Partitioning of dissolved organic matter-bound mercury between a hydrophobic surface and polysulfide-rubber polymer

Eun-Ah Kim, Richard G. Luthy*

Department of Civil and Environmental Engineering, Stanford University, Stanford, CA 94305-4020, USA

ARTICLE INFO

Article history:
Received 23 April 2011
Received in revised form 23 June 2011
Accepted 3 August 2011
Available online 11 August 2011

Keywords:
Dissolved organic matter
Polysulfide-rubber polymer
Mercury
Addition reaction
Adsorption reaction
Mercury complexation

ABSTRACT

This study investigated the role of dissolved organic matter on mercury partitioning between a hydrophobic surface (polyethylene, PE) and a reduced sulfur-rich surface (polysulfide rubber, PSR). Comparative sorption studies employed polyethylene and polyethylene coated with PSR for reactions with DOM-bound mercuric ions. These studies revealed that PSR enhanced the Hg-DOM removal from water when DOM was Suwannee River natural organic matter (NOM), fulvic acid (FA), or humic acid (HA), while the same amount of 1,3-propanedithiol-bound mercuric ion was removed by both PE and PSR-PE. The differences for Hg-DOM removal efficiencies between PE and PSR-PE varied depending on which DOM was bound to mercuric ion as suggested by the PE/water and PSR-PE/water partition coefficients for mercury. The surface concentrations of mercury on PE and PSR-PE with the same DOM measured by x-ray photoelectron spectroscopy were similar, which indicated the comparable amounts of immobilized mercury on PE and PSR-PE being exposed to the aqueous phase. With these observations, two major pathways for the immobilization reactions between PSR-PE and Hg-DOM were examined: 1) adsorption of Hg-DOM on PE by hydrophobic interactions between DOM and PE, and 2) addition reaction of Hg-DOM onto PSR by a complexation reaction between Hg and PSR. The percent contribution of each pathway was derived from a mass balance and the ratios among aqueous mercury, PE-bound Hg-DOM, and PSR-bound Hg-DOM concentrations. The results indicate strong binding of mercuric ion with both dissolved organic matter and PSR polymer. The FT-IR examination of Hg-preloaded-PSR-PEs after the reaction with DOM corroborated a strong interaction between mercuric ion and 1,3-propanedithiol compared to Hg-HA, Hg-FA, or Hg-NOM interactions.

1. Introduction

Methylmercury is a potent neurotoxin and has high bioaccumulation factors (Driscoll et al., 2007). A recent study showed an enhanced mercury methylation rate with Geobacter sulfurreducens when mercuric ion is bound to cysteine (Schaefer and Morel, 2009), a small organic molecule with a thiol group. This finding implies enhanced methylation of mercury in the presence of certain organic molecules in sediments, which may depend on the strains of the mercury methylating bacteria. Therefore, it is crucial to have an accurate estimation of the amount of mercury that could be
transformed into a source for methylation when there are
perturbations of the sediment organic carbon speciation due
to erosion, runoff, changes of pH/redox potentials, or sudden
input of sediment organic matter.

Since the mobile mercury is more readily bioavailable for
mercury methylation compared with solid-bound mercury
species (Benoit et al., 2001a,b; Skyllberg et al., 2009), the
mobile portion of mercury is a better proxy for methylmercury
concentration than the total mercury concentration. Mercury
mobilization is related the presence of other metal
binding ligands such as dissolved organic matter (DOM) and
organic or inorganic thiols/sulfides (Ravichandran, 2004;
Skyllberg, 2008). The latter would include DOM with reduced
sulfur functional groups that strongly bind mercuric ion and
prevent the mercury from precipitating as mercuric sulfide.
Dissolution of Hg-S(α) by DOM (Ravichandran et al., 1998;
Waples et al., 2005; Slowey, 2010) indicates a strong interact-
ion between DOM and Hg, and critical roles of DOM in
mercury mobilization.

