

USACE Symposium Summary

# Methylmercury In Dredging Operations and Dredged Sediment Reuse



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# Initial Questions

Question 1. Are environmental conditions in the San Francisco Estuary sufficiently different from those elsewhere that specific work is required?

Yes

Question 2. What, if any, information needs to be obtained to make predictions about methylation and bioaccumulation in the perspective of dredging operations?

Lots



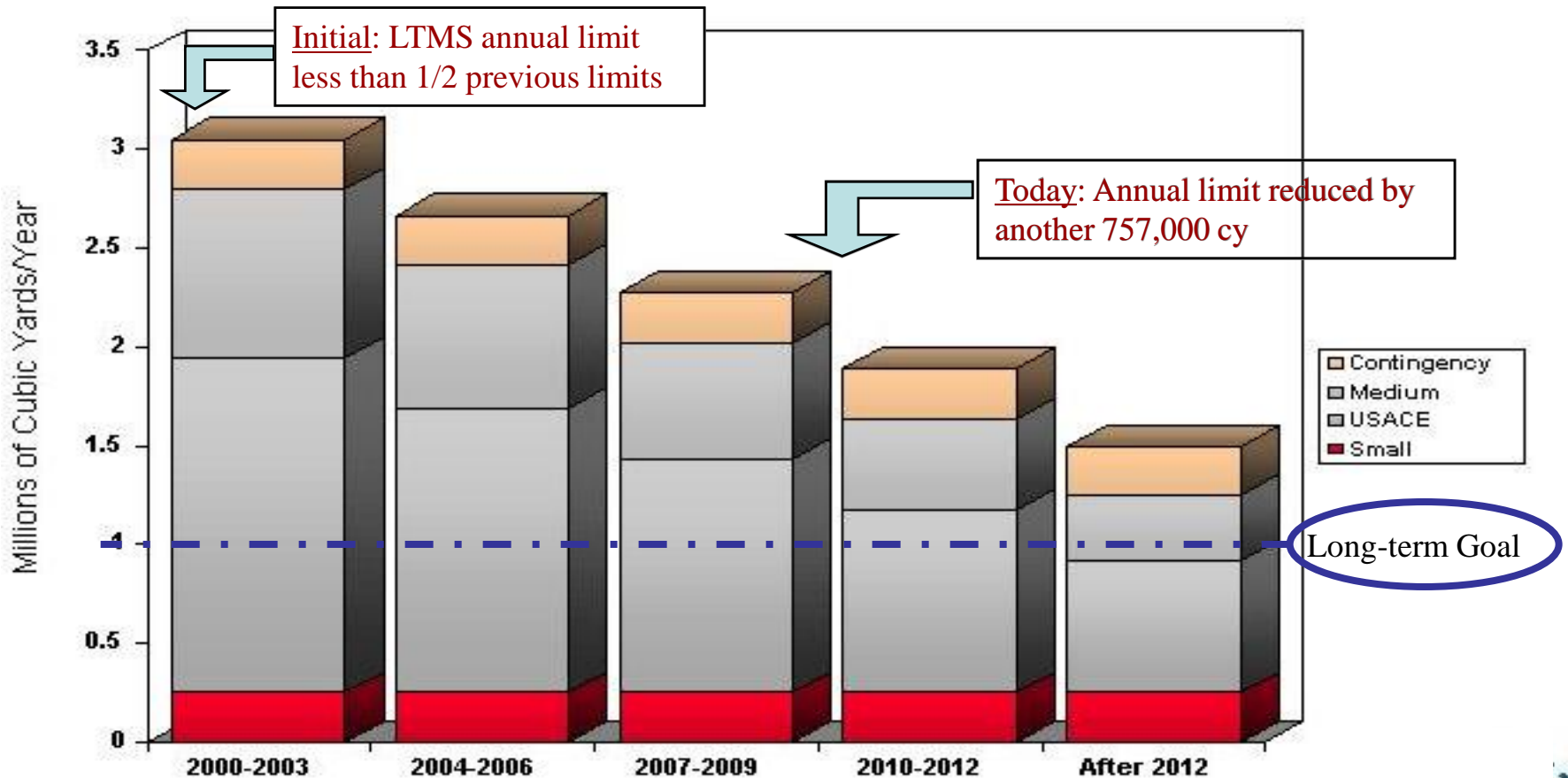
# Symposium Agenda

- Management context
- State of the science
  - Context
  - Case studies
- Strategies for monitoring
- Panel discussion / Q&A

# Management Context

# How to Get There?

## 12-Year Transition Period Reduces in-Bay Disposal Systematically





**Montezuma  
Wetlands Project**

**Sonoma Baylands  
& Carneros  
River Ranch**

**Hamilton Army  
Airfield/BMK**

**Middle Harbor  
Habitat Area**

**SF-8/Ocean Beach  
Nourishment Site**

**Bair Island**

# **Major Bay Area Beneficial Reuse Sites**





# CALFED Stakeholders Workshop 8-9 October 2002, Moss Marine Laboratory

## Research questions to be answered

1. What are the present levels of MeHg in SF Bay wetlands with respect to biota, sub-habitats, and location within the Bay?
2. What are the rates of MeHg production?
3. What factors control MeHg production? Can these be managed?
4. Are some wetlands larger mercury exporters than others?
5. Can we model/predict the effects of wetland restoration on MeHg production and export?

