Photochemical Transformation of Particulate Organic Carbon and its Impact on Mercury Cycling in Aqueous Systems

by

Claudia E. Gelfond
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Signature redacted

Department of Civil and Environmental Engineering
January 11, 2017

Signature redacted

Benjamin Kocar
Professor of Civil and Environmental Engineering
Thesis Supervisor

Signature redacted

Jesse Kroll
Professor of Civil and Environmental Engineering
Chair, Graduate Program Committee
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Submitted to the Department of Civil and Environmental Engineering on January 11, 2017 in Partial Fulfillment of the Requirements for the Degree of Master of Science in Civil and Environmental Engineering

ABSTRACT

Mercury (Hg) is a global pollutant with high toxicity that accumulates in biota and biomagnifies, posing a risk to organisms throughout the food chain. Mercury is known to strongly associate with natural organic matter (NOM), which, in turn, affects its speciation, solubility, mobility and toxicity. Numerous studies have examined Hg coordination with dissolved organic carbon (DOC), an important aqueous constituent that alters the reactivity and fate of Hg primarily through complexation with carboxyl and reduced sulfur (e.g. sulfhydryl) groups. However, less is understood of Hg reactions with particulate organic matter (POM), an important reservoir of NOM found within soils, sediments, and suspended in aqueous systems. Moreover, the chemistry of NOM changes when irradiated by sunlight, altering the composition and distribution of functional groups available for complexation with aqueous Hg. Accordingly, we investigate Hg complexation with POM derived from a natural source, Phragmites australis ("common reed"), and examined how photochemical processes impact Hg adsorption through chemical alteration of POM. Mercury adsorption to irradiated and non-irradiated POM was examined through performing isotherm experiments, using an environmentally-relevant range of Hg concentrations (2-500 ppb). First, we find that non-irradiated POM is a powerful sorbent of Hg$^2+$. Adsorption characteristics are indeed altered during POM photolysis, with a three-fold (based on $K_d$) increase in Hg adsorption observed for irradiated POM compared to dark controls. Further, we examine the speciation and oxidation state of adsorbed Hg$^2+$, and deciphered functional groups that contribute to mercury association with POM. Measurements of C, S, and Hg speciation and oxidation state were performed using synchrotron-based X-ray adsorption spectroscopy (XAS) and scanning transmission x-ray microscopy (STXM). These revealed a marked decrease in POM-reduced sulfur following irradiation, leading to fewer R-SH groups capable of strongly binding Hg. However, decreased Hg binding to irradiated POM was not observed owing to a large increase in the quantity of carboxyl groups formed through photochemical processes, which resulted in a higher overall capacity of irradiated POM to bind Hg. The large capacity of POM for binding Hg, as well as enhanced Hg binding following irradiation illustrates that POM is a chemically dynamic pool of NOM that warrants consideration when evaluating reservoirs and processes governing the global Hg cycle.

Thesis Supervisor: Benjamin Kocar
Title: Professor of Civil and Environmental Engineering
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1. Introduction

Mercury is a toxic heavy metal that affects the health and sustainability of environments, organisms and humans\(^1\). In some of its forms (e.g. methylmercury), mercury can act as a potent neurotoxin that can accumulate in organisms. Mercury has an affinity for sulfhydryl groups and as a result is observed in fatty tissue of animals. Thus, these toxic forms of mercury bioaccumulate and biogmagnify in contaminated organisms, posing health risks throughout the food chain.

Several anthropogenic sources of mercury are responsible for its elevated environmental concentrations, relative to natural levels, such as byproducts from coal-fired power plants and gold mining. Emissions from these sources are about 475 metric tons and 725 metric tons per year respectively (Mercury emissions EPA). The dominant species of mercury sourced from anthropogenic activities are elemental mercury, \(\text{Hg}^0\) and inorganic mercury, \(\text{Hg}^{2+}\) (observed in a particle bound phase in emissions – \(\text{Hg}(\text{p})\)). The total amount of mercury in the atmosphere is 5000 metric tons.

