Conceptual Model of Selenium in North San Francisco Bay

Technical Memorandum 4
Prepared by Tetra Tech
Bill Mills, Sujoy Roy, Limin Chen, and Tom Grieb

Presentation to
Advisory Committee
April 1, 2008
Objectives

- Explain important selenium-related processes to stakeholders, and to lay out broad areas of agreement in the scientific literature.
- Summarize spatial and temporal trends in selenium data, with a focus on concentrations in bivalves, waterfowl and fish, so that they can be compared against toxicological and health-based guidelines.
- Highlight data gaps and uncertainties of relevance to the TMDL.
- Guide the development of a numerical model that is proposed to be used to link selenium sources quantified in TM-2 to biota.
Selenium Cycling in North San Francisco Bay
Overview of Presentation

• Summary of processes in
  – Water column
  – Sediments
  – Phytoplankton/bacteria
  – Fish and birds

• Recent data from NSFB

• Next steps in analysis and data collection
Water Column Selenium

• **Selenium (+VI) (selenate):** Present in very oxidizing environments, and does not adsorb strongly to particulates.

• **Selenium (+IV) (selenite):** This form of selenium is common in oxygenated estuarine waters and can be taken up more readily than selenate by microbes and algae.

• **Selenium-II (selenide):** Selenides can form through the uptake of oxidized selenium by plankton or microbes, where the selenium is biologically reduced and incorporated into organic compounds.
Particulate Selenium

- **Mineral-particulate selenium**: Selenium can be adsorbed onto these particles as selenate, selenite, or organic selenide. Exchange between the water and sediments may be important source of mineral sediment-associated selenium. Riverine inputs from the Delta or from tributaries are also an important source.

- **Elemental selenium in zero oxidation state**: This form is stable in mildly reducing conditions, is very insoluble, and can be present in sediments or in suspended particulates.

- **Algal or bacterial associated selenium**: Selenium species, particularly selenite, can be taken up into the cytoplasm of these unicellular organisms as be converted into various organic forms such as seleno-methionine.

- **Selenium associated with organic detritus**: Selenium may be associated with non-living particulate organic carbon, which is likely to have originated in biologically associated selenium.
Bioaccumulation

• Little direct uptake from the dissolved phase for most species
• Uptake occurs through particulates and higher particulate selenium concentrations should result in greater bioaccumulation
Algal Uptake can be Non-Linear to Ambient Concentrations
Dissolved Selenium Concentrations

Low Flow

High Flow

Salinity

Dissolved Se (μg/L)

RMP (pre 07/98)
Cutter (pre 07/98)
RMP (post 07/98)
Cutter (post 07/98)
Selenite Concentrations

High Flow

Low Flow

% Se IV as total dis. Se

Salinity

% Se IV of total dis. Se

Salinity

Apr. 86

Jun. 98

Apr. 99

Sep. 86

Nov. 97

Oct. 98

Nov. 99
Particulate and Dissolved Se: Low Flow
(Source: Cutter Research Group papers)
Particulate and Dissolved Se: High Flow
(Source: Cutter Research Group papers)
Particulate Se As a Function of TSM
(Source: Cutter Research Group papers)

Low Flow

High Flow
Resident Bivalve Data (USGS)

Bivalve Data from Carquinez Strait

<table>
<thead>
<tr>
<th>Year</th>
<th>1976</th>
<th>1985</th>
<th>1995</th>
<th>1999</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se in Tissue (μg/g dry weight)</td>
<td>0</td>
<td>2</td>
<td>14</td>
<td>10</td>
</tr>
</tbody>
</table>

Refinery cleanup in 1998
White Sturgeon Muscle Tissue Data

Year

Muscle selenium concentration (μg/g)


Refinery Cleanup
Transplanted Bivalve Data (RMP)
Bivalves and Sediment Concentrations

- **Sediment, µg/g**
  - 0.59 - 0.66
  - 0.67 - 0.92
  - 0.93 - 1.03
  - 1.04 - 1.51
  - 1.52 - 3.30

- **Bivalves, µg/g**
  - 7.15 - 7.37
  - 7.38 - 7.88
  - 7.89 - 8.59
  - 8.60 - 11.59
  - 11.60 - 25.56

- **Locations**
  - Bilvalves Locations
  - Sediment Locations
  - Refineries
Concentrations in Diving Ducks

Selenium concentrations (muscle, μg/g)