The implications of strong Hg-DOM interaction are yet
unclear with respect to mercury partitioning in the presence of
a strong binding ligand for mercuric ion on a solid surface.
For example, with polysulfide-rubber (PSR) polymer, the DOM
may compete with PSR for mercury binding, or PSR may
simply provide additional binding sites for DOM-bound
mercric ion without competition. These interactions may
be examined by preparing polysulfide-rubber polymer-coated
polyethylene (PSR-PE) and conducting competitive sorption
studies with various forms of DOM. Assuming Hg-DOM
interaction mainly comprises a Hg–S bond, immobilization
of the Hg-DOM species on the reduced sulfur-rich sites can
occur via multiple Hg–S bond formation (Hesterberg et al.,
2001). In this case, the Hg ion would be encapsulated in DOM
and the PSR polymer simultaneously. An exchange of
mercric ion between DOM and PSR is also possible when
DOM-bound mercrnic ion is transferred to PSR, subsequently
reaching a new equilibrium between Hg-DOM and Hg-PSR.
In summary, the possible reaction pathways between PSR-PE
and Hg-DOM can be classified as 1) adsorption of Hg-DOM
on PE via hydrophobic interaction giving a Hg-PE-DOM species,
and 2) additional bond formation between PSR and
Hg-DOM giving a Hg-PSR species.

The purpose of this study is to assess the role of dissolved
organic matter on mercury partitioning between a hydro-
phobic surface (i.e., polyethylene) and a reduced sulfur-rich
surface (i.e., polysulfide-rubber polymer). Better under-
standing of the partitioning behavior of Hg-DOM with PSR-PE
or PE is expected to provide clues to delineate the Hg-DOM
immobilization processes on PSR-PE. The results indicate
that both PE and PSR participate in Hg-DOM removal from
water, and mercury complexation with PSR polymer (6.7% of
the total PSR-PE surface area) and DOM contributes greatly to
the overall immobilization reaction on PSR-PE in the presence
of Suwannee River natural organic matter, fulvic acid, and
humic acid. Depending on the relative affinities of a hydro-
phobic surface and a polysulfide-rich surface for DOM-bound
mercric ion, the mercury removal efficiency of a multi-
functional sorbent, for instance, PSR-coated activated carbon
(Kim et al., 2011), can be optimized by adjusting the coverage
of PSR polymer on activated carbon.

2. Materials and methods

2.1. Polymer coating on polyethylene strips

Polyethylene (PE) strips were pre-cleaned with methylenec-
chloride, methanol, and DI-water consecutively for one day at
each step. The PE was dried in a convection oven at 60 °C for
4 h and cut into 2 cm × 2 cm (18 ± 0.5 mg) pieces. The
polysulfide-rubber polymer was synthesized following the
procedure described by Kalae et al. (2009). Condensation
polymerization between sodium tetrasulfide and 1,2-
dichloroethane, using methytributylammonium chloride as
a phase transfer catalyst, produced a yellowish elastic solid in
water. One hundred mg of the PSR polymer in 40 mL toluene
was refluxed until the polymer block was completely dis-
solved. The solution was cooled to room temperature before it
was used for coating PE strips. A piece of PE was dipped into
the PSR solution for less than 1 min and taken out for an
immediate drying in air for 10 s. The PSR-PE was dried again
under vacuum for 1 h.

The sulfur content of the polymer-coated polyethylene
strip was determined in duplicate by elemental analysis
(Atlantic Microlab, GA).

2.2. Surface reactions of Hg-DOM on PE or PSR-PE

Suwannee River natural organic matter (NOM), and fulvic
acid (FA) were obtained from the International Humic
Substance Society (IHSS). Humic acid (HA) and 1,3-
propanedithiol were purchased from Sigma Aldrich and
Alfa Aesar. Because the source and the isolation method for
Sigma Aldrich HA are different from those for IHSS HA, the
differences between FA and HA reported in this paper do not
necessarily represent any FA and HA properties in a specific
natural system. Suwannee River NOM, Suwannee River fulvic
acid (FA) and Sigma Aldrich humic acid (HA) were dissolved in
250 mL borosilicate glass bottles to make 10 mg DOM L

