Survey of UCSC Mercury Work in and around San Francisco Bay. Hg complexation, salmonid uptake, algal blooms, fuel emissions… a whirlwind tour

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Estimate of mercury emission from gasoline and diesel fuel consumption, San Francisco Bay area
Christopher Conaway, R.P. Mason, D.J. Steding, and A. Russell Flegal

- Major refining center in North America
  - 95 million liters of crude oil per day capacity
  - Produced 20 million liters of gasoline in 1998
- Over 4.5 million vehicles, 13 billion liters of gasoline per year
- Crude oil and mercury deposits known to coexist
- Trace quantities of mercury could result in large emission.
• [Hg] similar to other reported gasoline values
• Lower than typical Hg in crude oil purchased by CA refineries
• Hg from gasoline is a small (< 3%) fraction of local emissions
Mercury deposition in a tidal marsh downstream of the historic New Almaden mining district

Christopher Conaway, Elizabeth Watson, J.R. Flanders, and A.R. Flegal

- Project designed to measure historic Hg contamination in San Francisco Bay
- Determine effects of the weathering of naturally-rich Hg mineralization in the Santa Clara Valley
- Mercury deposition studied in piston cores from a tidal marsh 30-km downstream of New Almaden and cores from South Bay
- Use of pollen appearance for core chronology
Results

• Pre-mining Hg in marsh core is similar to the pre-mining Hg in cores taken throughout the estuary.

• The extent of contamination from mining reflects both mining activity and watershed hydrology.
Methylmercury Toxicity to Developing Fish
Mary Langsner

• Overall Project Goals:
  – Evaluate the role of exposure route in toxicity to developing Chinook and Coho salmon
  – Use standard surrogate laboratory species zebrafish (*Danio rerio*) for methods development and exposure scenarios for MMHg
Zebrafish Development Studies

• Examine effect of MMHg exposure on mechanisms employed by larval fish to protect against xenobiotics.
  – Do general mechanisms also protect against MMHg?

• Project currently in Phase I: establishing methods to detect two multixenobiotic resistance transporters in larval zebrafish using fluorescence microscopy
Effect of a Spring Phytoplankton Bloom on Dissolved MeHg & Hg\textsubscript{T}  
Allison Luengen

- Predictable phytoplankton bloom in South Bay occurs when water column stratifies in spring (Cloern, 1996).

- The phytoplankton bloom depletes nutrients and some trace metals (Beck et al., 2002; Grenz et al., 2000; Luoma et al., 1998).

- This research has measured mercury at 3 sites before, during, and after the spring 2003 bloom in collaboration with Jim Cloern, USGS.
Preliminary Objectives

- The Spring 2003 bloom was an unusually large bloom.
- Did phytoplankton uptake MeHg & HgT from water, creating a pulse of bioavailable mercury to the food-chain?
- Did decay of the bloom remobilize mercury?
- Are blooms important for retaining metals in the estuary?
- Are nutrient-enriched phytoplankton blooms a management concern in the South Bay?
Speciation and Complexation of Inorganic Mercury in Oxic Freshwaters: Role of Wetlands and Reduced Sulfur Ligands

Frank Black and A. Russell Flegal
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Project Objectives

• Quantify Hg(II) complexation in aquatic systems

• Determine role of reducing environments as source of ligands responsible for Hg(II) complexation

• Evaluate importance of sulfide and thiols in Hg(II) complexation

• Determine relative bioavailability of Hg(II) complexed in different natural freshwater systems
Field Campaigns
Alamitos Creek

Alamitos Creek Site 1
Alamitos Creek Site 2

New Almaden mining district
Hg(II) Complexation Capacity
Alamitos Creek Sites 1 and 2

\[ \text{log} [\text{Hg}^{2+}] (\text{M}) \]

\[ \text{log} [\text{Hg}] \text{nat} (\text{M}) \]
Hg(II) Complexation Capacity
Alamitos Creek and Panoche Creek

The diagram shows the log transformation of [Hg^{2+}] (M) and [Hg]_{nat} (M) for different sites and ligand models. The x-axis represents log [Hg]_{nat} (M) and the y-axis represents log [Hg^{2+}] (M). The graph includes data points for Panoche Site A Hydrophilic, Panoche Site A Hydrophobic, Panoche Site B Frozen Hydrophilic, Panoche Site B Frozen Hydrophobic, Alamitos Site 1 Hydrophilic, Alamitos Site 2 Hydrophilic, Alamitos Site 2 Hydrophobic, 1 ligand model, 2 ligand model, 1 ligand model A, 1 ligand model B, and 2 ligand model.
## Ligand Fitting Results Comparison

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>[L']</th>
<th>logK_{cond}^{HgL'}</th>
<th>Method</th>
<th>Working Window</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh/waste water</td>
<td>90-500 pM</td>
<td>&gt;30</td>
<td>CLE-SPE</td>
<td>similar</td>
<td>Hsu and Sedlak, 2003</td>
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<tr>
<td>DOC isolates</td>
<td>-</td>
<td>29.6-31.6</td>
<td>CLE-eq dialysis</td>
<td>similar</td>
<td>Haitzer et al, 2002</td>
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<tr>
<td>DOC isolates</td>
<td>-</td>
<td>18.4-19.8</td>
<td>CLE-LLE</td>
<td>much higher</td>
<td>Benoit et al., 2001</td>
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<tr>
<td>Fresh/sea water</td>
<td>1-60 nM</td>
<td>21-24</td>
<td>Reducible Hg</td>
<td>higher</td>
<td>Lamborg et al., 2003</td>
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<tr>
<td>Fresh/sea water</td>
<td>1.4-4.5 nM</td>
<td>9.7-10.8</td>
<td>OSW-ASV</td>
<td>much higher</td>
<td>Wu et al., 1997</td>
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<tr>
<td>Freshwater</td>
<td>0.01-3.5 nM</td>
<td>26.9-34.2</td>
<td>CLE-SPE</td>
<td></td>
<td>This study</td>
</tr>
</tbody>
</table>

\[
\log K_{cond}^{HgHS_2^-} = 37.1^1 \\
\log K_{cond}^{Hg(GSH)_2} = 30.8^1 \\
\log K_{cond}^{Hg(2,3-dimercaptopropanol)} = 21.6^1 \\
\log K_{cond}^{Hg(HEDTA)^{2-}} = 13.9^2 \\
\log K_{cond}^{Hg(Citrate)^2} = 9.6^2 \\
\]

1 pH = 7.4; 2. pH 7.1, 1 mM Ca^{2+}
Kinetics Study Results, Alamitos Creek Site 1 Amended to 39 uM TSA, spiked to 100 ppt Hg

[Hg] (ppt) in column passing fraction

Hours between TSA added and extraction carried out

Group 1, 2 hours
Group 2, 6 hours
Group 3, 12 hours
Group 4, 24 hours
Group 5, 48 hours
Group 6, 72 hours
Preliminary Conclusions

- Concentrations and conditional stability constants of natural ligands complexing Hg(II) similar to those of reduced sulfur compounds

- Wetlands may be a source of both reduced sulfur compounds and ligands capable of complexing Hg(II), but strong complexation was observed at all sites
Future Work

• Kinetic studies of competing ligand degradation

• CLE-SPE transects along Alamitos Creek

• Lab studies of Hg(II) complexes with sulfide and known thiols in natural waters during SPE

• Determine if complexation of Hg(II) in these natural freshwaters renders Hg(II) more or less bioavailable