Delta Mercury Control Program Stakeholder Process

Scientific Foundation for TMDL Development & Basin Planning

** Part 2 **

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25 June 2009

Scientific Foundation

Outline

- Methylmercury (MeHg) Cycling
- MeHg Persistence
- Controllable Processes
- Unknowns

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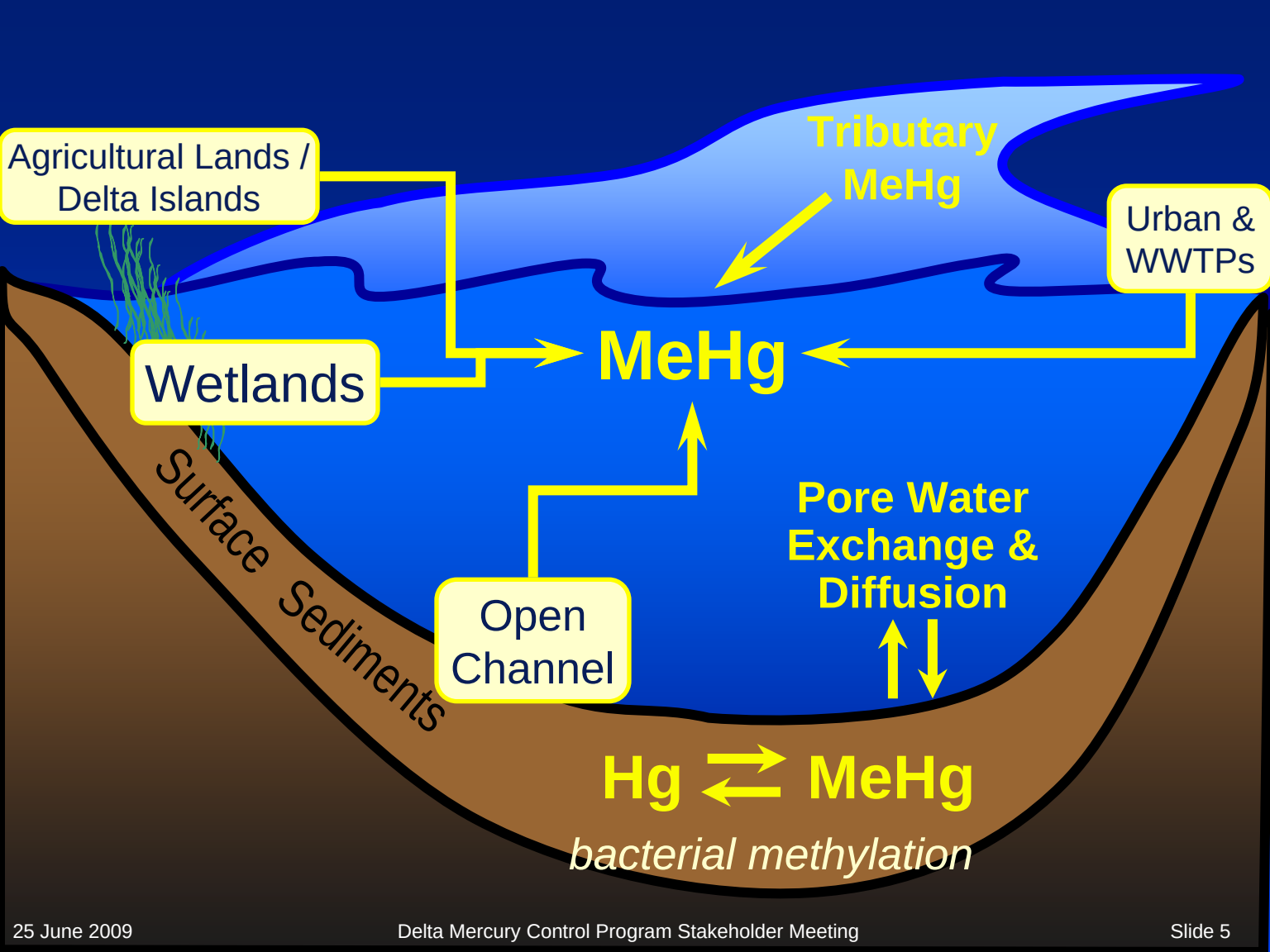
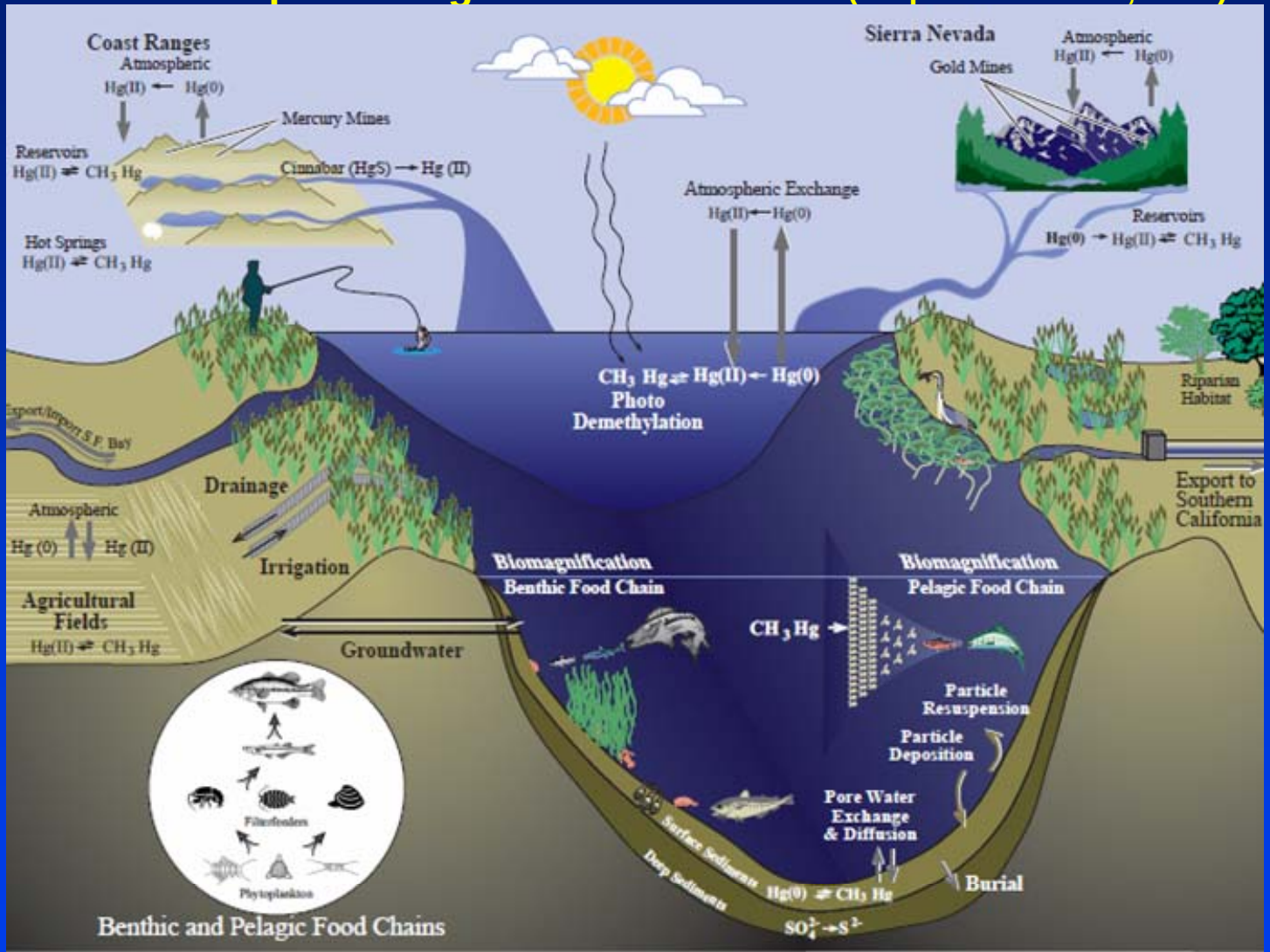
Please save questions until halfway point since we only have an hour today.