solutions. Suwannee River NOM and FA dissolved in water
readily, but the HA solution was sonicated until its complete
dissolution. The solutions were filtered through 0.45 μm
polyvinylidene fluoride (PVDF) membrane filters to remove
particulate matter. An aqueous solution of 1,3-propanediol
was freshly prepared by dissolving 1,3-propanediol in 1 M
NaOH and diluted 400 fold to make 5.41 mg mL

solutions. Because Suwannee River NOM, FA, and HA have
0.65 wt%, 0.44 wt% and 0.96 wt% sulfur respectively, accord-
ing to the elemental analysis results reported by IHSS and
Pitois et al. (2008), 10 mg L

DOM solutions have 1.4–3.0 μM sulfur, which is an excess amount for mercury binding in
50 nM Hg solutions. The pH was adjusted to 7 with 0.01M
potassium monophosphate buffer. The mixtures of mercrnic
ion and DOM were shaken for one week to allow sufficient
reaction time for forming Hg-DOM. One piece of PE or PSR-PE
was in contact with 40 mL of these solutions for 4 weeks. The
PE or the PSR-PE strip was taken out, washed with DI-water,
and gently pressed on Kimwipes to remove water on a PE or
a PSR-PE strip. PSR-PESs after the reaction with Hg-DOM were
washed with MilliQ water followed by drying in vacuum for 1 h. The remaining aqueous solution was preserved by adding 400 μL of BrCl.

2.3. DOM contact with Hg pre-loaded PSR-PE

HgCl₂ stock solution in 1 M HCl was used to make 10 ppm Hg solution in 0.01M potassium monophosphate buffer to maintain the pH at 7. One piece of PSR-PE was in contact with 40 mL of 10 ppm Hg solutions for 1 week. The PSR-PE strips were taken out, washed with DI-water, and gently pressed on Kimwipes to remove water on the PSR-PE strip. The Hg-loaded PSR-PE was then in contact with 40 mL of 10 mg L⁻¹ NOM, FA, HA, or 5.41 mg L⁻¹ 1,3-propanedithiol for 4 weeks. The PSR-PE strips were taken out after the reactions, washed with DI-water, and gently pressed on Kimwipes to remove water on the PE strips. The PSR-PE strips were dried for 1 h in vacuum and analyzed by Fourier transform infra-red spectroscopy (FT-IR) and x-ray photoelectron spectroscopy (XPS). The remaining aqueous solution was preserved by adding 400 μL of BrCl to the reaction vessels.

2.4. Total mercury analysis

Four mL of preserved duplicate samples was filtered through 0.45 μm polyvinylidene fluoride (PVDF) membrane filter. The filtrate was diluted to ensure mercury concentrations were within the detection range of 0.5–400 ng L⁻¹. The total mercury concentrations were measured by Tekran 2600 cold vapor atomic fluorescent spectrometry (CVAFS) following the US EPA (Environmental Protection Agency) method 1631 revision E.

2.5. X-ray photoelectron spectroscopy (XPS)

XPS techniques were used to determine the surface concentrations of sulfur and mercury on PSR-PE, PE, or Hg-preloaded PSR-PE before and after the reactions with Hg-DOM or DOM. Three spots for each sample were analyzed to account for non-uniform distributions of sulfur and mercury atoms on the PSR-PE surface. PHI 5000 Versa-Probe scanning XPS microprobe with Al Ka x-ray radiation (1486 eV) was used under high vacuum condition (below 10⁻⁵ Pa). Charging effects by the poor surface conductivity were minimized by applying 10 eV argon ions. Analytical sample size for the effects by the poor surface conductivity were minimized by applying 10 eV argon ions. Analysing sample size for the IR beam passes through perpendicularly. Forty scans were averaged for each spectrum.

2.6. FT-IR analysis of PSR-PE

Far infra-red (FIR) spectra of Hg-pre-loaded PSR-PE (Hg-PSR-PE) after the reaction with DOM were obtained with Bruker Vertex 70 FT-IR spectrometer using a deuterated triglycine sulfate (DTGS) detector. A piece of PSR-PE was placed where the IR beam passes through perpendicularly. Forty scans were averaged for each spectrum.