Refinery cleanup
### Uncertainty in Predicting Bioaccumulation

<table>
<thead>
<tr>
<th>Selenium in Different Compartments</th>
<th>Dissolved</th>
<th>Particulate</th>
<th>Prey Items</th>
<th>Predators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenate, Selenite, and Organic Selenide</td>
<td>Conversion to particulate form, and thus bioavailability, varies by selenium speciation. Concentrations and speciation change with season and with the volume of rainfall during the wet season. However, selenium speciation data (i.e., whether in selenite, selenate, or organic selenide form) are available for limited times in the bay.</td>
<td>Algal selenium uptake varies significantly depending on algal species, and may respond only weakly to changes in dissolved selenium concentrations. Recent changes in phytoplankton concentrations may have unknown impacts on bioaccumulation. Bacterial uptake may also occur and result in higher cellular concentrations although data are limited.</td>
<td>Although uptake in prey items can be represented by a simple function, there are several variables, especially feeding rate, assimilative efficiency, and loss rate, that make a significant difference to the prey tissue concentrations. These variables are a function of the species of interest and of the particulate form of selenium. Published bivalve data show some spatial patterns, but there are differences in behavior among resident and transplanted species. For data from transplanted species, different species are used in different salinities in the bay. In recent years, bivalve populations may have changed because of predation. Zooplankton data in the bay are limited although they do not show significant spatial variations.</td>
<td>Based on a limited amount of data, much of it from the 1980s, predator selenium concentrations are generally presented as a linear function of selenium concentration in prey items. There is limited recent data to evaluate changes in response to changes in water column and prey concentrations. There is little direct information on the assimilative efficiency of selenium from different prey items.</td>
</tr>
</tbody>
</table>

#### Key Drivers of Uncertainty

- **Conversion to particulate form, and thus bioavailability** varies by selenium speciation. Concentrations and speciation change with season and with the volume of rainfall during the wet season. However, selenium speciation data (i.e., whether in selenite, selenate, or organic selenide form) are available for limited times in the bay.

- **Algal selenium uptake** varies significantly depending on algal species, and may respond only weakly to changes in dissolved selenium concentrations. Recent changes in phytoplankton concentrations may have unknown impacts on bioaccumulation. Bacterial uptake may also occur and result in higher cellular concentrations although data are limited.

- **Although uptake in prey items** can be represented by a simple function, there are several variables, especially feeding rate, assimilative efficiency, and loss rate, that make a significant difference to the prey tissue concentrations. These variables are a function of the species of interest and of the particulate form of selenium. Published bivalve data show some spatial patterns, but there are differences in behavior among resident and transplanted species. For data from transplanted species, different species are used in different salinities in the bay. In recent years, bivalve populations may have changed because of predation. Zooplankton data in the bay are limited although they do not show significant spatial variations.

#### Data Sources

- Cutter and Cutter, 2004; Doblin et al., 2006; Regional Monitoring Program in San Francisco Bay
- Baines and Fisher, 2001; Hogue et al., 2001; Cloern et al., 1992; Cloern et al., 2007
- Regional Monitoring Program in San Francisco Bay; Linville et al., 2002; Stewart et al., 2004; Luoma and Rainbow, 2005; Luoma et al., 1992; Schlekat et al., 2002
- White et al., 1987, 1988, 1989; Luoma and Presser, 2006; SFEI 2006
Key Findings and Next Steps-1

• For key biological indicators, data beyond 2001 were not available in the public domain.

• In addition to the load changes, there have been recent changes in the ecology of the bay, primarily an increase in phytoplankton productivity to levels seen prior to the *P. amurensis* invasion.

• There is no information now on what the *P. amurensis* populations are, and whether a decline in its numbers may reduce the levels of bioaccumulation in the future.

• Laboratory data show the dramatic effect of algal species on selenium uptake, although this information is not collected in the field.

• Field data show minimal change in particulate selenium concentrations (expressed as μg/g) despite substantial changes in dissolved concentrations in the late 1990’s.
Key Findings and Next Steps-2

• Although 1999-2001 particulate, bivalve, and white sturgeon selenium data do not show decreases from prior periods, the very small amount of bird muscle data does indicate a decrease.

• The role of particulates in the uptake of selenium implies that the modeling of the freshwater residence time and uptake in the bay is critical to understanding potential risk.

• From the sediment coring performed to date, there is limited knowledge of the historical signal of selenium in the bay, especially conditions that were prevalent prior to large scale irrigation in the San Joaquin Valley.