Agricultural Lands / Delta Islands
Tributary MeHg
Urban & WWTPs
Wetlands
MeHg
Surface Sediments
Open Channel
Pore Water Exchange & Diffusion
Hg ⇄ MeHg
bacterial methylation

Delta Conceptual Biogeochemical Model (Stephenson et al., 2003)



MeHg concentrations in aquatic ecosystems are the result of two competing processes:

- MeHg Production
- MeHg Loss

Methylation

- MeHg = byproduct of the metabolism of sulfate- and iron-reducing bacteria typically in sediment, sometimes in water
- The amount of MeHg produced is a function of:
  - Amount of active bacteria
  - Availability of inorganic mercury
  - Conditions that affect bacterial growth (e.g., nutrients, temperature, pH).
  - Sulfate-reducing bacteria will produce MeHg even if MeHg is present in the surrounding environment (i.e., MeHg production is not controlled by chemical equilibrium)

Factors Controlling MeHg Production

- Sulfate and pH concentration of the water
- Percent organic content of the sediment
- Creation of new water impoundments
- Amount of permanent or seasonally flooded wetland and floodplain in a watershed
- Amount and kind of inorganic mercury present in the sediment

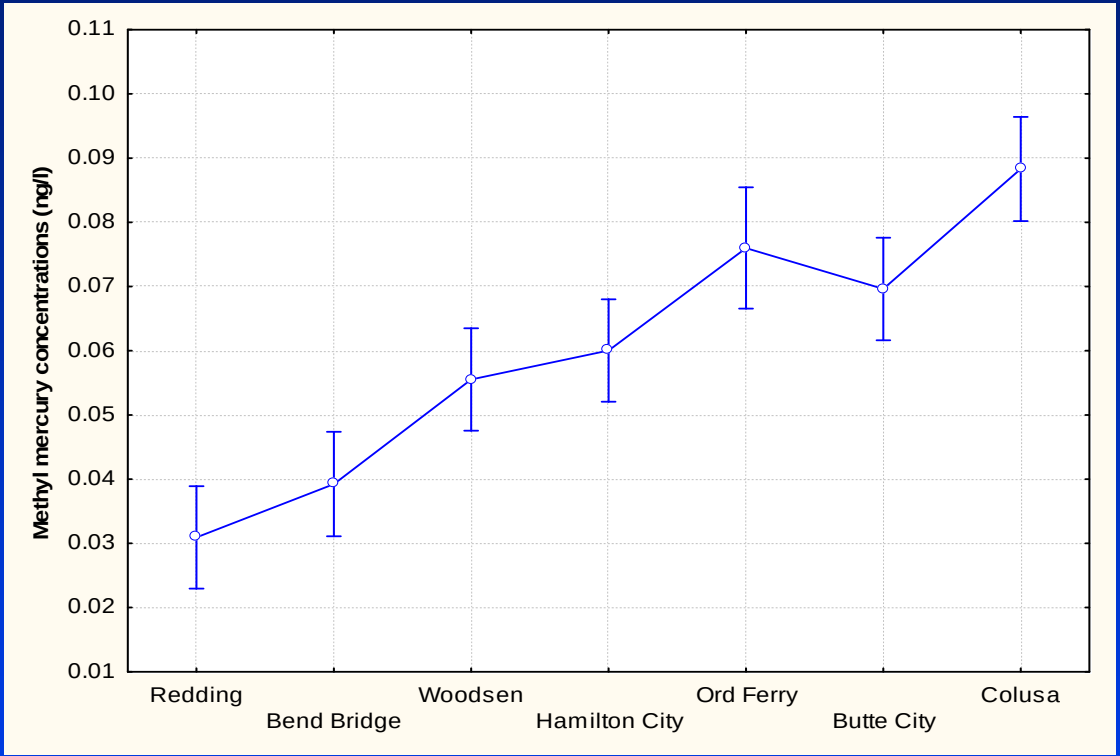
MeHg Loss Processes

- Demethylation:
  - Biotic: Sulfate-reducing and methanogen-type bacteria have been reported to demethylate MeHg in sediment
  - Abiotic: Photodegradation of MeHg in the water column
- Sedimentation & Burial

MeHg Persistence

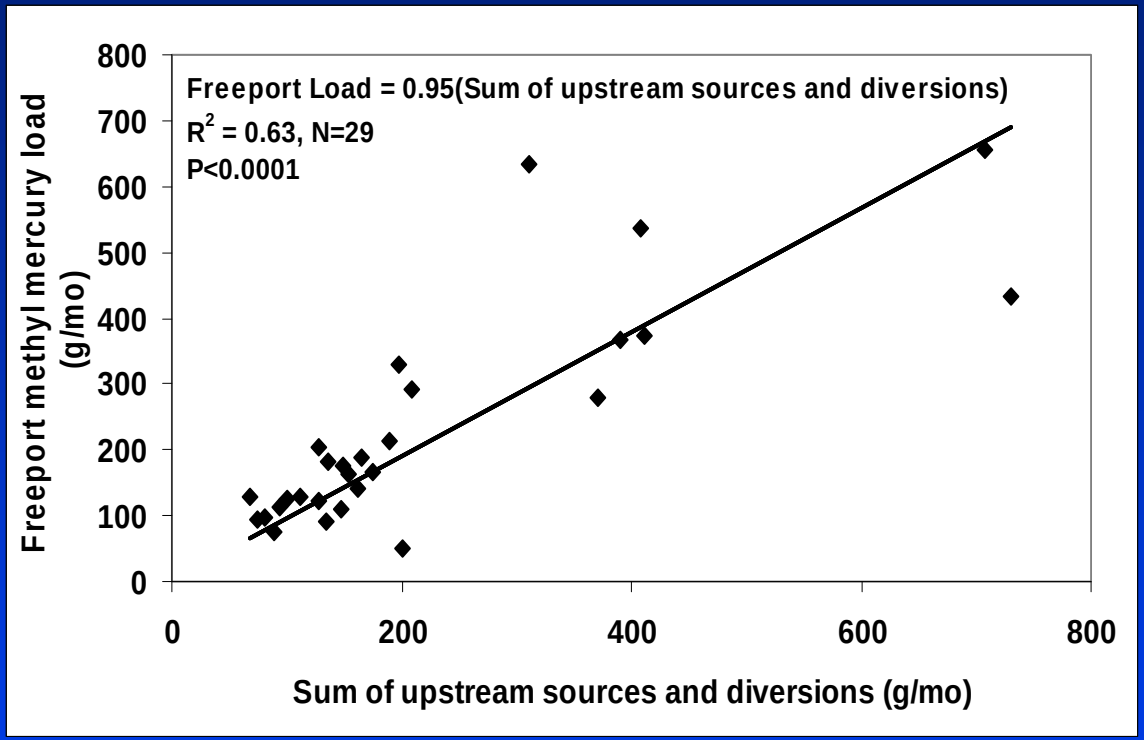
- MeHg is not very reactive left on its own:
  - EPA Method 1630 – 2 day hold time before preservation is needed
  - 50-60 dark/light bottle experiments: Persistent for 8 hours to 10 days
- It behaves conservatively in some river reaches

MeHg Persistence: Transport in Sacramento River



Average MeHg (ng/l) in the Sacramento River between March 2003 and June 2006 (n=30). [The graph does not include storm events.]
(Foe, Louie & Bosworth, 2008 CalFed study)

Transport in Sacramento River – *An example of conservative transport*



MeHg loads in Sacramento River at Freeport as a function of the sum of upstream sources and diversions downstream of Colusa.
(Foe, Louie & Bosworth, 2008 CalFed study)