3. Results and discussion

3.1. Synthesis of PSR-PE and proposed reaction pathways

The acronyms, definitions, and units for the terms used in this paper are summarized in Table 1. The synthesis procedure for PSR-PEs involves a solution casting of PE strips with PSR polymer solution in toluene, and drying in vacuum to produce a thin layer of PSR polymer over the PE surface as depicted in Fig. 1. The surface areas of PSR and PE are assumed to be proportional to the atomic counts of the constituting atoms (C and S for PSR, and C for PE) based on the XPS analysis of PSR-PE before the reactions with DOM-bound Hg. The PSR is constituted of the repeating \(-\text{C}_n\text{S}_x\) segments, and with the average atomic % of sulfur on PSR at 4.0 atom%, the contribution of PSR to the total carbon atomic count is approximately 2.0 atom%. Accounting for the different atomic radii of sulfur and carbon, 0.109 nm and 0.091 nm respectively, the average fractions of PSR (f_{PSR}) and PE (f_{PE}) on a PSR-PE strip were determined as \(f_{PSR} = 0.067\) and \(f_{PE} = 0.933\). The possible reactions of DOM-bound mercuric ion with a PE strip or a PSR-PE strip are illustrated in Fig. 2. Each Hg-DOM species (NOM, FA, HA, or 1,3-propanedithiol) was reacted with PE or PSR-PE separately for comparison. As illustrated schematically in Fig. 2, Hg-PSR and Hg-DOM-PE are proposed as the products of the two possible reaction pathways after the DOM-bound mercuric ion encounters PSR-PE. These reactions represent the sorption of Hg-DOM to the surface via direct Hg-sulfur interactions (Hg-PSR) or indirectly by DOM-PE hydrophobic interactions (Hg-DOM-PE).

The reaction represented by Hg-PSR differs from that for Hg-DOM-PE in terms of where a mercuric ion is situated. Mercuric ion binds both with DOM and polysulfide in Hg-PSR, after which DOM may be detached from mercuric ion. However, in the case of the Hg-DOM-PE pathway, which utilizes DOM hydrophobic interaction with polyethylene,
mercuric ion does not form a chemical bond with polysulfide. The total aqueous mercury concentration measured after the reaction between PSR-PE and Hg-DOM is defined as \([\text{Hg-DOM}]\). Due to the 1000-fold mass ratio of DOM to Hg and the high stabilization constants for the association reactions between mercuric ion and DOM (Benoit et al., 2001a,b; Khwaja et al., 2006; Miller et al., 2009; Dong et al., 2010), DOM-bound mercuric ion would be the major constituent of total mercury concentration in the aqueous phase. \([\text{Hg}]_{\text{sorbed}}\) can be defined by using a mass balance with the total aqueous mercury concentrations before and after the reaction with DOM-bound mercuric ion (equation (1), (2)).

\[
\text{Hg}_{\text{tot}} = V_{aq} \cdot [\text{Hg} - \text{DOM}] + S_{\text{PSR-PE}} \cdot [\text{Hg}]_{\text{sorbed}}
\]

(1)

\[
[\text{Hg}]_{\text{sorbed}} = [\text{Hg} - \text{PSR}] + [\text{Hg} - \text{DOM} - \text{PE}]
\]

(2)

By our experimental methods, \([\text{Hg-DOM}]\) includes the amount of aqueous phase mercury and any mercury loss by the reaction vessel (glass vial) because BrCl, a strong oxidant, was directly spiked to the vial after PSR-PE strip was removed so that BrCl would oxidize and extract any trace mercury from the glass wall and the lid. However, such mercury partitioning on the glass vial was negligible because the mercuric ion loss by the same glass vial with the same or higher DOM concentration was not significant according to the previous experimental data not reported here. Hg-DOM-PE.

