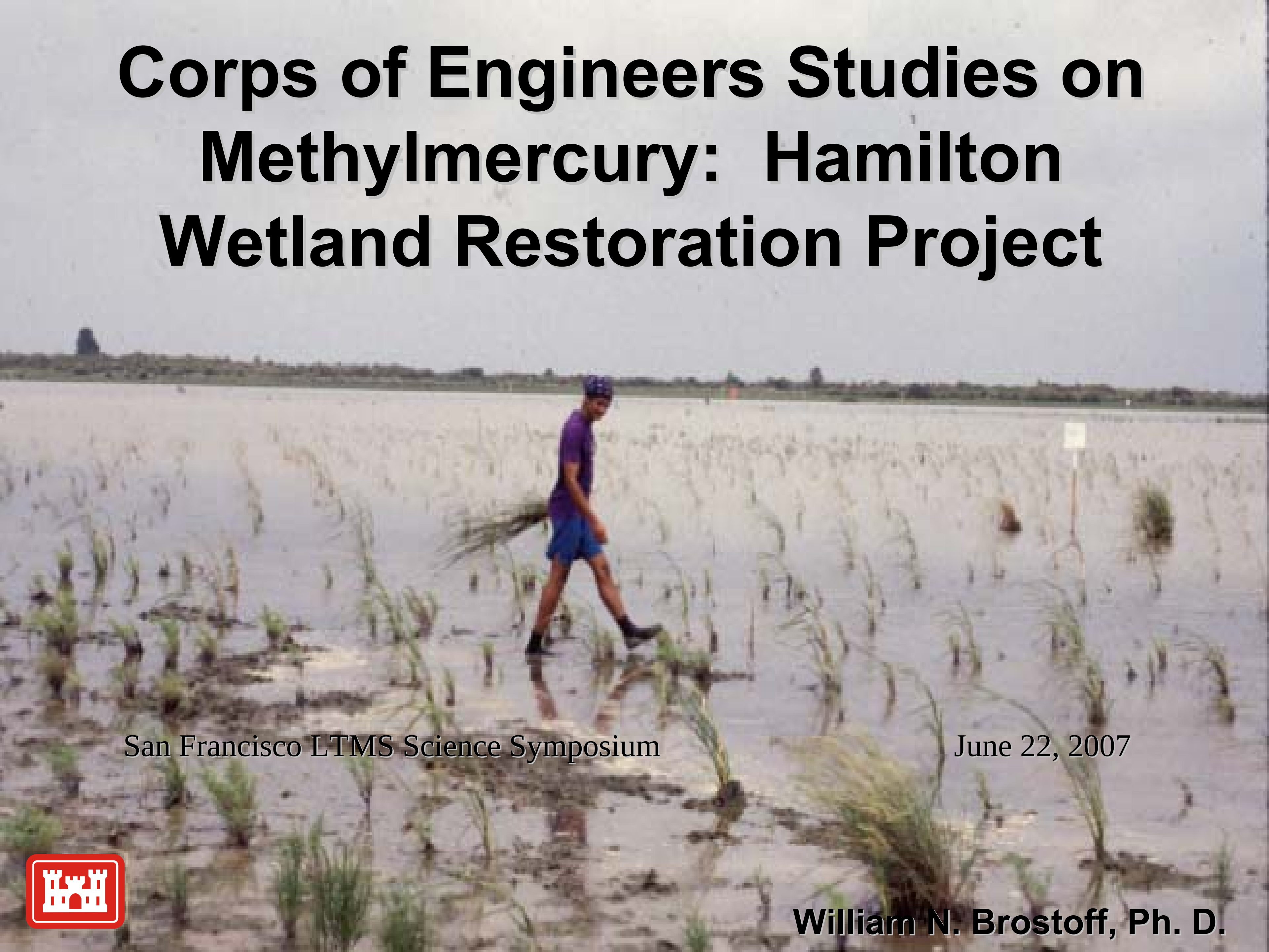
Corps of Engineers Studies on Methylmercury: Hamilton Wetland Restoration Project