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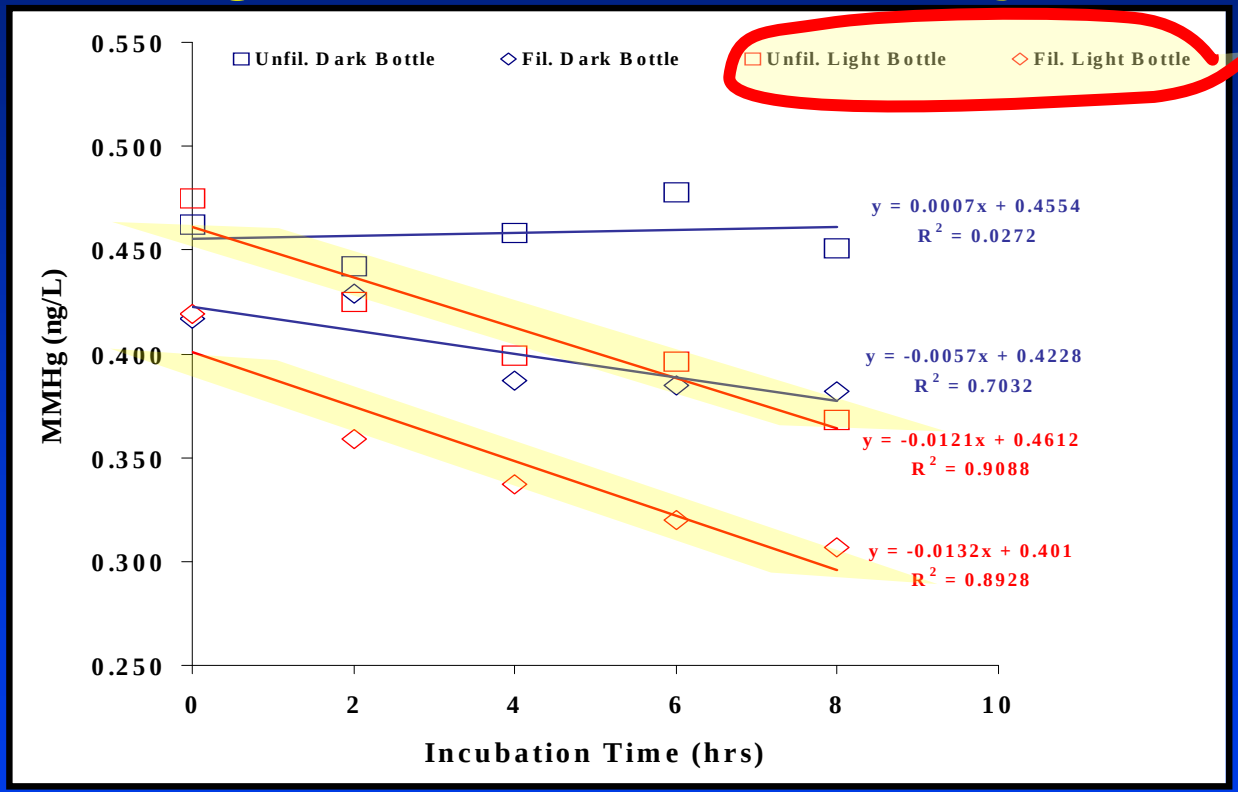
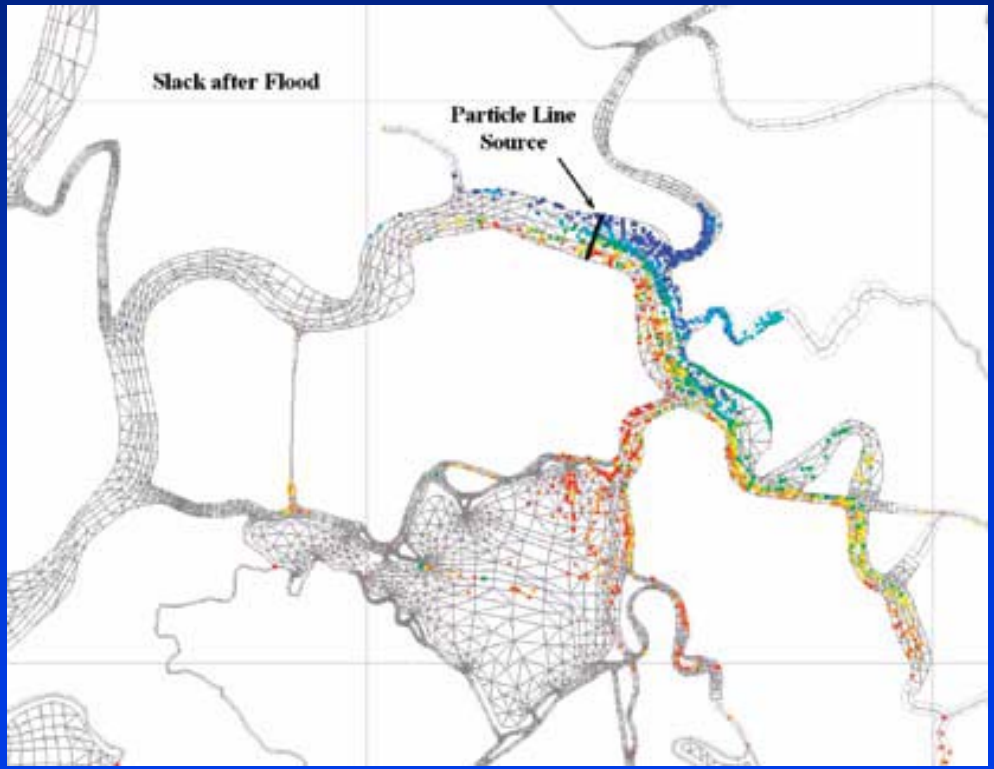
MeHg Persistence: Photodegradation rate 22%/day in Delta



(Gill, Byington et al., 2008 CalFed study (http://mercury.mlml.calstate.edu))

Particle Tracking Model
(Resource Management Associates)



Estimating MeHg loss in the Delta using the RMA Particle Tracking Model

4 Major Inputs:

Sac. R. @ Freeport

San Joaquin River

Prospect Slough

Mokelumne R.