### 3.2. Surface reaction of DOM-bound mercuric ion on PSR-PE

In order to estimate overall Hg-DOM removal efficiencies by PSR-PE, dissolved mercury concentrations after the reactions were measured and compared with the Hg-DOM solutions without any sorbents. Because dissolved humic substances, especially those with reduced sulfur groups are the main competitors for mercuric ion, we tested dissolved natural organic matter, fulvic acid, humic acid, and 1,3-propanedithiol (PDT) as representatives of reactive constituents in sediment pore water. The results are depicted in Fig. 3, showing a strong partitioning of PDT-bound mercuric ion as well as HgCl₂ by PSR-PE. The partition coefficient \(K_1\) is defined as the ratio of the total mercury concentration on PSR-PE surface to the total aqueous mercury concentration (equation (3)).

\[
K_1 = \frac{[\text{Hg}]_{\text{sorbed}}}{[\text{Hg}]_{\text{aqueous}}} = \frac{[\text{Hg}]_{\text{sorbed}}}{[\text{Hg} - \text{DOM}]} \frac{V_{aq} \cdot [\text{Hg} - \text{DOM}]}{S_{\text{PSR-PE}} \cdot [\text{Hg} - \text{DOM}]} \text{[Lm}^{-2}\text{]}
\]

(3)

Thus, the overall removal processes incorporated in \(K_1\) represent the combination of the two proposed reaction pathways. As shown in Fig. 3, the partition coefficients vary from 13 to 115 L m⁻².
3.3. Reactions between PE strip and DOM-bound mercuric ion

Because the complexation of mercuric ion with DOM itself transforms ionic mercury into a more hydrophobic species, namely Hg-DOM, the PE surface can provide sorption sites for Hg-DOM via a favorable DOM-PE hydrophobic interaction, i.e., the second pathway in Fig. 2. The PE/water partition coefficient with Hg-DOM gives a good criterion to estimate how much Hg-DOM sorption on PE alone contributes to the overall reaction between PSR-PE with Hg-DOM. A hydrophobic partition coefficient assigned for this reaction equals the ratio of \([\text{Hg-DOM-PE}]\) to the total aqueous mercury species (equation (4))

\[
K_2 = \frac{[\text{Hg-DOM-PE}]}{[\text{Hg-DOM}]} = \frac{f_{\text{PE}}[\text{Hg-DOM-PE}]_{\text{PE-only}}}{[\text{Hg-DOM}]} \tag{4}
\]

where Hg-DOM-PE denotes PSR-PE-bound Hg-DOM due to a favorable hydrophobic interaction between DOM and PE. As shown in Fig. 4 and 1,3-propanedithiol-bound mercuric ion has a high affinity for PE, which indicates a significant encapsulation of mercuric ion with a hydrophobic bidentate ligand, and a large contribution of the adsorption reaction to the overall reaction between PSR-PE and Hg-PDT. In contrast, the mercuric ion complexed with Suwannee River natural organic matter, fulvic acid, or humic acid as well as HgCl\(_2\) does not exhibit high removal efficiency by PE alone (Fig. 4) compared with that by PSR-PE (Fig. 3). These differences suggest the overall reactions between PSR-PE and Hg-DOM (NOM, FA, or HA) comprise other reactions than the hydrophobic adsorption reactions between DOM and the PE itself.

3.4. Comparison on the atomic % of mercury on PSR-PE and PE surfaces after the reactions with Hg-DOM

The surface concentrations of mercury on PSR-PE and PE were measured after the reaction with Hg-DOM. The XPS analyses were used to estimate the proportion of the easily accessible (i.e., not significantly covered by organic matter) mercury among the total immobilized mercury on PSR-PE. Because XPS is a surface sensitive technique that measures the atomic compositions in the top \(\sim 10\) nm layer, any deposition of organic substances over mercuric ion will shield the escaping electron and reduce the signal. Therefore, we can qualitatively estimate the extent of the shielding effect from DOM or PSR by comparing the total immobilized mercury concentrations on PSR-PE or PE as exhibited in Fig. 3 or Fig. 4 and the XPS results as shown in Fig. 5. Whereas the Hg-DOM removal efficiency of PSR-PE (Table S1) ranges from 96% to 531% of the same Hg-DOM removal by PE, the estimated surface concentrations of mercury on PSR-PE and PE (Fig. 5) after the reactions with the same Hg-DOM species are not significantly different with each other. This indicates that Hg-DOM removal by PSR-PE involves partial covering of Hg ions with DOM, or migration of mercuric ion into the inner PSR layer.