The main naturally occurring sources of mercury discharge are volcanic eruptions and cinnabar dissolution. Volcanic eruptions contribute substantial quantities of \(\text{Hg}^0\) and particle bound \(\text{Hg}^{2+}\) to the atmosphere. Though cinnabar is relatively insoluble \((K_{sp} = 10^{-36.8})\)^3, its dissolution is amplified in the presence of organic matter\(^1\). Studies using DOM isolated from the Florida Everglades indicate the enhancement of a large release of mercury (35uM dissolved Hg) from cinnabar\(^4\). These sources, natural and anthropogenic, emit mercury to the atmosphere where it undergoes a variety of transformations and is eventually deposited into aquatic and terrestrial environments\(^5\). The atmospheric lifetime of \(\text{Hg}^0\) is 0.8-1.7 years\(^6\), whereas the lifetime of \(\text{Hg}^{2+}\)
and Hg_{(p)} are much shorter, on the order of weeks. This difference in atmospheric lifetime is due to the fact that Hg^{2+} and Hg_{(p)} are more soluble than Hg^{0} and are prone to wet deposition to aquatic and terrestrial systems.

Once deposited, Hg^{2+} can undergo reaction transformations through several different pathways. One is biotic transformation to toxic methylmercury (HgCH_{3}^{+}), a known neurotoxin, which is particularly hazardous as it biomagnifies in lipids of animals. However, the major pathway for transformation in aquatic systems is the reduction of Hg^{2+} to Hg^{0}. In comparison to HgCH_{3}^{+}, Hg^{0} is a lesser threat to bioaccumulation because it is volatile and capable of outgassing from aquatic systems. The outgassing of Hg^{0} from aquatic systems is referred to as a legacy emission and remains a large unknown in the cycling of mercury. The magnitude of this legacy emission is estimated at 5000 Mg/year, which is equivalent to the emission of all other natural and anthropogenic sources combined\(^7\). Despite the fact that this emission is the largest single source of mercury to the atmosphere, there is a large amount of uncertainty attributed with the aforementioned value. A recent publication noted “the natural and legacy Hg emissions inputs to models currently demonstrate factor of five differences”\(^8\). Because the rate of this re-emission to the atmosphere remains uncertain, it is difficult to devise global chemical transport models that accurately depict the cycling of mercury in the environment\(^6,8\). A deeper understanding of the transformations leading to this emission is necessary in order to fully understand the cycling of mercury in the environment.

While the rate and magnitude of this re-emission is not well constrained, it is largely accepted that this transformation mainly occurs through abiotic light and organic matter mediated transformation of mercury\(^9,10\). An early study showed that sunlight leads to an increase in the concentration dissolved gaseous mercury (DGM), with an increase in the photoreduction
in areas with high DOM. Reduced sulfur groups are believed to be the primary functional
groups responsible for sorption of mercury. As a result recent studies have shown that DOM
type (as variable by location) can have a large effect on the amount of Hg produced. It was
observed that the highest amount of DGM was produced in terrestrial regions, where DOM
concentration was higher than in marine environments. This study suggests that DOM is an
important driver in Hg reactivity. Following, functional groups can also play an important role in
the extent of photoreduction. For example, the production of Hg was greater in the presence of
anthranilic acid than in the presence of salicylic acid, suggesting that functional groups can
change the reactivity of Hg in a system.

Natural organic matter (NOM) serves as an important vehicle for the transport of trace
metals in the environment, and may act as a source and sink of electrons that drive redox
reactions, including those initiated through photochemistry. Though these electron transfer
mechanisms between Hg and NOM are poorly understood, photo-reductive studies of other
metals have been used to understand their redox cycling and speciation in natural waters. Similar to Faust, who studied the photochemical reactions of Cu(II) with organic matter, this
work aims to constrain the foundation for mechanisms and rates of photochemical Hg reduction
in aquatic systems.

It is known that irradiation by sunlight represents a dominant process that alters the
chemistry of dissolved fractions of organic matter (DOM) and associated redox-active trace
metals. However, the effects of irradiation on the chemical transformation of particulate organic
matter (POM) – one of the major forms of carbon found in terrestrial and aquatic environments –
is comparatively much less understood. The role of POM both as an important environmental
sorbent and photo-reactive solid must be deciphered to better understand the cycling of mercury in the environment.

Due to a higher density of reactive functional groups than DOM, POM has a higher capacity to complex trace metals. This results in a larger pool of metals susceptible to photo-induced reactions. While some studies have looked at interactions between mercury and organic matter and sunlight in separate cases, few have looked at the interactions between sunlight, mercury, and POM in conjunction. Mercury is known to strongly associated with DOM, which in turn affects its speciation, solubility, mobility, and toxicity. Additionally, mercury sorbs to POM in soils. Studies using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy have provided evidence of coordination with sulfur functional groups. Similar studies have been conducted using DOM to confirm similar coordination in aquatic systems. Sulfur bearing functional groups have also been shown to play an important role in reactions involving Hg-DOM complexes.