# TMDL Implementation

## Dredging and In-Bay Disposal

- Load Allocation = Zero
  - Implement LTMS
- Restrictions on In-Bay Disposal
  - Sed. Hg conc. < ambient (0.53 ppm)
- Operations shall not cause an increase in Hg bioavailability







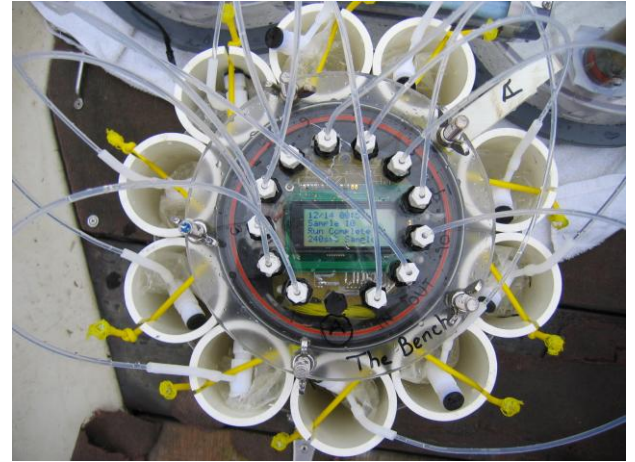
# WDL Implementation Wetlands Creation & Restoration

- No net increase in Hg or MeHg loads
  - Requirements in WDRs/401 WQ Certs to manage existing wetlands and ensure newly constructed wetlands are designed to minimize MeHg production and biological uptake
  - Pre- and post-restoration monitoring
  - Adaptive Implementation

# State of the Science

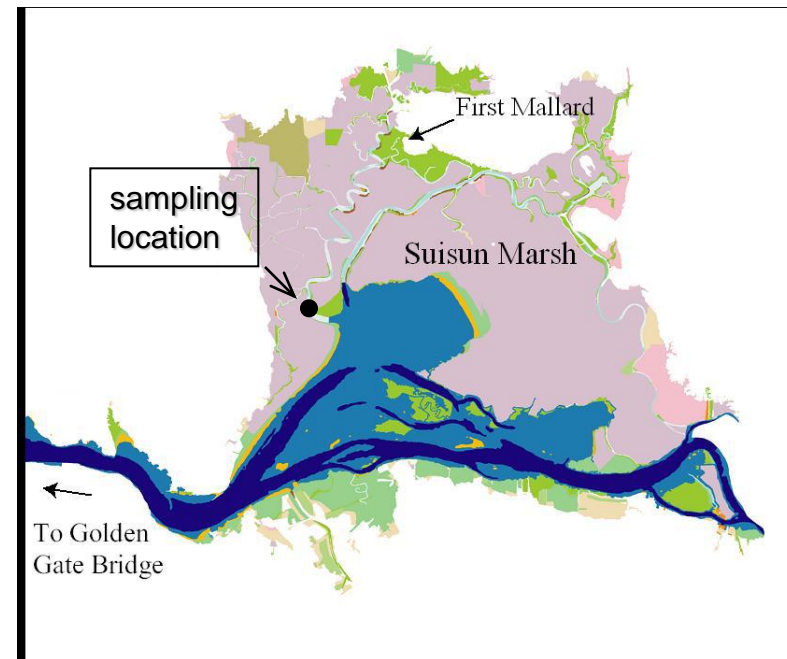
# Methods – how do you measure MMHg loads in tidal wetlands?

- Collected discrete water samples (n = 20) over tidal cycle using hand built autosamplers



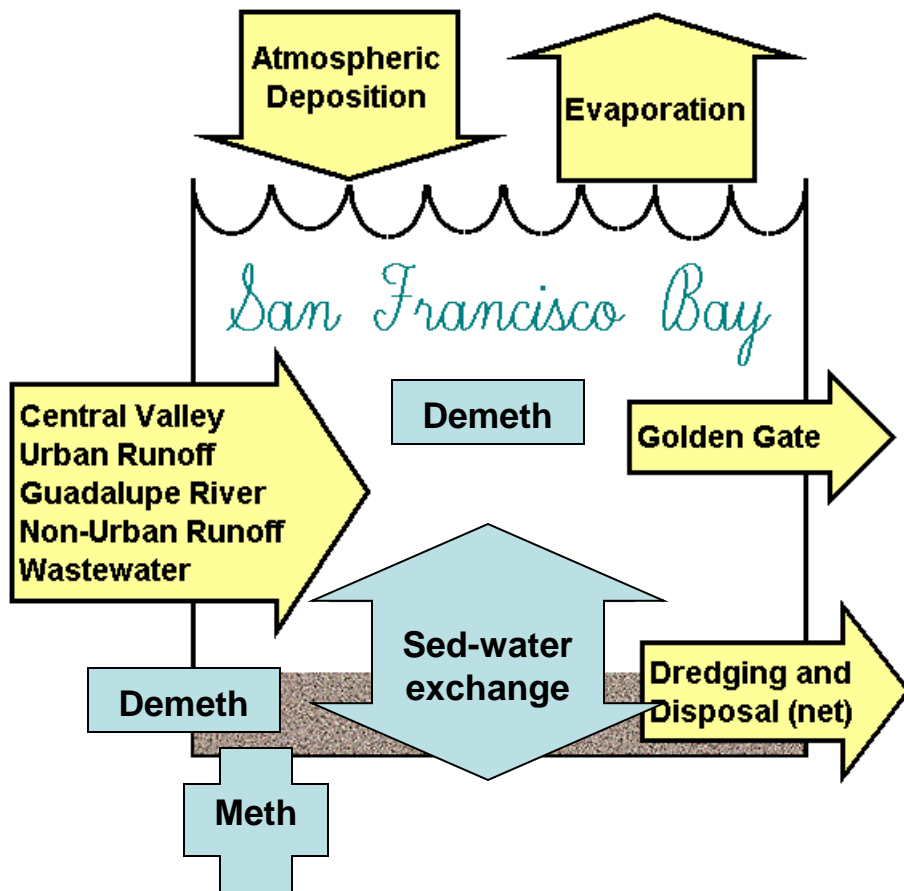
# Results – Suisun Slough

<u>Date</u>	<u>MMHg (mg/tidal cycle)</u>
June – 2005	← 186.0 in
July – 2005	← 289.7 in
Nov – 2005	← 701.2 in
Jan – 2006	→ 32.93 out





# Methylmercury Budget



Need to track **MeHg**

- MeHg <1% of totHg
- Poor MeHg:totHg correlation

Differences from Hg Budget

- Methylation & demethylation
- Potentially rapid response (days-months)



# Mass Budget Base Case

- **Water Mass**
  - Net sediment to water exchange, external load = GG outflow >, degradation, >> bio-uptake, volatilization
- **Total (Water+Sediment)**
  - Production ~balances degradation >> all other processes