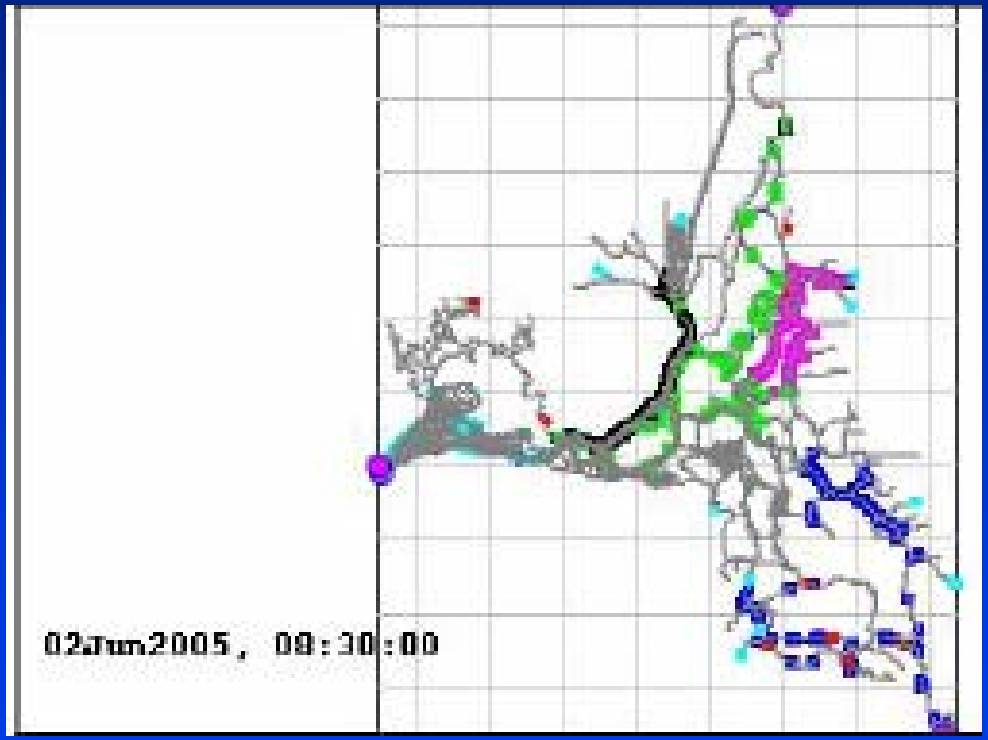
3 Major Exports:

Mallard Island

(Suisun Bay)

