offer a

mechanism for this phenomenon. The mechanism proposed is a mixture of desorption of gaseous mercury trapped in the soil air space and displacement due to water penetration into each soil horizon. This, however, does not explain how, upon multiple wet and dry phases, there seems to be an increase and subsequent decrease in mercury emissions. Either some chemical change of the soil that allows subsequent water additions to liberate mercury more easily from the soil is at play, or a biological process that intensifies upon each water addition is occurring.

If bacterial growth is stimulated by the presence of water, and not the wet/dry cycles, then a sample that was wet for cumulatively a longer amount of time would show a larger mercury flux later in the experiment. This was not seen in our results. From our experiments, the frequently watered sample was wet for more time overall and was speculated to then stimulate more bacterial growth. Bacterial activity was not explicitly studied in my research but is an area of future research.

## 5. Conclusion

As seen in our results, the processes that control soil mercury emissions are multifaceted. Each part of these experiments show that our current understanding of mercury emissions does not fully explain this phenomenon and future research is needed to generate a fuller understanding.

Our HA experiments show organic matter strongly inhibiting photoreduction of  $\text{HgCl}_2$  in a simplified sample. The question of the specific mechanism is still left unanswered, with two possible explanations of interest. There is the idea that HA blocks light from reaching the Hg in our sample and thus unable to be photoreduced into

elemental mercury, and the other explanation is that HA binds strongly to mercury making it unavailable for reaction. Given the very small amount of HA that was needed to suppress mercury emissions from our sample, we propose that the binding mechanism more likely explains this phenomenon than the light suppression mechanism. This is an area of future research as HA analogues could be used to test these hypotheses.

Finally, with the frequent water addition experiments, we observe little difference when looking at the duration of the wet phase as it relates to subsequent potentiation of mercury emissions in response to water. The latter peaks do not show a measurable difference if a sample is watered once or is kept wet for a prolonged period. While a specific mechanism of action cannot be determined with these experiments alone, they do cast doubt on the current mechanism proposed by Gustin and Stamenkovic (2005), which explained gaseous mercury released and vertical transport of dissolved mercury were the mechanisms driving mercury emissions when water is added to dry soil. Further research is still needed to develop a more complete understanding of mercury emissions in soil in the presence of water.

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