<b>Mass in Water</b>	<b>0.38</b>	<b>kg</b>
Ext. Load	0.024	kg/d
Sed to Water*	0.0064	kg/d
Water Degrade	<b>0.0075</b>	kg/d
GG Outflow	<b>0.023</b>	kg/d
Bio-uptake	<b>&lt;0.001</b>	kg/d
Volatilize	<b>&lt;0.001</b>	kg/d
<b>Mass in Sediment</b>	<b>31</b>	<b>kg</b>
Methylate	1.82	kg/d
Sed Degrade	<b>1.80</b>	kg/d
Sed to Water	<b>0.0064</b>	kg/d
Burial	<b>0.0074</b>	kg/d



# Dredging Context

- **LTMS 2012 target 1.25 mcy per year**  
=0.96 mcm per year dredged
- **Volume of sediment in budget = 110 mcm**
- **Mass of methylmercury in sediment = 31 kg**
- **If ALL methylmercury in dredged sediment immediately entered the water, 0.3 kg/yr added (0.7 g/day, about 3% of daily external loads)**
  - **Worst case scenario, unlikely**
- **Most MeHg from (on-site) sediment de/methylation**
  - **Control methylation or demethylation?**

# Management Strategies – Dr. Evil



**Acquire \$1 Million**

**Control Methylation:**

- **Sterilize the Bay (thermonuclear device)**

**Control Demethylation:**

- **Equip sharks w/ UV lasers to photodemethylate**





# Management Strategies (Real World)

- **Local impact will be more significant**
  - **Smaller parcel of water (ponds, wetlands)**
  - **Spread over shorter time (esp if times of bio growth)**
  - **i.e. Evaluate/monitor/manage locally rather than bay-wide**

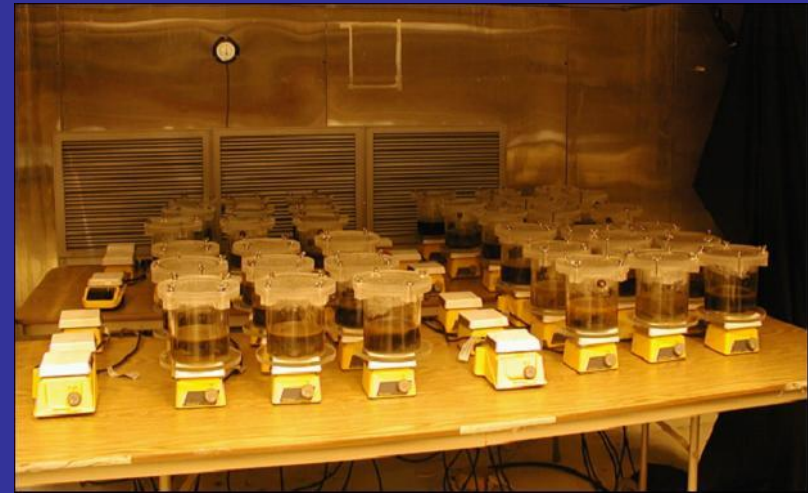
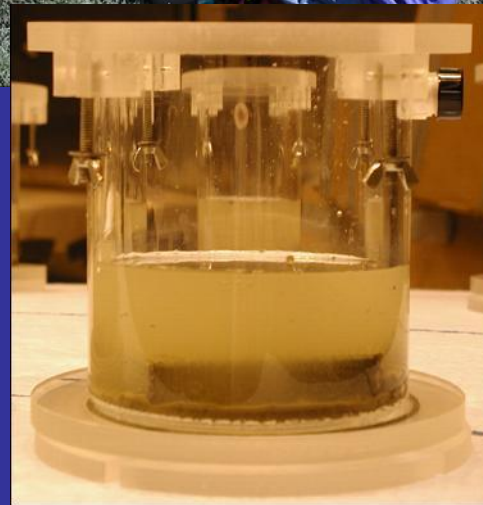
Action	Local Effect	Regional Effect
Dredging		<b>Small</b>
Bay disposal		<b>Small</b>
Ocean disposal		<b>Tiny</b>
Wetland disposal	<b>Larger</b>	<b>Small</b>
Upland disposal	<b>Larger</b>	

# Zero Sum Game?

- Wetland/Upland Reuse
  - Larger effects local biota (birds, mice, small fish)
  - New habitat
    - Some MeHg forming
  - Offset subsidence
  - Protection from storm surges, sea level rise
- Bay Disposal
  - Smaller effects widespread (sportfish, seals)
  - (Mostly) unchanged habitat
    - Status quo w/r to MeHg
  - Continued subsidence
  - Need other sources of sediment

# Mercury Dynamics in the Wetland Detritus Cycles

Decaying plant mass becomes a complex system in itself



- ❖ Concentrations of detritus-MeHg sharply increased from 0 up to 25 ng/g during incubation with water and sediment, and decrease exponentially afterwards
- ❖ Implications for detritivores and higher order consumers



# Lessons Learned and Recommendations for an Adaptive Management Approach

## GOALS:

1. Reduce total mercury loads into the bay.  
Not expected to have a large effect.
2. Reduce methylmercury production.  
Create/manipulate wetlands to minimize conditions favoring net MeHg production (avoid low salinity and fluctuating redox potential).
3. Monitor and focus studies on understanding Bay system.  
Use chemical and biological monitoring in combination,  
Data gaps in:
  - i. speciation and concentrations of Hg & redox species
  - ii. food web structure & processes
4. Encourage actions that address multiple contaminants.  
See 1-3.







