Mercury and ISTD: Research Overview and Perspectives

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Mercury is one of the most common metals identified at Superfund sites
## Mercury Exposure & Toxicity

- Hg$^0$ and MeHg are **NEURO- and NEPRHOTOXINS**

<table>
<thead>
<tr>
<th>Species</th>
<th>Important Exposure Pathway</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg$^0$</td>
<td>Inhalation</td>
</tr>
<tr>
<td>MeHg</td>
<td>Ingestion</td>
</tr>
</tbody>
</table>

- Facile tissue transport of MeHg:
  - Causes biomagnification up the food chain
  - Makes MeHg an important teratogen

# Common Forms of Hg

<table>
<thead>
<tr>
<th>Chemical Properties</th>
<th>Inorganic Mercury</th>
<th>Organic Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hg&lt;sup&gt;0&lt;/sup&gt;</td>
<td>HgCl&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>M.W. [g/mol]</td>
<td>200.59</td>
<td>271.50</td>
</tr>
<tr>
<td>Melting Point [°C]</td>
<td>-38.87</td>
<td>276</td>
</tr>
<tr>
<td>Boiling Point [°C]</td>
<td>356.9</td>
<td>302</td>
</tr>
<tr>
<td>Density at 20°C [g/mL]</td>
<td>13.546</td>
<td>5.44 at 25°C</td>
</tr>
<tr>
<td>Vapor Pressure [mmHg]</td>
<td>1220 at 20°C</td>
<td>834000 at 25°C</td>
</tr>
<tr>
<td>Solubility in H&lt;sub&gt;2&lt;/sub&gt;O [g/L]</td>
<td>5.6 x 10&lt;sup&gt;-5&lt;/sup&gt; at 25°C</td>
<td>69 at 20°C</td>
</tr>
<tr>
<td>K&lt;sub&gt;OW&lt;/sub&gt;</td>
<td>4.15</td>
<td>3.33</td>
</tr>
</tbody>
</table>
Key Points that affect remediation

- Elemental Hg is a DNAPL
- Elemental Hg and HgCl$_2$ are volatile
- HgCl$_2$ is soluble
- Hg speciation includes both inorganic and organic forms
- Organic mercury bioaccumulates
Aqueous Speciation of Hg(II) in Aerobic Environments

- **Graph a**: 
  - % Hg(II) Distribution vs pH
  - Species: Hg$^{2+}$, Hg(OH)$_2^0$, HgNO$_3^-$

- **Graph b**: 
  - % Hg(II) Distribution vs pH
  - Species: HgCl$_2^0$, Hg(OH)$_2^0$, HgOHCl$^0$, HgCl$_3$
Inorganic Speciation in Water

With DOM

With \([S^=] + \text{DOM}\)

DOM speciation
Dominates except at high \([S^{2-}]\)

- freshwater conditions
- marine conditions
- polysulfides absent

Skullberg, U. (2012), Environmental chemistry and toxicology of mercury, pg 215
• Methylation is an accidental byproduct of microbial activity – sulfate reducing bacteria

• Mercury-sulfur speciation is the key to understanding mercury methylation and affects a) bioavailability and b) mercury solubility
• Mercury vs. methyl mercury (MeHg)

  - Methylation is an accidental byproduct of microbial activity

  - sulfate reducing bacteria

\[
Hg^{2+} \rightarrow \text{Methyl Mercury} \Rightarrow CH_3Hg^+
\]

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\]
Methylation Paradigm

- Mercury vs. methyl mercury (MeHg)
  - Methylation is an accidental byproduct of microbial activity

\[ \text{Inorganic Mercury} \quad \Rightarrow \quad \text{Methyl Mercury} \]

\[ \Rightarrow CH_3Hg^+ \]

\[ \text{uncharged, bioavailable mercury-sulfide} \]
Atmospheric Deposition

Sources of Hg emission

- Utility Boilers: 32.8%
- Municipal Waste Incinerators: 18.7%
- Industrial Boilers: 17.9%
- Medical Waste Incinerators: 10.1%
- Manufacturing: 10.0%
- Hazardous Waste Incinerators: 4.4%


### Sources of Mercury Emissions in the U.S.

<table>
<thead>
<tr>
<th>Industrial Category</th>
<th>1990 Emissions (tpy)</th>
<th>2005 Emissions (tpy)</th>
<th>Percent Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Plants</td>
<td>59</td>
<td>53</td>
<td>10%</td>
</tr>
<tr>
<td>Municipal Waste Combustors</td>
<td>57</td>
<td>2</td>
<td>96%</td>
</tr>
<tr>
<td>Medical Waste Incinerators</td>
<td>51</td>
<td>1</td>
<td>98%</td>
</tr>
</tbody>
</table>