Photo reduction of Hg$^{2+}$ in the presence of DOM has been observed. However, the mechanisms for these reactions are poorly constrained. Though potential modes for electron transfer mechanisms between mercury and DOM are poorly understood, photo-reductive studies of other metals have been used to understand their redox cycling and speciation in natural waters.

Since it is known that organic matter and light play an important role in the transformation of mercury, the goal for this project was to understand how both the POM changes with exposure to sunlight, as well as how mercury's association with the POM changes with irradiation. To address these objectives, batch sorption isotherms were performed using control and irradiated POM to determine how sorption capacity changes as POM is degraded.
Samples of POM were also analyzed at Stanford Synchrotron Radiation Light Source (SSRL) in order to determine the speciation, coordination, and distribution of mercury and sulfur within our samples. The model POM source for these experiments was also analyzed in collaboration for this project. Several techniques were used including Scanning Transmission X-ray Microscopy (STXM) to determine how the surface chemistry of the POM changed with irradiation.
2. Experimental

2.1 POM Collection, Preparation, and Irradiation

A source of model POM was derived from *Phragmites australis*, a ubiquitous and invasive plant with high lignocellulose content. This species was chosen as a source of model POM because it is widely distributed within wetlands where Hg cycling is known to occur (e.g. near coal-fired power plants), it is a substantial source of organic matter to wetland sediments and aqueous environments, and it is easily harvested from local sites. Senescent *Phragmites australis* was collected in a wetland near Revere, MA, dried for 24 hours, and ground to a particle size representative of natural POM found in freshwater environments (43-90 microns). It was then suspended in MilliQ water and filtered to remove highly soluble inorganic and organic compounds.

POM samples were suspended in a quartz reactor at loadings of 100 mg/L for batch isotherm experiments, or 1000 mg/L to examine irradiation-induced changes in S oxidation state. Suspensions were exposed to a 350W xenon lamp equipped with an AM 1.5 filter, which approximates the spectral irradiance of sunlight at mid-latitude at mid-year. Suspensions were exposed to irradiation for one week, simulating exposure to sunlight for one month (based on reported flux values for this instrument, Newport-Oriel, inc.). After irradiation, POM was collected by filtering the sample and was rinsed to remove weakly adsorbed (photo-produced) DOM.
2.2 Batch Sorption Isotherms and Mercury Analysis Using ICP-MS

Time series data for a selected concentration (12 ppb Hg) was used to determine an appropriate equilibration time of 2 days (Figure 1) used in batch isotherm experiments. This was accomplished by equilibrating 100 mg/L POC suspensions with 12 ppb Hg\(^{2+}\) (as Hg(NO\(_3\))\(_2\)) and shaking for various lengths of time before being filtered and prepped for ICP-MS analysis. The times for incubation ranged between 30 minutes and two weeks to determine the time point for equilibrium. Batch sorption isotherms were then performed to determine the extent of mercury sorption to dark and irradiated POM. For each case, ground phragmites were suspended to 100 mg/L and Hg(NO\(_3\))\(_2\) was added ranging in concentration from 0.2 ppb to 100 ppb. Additional samples for the irradiated phragmites were prepared at elevated concentrations: 150 ppb, 250 ppb, and 500 ppb to determine the maximum extent of sorption. These concentrations range from safe drinking water concentrations to levels observed in contaminated freshwater systems. All samples were prepared in triplicate.

*Figure 1* Time series indicates equilibrium was reached after 2 days. Fast sorption is observed at the beginning of the time series. It is possible that slow sorption mechanisms are important for this case as a decrease in solution concentration is observed after four days. Error bars indicate standard deviation between sample runs.
Total aqueous mercury was determined using ICP-MS. First, samples were filtered through a 0.45 micron filter to remove suspended POM; filtrate was then acidified using 50% nitric acid to bring sample to 2% nitric and spiked with gold acetate, to reach 1 ppm concentration, to prevent Hg adsorption to container and tubing surfaces. To construct an Hg standard curve, total counts were recorded at masses 198, 199, 201, and 202 a.m.u. for known Hg concentrations. These curves were then used to determine Hg concentrations in experimental (unknown) samples.