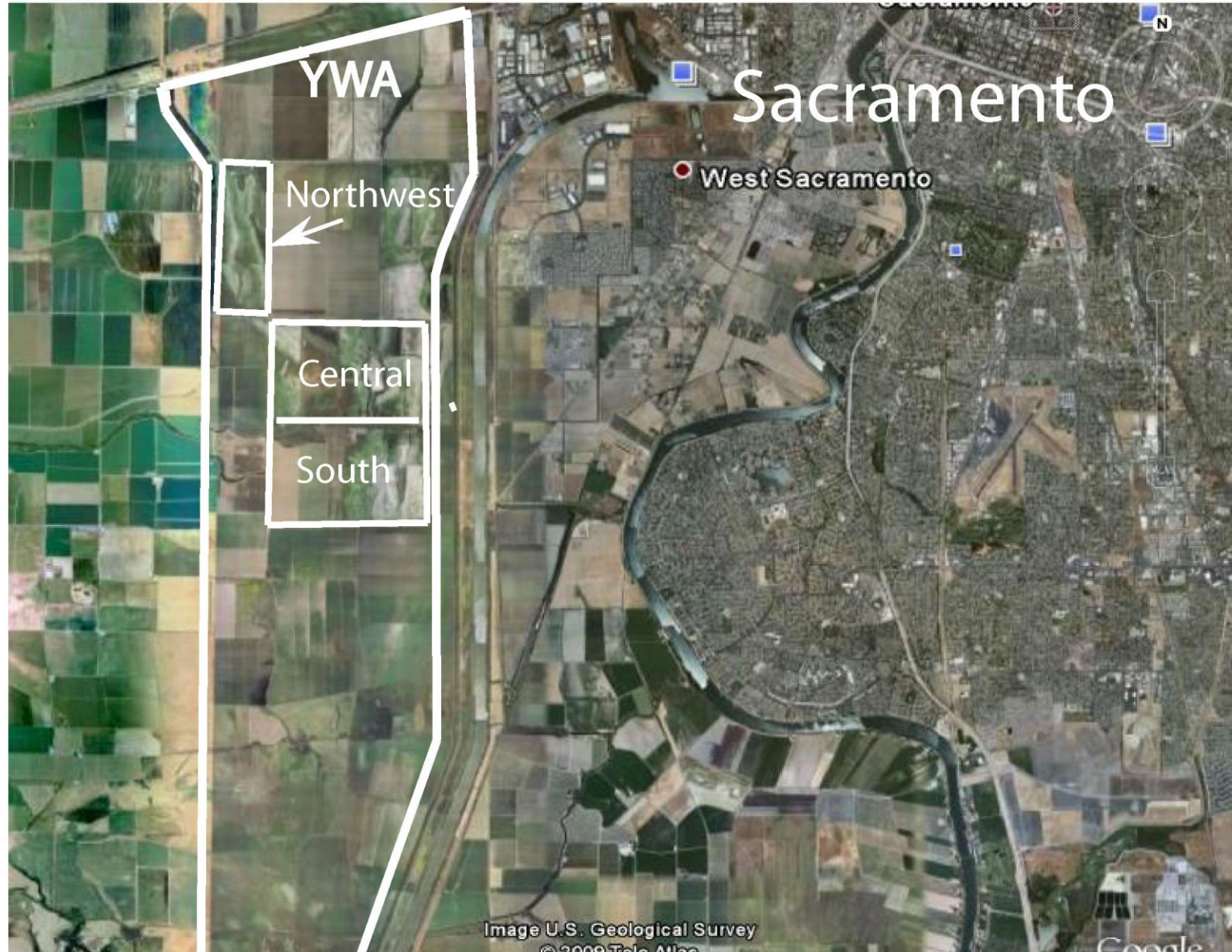
# Reactive Hg Studies

- Not all Hg immediately available for methylation
- “Reactive” Hg
  - Marvin-Dipasquale (USGS Menlo Park) lab  
operational measure of chemically available Hg
- Alviso Slough & Yolo samples <1% of sediment total Hg “reactive”, but dissolved reactive Hg increased over ~1 week