Delta Mendota Canal

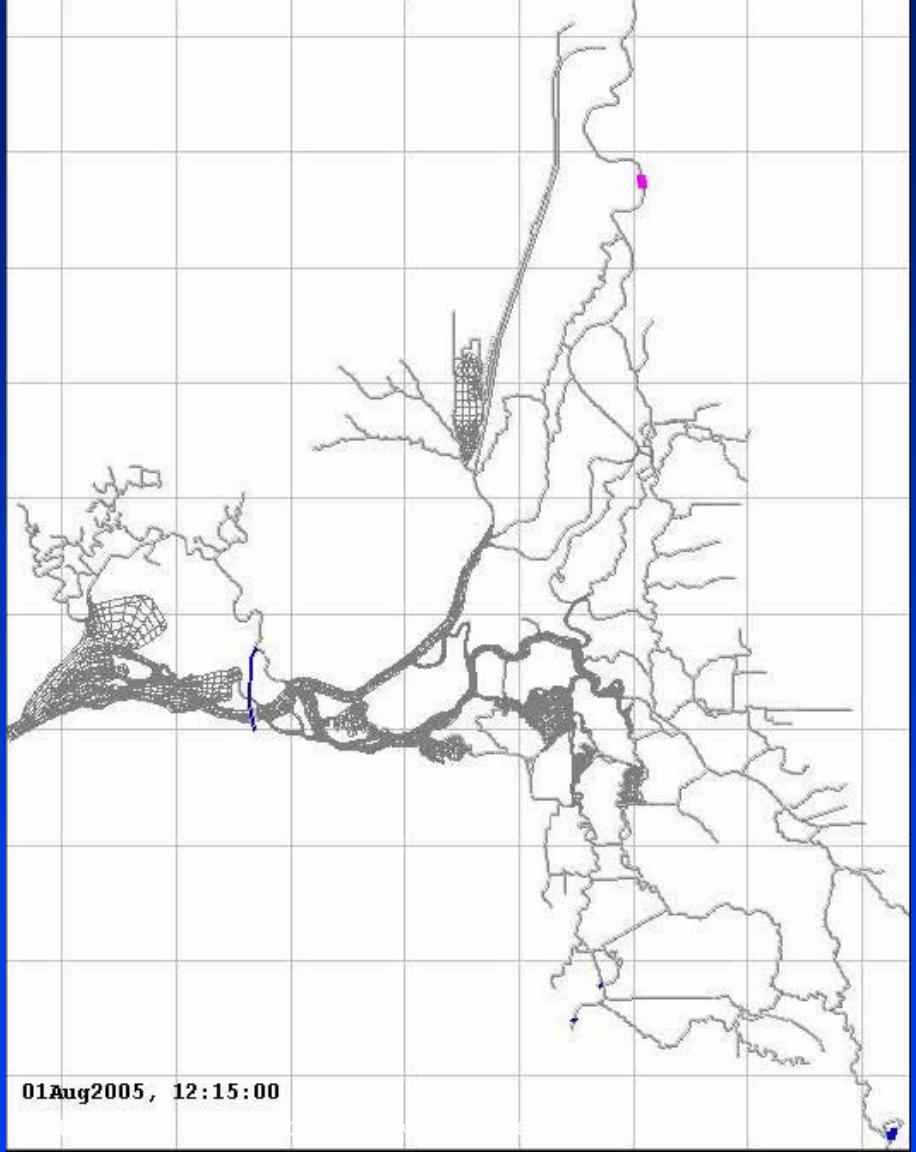
State Water Project



(Stephenson et al., 2008 CalFed study)

MeHg Mass Tracking Model for August 2005

(Movie courtesy of Mark Stephenson)



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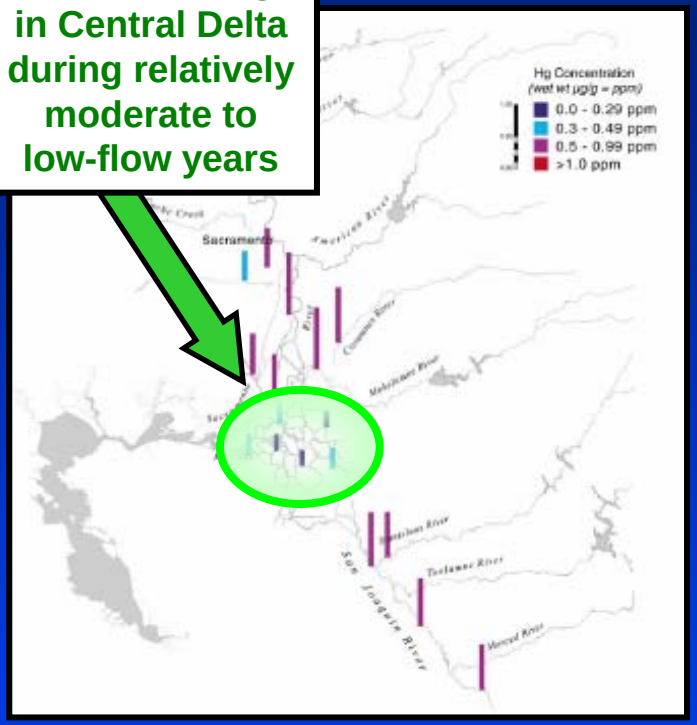
- MeHg persists long enough in tributary and Delta waters to be reflected in fish uptake, with regional patterns that stay consistent over years

CalFed Mercury Program Fish Sampling

Lower fish Hg in Central Delta during relatively moderate to low-flow years



Average Hg Concentrations in largemouth bass, 2000 (Davis *et al.*, 2003)

Inland silverside Hg & MeHg Concentrations, Fall 1999 (Slotton *et al.*, 2002)

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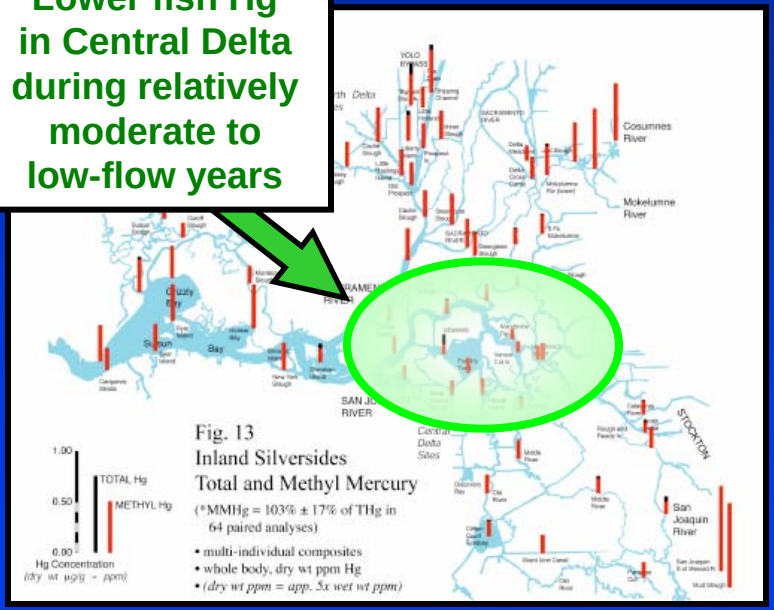

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- MeHg persists long enough in tributary and Delta waters to be reflected in fish uptake, with regional patterns that stay consistent over years
- The Water Boards regulate other chemicals that are more reactive than MeHg (e.g., ammonia and chlorine) and that sorb/desorb to sediment (e.g., copper)

Outline

- Methylmercury Cycling
- MeHg Persistence
- Controllable Processes
- Unknowns

Questions?

Factors Controlling MeHg Production & Loss

- Sulfate and pH concentration of the overlying water
- Organic content of the sediment
- Creation of new water impoundments
- Acres of permanent or seasonally flooded wetland and floodplain in a watershed
- Amount and kind of inorganic mercury present in the sediment
- Sedimentation
- Photodegradation

pH may not be controllable

MeHg Control: Decrease "Food" (carbon)?