The difference between mercury in solution and the initial concentration was used to determine the extent of sorption to the particles. Assumption of mass balance is valid, as XAS revealed no transformation of Hg$^{2+}$ to volatile Hg$^0$. Data was fitted to a Freundlich isotherms to determine the sorption trend as well as overall sorption capacity. A linear regression was fit to the linear regions of each isotherm to determine $K_d$ values (where $K_d = [\text{Hg}]$ in organic matter/$[\text{Hg}]$ in solution) that would indicate the extent of sorption in systems with low mercury concentrations.

### 2.3 X-Ray Absorption Spectroscopy (XANES) of Sulfur and Mercury Associated with POM

Bulk X-ray adsorption near-edge spectroscopy (XANES) was performed on dark and irradiated POM samples to characterize initial S oxidation state, and examine changes in S speciation following irradiation (Stanford Synchrotron Radiation Lightsource [SSRL], beamline 4-3, 11-2). Owing to low solid-phase concentration of S, a high concentration of POM (1000 mg/L) was irradiated to ensure a S quantity sufficient for S XANES analysis. Irradiated samples
were filtered, dried, and fixed onto 1 Mil, PET/Acrylic adhesive (Saint Goblin Performance Plastics CHR M-Series) and mounted on an aluminum sample holder. XANES analysis was performed on BL 4-3 (SSRL) in a He-purged chamber equipped with a LYTLE detector. Spectra were collected at 0.15 eV increments across the K-edge (2440 – 2495), and at 0.5 eV increments above and below 2420 and 2695 eV for defining post and pre-edge regions, respectively. Spectra of standards were also collected, including methionine, cysteine, and dimethyl sulfone. These standards were also spiked with Hg (120 ppb) to examine S chemical alteration when associated with Hg$^{2+}$ (results for these additional experiments in Appendix).

Mercury L$_{III}$-edge X-ray Absorption Near Edge Structure (XANES) spectra were collected for POM incubated in a solution of 120 ppb Hg$^{2+}$ as well as a Hg(NO$_3$)$_2$ standard. Dilute standards were made by mixing concentrated Hg(NO$_3$)$_2$ with an X-ray transparent material (boron nitride) that is essentially transparent to X-ray energies and mounted on a nylon sample holder. Experimental solids (POM) were collected through filtration onto combusted glass fiber filters, which contain low concentrations of background Hg. Samples and standards for mercury L$_{III}$-edge analysis were subsequently encapsulated in Kapton tape in preparation for beam line analysis. XANES analysis was performed on BL 11-2 (SSRL) in a chamber equipped with a germanium detector. Spectra were collected at 0.15 eV increments across the L-edge and at 10 eV increments above and below the edge for defining post and pre-edge regions, respectively.

For Hg XANES, dark and irradiated samples were suspended to a concentration of 330 mg/L. These samples were spiked with different concentrations of Hg(NO$_3$)$_2$ to yield final solution concentrations between 12-120 ppb. Samples were placed on a shaker table for one week.
POM was suspended at a concentration of 1 mg/mL. These samples were spiked with Hg(NO₃)₂ to various extents, yielding final solutions at a range from 12-120 ppb. Control samples were also prepared without the addition of Hg(NO₃)₂. Samples were placed on a shaker table for one week.

2.4 Synchrotron-based Chemical Mapping and Speciation of Mercury, Sulfur and Carbon

X-Ray Fluorescence (XRF) mapping and μ-XANES were also used to analyze mercury and sulfur distribution and speciation in POM particles. In this technique, a sample is rastered across a microfocussed x-ray beam (~2 micron spot size) and x-ray fluorescence associated with excited elements is measured. This generates a map of elements with edges (usually K or L) below the selected X-ray energy. Further, multiple energies can be mapped across the edge of a selected element (e.g. S K-edge) to generate “chemical maps” of the chosen element. Hence, XRF mapping can be used to examine both the spatial extent and form of one or more elements in a 2 dimensional sample (usually a thin section or partial mount), which aids in elucidating chemical complexity and heterogeneity within a sample. Further, a μ-XANES analysis can be performed at selected points in a map for more detailed chemical analysis within microscopic regions of a sample.

