Kinetics of abiotic mercury(II) reduction by iron(II): Homogeneous and heterogeneous catalysis

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Biogeochemical cycling of Hg at the solid-water interface
Hg(0) in ground water

Reduction Fe and Hg Species in MMR Plume

- samples where Hg$^\circ$ is a very small % of total Hg
- slope = 9.3 n mole Hg/mole Fe
  - approx. sed ratio = 5 n mole Hg/mole Fe

(Lamborg and Kent, unpublished results)
Fe(II) and dissolved organic matter reduce Hg(II) in the dark. Limited data exist on the kinetics and mechanism of these reactions. The existing studies point to relatively fast kinetics with half lives in the order of tens of minutes.

Hg reduction pathways

- **Biotic pathways**
  Hg resistant (mer) operon is found in the majority of bacteria that have evolved resistance to mercury; merA reduces Hg (II) to Hg(0).

- **Abiotic pathways (dark)**
  Fe(II) and dissolved organic matter reduce Hg(II) in the dark.

  Limited data exist on the kinetics and mechanism of these reactions.

Hg resistant (mer) operon is found in the majority of bacteria that have evolved resistance to mercury; merA reduces Hg (II) to Hg(0).
Objectives

- To understand the mechanism for abiotic Hg(II) reduction by Fe(II)
- To develop a kinetic model for this reduction reaction that can be incorporated into fate and transport models
Experimental setup

Hg(0) measured with CV-AFS directly from the gold traps at different times.

Teflon vessel

flow meter

Fe^{II}/Fe^{III}
trap to scrub residual O_2

moisture scrubber

gold trap to scrub residual Hg

N_2

moisture scrubber

gold trap to remove Hg(0)
Experimental setup, cont’d

- Hg(II) initial concentration = 50 pM (10 ng L\(^{-1}\))
- Fe(II) concentration = 0.1 – 1 mM
- Goethite (\(\alpha\)-FeOOH), 45 m\(^2\) g\(^{-1}\)
  Hematite (\(\alpha\)-Fe\(_2\)O\(_3\)), 43 m\(^2\) g\(^{-1}\)
  \(\gamma\)-Al\(_2\)O\(_3\), 97 m\(^2\) g\(^{-1}\)
- pH = 5.5 - 8
- Ionic strength at 0.1 M with NaNO\(_3\)
- Experiments conducted in the dark in an anaerobic chamber
Conceptual model for Hg(II) reduction by Fe(II)

Homogeneous reduction

Surface-catalyzed reduction

Hg(II) reduction by Fe(II)

Water

Solid

Surface coordination

Surface-catalyzed reduction
Model for homogenous reduction of Hg(II) by Fe(II)

\[ \text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{(II)}(\text{OH})^+ \]

Aqueous hydrolysis of Fe\(^{2+}\)
(equilibrium \(\log K = 4.5\))

\[ \text{Hg}^{(II)}(\text{OH})_2 \]

One-electron reduction of Hg(II)
(irreversible kinetic – rate determining)

\[ \text{Hg}^{(I)}\text{OH} + \text{Fe}^{(III)}(\text{OH})_2^+ \]

\[ \text{Fe}^{(II)}(\text{OH})^+ \]

\[ \text{Hg}^{(0)} + \text{Fe}^{(III)}(\text{OH})_2^+ \]

One-electron reduction of Hg(I)
(irreversible kinetic – very fast)
Homogeneous reduction of Hg(II) by Fe(II)

Strong pH dependence shows that the FeOH$^+$ species, and not total Fe (II), reduce Hg(II):

$$r_{\text{hom}} = 7.19 \times 10^3 [\text{Hg(OH)}_2] [\text{Fe(OH)}^+]$$
Model for surface-catalyzed reduction of Hg(II) by Fe(II)

Al/Fe(III)\(\text{-O-H}\)

Surface acid-base reaction (equilibrium; from literature)

Al/Fe(III)\(\text{-O}^- + H^+\)

Fe(II) coordination with surface sites; includes >Fe(III)OFe(II)+ and >Fe(III)OFe(II) OH species (equilibrium; from literature)

Al/Fe(III)\(\text{-O}^- + \text{Fe}^{(II)}\)

Al/Fe(III)\(\text{-O}^- \text{-Fe}^{(II)}\)

Hg(II) coordination with surface sites (reversible kinetic – slow)

Al/Fe(III)\(\text{-O-H + Hg(OH)_2} + H^+\)

Al/Fe(III)\(\text{-O-Hg}^+ + 2\text{H}_2\text{O}\)

Hg(II) coordination with surface sites (reversible kinetic – slow)

Al/Fe(III)\(\text{-O-Fe}^{(II)} \text{+ Hg(OH)_2}\)

Al/Fe(III)\(\text{-O-Fe}^{(II)-Hg(OH)_2}\)

Hg(II) interaction with the reducing sites (reversible kinetic – slow)

Al/Fe(III)\(\text{-O-Fe}^{(III)} + \text{Hg}^{(I)}\)

Electron transfer and Hg(I) release (irreversible kinetic – fast)

Al/Fe(III)\(\text{-O-Fe}^{(III)} + \text{Hg}^{(I)}\)

Hg(I) reduction to Hg(0) at the surface or in solution (irreversible kinetic – fast)

mineral-water
Adsorption of Fe(II) onto mineral surfaces

Fe(II) adsorption to goethite (Dixit et al., 2006)
Tot Fe(II) = 0.215 mM
Tot Fe(III) surface site = 0.448 mM

Fe(II) adsorption to hematite (Liger et al., 1999)
Tot Fe(II) = 0.160 mM
Tot Fe(III) surface site = 0.200 mM