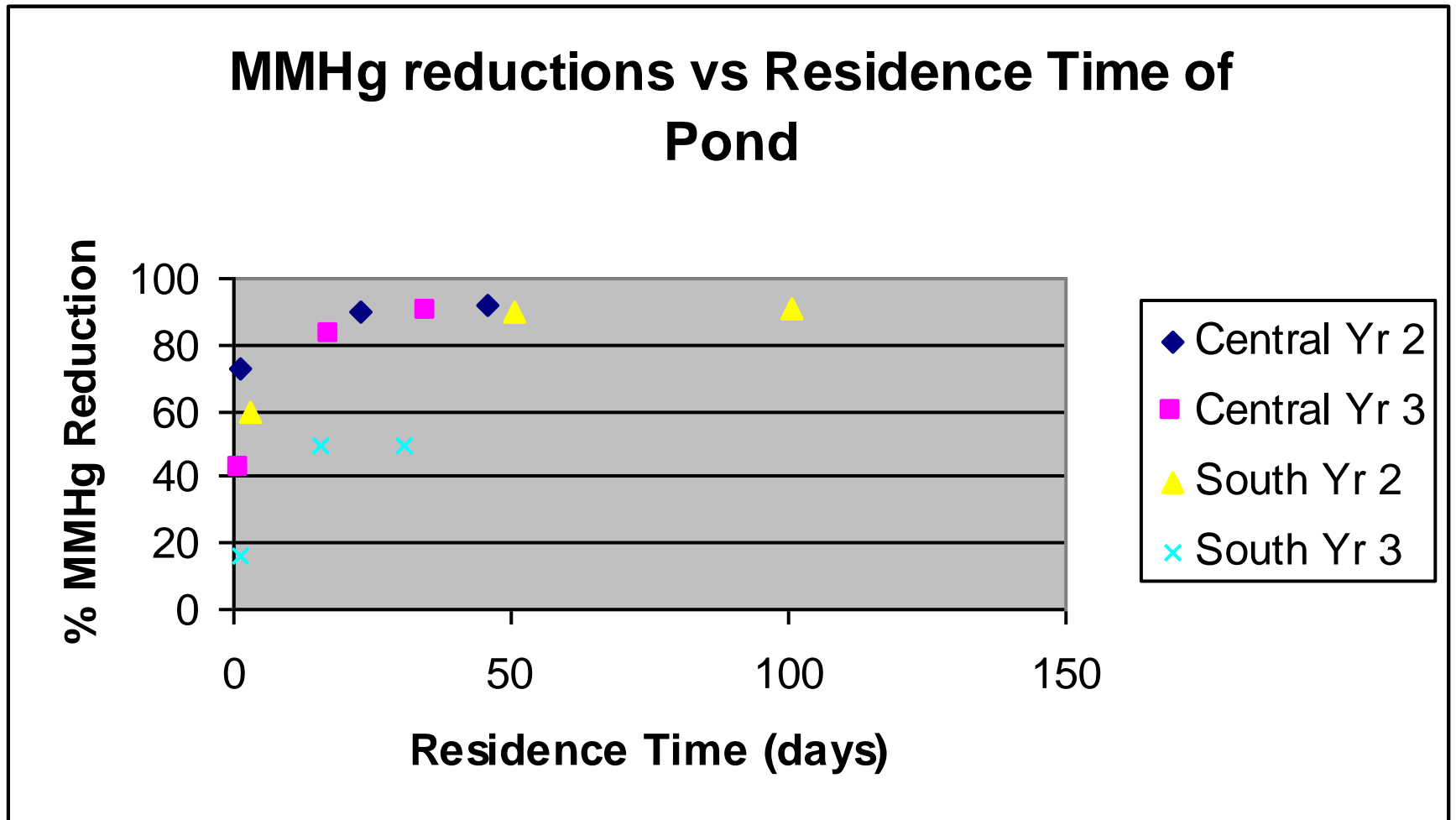
# Take Home Messages- Reactive Hg

- The mobilization of buried sediment can lead to an increase in Hg(II) reactivity.
- Mixing experiments suggest MeHg production can be stimulated in down stream 'receiving' environments
- Dredging & restoration projects should be aware of this potential and pre-test material for it's capacity to form MeHg in environments receiving dredge material.