For XRF mapping, dark and irradiated samples were suspended to a concentration of 250 mg/L. Each sample was spiked with mercury to bring to a final concentration of 5 ppb. Samples were placed on a shaker table for one week. Samples of S and Hg-bearing POM were fixed on 1
Mil PET/Acryclic adhesive (sulfur free mylar) and mounted on a sample holder for analysis. Small areas of samples were scanned (roughly 2 mm by 2 mm) and Hg (LIII-edge) and S (K-edge) μ-XANES spectra were collected at points of interest.

Microscopic measurements and mapping of C chemical speciation were performed using a different synchrotron-based technique – Scanning Transmission X-Ray Microscopy (STXM – 5.3.2 at the Advanced Light Source – Berkeley, CA and SM beamline at Canadian Light Source – Saskatoon, SK) In this technique, a sample is placed on a fine stage in order to raster scan the sample through a range of energies. A sequence of images is measured as a function of photon energies, which yields a “stack” or a three dimensional spectral data set. For the samples analyzed in this experiment, stacks for C and O were obtained, focused around the C K-edge and the O K-edge respectively. Samples of dark and irradiated phragmites were prepared by drop casting suspended particles onto 20 nm thick silicon nitride membranes.

2.5 Synchrotron Data Reduction and Analysis

All spectra collected were analyzed using SixPACK powered by IFEFFIT22. XANES spectra for each sample were averaged and normalized. XRF maps were analyzed using SMAK micro toolkit. Correlation plots of mercury and sulfur intensity from the XRF maps were prepared to determine if and how Hg-POM interactions changed between the dark and irradiated samples.

For STXM analysis, maps of edges of the POM were used to determine changes in chemical composition between samples using pixel-by-pixel curve fitting. Spectra were corrected by subtracting both linear background and the contribution from the carbon K-edge
(modeled as an arctangent step function) centered at 290 eV. The relative abundances of major organic functional groups between the two samples were determined by fitting multiple Gaussian curves to each spectrum at energies relevant to specific functional groups (e.g. ketone, carboxylic acid, etc...)

### 2.6 Brunauer-Emmett-Teller (BET) Analysis

Samples of dark and irradiated phragmites were characterized by specific surface area determination, Brunaur-Emmet-Teller (BET) analysis. This analysis was performed to determine if there was a significant increase in surface area after irradiation of the phragmites. Samples were analyzed by Sovanndara Hok (Kim group) at Chapman University.
3. Results

3.1 Batch Sorption Isotherms

Time series data of Hg adsorption to POM reveals that a quasi-equilibration state is achieved after 2 days. Results (Figure 2) from the batch isotherms show a significant difference in the extent of mercury sorption between the dark and irradiated phragmites. Freundlich isotherms were fit to data and $K_F$ values were determined to be 0.011 L/mg for the irradiated phragmites and 0.0086 L/mg for the dark phragmites. A Freundlich fit was used because the time

![Light v Dark Isotherms](image)

*Figure 2* Light vs. Dark Isotherms show a significant increase in the extent of sorption between the dark and irradiated phragmites.
series suggests that slow sorption\textsuperscript{23} could be relevant in this case and that the extent of sorption might not be dependent on a finite number of surface sorption sites.

$K_d$ values were also calculated at for both plots at low concentration. For the irradiated POM sample, $K_d = 0.003$ L/mg. For the dark POM sample, $K_d = 0.0012$ L/mg. From these constants it is apparent that mercury association with POM is roughly three times higher for the irradiated sample, signifying a significant change in the surface chemistry between the dark and irradiated POM. BET analysis showed consistency between the surface areas of both the dark and irradiated phragmites samples.

3.2 Synchrotron Analysis

The mercury L\textsubscript{III}-edge XANES spectra (Figure 3) of the two samples were nearly identical, exhibiting a pre-edge peak at 12,282 eV consistent with Hg-complexation with carboxyl functional groups\textsuperscript{24}. Additionally, no difference was observed between spectra first derivatives, which are often examined to identify subtle differences in Hg local atomic

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{The figure on the left overlays the mercury L\textsubscript{III}-edge XANES spectra for the dark and irradiated Hg-POM complexes as well as an Hg(NO\textsubscript{3})\textsubscript{2} standard. The pre-edge peak can be observed at 12,282 eV. The figure on the right shows the first derivative of the Hg-POM complexes and the Hg(NO\textsubscript{3})\textsubscript{2} standard. Differences in peak height and location in this first derivative plot gives insight into the coordination environment of mercury in samples.}
\end{figure}
environment that might not be apparent in raw signals. Though there is no significant change between the two samples, the \( \text{Hg(NO}_3\text{)}_2 \) standard illustrates how spectroscopy can give insight to the specific coordination environment.