Fe(II) adsorption to γ-Al2O3 (Nano et al., 2006)
Tot Fe(II) = 0.10 mM
Tot Al(III) surface site = 1.83 mM

Used surface complexation with diffuse double layer to model existing data in literature.
Surface-catalyzed reduction of Hg(II): Goethite + Fe(II)

\[
\begin{align*}
    r_{ads} &= k_{ads} \left[ >SOH \right] \left[ Hg(OH)_2 \right] \\
    r_{des} &= k_{des} \left[ >SOHg^+ \right] \\
    r_{red} &= k_{red} \left[ >SOFe^{(II)_T} \right] \left[ Hg(OH)_2 \right]
\end{align*}
\]
Surface-catalyzed reduction of Hg(II): Hematite + Fe(II)

Fe(II) = 1 mM
Tot hematite = 5 m² L⁻¹
pH = 7.3

Hg(0) concentration (pM)

Time (min)

6.2

Fe(II) = 1 mM
Tot hematite = 5 m² L⁻¹
pH = 7.3

Hg(0) concentration (pM)

Time (min)

6.2

Tot hematite = 10 m² L⁻¹
pH = 7.4

6.8

6.1
Surface-catalyzed reduction of Hg(II): $\gamma$-Al$_2$O$_3$ + Fe(II)
## Kinetic and equilibrium expressions and constants

<table>
<thead>
<tr>
<th>reaction and rate expression</th>
<th>homogeneous $k$</th>
<th>surface-catalyzed $k$</th>
<th>$\gamma$-Al$_2$O$_3$ $k$</th>
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</thead>
<tbody>
<tr>
<td><strong>kinetic</strong></td>
<td></td>
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<tr>
<td>Fe$^{2+}$ + OH$^-$ ⇌ Fe(OH)$^+$</td>
<td></td>
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<tr>
<td>homogenous Hg(II) reduction (kinetic)</td>
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<tr>
<td>2FeOH$^+$ + Hg(OH)$_2$ → Hg$^0$ + 2Fe$^{3+}$ + 4OH$^-$</td>
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<tr>
<td>$r_{hom} = k_{hom} [\text{FeOH}^+] [\text{Hg(OH)}_2]$</td>
<td>7.19×10$^3$</td>
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<tr>
<td>surface acid-base (equilibrium)</td>
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<tr>
<td>$&gt;$SOH + H$^+$ ⇌ $&gt;$SOH$_2^+$</td>
<td>6.19</td>
<td>8.41</td>
<td>7.7</td>
</tr>
<tr>
<td>$&gt;$SOH ⇌ $&gt;$SO$^+$ + H$^+$</td>
<td>-10.41</td>
<td>-10.57</td>
<td>-10.2</td>
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<tr>
<td>Fe(II) adsorption (equilibrium)</td>
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<tr>
<td>$&gt;$SOH + Fe$^{2+}$ ⇌ $&gt;$SOFe$^+$ + H$^+$</td>
<td>-1.29</td>
<td>-0.48</td>
<td>-3.70 and -0.66</td>
</tr>
<tr>
<td>$&gt;$SOH + Fe$^{2+}$ + H$_2$O ⇌ $&gt;$SOFe(II)OH + 2H$^+$</td>
<td>-9.85</td>
<td>-9.18</td>
<td></td>
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<tr>
<td>Hg(II) adsorption (kinetic)</td>
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<tr>
<td>$&gt;$SOH + Hg(OH)$_2$ → $&gt;$SOHg$^+$ + H$_2$O+ OH$^-$</td>
<td>8.98×10$^3$</td>
<td>3.07×10$^5$</td>
<td>1.36×10$^1$</td>
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<tr>
<td>Hg(II) desorption (kinetic)</td>
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<tr>
<td>$&gt;$SOHg$^+$ + 2H$_2$O → $&gt;$SOH + Hg(OH)$_2$ + H$^+$</td>
<td>1.89×10$^{-2}$</td>
<td>2.24×10$^{-1}$</td>
<td>6.13×10$^{-3}$</td>
</tr>
<tr>
<td>surface-catalyzed Hg(II) reduction (kinetic)</td>
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<tr>
<td>2$&gt;$SOFe(II)OH + Hg(OH)$_2$ → Hg$^0$ + 2$&gt;$SOFe(III)OH</td>
<td>4.69×10$^+3$</td>
<td>8.22×10$^+3$</td>
<td>1.11×10$^{+2}$</td>
</tr>
</tbody>
</table>
Conclusions

- Hg(II) reduction rate is controlled by Fe(II) speciation and not just total Fe(II) concentration.
- Kinetics of Hg(II) reduction by adsorbed Fe(II) may be described as a set of surface-controlled adsorption and reduction processes.
- Depending on their type and concentration, minerals can accelerate or slow down the Hg(II) reduction rate by Fe(II).
- The model developed here may be easily incorporated into reactive transport models to simulate Hg(II) reduction by Fe (II).
Hg in ground water is not well studied.

A series of studies in coastal New Jersey sand aquifers showed that 6-10% of 147 water well samples had Hg ≥ 2 µg L⁻¹ or 10 nM (Julia Barringer, USGS).

It was proposed that onset of anoxia releases the iron oxide coating that promotes Hg mobility.
Modeling data

- Existing data on mineral surface acid-base and Fe(II) adsorption reactions were modeled using the diffuse double layer model with the computer program, Fiteql.

- Computer program, Phreeqc, was used to model the kinetic and equilibrium data for homogeneous and surface-catalyzed reactions.

- Fits to kinetic the data were provided by varying rate constants for Hg(II) interactions with dissolved and sorbed Fe(II); Matlab was used to provide best fit to the data.