Decaying plant matter stimulates MeHg production

Possible control: Reduce plant matter before flooding by disking, mowing, or grazing

Initial Study: DFG and USGS study of wetlands & rice in Yolo Bypass Wildlife Area

MeHg control: Wetland design?

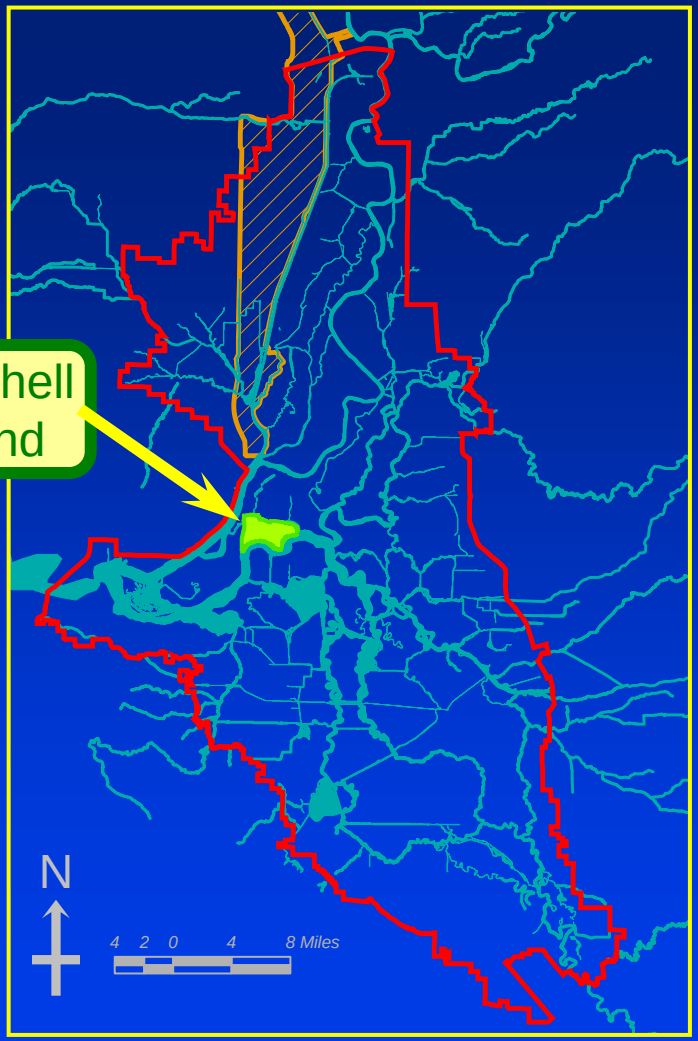
Wetland design affects MeHg levels:

- Tidal versus non-tidal
- Portion that will be seasonally versus permanently flooded
- Depth of water
- Density and type of vegetation
- Locations with high THg concentration in sediment

Proposed study at Dutch Slough Restoration Site: Evaluate effects on MeHg of variations in channel design and elevation; test THg concentration in area that may be flooded.

MeHg Loading from Delta Wetlands

TMDL based on evaluation of MeHg production at two experimental ponds on **Twitchell Island**



Wetland MeHg Characteristics
Preliminary Summary

Watershed	Site	Marsh Type	MeHg Characteristics
Delta	Twitchell Island	2 Permanent (test ponds)	Both **sources** (one with 10x the summer production)
	Browns Island	Permanent, tidal	Small **source**
	Sycamore Slough	Permanent, tidal	**Sink**
Cache Creek	Anderson Marsh	Permanent	**Source**
	Cache Creek Conservancy	Permanent	**Source**
Mud Slough	San Luis Wildlife Refuge	2 Permanent	Both neutral
		6 Seasonal	All **sources**
Suisun Marsh	First Mallard Branch (interior marsh)	Permanent, tidal	**Source**
	Suisun Slough (mouth)	Permanent, tidal	**Sink**

MeHg control: Aeration & circulation?

- Maximum MeHg production occurs at the oxic-anoxic boundary in sediment, usually several centimeters below the surface
- MeHg also may be formed in anaerobic water

Guadalupe Reservoir Study:
Santa Clara Valley Water District's ongoing study, "Reduction of methyl mercury concentrations in an urban lake using a solar-powered circulator", observed **>96%** decrease in unfiltered MeHg in water in 2006 from 2005 levels.

MeHg control: Sulfate?

- Sulfate additions have been observed to both stimulate and inhibit MeHg production
- Factors influencing sulfate concentrations:
  - Water quality objectives for electrical conductivity (EC)
  - Ratio of San Joaquin River to Sacramento River water

Both are controllable water quality factors and result from water management decisions made by the State of California.

Studies are needed to determine whether sulfate concentration in overlying Delta water affect MeHg production in Delta sediments.

MeHg control: Manage water discharge?

Limiting flow from agricultural fields and wetlands decreases MeHg loads.

Possible control: Limit volume and/or timing of discharge

Initial study: Discharge volume and MeHg loads from rice fields during growing season were small. But, draining wild rice fields during harvest caused spike in MeHg export (DFG and USGS, 2008).

MeHg Control: Increase removal from water column?