3.5. Overall Hg-DOM immobilization reaction pathways with PSR-PE

Table 2 summarizes two partition coefficients obtained from the two sets of surface reactions, one with PSR-PE and Hg-DOM, and the other with PE and Hg-DOM. Since \(K_1\) and \(K_2\) formulate two equations for three unknowns, the two classes of sorbed mercury concentrations, \([\text{Hg-PSR}]\) and \([\text{Hg-DOM-PE}]\), can be expressed as functions of the aqueous mercury concentration, \([\text{Hg-DOM}]\). With these constants and the following reaction model equations (5)–(7),

\[
f_{\text{add}} : \text{PSR} + \text{Hg} + \text{DOM} \rightarrow \text{Hg} + \text{PSR} \tag{5}
\]
Summary of the partition coefficients and the error in their estimation. The columns represent the average values of the triplicates, and the error bars correspond to the standard deviations.

Overall reaction:

\[ \text{PSR – PE + Hg – DOM} \rightarrow f_{\text{add}} \text{Hg} + f_{\text{ads}} \text{Hg – DOM – PE} \quad (7) \]

we can calculate how much each reaction pathway contributes to the overall reaction. By definition, a contribution factor \( f_{\text{add}} \) or \( f_{\text{ads}} \) means the fractions of addition (via pathway 1) or adsorption (via pathway 2) reaction to the overall reaction, which can be defined as a ratio of each corresponding reaction product concentration to the total surface mercury concentration (equations (8)–(10)).

\[
f_{\text{add}} = \frac{\text{Hg – PSR}}{\text{Hg}_{\text{adsorbed}}} \quad (8)
\]

\[
f_{\text{ads}} = \frac{\text{Hg – DOM – PE}}{\text{Hg}_{\text{adsorbed}}} \quad (9)
\]

The definitions of the reaction constants and the solutions for \( f_{\text{add}} \) and \( f_{\text{ads}} \) are summarized in Table 3. The results shown in Table 4 reveal that the reaction of Hg-DOM on PSR-PE is mainly by the addition reaction, i.e., via pathway 1, with complexation of mercuric ion with PSR, except for the case with 1,3-propanedithiol. The hydrophobic partitioning reaction has the highest importance in the PDT-mediated mercury sorption on PSR-PE.

The dependence of the major reaction pathway on DOM may stem from the Hg-DOM binding strength or the bulkiness of Hg-DOM, which varies with DOM. Suwannee River NOM, FA, and HA solutions have excess amounts of sulfur (1.4–3.0 \( \mu \text{M} \)) for mercury binding in 50 \( \text{nM} \) Hg solutions, and the proportion of reduced sulfur groups in river DOM ranges from 13 to 36% of the total sulfur (Ravichandran, 2004). Therefore, the amount of reduced sulfur atoms in the DOM solutions would not affect the overall affinity of DOM for mercuric ion. Instead, the interaction of mercuric ion with

---

**Table 2** – Summary of the partition coefficients \( K_1 \) and \( K_2 \).

<table>
<thead>
<tr>
<th>DOM</th>
<th>( K_1 ) (( \pm \text{error} )) [L m(^{-2})]</th>
<th>( K_2 ) (( \pm \text{error} )) [L m(^{-2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>86.6 (( \pm )4.3)</td>
<td>6.61 (( \pm )0.66)</td>
</tr>
<tr>
<td>Suwannee River</td>
<td>13.2 (( \pm )6.4)</td>
<td>4.15 (( \pm )0.50)</td>
</tr>
<tr>
<td>natural organic matter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suwannee River fulvic acid</td>
<td>38.2 (( \pm )17.7)</td>
<td>4.15 (( \pm )0.53)</td>
</tr>
<tr>
<td>Humic acid</td>
<td>14.8 (( \pm )2.2)</td>
<td>2.71 (( \pm )0.89)</td>
</tr>
<tr>
<td>1,3-propanedithiol</td>
<td>115 (( \pm )5.4)</td>
<td>122 (( \pm )32.1)</td>
</tr>
</tbody>
</table>