# Can MeHg in seasonal pond tailwater be reduced?

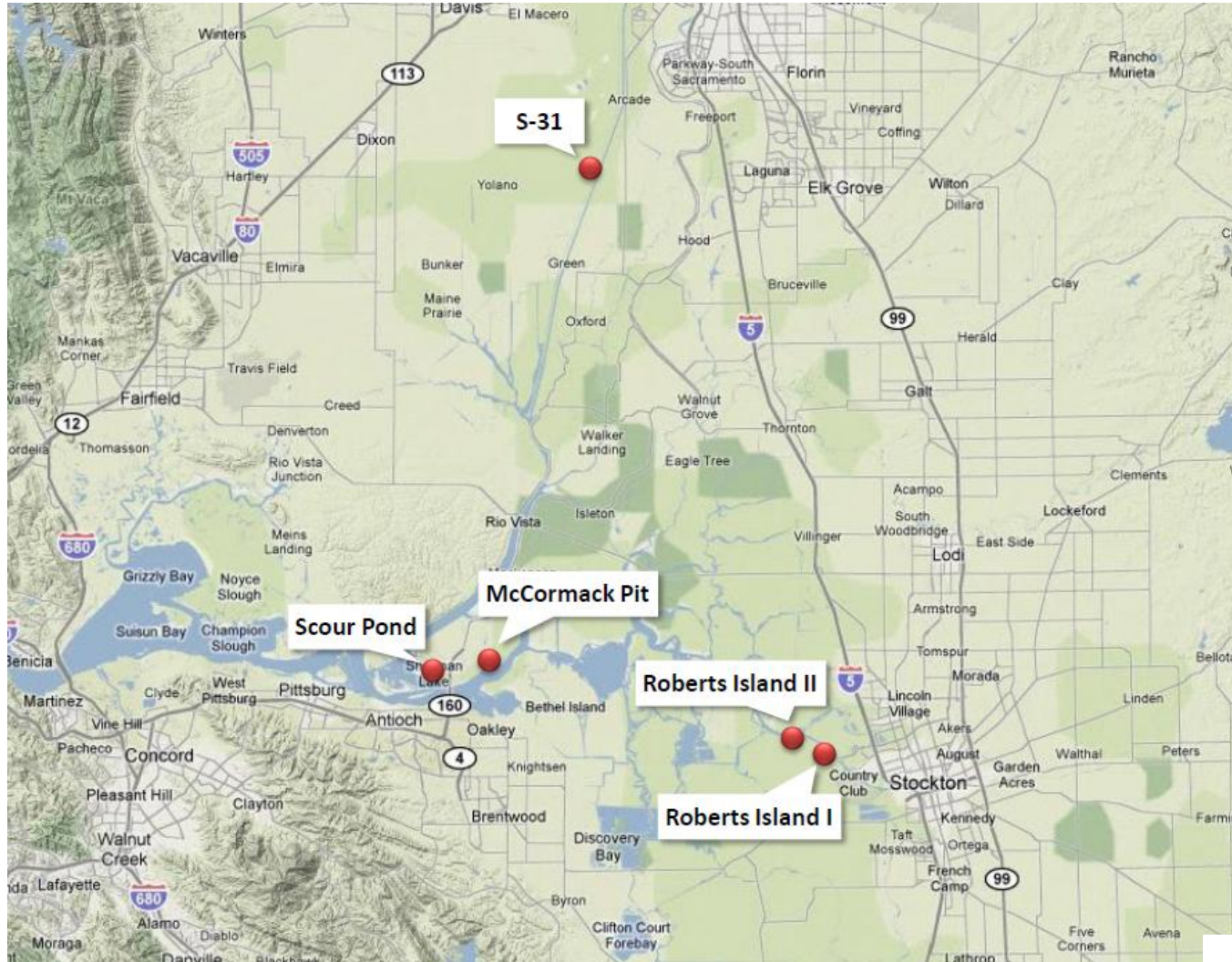


# Demethylation Over Time

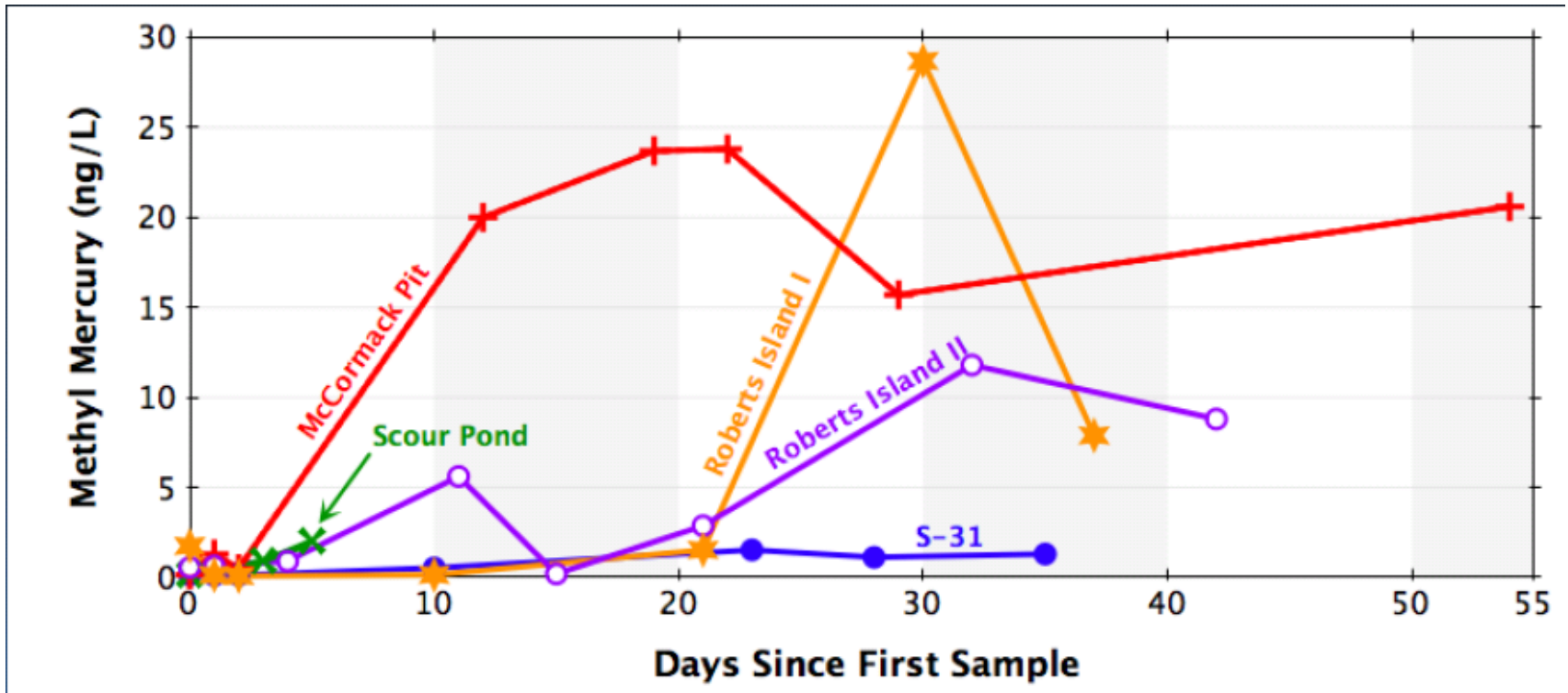




# Dredged Material Placement Ponds



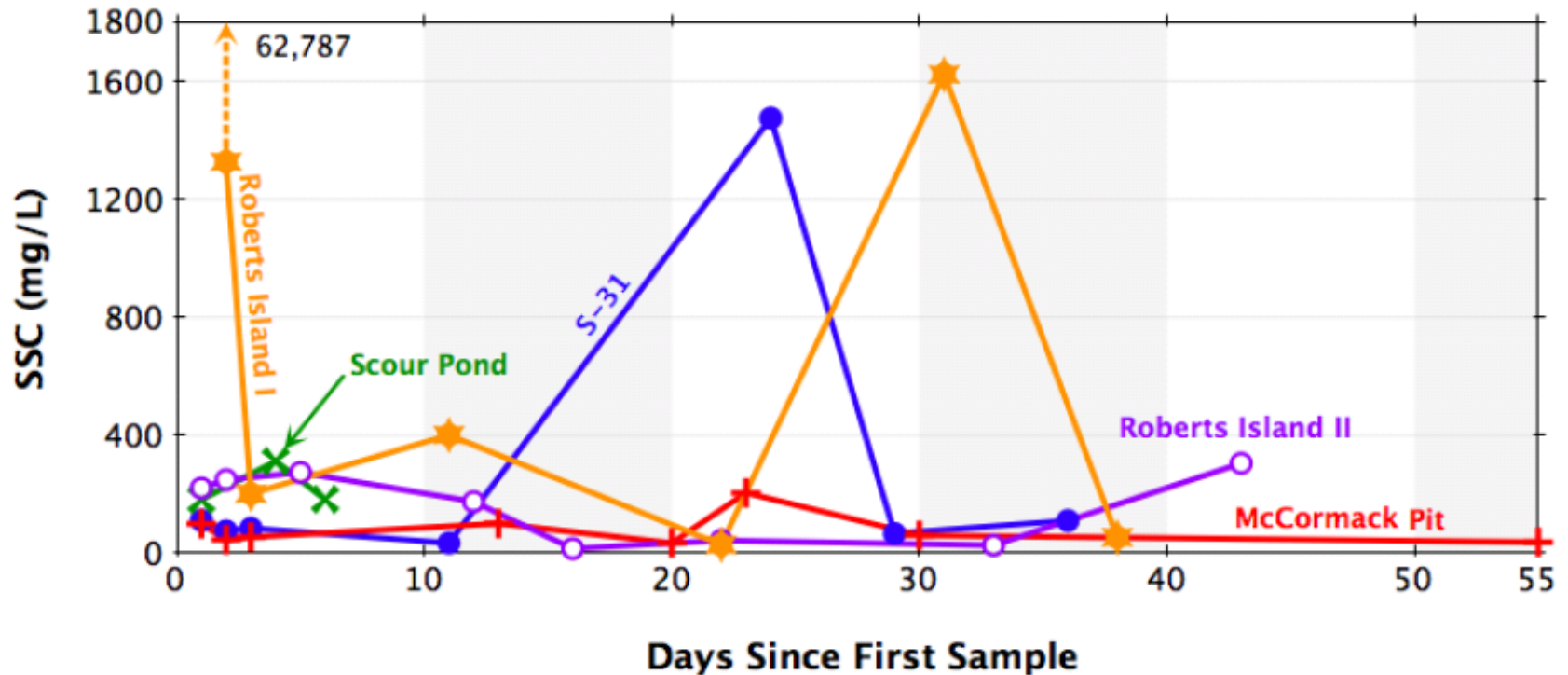
# MeHg Rises in Shallow Ponds



- Highest in high organic sites
- Stays high >4 weeks



# Sediments Resuspended



- Re-supply of MeHg to water column?

