San Francisco Bay Mercury TMDL – Implications for Constructed Wetlands

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Total Maximum Daily Load (TMDL)

Definition

- **1972 Federal Clean Water Act [§ 303(d)]** – essentially requires USEPA to manage the nation’s water quality on a watershed basis.

- Calculation of the maximum amount of a specific pollutant that a water body can receive and still meet Water Quality Standards

- Allocation of that (maximum) amount to the various pollutant’s sources

\[ \text{TMDL} = \sum \text{WLA} + \sum \text{LA} + \sum \text{MOS} \]

(from Steve Silva, EPA Region 1)
Total Maximum Daily Load (TMDL)

Process

1. Identify impaired water – “303(d) List”.
2. Determine maximum quantity of a pollutant that a water body can assimilate without exceeding a Water Quality Standard.
3. Quantify current sources of pollutant.
4. Determine necessary load reductions.
5. Allocate maximum pollutant loads to each source.

(from Steve Silva, EPA Region 1)
Mercury – an Environmental Pollutant

Human Exposure


- Neural impairment – children most susceptible
- Level of Concern in Blood = 5.8 THg μg per L
- 6% of U.S.A. childbearing-aged women, blood levels at/above 5.8 (1999-2002)
- Hair Hg levels 20% of U.S.A. childbearing-aged women greater than Federal health standards (UNC Asheville)
- 60,000 U.S.A. births per year Hg impaired (NAS, July 2001)
- Methylmercury (MeHg) is bioavailable form
Mercury – an Environmental Pollutant

Human Exposure Route - Mainly through eating fish

<table>
<thead>
<tr>
<th>Fish Consumption Frequency</th>
<th>Average Hg Hair Concentration (µg/g of hair)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>2.0</td>
</tr>
<tr>
<td>Less than 1 fish meal/month</td>
<td>1.4 (range 0.1 to 6.2)</td>
</tr>
<tr>
<td>Fish meals twice/month</td>
<td>1.9 (range 0.2 to 9.2)</td>
</tr>
<tr>
<td>One fish meal/week</td>
<td>2.5 (range 0.2 to 16.2)</td>
</tr>
<tr>
<td>One fish meal/day</td>
<td>11.6 (range 3.6 to 24.0)</td>
</tr>
</tbody>
</table>

World Health Organization Programme for Chemical Safety
Cited in EPA’s Mercury Study Report to Congress December 1977
Mercury – an Environmental Pollutant

Environmental Effects

- MeHg accounts for 75% of USA fish advisories
- 2073 MeHg fish advisories in 41 states

Fish Consumption Advisories for Mercury

The EPA Web site for this information is: http://www.epa.gov/ost/Fish
SF Bay Mercury Total Maximum Daily Load (TMDL)

GOALS:
1. Reduce total mercury loads into the bay.
2. Reduce methylmercury production.
3. Monitor and focus studies on understanding Bay system.
4. Encourage actions that address multiple contaminants.
Mercury Total Maximum Daily Load (TMDL)

303(d) Impairment – Sports fishery, Endangered species, Habitat

SF Bay Fish Tissue THg Concentration Compared to US EPA Criterion

SF Bay Bird Egg THg Concentration Compared to No Effect Level

California Regional Water Quality Control Board
http://www.swrcb.ca.gov/rwqcb2/sfbaymercurytmdl.htm
Mercury Total Maximum Daily Load (TMDL)

Levels of Particulate Total Mercury in the Water Column

Measured THg Levels

Predicted aqueous THg Levels by reducing sediments by 50%

California Regional Water Quality Control Board
http://www.swrcb.ca.gov/rwqcb2/sfbaymercurytmdl.htm
## Mercury Total Maximum Daily Load (TMDL)

### Mining Legacy vs Contemporary Atmospheric Loading

#### Current Mercury Loads /Proposed Allocations

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>Existing kg/yr</th>
<th>Allocation kg/yr</th>
<th>Per Cent Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediments</td>
<td>460</td>
<td>220</td>
<td>53%</td>
</tr>
<tr>
<td>Upstream Sources (Central Valley)</td>
<td>440</td>
<td>330</td>
<td>25%</td>
</tr>
<tr>
<td>Urban Runoff</td>
<td>160</td>
<td>82</td>
<td>49%</td>
</tr>
<tr>
<td>Rural Runoff</td>
<td>25</td>
<td>25</td>
<td>0%</td>
</tr>
<tr>
<td>Historic Mercury Mine Drainage (Guadalupe River)</td>
<td>92</td>
<td>2</td>
<td>98%</td>
</tr>
<tr>
<td><strong>Atmosphere</strong></td>
<td><strong>27</strong></td>
<td><strong>27</strong></td>
<td><strong>0%</strong></td>
</tr>
<tr>
<td>Wastewater</td>
<td>16</td>
<td>16</td>
<td>0%</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>1,220</strong></td>
<td><strong>702</strong></td>
<td><strong>42%</strong></td>
</tr>
</tbody>
</table>

http://www.swrcb.ca.gov/rwqcb2/sfbaymercurytmdl.htm

SF Bay Catchment - ~40% area of CA; 47% of CA runoff
Comparison of Rates of Atmospheric Mercury Deposition