a  The errors in \( K_1 \) and \( K_2 \) are:

\[
K_1 = \left( \frac{\text{error in[Hg}_{\text{adsorbed}}]}{\text{Hg}_{\text{adsorbed}}} \right)^2 + \left( \frac{\text{error in[Hg – DOM]}}{\text{Hg – DOM}} \right)^2
\]

\[
K_2 = \left( \frac{\text{error in[Hg – PE]}}{\text{Hg – PE}} \right)^2 + \left( \frac{\text{error in[Hg – DOM]}}{\text{Hg – DOM}} \right)^2
\]

(Valcárcel, 2000).

---

**Table 3** – Summary of the partition coefficients and the solutions of the contribution factors, \( f_{\text{add}} \) and \( f_{\text{ads}} \), expressed in terms of the defined constants, \( K_1 \) and \( K_2 \).

- \( \text{Hg}_{\text{adsorbed}} / \text{Hg – DOM} \) = \( K_1 \)
  \[
  f_{\text{add}} = \frac{\text{Hg – PSR}}{\text{Hg}_{\text{adsorbed}}} - \left( \frac{K_1 - K_2}{K_1} \right) = 1 - f_{\text{ads}}
  \]
- \( \text{Hg – DOM – PE} / \text{Hg – DOM} \) = \( K_2 \)
  \[
  f_{\text{ads}} = \frac{\text{Hg – DOM – PE}}{\text{Hg}_{\text{adsorbed}}} = \frac{K_2}{K_1}
  \]

a  \( K_1 \) is derived from the reactions of Hg-DOM with PSR-PE; \( K_1 \) is the ratio of the total surface mercury concentration to the total aqueous mercury concentration. \( K_2 \) is a partition coefficient of Hg-DOM between water and PE obtained from the Hg-DOM adsorption study with the PE strips; \( K_2 \) from the Hg-DOM reaction with pure PE is multiplied by \( f_{\text{PE}} \) to reflect the PE surface area on PSR-PE.
a reduced sulfur group in a DOM molecule and other adjacent reactive binding sites in DOM would determine Hg-DOM binding strength. The different DOM molecule sizes can also explain the difference in \( f_{ads} \) because the limited PSR surface area (0.536 cm\(^2\)) can only accommodate 4.5 \( \times 10^{-10} \)–5.6 \( \times 10^{-16} \) mol of Hg-DOM out of 2 \( \times 10^{-9} \) mol of the total Hg-DOM when Hg-DOM is assumed to be a sphere with diameter 0.5–450 nm, where 0.5 nm corresponds to the approximate size of one 1,3-propanedithiol molecule, and 450 nm corresponds to the filter pore size that the NOM, FA and HA molecules passed in preparation of the DOM solutions. Therefore, when the surface area is the limiting factor, a smaller Hg-DOM molecule would be able to react more extensively with PSR regardless of the Hg-DOM bond strength, and \( f_{ads} \) may not provide information about the relative binding strength of Hg-DOM among the tested DOM. In this case, an analogous experiment with excess surface area of PSR for accommodating Hg-DOM may reveal the relative Hg-DOM bond strength.