# Take Home

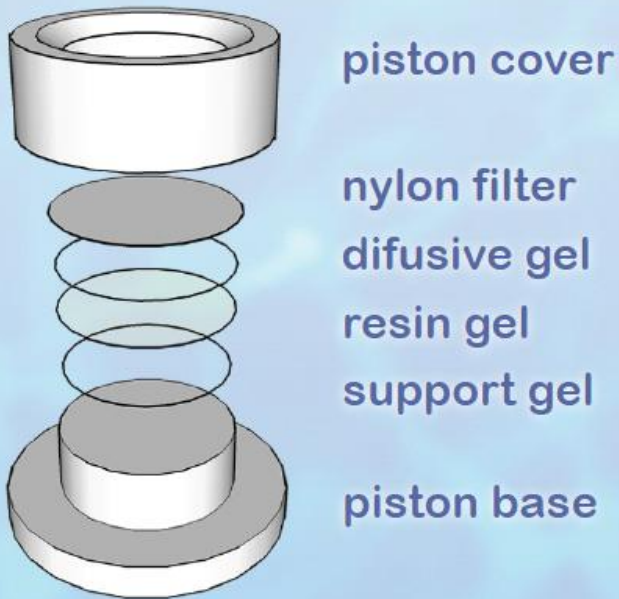
Little special w/ dredged sediments if Hg ~ avg.



- “It’s not where you take things from - it's where you take them to.” (J.L. Godard)
  - MeHg determined mainly by conditions where placed
  - Avoid worst sediments in worst places

# Monitoring Strategies

# DGT (Diffusive Gradient in Thin film)



Based on the Fick's First law of diffusion

$$F = \frac{M}{At} = D \frac{C_b}{\Delta g} \quad \rightarrow \quad C_b = \frac{M \Delta g}{DA t}$$

F : flux

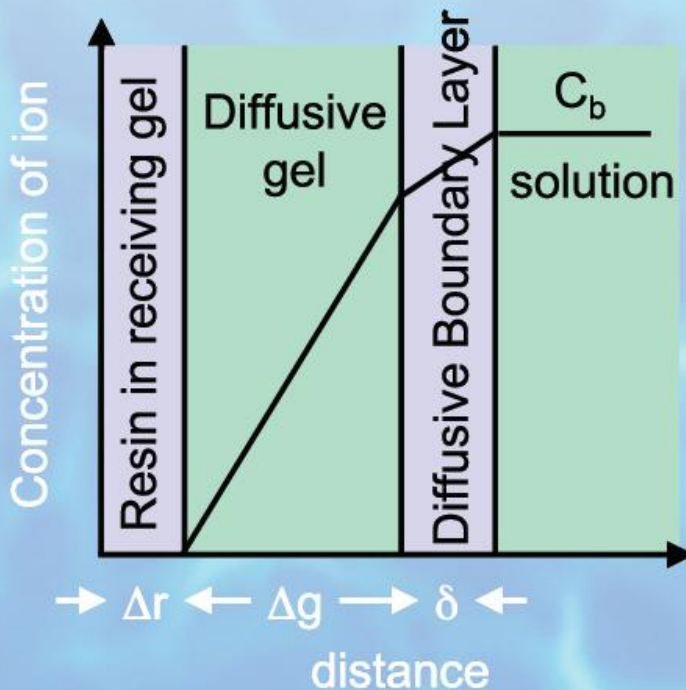
M : mass of the specie accumulated by the resin

A : diffusive gel area      t : gel exposure time

D : Diffusive coefficient

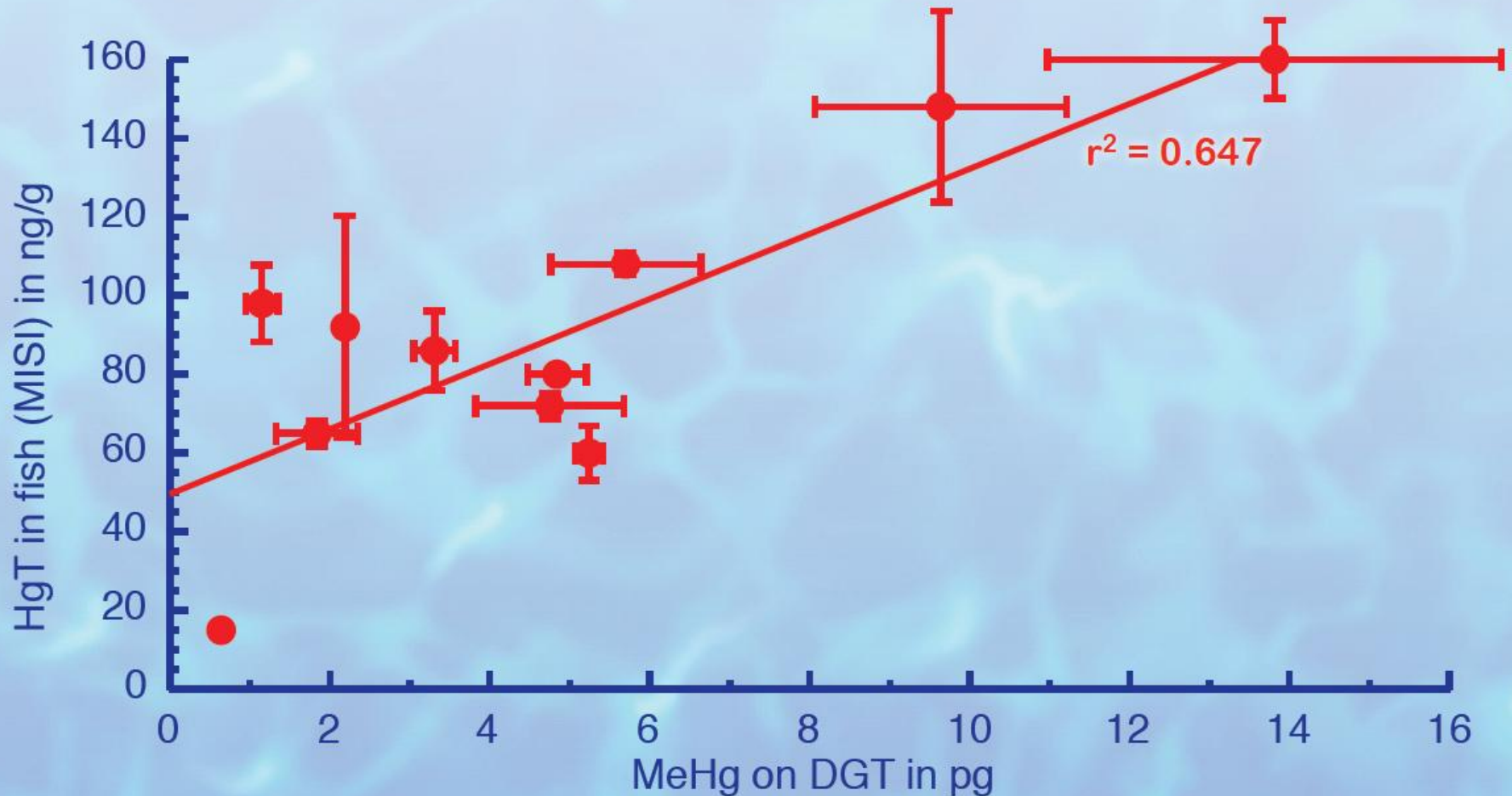
$C_b$  : specie concentration in solution