Newly deposited Hg more bioavailable than that in sediment (Benoit et al, 2003)
Mercury TMDL Compliance Issue #1

- Atmospheric deposition of mercury is an important source.
- States lack interstate regulatory jurisdiction
Mercury Total Maximum Daily Load (TMDL)

Mercury TMDL Compliance Issue #2

- Linkages between particulate THg and MeHg and fish body burdens are not clear.
- Net MeHg production is site specific
- MeHg uptake and biomagnification is foodweb specific.
San Francisco Bay Mercury TMDL –
Implications for Constructed Wetlands

San Francisco Bay Wetland Reconstruction

“… the restored wetland be designed and operated to minimize methylmercury production and biological uptake, and result in no net increase in mercury or methylmercury loads to the Bay.”

California Regional Water Quality Control Board
Basin Plan Amendment – Resolution R2-2004-008
San Francisco Bay Wetlands - Ecological Importance

- Loss >90% of marsh wetlands since 1900
- West coast flyway
- Critical habitat for endangered species

California Clapper Rail
Salt marsh harvest mouse
California Least Tern

Western San Francisco Bay Wetlands: Ecological Importance

Cumulative Effects of SF Bay Wetland Restorations

San Francisco Bay Area Wetlands Ecosystem Goals Project

- HAAF represents only 203 hectares (0.8 %) of 26,300 hectares to be restored by 2055
- Many restoration sites will require fill material
- Intertidal wetlands are potential source of MeHg
Port of Oakland - Commercial Importance

Most important on west coast ($30 B pa)

Potential Win – Win

1. Reduce DM disposal costs.
2. Avoid material & transport cost.

Deep Ocean Disposal Site
Hamilton Army Airfield – FUDS Site

- HAAF will require <10 M yd³ of dredged material
- Upland disposal – Out of Bay (Hg Mass Balance)
China Camp State Park – Reference Site

Spartina foliosa

Salicornia virginica
THg and MeHg in surface (0-4 cm) sediments from various wetlands

- Only a loose relationship between THg and MeHg levels (log – log plot).
- Despite history of mining level of THg and MeHg are median among contaminated sites.
- However, potential for a 10X increase/decrease in MeHg levels.

Benoit et al., 2003
Question:

How do ppb levels of Hg in soil, water and sediment become ppm levels in top aquatic predators? (Benoit et al., 2003)

Clues:

MeHg generally comprises <1% of the THg in soils and sediments, but comprises 99% of the total Hg in fish biomass.

Sulfate-reducing bacteria methylate mercury.
Methylmercury is the species of highest concern

**Food Web**

- **Bacteria in sediment catalyze antagonistic methylation and demethylation reactions.**
- **These reactions are very rapid.**
- **The availability of mercury to methylating bacteria limits MeHg production.**
- **Extent of biomagnification is foodweb specific.**
Macro Drivers of Net Methylation

Wet Season vs Dry Season

San Rafael Average Temperature and Rainfall

- Temperature, °F
- Precipitation
- Minimum Temp
- Maximum Temp

Rainfall, Inches

- January to December

- Number in Interval

- Wet Season
  - Relative MeHg levels (% THg) are 3X greater on average in the wet season.

- Dry Season

Percent MeHg in THg

- 0 to 15

- 0.1 to 10
## Macro Drivers of Net Methylation

### Position in Salinity Gradient

<table>
<thead>
<tr>
<th>Site</th>
<th>THg (ng/gDW)</th>
<th>MeHg (ng/g DW)</th>
<th>Meth. rate (ng/gDW/d)</th>
<th>Dem. rate (ng/gDW/d)</th>
<th>M/D</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Jul-04</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Petaluma River Mud</td>
<td>397 (2)</td>
<td>1.33 (0.32)</td>
<td>7.74 (2.21)</td>
<td>1.26 (0.39)</td>
<td>6.19 (0.99)</td>
</tr>
<tr>
<td>Sonoma Fringe Marsh Mud</td>
<td>358 (10)</td>
<td>0.49 (0.07)</td>
<td>2.80 (0.28)</td>
<td>0.42 (0.14)</td>
<td>7.36 (3.34)</td>
</tr>
<tr>
<td>Sonoma Baylands Mud</td>
<td>296 (10)</td>
<td>2.75 (0.16)</td>
<td>13.21 (3.18)</td>
<td>2.64 (0.14)</td>
<td>5.03 (1.33)</td>
</tr>
<tr>
<td>HAAF Fringe Marsh Mud</td>
<td>299 (117)</td>
<td>1.97 (0.89)</td>
<td>6.59 (4.87)</td>
<td>1.60 (0.91)</td>
<td>4.18 (1.44)</td>
</tr>
<tr>
<td>China Camp Mud</td>
<td>362 (35)</td>
<td>3.71 (0.59)</td>
<td>9.43 (0.19)</td>
<td>3.27 (0.71)</td>
<td>3.00 (0.81)</td>
</tr>
</tbody>
</table>