3.6. Changes in the chemical bonding between PSR and mercuric ion in the presence of DOM

The reaction between Hg-preloaded PSR-PE with DOM provides information about the Hg-PSR bond strength, as DOM can dissolve Hg ions from PSR. Mercuric chloride was pre-loaded on PSR-PE, which produced Hg-PSR-PE. This surface was then reacted with DOM for one month. As the addition reaction proceeds, the PSR-PE surface would be covered with DOM, and Hg-DOM could be dissolved into the water depending on the Hg-DOM binding strength. It is also possible to have a subsequent migration of DOM-bound mercuric ion toward the hydrophobic PE surface. Our data on the aqueous mercury concentration after the reaction with each DOM (Table S2) reveal that the total amount of the immobilized mercury remaining on PSR-PE is close to that without DOM, which indicates an insignificant amount of remobilization of PSR-PE-bound mercuric ion by DOM.

One way to assess the amount of Hg-PSR bond breakage or weakening by DOM is to analyze FT-IR spectra around 350–390 cm\(^{-1}\) for the characteristic IR peaks for Hg-S (Al-Jeboori et al., 2010). As shown in Fig. 6, without any DOM, the major peak for Hg-S appears at 354 cm\(^{-1}\), which is lower than the emerging peaks at around 376 cm\(^{-1}\) in the presence of DOM. This change indicates that new Hg-S bonds are formed with DOM and existing bonds between polysulfide and mercuric ion are weakened or broken. The extent of the change is most prominent with 1,3-propanedithiol, which has two highly reactive thiol groups per molecule to compete with PSR for mercuric ion. According to the decrease in the absorbance intensities at 354 cm\(^{-1}\) with respect to those at 376 cm\(^{-1}\) as shown in Fig. 6, the extent of perturbation to Hg-PSR bond is comparable among NOM, FA, and HA. A diminished binding strength of Hg-PSR does not necessarily imply a lower stability of the immobilized mercuric ion unless Hg-DOM formation results in its transport into the water. The favorable interaction between DOM and hydrophobic PE surface or fouling of Hg-PSR by the DOM

![Fig. 6 – FT-IR spectra (far-infrared region) of Hg-PSR-PE after the reaction with various DOM for one month. Hg-PSR-PE-buffer represents a control group that has no dissolved organic matter.](image)
could compensate for any diminishment of Hg-PSR bonding and keep the immobilized mercury from being released into the solution.

4. Conclusion

A comparison of Hg-DOM interactions with a hydrophobic surface (PE) and a sulfur-rich surface (PSR-PE) showed the stronger interactions of Hg-DOM with PSR-PE. A greater amount of Hg-DOM was removed by PSR-PE than PE when NOM, FA, or HA was present in the solution, during which DOM accumulation over mercury or migration of mercuric ion into the inner PSR layer occurred. This implies a significant contribution of the PSR-mediated reaction to the overall Hg-DOM immobilization reaction. The organic compound, 1,3-propanedithiol, was examined as a strong competing ligand for mercuric ion, and 1,3-propanedithiol-bound mercuric ion was most effectively removed via an adsorption reaction pathway. The changes in the relative peak intensities at 354 cm\(^{-1}\) and 376 cm\(^{-1}\) in the FT-IR spectra of HgCl\(_2\)-preloaded PSR-PE after the reaction with DOM suggest that partial breakage or weakening of PSR-Hg bonds took place with additional complexation with DOM. The magnitude of the change is most prominent with 1,3-propanedithiol. Since both PSR and PE participate in Hg-DOM removal from water, it is beneficial to develop a multi-functional sorbent that has high affinities for both DOM and mercuric ions in order to achieve high mercury removal efficiencies in sediments. Depending on the \(f_{\text{add}}\) and \(f_{\text{ads}}\) values for the Hg-DOM of concern, different ratios of hydrophobic/reduced-sulfur-rich sorbent can be determined for an optimum Hg-DOM removal efficiency.

Acknowledgments

The authors acknowledge the National Institute of Environmental Health Sciences (NIEHS), grant number R01 ES016143-02, for the financial support of this study.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.watres.2011.08.003.

References


Skyllberg, U., 2008. Competition among thiols and inorganic sulfides and polysulfides for Hg and MeHg in wetland oils and sediments under suboxic conditions: illumination of controversies and implications for MeHg net production. J. Geophys. Res. 113, G00C03.