$\Delta g$  : diffusive gel thickness



After retrieval, resin gel is peeled.  
Species bound to the resin are eluted and analysed.  
With M measured, it is easy to calculate  $C_b$

# Comparison of DGT and fish (MISI) data



# Q1: How should the mercury problem be assessed?

- Measure mercury concentrations in wildlife species indicative of restoration habitat endpoints
- Beneficial use target = monitoring tool
- Carefully selected biosentinels
  - Endpoints: tidal marsh and managed pond
  - Habitat-specific
  - Highly localized



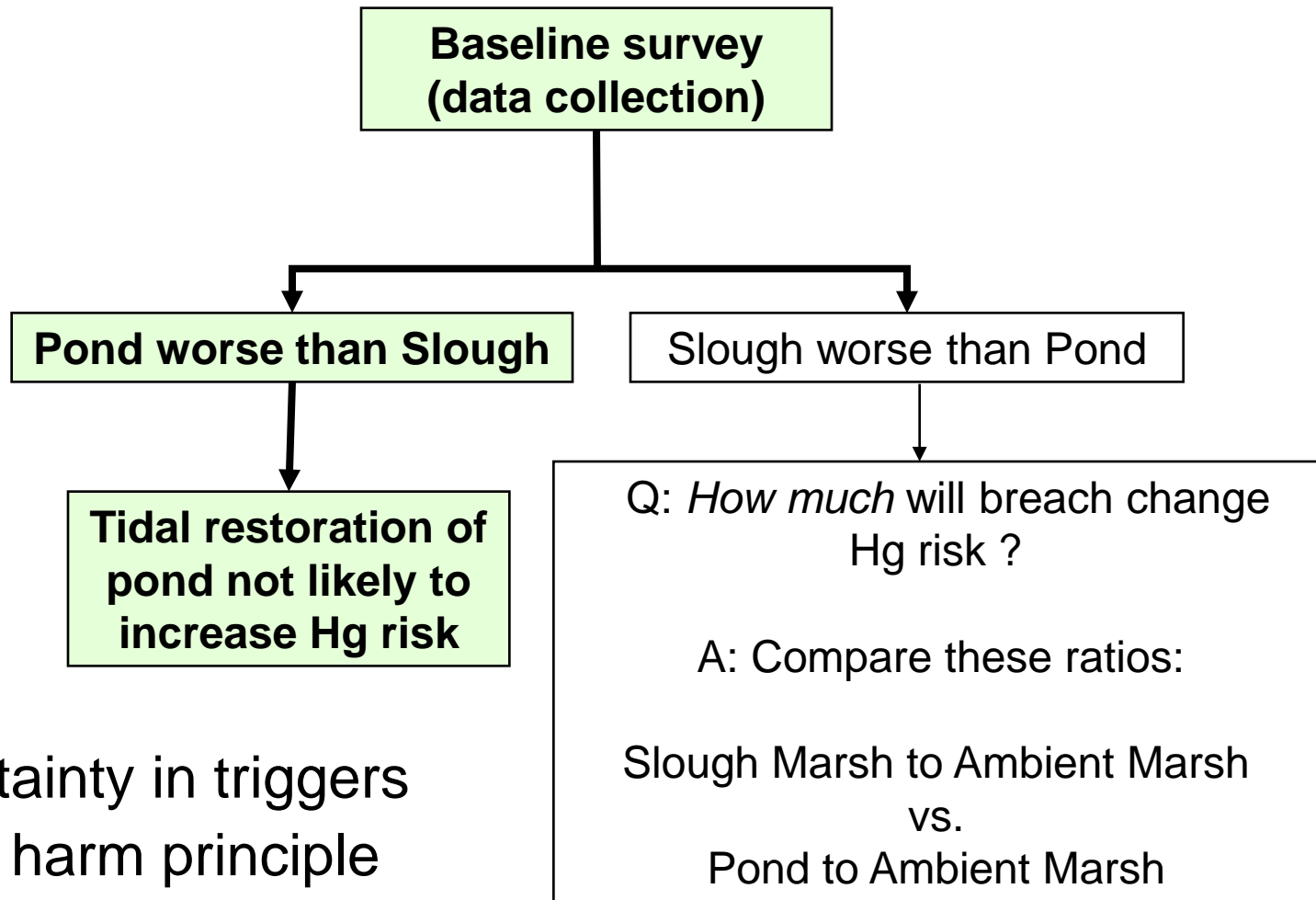


# Match biosentinels to management questions

- Bay regional
  - Sport fish
  - Cormorants
  - Terns
- Shallow-water margins
  - Small fish
- Wetlands
  - Song sparrows
  - Longjaw mudsuckers
  - Brine flies



# Pond Action Decision Tree



- Uncertainty in triggers
- Do no harm principle

# Grand Take Home Messages

- Local processes, effects, solutions
  - Not one-size fits all
- Identify priorities
  - No “ideal” solutions, question of better or worse
- MeHg becomes a problem when you
  - Make it → move it → eat it
  - Avoid links to mitigate the problem
- Monitoring needed
  - Choose your tools to fit your priorities/situation
  - Feedback for “adaptive management”

# Strategies Moving Forward

- Use local lessons to build regional understanding
  - Don't reinvent wheel
    - Similar problems, data needs
    - Build on previous work
  - Not always similar solutions, but a similar process for getting there
    - Structured evaluation framework, monitoring tools