- Chlor-alkali plants have phased out Hg cells in favor of membranes
- More stringent regulations promoting control technologies such as:
  - Selective catalytic reduction with flue-gas desulfurization (SCR-FGD)
  - Activated carbon injection (ACI) with fabric filter (FF) or electrostatic precipitators (ESP)
- Medical industry phase-out of mercury thermometers

For more information:
- [http://www.ehjournal.net/content/8/1/2](http://www.ehjournal.net/content/8/1/2)
- [http://www.epa.gov/mats/powerplants.html](http://www.epa.gov/mats/powerplants.html)
Atmospheric deposition has decreased…

But legacy deposition and mining sites have left contaminated soils & sediments

Provide constant flux to ground & surface waters

Stumm, W., & Morgan, J.J. (1996), Aquatic chemistry: chemical equilibria and rates in natural wates
Diverse Site Speciation: Solid & Liquid Phases

Relative maximum compositions for:
1. chlor-alkali deposition
2. Au|Ag|Hg mine processing
3. military/industrial spillage

Davis, J (2012)
NOM is important in both pore water and solid speciation:

WHENEVER ORGANIC MATTER IS PRESENT, IT TENDS TO DOMINATE

Ligand binding strength: \( \text{Hg}–\text{S} > \text{Hg}–\text{N} \approx \text{Hg}–\text{O} > \text{Hg}–\text{Cl} \)

Hg(SR)\(_2\), \(\alpha\)-HgS, \(\beta\)-HgS & thermodynamically favored

Enhanced stability of NOM:

strong linear bridge with weaker contributions from C, N or O ligands

1. Electro-remediation

- Description
  - Uses electrodes to form and extract metal complexes
  - Electromigration, electroosmosis and electrophoresis

- Advantages
  - In-situ, chemical-free treatability
  - Permanent removal of Hg
  - Simultaneous treatment of other metals
  - Effective for soils of low hydraulic permeability

- Disadvantages
  - Interference by non target ions
  - Separation of HgS, generating larger waste volumes
  - May require chemical addition if Hg$^0$ dominates speciation (low solubility in soils)

2. Stabilization/solidification

- **Description**
  - Promotes formation of stable HgS or solidified in sulfur polymer cement

- **Advantages**
  - *In-situ*, low cost treatability
  - Waste volume reduction

- **Disadvantages**
  - Hg is not removed from the soil column
  - Long-term monitoring may be required

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3. Nanotechnology

• Description
  o Uses FeS nanoparticles to immobilize Hg

• Advantages
  o In-situ, low cost, low energy treatability
  o No additional waste volume

• Disadvantages
  o Effects of soil pH need to be determined
  o Effects on soil microorganisms need to be determined

4. **Phytoextraction**

   **Description**
   - Uses living plant roots to extract Hg from contaminated soils

   **Advantages**
   - *In-situ*, low cost, low energy treatability
   - Permanent removal of Hg
   - No additional waste volume reduction

   **Disadvantages**
   - Effective only remediates surface soils
   - No hyperaccumulator plant species have been identified
   - Chemical additives may be required for effective removal

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From 1950-1982 estimates of 240,000 pounds of mercury released from Y-12 to Upper East Fork Poplar Creek. An estimated 2 million pounds of mercury was unaccounted for.
Thermal Desorption


Thermal Desorption

In-situ Thermal Desorption

Why thermal desorption works:

- The graph shows the relationship between temperature (T °C) and pressure (PRES (mm Hg)) for various substances.
- The equation $1000/T = 1000/K$ is used to plot the data.
- Substances such as Benzene, Water, Mercury, Naphthalene, PCB 1242, PCB 1260, Benzene, Water, Mercury, Naphthalene, PCB 1242, and PCB 1260 are depicted.
- The table below provides vapor pressure data for Hg (Hg$^0$) and HgCl$_2$:

<table>
<thead>
<tr>
<th>Substance</th>
<th>pVap (mm Hg)</th>
<th>Hg$^0$</th>
<th>HgCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.22E3 @ 20 °C</td>
<td>8.34E5 @ 25 °C</td>
</tr>
</tbody>
</table>

