ASSESSMENT AND REMEDIATION OF MERCURY CONTAMINATED SITES

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Primary Source Sites for SF Bay Region Waterbodies

Images Library of Congress, Sierra Fund, UC Davis, Lumicrest
FISH Hg LINKED TO MINING

- Higher fish [Hg] associated w/watersheds more historical mining
- Only waterbodies downstream of Hg associated mines NOT impaired remediated or not actually connected

Alpers et al, 2016
What are stable isotopes?
Forms of the same element that contain equal numbers of protons but different numbers of neutrons and as a result have different atomic masses

**Mercury Isotopes:**
7 stable isotopes with range in mass from 196 to 204 amu

**Mass dependent fractionation:**
Lighter isotopes react faster and become enriched in the products
Hg stable isotope analysis has provided insights into different sources of Hg—requires unique end-members (and minimal post-source transformation)

- Mines significant source downstream

**Site Assessment: Source attribution using stable isotopes**

- Black Butte Hg Mine, OR
- Wanshan Hg Mine, China
- San Francisco Bay, CA

(Jannsen) (Yin et al, 2013) (Donovan et al, 2013)
Source control has been effective, but enough?

- Uncertainties may be significant, different:
  - Types of sites (3 mines)
  - Remediation strategies
  - Fish sampled
  - Temporal scales
- Downstream mitigation needed
- Improved source control needed

**Graphical Data:**
- Hg levels in fish from different sites.
- Pre-Remediation vs. Post-Remediation.
- US Fish Tissue Criteria: 0.3 mg/kg.
- SF Bay human health criterion: 0.2 mg/kg.
Site Assessment: Source/Site characterization

- Delineate extent of contamination
- High measurement density resolves soil heterogeneity, limited sampling
- Reduce cost/effort

Recommendations for quality data:
- Site/Source-specific reference materials, analysis times
- Aggregate measurements (ISM)
- Reliable limit 2xmdl (~15mg/kg)
- Lab comparison with HF digestion near action levels (or minimal false negatives)

Images: Golder Associates & Eckley et al, 2020
Site Assessment: Risk Assessment

- Speciation/Chemical Extractions
- Reduce cost/effort of cleanup
- Identify environmentally available Hg (EA-Hg potentially harmful/methylatable)
- Support risk assessment
- Target “harmful” Hg rather than “locked” Hg
- SSE recommendation after Bloom, F0-F3 (~F4)

Selective Sequential Extraction & Thermal Desorption

X-Ray Absorption Fine Structure

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<table>
<thead>
<tr>
<th>k^3 * Y(k)</th>
<th>k (Å⁻¹)</th>
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<tbody>
<tr>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
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<td>6</td>
<td>4</td>
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<tr>
<td>5</td>
<td>6</td>
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<tr>
<td>4</td>
<td>8</td>
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- 42% Cinnabar, HgS (hex)
- 39% Metacinnabar, HgS (cub)
- 19% Schuetteite, Hg₃O₂SO₄

Residual = 0.057
Target EA-Hg Target Remedial Method

Enhanced Containment Vapor Mitigation

<table>
<thead>
<tr>
<th>SSE Fraction</th>
<th>Common Mine Source</th>
<th>Primary Exposure Routes</th>
<th>Transformation Exposure Routes</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0 Hg⁰ (elemental, volatile)</td>
<td>Equipment, waste, &amp; spills from ore processing, Overburden (typically low percentage)</td>
<td>Vapor inhalation</td>
<td>Oxidation to reactive, potentially methylatable form (F-1 through F-3)</td>
</tr>
<tr>
<td>F1 water soluble (~DI WET)</td>
<td>Calcines (tailings), Ore (typically low percentage), Overburden (typically low percentage), Equipment, waste, &amp; spills from ore processing, Native soil contaminated by atmospheric fallout</td>
<td>Dust inhalation, Dust ingestion</td>
<td>Methylation or can be (mobilization to aquatic environment, bioaccumulation, fish consumption)</td>
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<tr>
<td>F2 weak acid soluble (~TCLP)</td>
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<td></td>
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<tr>
<td>F3 organically complexed</td>
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<tr>
<td>F4 strongly complexed</td>
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<td></td>
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<tr>
<td>F5 mineral phase</td>
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Cleanup Goal

96%
Releases are a concern due to the potential for downstream methylation & bioaccumulation

- Stormflow flux >>> baseflow flux
- Annual loads dominated by a few large events
- Mobilization from erosion of particles/sediment entrainment

**Example:** Cinnabar Mine, ID

[Diagram showing discharge, THg-F load, and THg-P load for different seasons.]
• Positive relationship between THg and total suspended solids (TSS).
• Most regression slopes not significantly different.
• Most intercepts were significantly different and were correlated with the distance downstream from the contaminated source area.
To sieve or not to sieve?

Figure 2. Zones of erosion, transport, and deposition, and the river channel as conveyor belt for sediment. (Reprinted from Kondolf 1994, with kind permission of Elsevier Science-NL.)
### WILDLIFE PROTECTION FISH CRITERIA

- \([\text{Hg}]_{aq}\) necessary to exceed SF Bay Basin Plan Fish Criteria

<table>
<thead>
<tr>
<th>MeHg/HgT range: Coastal = Black et al; ES&amp;T 2009; SF Bay Delta = Choe et. al. Limnol. Oceanogr. 2004; Tidal Marsh = Zhang et. al. ES&amp;T 2014</th>
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<td>Small fish criteria= 0.03 mg/kg</td>
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<tr>
<td>Large fish criteria= 0.2 mg/kg</td>
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### HUMAN HEALTH FISH CRITERIA

- Assumptions:
  - MeHg/HgT 1% to 50%
  - Herbivorous fish, trophic level 3 to 4
  - Biomagnification range 2 to 10

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<tr>
<td>0.000004 to 0.0005ug/L</td>
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<tr>
<td>0.000006 to 0.015ug/L</td>
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Relative magnitude of surface-air versus water flux depends on hydrological/meteorological conditions.

Annual fluxes to the air can be 50-100 kg/year from some contaminated sites.

Soil Hg speciation (along with several environmental parameters) affect surface-air fluxes.

Site Assessment: Pathways of release—flux to air

Source: Eckley et al, 2011
Source: Kocman & Horvat, 2011
Source: Eckley et al, 2020
Site Remediation: Improve Containment

Vapor Barrier

Enhanced Erosion Control
Site Remediation: Sequester environmentally available Hg

Other options:
- Soil-washing
- Solidification/stabilization
- Thermal treatment
- Electrochemical/kinetic recovery
- Bioremediation/biotreatment
- Phytoremediation/stabilization
- Chelating agents
We need to and can optimize Hg source control by:

• Using stable isotope fractionation to identify sources of contamination
• Improving site assessment:
  • Resolve spatial heterogeneity with increased sample density, XRF
  • Identify EA-Hg forms/speciation that are mobile, labile, &/or toxic with speciation/SSE
• Improving site remediation:
  • Prioritize/Target environmentally available-Hg
  • Implement enhanced remedial methods

Next Steps:
• Novel approaches to addressing contaminated sites have been identified at the laboratory and test plot scale;
• However, more examples of large-scale applications are needed to encourage broader adoption of these methods – SF Bay Water Board is implementing several currently
THANK YOU!

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“Freddie Mercury” by Pablo Bustos