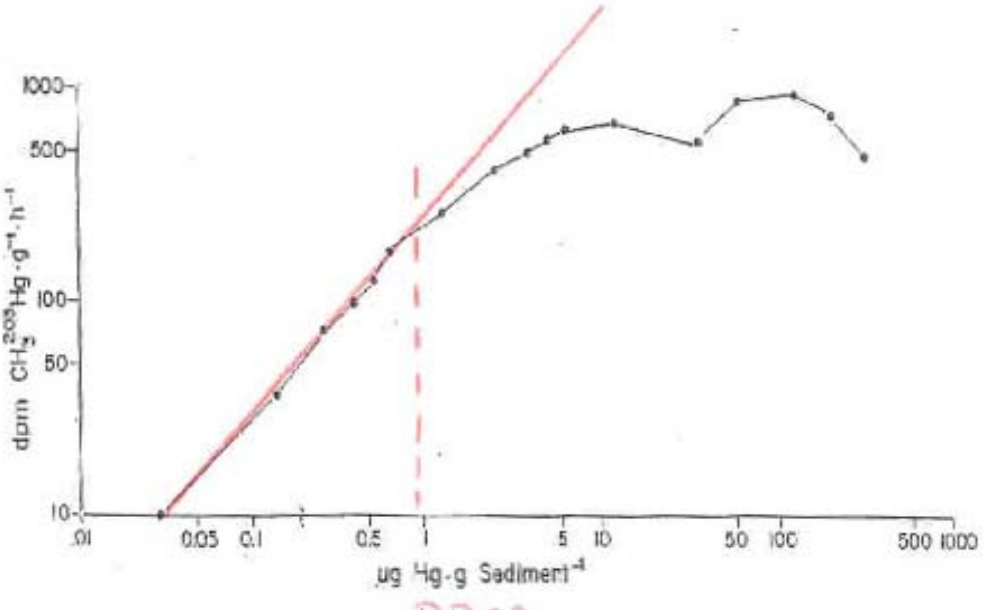
MeHg is removed by settling with particles and by photodegradation

Possible control: Manage water transport and/or retention to maximize the loss processes

Initial Study: DFG testing routing water from seasonal wetland through permanent wetland

MeHg control: Remove THg?

Reducing concentration of inorganic Hg in sediment will lower MeHg production



Influence of inorganic mercury additions in the laboratory on methylmercury production rates in sediment.

From Rudd *et al.*, 1983

Where does inorganic Hg come from?

Delta Sources:

- Wastewater treatment plants (dental, medical, household)
- Atmospheric deposition (local & global emissions)
- Urban runoff
- Tributaries

Where does inorganic Hg come from?

Tributary Sources [~97%]:

- Historic mining activities in tributary watersheds
- WWTP, atmospheric deposition & urban runoff
- Naturally mercury-enriched soils
- Geothermal springs

Legacy Mercury

- Millions of kilograms were released to waterways by historic mining operations.
- >8,000 mines, ~80% of historic mine sites are upstream of dams
- Recent cleanup projects: Sulphur Bank, Abbott-Turkey, Polar Star and Sailor Flat

Historic Mine Sites

- Hg released before dams were built
- Dams trap mercury from upstream mines
- Upstream mine cleanups will benefit reservoirs and upstream creeks but may not have much direct effect on the Delta
- Need to focus on legacy Hg upstream & downstream of dams

Movement of metals in sediment and soil is slow

- Plutonium in Los Alamos Canyon: After 60 years, most Pt remains within 12 miles of source; concentration has decreased 100x.
  Graf, 1996. Geological Society of America Bulletin 108:1342

- Lead in River Swale, England: After heavy mining in 1700-1900, >70% of deposited Pb remains within 30 miles of source; some concentration “hot spots” in downstream floodplains.
  Coulthard & Macklin, 2003. Geology 31:451

Movement of Hg in sediment and soil is slow

- Mercury entering into Harley Gulch from Abbott Mine: 12,000 kg in tailings pile eroding by 0.3-1.1 kg/year
  (Churchill and Clinkenbeard, 2003 CalFed Report)

MeHg control: Remove THg?

Reducing concentration of inorganic Hg in sediment will lower MeHg production.

Proposed study: Nevada Irrigation District and USGS to test THg removal from reservoir sediments by processing dredged material through centrifuge.

Need to identify additional projects to remove in-channel mercury-contaminated sediments.

Unknowns

- Better characterization of existing MeHg sources in the Delta and its tributary watersheds
  - We have limited data for nonpoint sources in tributary watersheds: *Wetlands, Ag, Forests, Rangeland, Open Water*
  - Reservoir Processes: *Will reducing TotHg sources to reservoirs substantially reduce MeHg concentrations in discharges from reservoirs and benefit the Delta?*

Unknowns

- Inorganic Hg reduction projects that will reduce sediment Hg in the Delta
  - Cache Creek Settling Basin: Improvements could reduce Hg to the Yolo Bypass and SF Bay
  - Need to identify other projects that could lead to benefits in the Yolo Bypass and elsewhere in the Delta

Initial Study: Tetra Tech EM Inc. evaluated feasibility of THg removal in Sacramento River basin downstream of major dams

Unknowns

How exactly do we reduce MeHg discharges from point and nonpoint sources?

- 2003 & 2008 CALFED and other studies gave us characterization and process information
- Wetland management practices studies are underway in the Yolo Bypass
- *We need more specific management studies & pilot projects for point and nonpoint sources*

Unknowns

Are there other controllable processes that can be manipulated?

- Mercury exists in many chemical forms; can control focus on the most reactive forms?
- Adding iron reduces MeHg formation; does the effect persist?

Questions?