Stegemeier, G. L., & Vinegar, H. J. (2000), *Hazardous and radioactive waste treatment technologies handbook* (pp. 4.6–1 – 4.6–38)
Experimental Evaluation

Thermal Remediation

Off-Gas Treatment

Courtesy of George Stegemeier
Experimental Evaluation

Thermal Remediation

Sample Vial contains 5% HNO₃/10% H₂O₂

Impinger 1: 5% HNO₃/10% H₂O₂
Impinger 2: 4% KMnO₄/10% H₂SO₄
Impinger 3: 4% KMnO₄/10% H₂SO₄

Off-Gas Treatment

Courtesy of George Stegemeier
Vapor Pressure-Temperature Correlations

Temperature (°C)

Vapor Pressure (atm)

C10F18 correlation (29)

Mercury data (30)

C10F18 data
Perfluorodecalin can be used as a surrogate for elemental mercury.

Experimental Evaluation: Controlled Experiments

Experimental Evaluation: Controlled Experiments

Elemental mercury removal compared to STARS simulation

Two approaches:

1. Thermodynamic modeling
2. Standard thermo-desorption curves
Experimental Approach: Field Samples

Speciation determined by comparing thermal desorption of field soils to thermodynamic modeling (FactSage)

Experimental Approach: Environmental Samples

Speciation using thermodynamic modeling

<table>
<thead>
<tr>
<th>Model species</th>
<th>Mercury (M)</th>
<th>Inorganic ligands (M)</th>
<th>Redox condition</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$Hg^{2+}$</td>
<td>$Hg_2^{2+}$</td>
<td>$Cl^-$</td>
</tr>
<tr>
<td>$Hg(l)$</td>
<td>2.4</td>
<td>9.0e-7</td>
<td>&lt; 1.0e-1</td>
</tr>
<tr>
<td>$HgS(s)$</td>
<td>2.4</td>
<td>1.0e-8</td>
<td>-</td>
</tr>
<tr>
<td>$HgCl_2(s)$</td>
<td>2.4</td>
<td>1.0e-8</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Phase transition simulation of $Hg(\ell)$

Phase transition simulation of $HgS(s)$

Experimental Approach: Environmental Samples

Speciation using thermodynamic modeling

Phase transition simulation of HgCl$_2$(s)

```
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<td>&lt; 4.4</td>
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<td>1.0e-8</td>
<td>-15</td>
</tr>
<tr>
<td>HgCl$_2$(s)</td>
<td>2.4</td>
<td>1.0e-8</td>
<td></td>
</tr>
</tbody>
</table>
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HgCl$_2$(s) $\rightarrow$ HgCl$_2$(g)

Experimental Approach: Environmental Samples

Speciation using standard thermo-desorption curves

Probability distributions of thermally desorbed standards

Experimental Approach: Environmental Samples

Speciation using standard thermo-desorption curves

Experimental Approach: Environmental Samples

Speciation using standard thermo-desorption curves

- Elemental
- Chlorides
- Sulfides & Cinnabars
- Humic & Acetic Acids, Oxides, Sulfates, & Nitrate

References:
- Watling et al. (1972)
- Bombach et al. (1994)
- Windmoller et al. (1996)
- Bäster & Nehrke (1997)
- Bäster & Scholz (1997)
- Bäster et al. (2000)

EPA Method 7473 T > 750°C

Eddy-Dilek, C. et al. (2012), Remediation of Chlorinated and Recalcitrant Compounds Conference
## Post-treatment: Scrubbing

<table>
<thead>
<tr>
<th>Traditional scrubbing techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet scrubbing</td>
</tr>
<tr>
<td>Activated carbon injection</td>
</tr>
<tr>
<td>Sulfur-impregnated activated carbon</td>
</tr>
<tr>
<td>Gold amalgamation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Advanced scrubbing techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver-promoted molecular sieves</td>
</tr>
<tr>
<td>Metal-sulfide systems</td>
</tr>
</tbody>
</table>


Post-treatment: Schematic

Post-treatment Remediation: Hg(II) Adsorption to Fe Oxides
Where do we go from here?

1. Obtain more experimental data regarding:
   • Speciation effects
   • Matrix-binding effects (e.g. FeS–Hg, NOM–Hg)
   • Mixed-Waste
2. Perform mechanistic analyses, account for variation among similar species
3. Validate and improve thermodynamic models
4. Improve field characterization methods
5. Perform optimization studies
6. Construct pilot projects
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