**Site**
- Hamilton Army Airfield
- Petaluma River
- Sonoma Fringe Marsh
- Sonoma Baylands
- HAAF Fringe Marsh
- China Camp

The table shows the concentrations of THg, MeHg, Methylation rate, Demethylation rate, and Methylation/Demethylation ratio for different sites sampled in July 2004.
High Primary Production – Hallmark of Intertidal Wetlands

San Pablo Bay Wetland Trophic Structure

Salicornia virginica
epipelon
Spartina foliosa
MeHg Biomagnification at the Base of the Foodweb

Mercury Bioaccumulation Factors (BAF)

Hemigrapsus oregonensis

Geukensia demissa

Nassarius obsoletus

\[
\text{Mercury Bioaccumulation Factors (BAF)}
\]

\[
\text{MeHg Tissue/Sediment BAFs}
\]

\[
\text{THg Tissue/Sediment BAFs}
\]
Use of Isotopic Ratios of C, N and S to Unravel San Pablo Bay Wetland Foodwebs?

You are what you eat

<table>
<thead>
<tr>
<th>Species</th>
<th>Marsh Habitat</th>
<th>$\delta^{13}C \pm SD$</th>
<th>$\delta^{15}N \pm SD$</th>
<th>$\delta^{34}S \pm SD$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary producers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Macrophytes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Spartina foliosa</em></td>
<td>Low marsh</td>
<td>-15.1 ± 0.2</td>
<td>10.3 ± 0.3</td>
<td>11.5 ± 0.5</td>
</tr>
<tr>
<td><em>Salicornia virginica</em></td>
<td>High marsh</td>
<td>-26.7 ± 0.2</td>
<td>11.0 ± 1.2</td>
<td>12.3 ± 2.2</td>
</tr>
<tr>
<td>Microalgae</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Microcystis</em> sp.</td>
<td>Marsh pool</td>
<td>-17.7</td>
<td>5.1</td>
<td>9.5</td>
</tr>
<tr>
<td>Macroalgae</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Rhizoclonium</em> sp.</td>
<td>Mid marsh</td>
<td>-20.2</td>
<td>9.6</td>
<td>17.5</td>
</tr>
<tr>
<td><strong>Consumers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Birds</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-F Clapper rail</td>
<td>Low marsh</td>
<td>-18.4 ± 0.2</td>
<td>17.9 ± 0.1</td>
<td>14.6 ± 1.2</td>
</tr>
<tr>
<td>Fish</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arrow goby</td>
<td>Channel</td>
<td>-18.4 ± 0.2</td>
<td>17.9 ± 0.1</td>
<td>14.6 ± 1.2</td>
</tr>
<tr>
<td>Striped mullet</td>
<td>Channel</td>
<td>-16.1 ± 0.2</td>
<td>16.0 ± 0.2</td>
<td>7.4 ± 0.2</td>
</tr>
<tr>
<td>Invertebrates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Mytilus edulis</em></td>
<td>Channel</td>
<td>-18.0</td>
<td>10.0</td>
<td>13.7</td>
</tr>
<tr>
<td><em>Orchestia traskiana</em></td>
<td>Mid marsh</td>
<td>-21.5</td>
<td>11.5</td>
<td>14.1</td>
</tr>
</tbody>
</table>

Dr. Joy Zedler’s Study (1997) of Tijuana Estuary
Fish are trophically linked to *Spartina* derived carbon in the low marsh.
SUMMARY

HAAF Mercury Mass Balance

- Marshes may become net Hg exporters as they mature
- Linkage between particulate THg and fish/egg burdens tenuous
- Antagonistic microbial methylation/demethylation rates are both fast (net MeHg)
  - Large temporal and spatial variability
- Macro drivers of net methylation
  - Wet season
  - Marsh position in salinity gradient
- Uncertainty due to lack of knowledge
  - Availability for methylation
  - Trophic structure and biomagnification
- Adaptive management is essential
Questions?

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