The S K-edge XANES spectra (Figure 4) of the two samples did reveal more appreciable differences between the particles. While each sample contained three main peaks, \( \sim 2472 \text{ eV (R-S-H or R-S CH}_3\text{)}, \sim 2475 \text{ eV (R}_2\text{-S-O or R-S-O}_3\text{)}, \) and \( \sim 2480 \text{ eV (ester or sulfate)}^{25} \), the relative ratios of these peaks differed between the samples. In the dark sample, there is a greater relative amount of reduced sulfur species than in the irradiated sample. This suggests that as the POM is irradiated the sulfur-bearing functional groups are being oxidized. Because mercury binds strongly with reduced sulfur, this data would suggest that as the POM is irradiated, a decrease in the extent of sorption should be observed. However, based on the results from the batch sorption isotherms and the XRF maps, this is not the case.

XRF maps (Figure 5) give information about both the intensity and spatial distribution of mercury within the two samples. For the dark sample, the distribution of mercury is heterogeneous, with a few distinct areas of higher mercury sorption, but otherwise relatively low.

Figure 4 The above shows sulfur K-edge XANES spectra. The top figure includes spectra for dark and irradiated POM. The bottom figure contains spectra for standard compounds. Methionine and cysteine both contain reduced sulfur functional groups. Dimethyl sulfone contains an oxidized sulfur functional group.
Figure 5: X-Ray Fluorescence Maps indicating mercury intensity. Data was collected using a microprobe with a spot size of 2 µm. Intensity is expressed on a logarithmic scale.

Sorption. In the irradiated sample, there is a more homogenous distribution of mercury. Though the overall mercury intensity in the irradiated sample is lower than the mercury intensity of the hot spots in the dark sample, the average mercury intensity in the irradiated samples is 20% higher than the average mercury intensity in the dark sample. This difference between the samples signifies that a change in surface chemistry leads to an enhancement in sorption. Despite the fact that reduced sulfur groups are being oxidized, there is an increase in mercury sorption. This suggests that there are changes in chemical properties of the...
surface of the particles that are contributing to different chemical interactions than observed in
the dark scenario. STXM results show no significant change in the relative abundance of alkene
and aromatic functional groups, increases in ketone and carboxylic acid/ether functional groups,
and a decrease in alkyl and alcohol/amid functional groups. (Figure 6, see table in appendix)

3.3 BET Analysis

Dark phragmites have a surface area of 2.940 m²/g. Irradiated phragmites have a surface
area of 2.497 m²/g. BET analysis showed consistency between the surface areas of both the dark
and irradiated phragmites samples. (add figure to appendix)
4. Discussion

4.1 Batch Sorption Isotherms

Isotherm data support conclusions drawn from the XRF experiments. Although irradiation oxygenates reduced sulfur species, we observe an overall increase in sorption capacity. This is counter-intuitive since mercury binds very strongly with reduced sulfur; as the quantity of these groups decrease, we would expect sorption to decrease with it. However, the data suggests that there are other important organic interactions between mercury and the POM that lead to the enhanced sorption observed. The $K_F$ and $K_D$ values calculated from these experiments suggest a large change in the association of mercury with POM as it is irradiated that could only be attributed to a significant change in surface chemistry, given an insignificant change in surface area.

Alterations in POM chemistry were observed, and attributed to photochemical processes. For example, data from Scanning X-ray Transmission Microscopy (STXM), performed at the Canadian Light Source (CLS), shows an increase in oxygen content as POM is irradiated. More specifically, an increase in ketones and carboxylic acid/ether functional groups are observed in conjunction with a decrease in alkyl and alcohol/amide functional groups.

Because the BET analyses showed no significant change in the surface area between the dark and irradiated samples, we can conclude that the increase in the extent of sorption is primarily caused by a change in surface chemistry and not just a change in the amount of exposed surface.
4.2 Synchrotron Analysis

X-ray Fluorescence mapping data reveals a heterogeneous distribution of mercury within non-irradiated (dark control) samples; the overall intensity of mercury fluorescence is weak, but there are a few hot spots signifying a high extent of mercury sorption. However, as the sample is irradiated, a more homogenous distribution is observed as well as an overall increase in average mercury intensity. This suggests that as the particulate organic matter is irradiated, there are significant changes to the surface chemistry that results in this overall increase in sorption capacity.

Because mercury and sulfur typically form strong complexes, examining the correlation between mercury and sulfur (Figure 7) was useful to determine if these interactions were changing. Within the correlation plot, there are a few points of interest. In the dark sample, there are a variety of different categories or groups of particulate associated mercury. Consistent with the hotspots, there is a region of very high mercury intensity coupled with typical sulfur intensities. This group disappears with irradiation of the particulate organic

![Figure 7](image-url) Correlation plots derived from XRF data shows the correlation between mercury and sulfur intensity at each point analyzed. The green circles indication regions in which we observe different groupings of mercury and sulfur intensities. The subplots in the upper right corner show regions of lower mercury intensity with more detail. In the subplots the dark and irradiated data are separated to show regions that were overlapping the main plot.
matter. This suggests that as we irradiate the particulate organic matter, there is a change in the chemistry of the sulfur bearing functional groups that decreases their capacity to complex with mercury. This shift is likely a decrease in the presence of reduced sulfur bearing functional groups that bind mercury strongly. With a decrease in these functional groups, mercury is likely associating with other organic functional groups on the surface of the organic matter.

The bulk sulfur data shows us that as the particulate matter is irradiated, there is a shift in the distribution of sulfur functional groups. In the dark particulate matter, the speciation of the sulfur functional groups is more reduced. We can compare this data to standards that have more delineated sulfur signatures that were analyzed at the beam line. For example, methionine and cysteine contain only reduced sulfur bearing functional groups that are observable at 2472 eV. Conversely, dimethyl sulfone contains only oxidized sulfur bearing functional groups which are observed at 2478 eV. In both samples there are a variety of different sulfur signatures, consistent with both oxidized and reduced species.

The bulk mercury data shows that there is no significant change in the speciation or coordination of mercury between the two samples. As these studies did not include mercury in the sample until after it was already irradiated, this result is not surprising. Future experiments will include irradiation of the Hg-POM complex. Here we might expect to see differences in mercury-organic interactions as well as the evolution of elemental mercury. These changes would result in visible differences in both the mercury XANES spectra and the more sensitive first derivative curves. From the first derivative curves in particular, we can learn more about the functional groups that mercury may be interacting with.

STXM data shows an increase in oxygenated functional groups in the irradiated sample. This oxygenation could lead to the increased extent of mercury sorption of POM after irradiation.
due to an increase in carboxyl groups. The results suggest that photodegradation of POM proceeds through an indirect pathway because there is no major change in the amount of aromatic functional groups.
5. Conclusion

The work completed in this project begins to make clear the roles of both POM and light on the transformation of mercury in aquatic systems. The experiments have elucidated the predominant interactions between mercury and organic matter and how these interactions change when organic matter is degraded via sunlight. While mercury binds strongly with reduced sulfur and increases the extent of sorption in areas where this form of sulfur is found, mercury also has significant interactions with other organic functional groups. From the XRF mapping data as well as the batch isotherms, it is apparent that these interactions between mercury and oxygenated functional groups on the surface of POM can actually cause the extent of sorption to be much higher than would be expected. These findings suggest that as POM is degraded by sunlight, mercury will actually sorb more readily, which could lead to an increased rate of reduction to $\text{Hg}^0$. Further studies in which the POM is irradiated for different lengths of time should be conducted in order to determine how quickly the surface chemistry of the particles is changing and how this affects the extent of mercury sorption.
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(18) Miller, C. L.; Southworth, G.; Brooks, S.; Liang, L.; Gu, B. Kinetic controls on the


Initial time series data including time points taken between 30 minutes and 1 day show a quick uptake of Hg by POM. Figure 1 omits these data points to highlight the overall trend of sorption after this initial quick step.
S XANES data shows samples of phragmites and standards that have been spiked with Hg as well as controls. We observe in the standards that an addition of Hg drastically alters the sulfur speciation as observed in the methionine and cysteine spectra. With the addition of mercury to the dark and irradiated phragmites however, we see minimal changes in the speciation of the sulfur functional groups. This suggests that other functional groups are responsible for coordinating the added Hg.
STXM results show relative changes in abundances of functional groups listed above.

There is minimal change in the abundance of alkene/aromatic functional groups. We see a relative decrease in alkyl and alcohol/amide functional groups with irradiation and a relative increase in alkyl and carboxylic acid/ether functional groups.