San Francisco LTMS Science Symposium

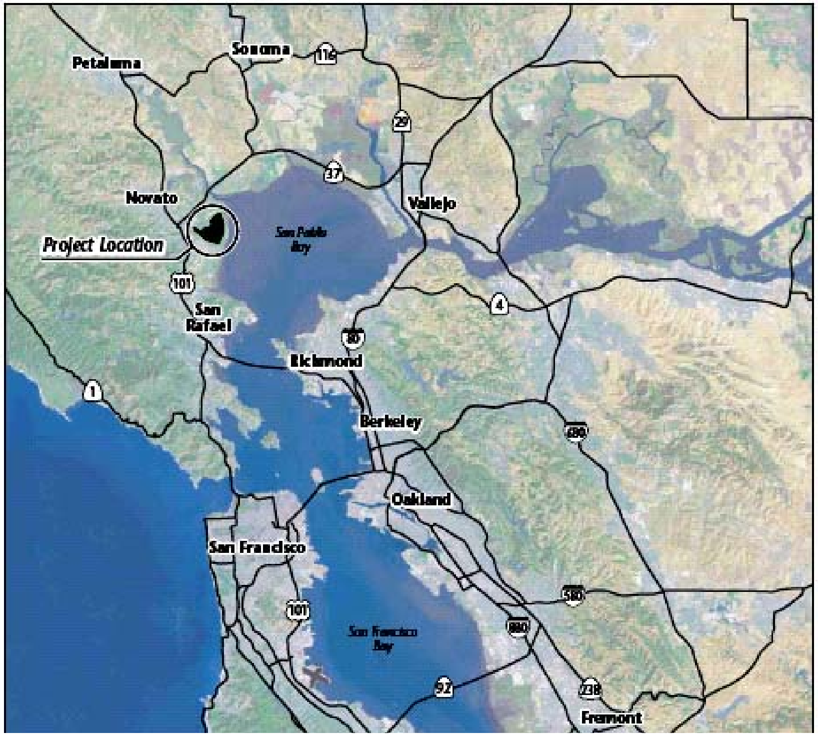
June 22, 2007

William N. Brostoff, Ph. D.

OUTLINE

- Overview & Status of Hamilton Wetland Restoration Project (HWRP)
- Overview of mercury concerns in wetlands
- Goals of Methylmercury Study
- Current projects & interim results
  - Basic & Applied Science Studies
  - Monitoring & Adaptive Management Plan
  - Future direction
- My role and impressions

HWRP Background



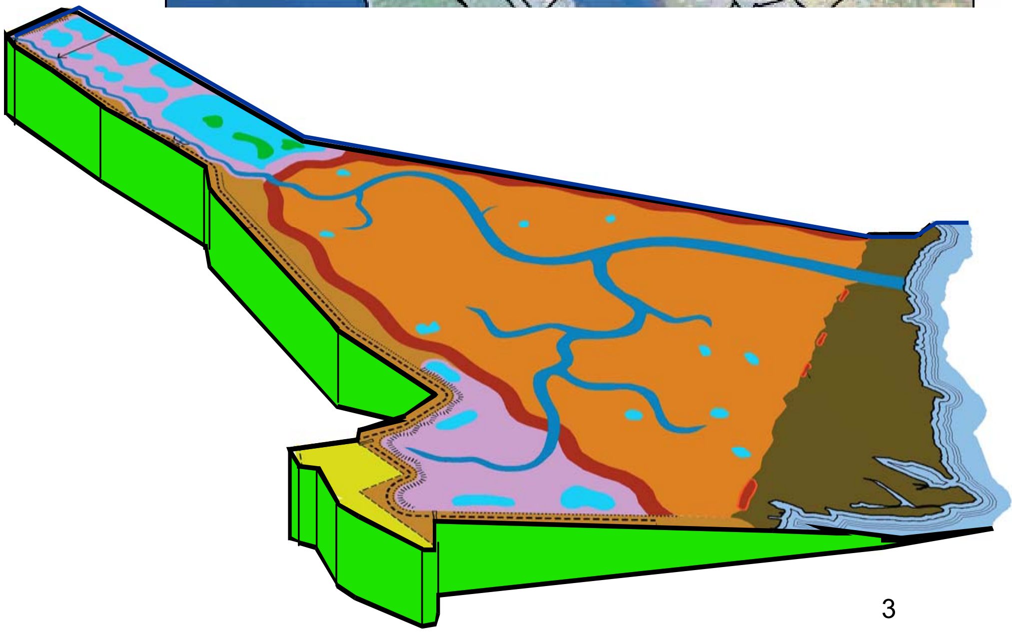
- Site was originally wetland/intertidal salt marsh.
- Diked and drained for agricultural use in mid-19th century.
- Ag lands converted to Army Air Base in 1932.
- Base Realignment and Closure (BRAC) in 1980's.
- Project intent:

  'ecosystem restoration'.

  dredged material disposal.

  ≈ 630 acres of wetland.

  ≈1000 acres total project.
- Sponsor: California State Coastal Conservancy.



Wetland Restoration and Mercury Methylation:
Between the devil and the deep blue sea…

- Trade-offs between functions and values with possible risks of methylmercury (MeHg) accumulation in the food chain.
- Large number of multidisciplinary groups addressing various aspects.

Wetland Restoration and Mercury Methylation:

- Mercury is converted from a relatively inert form to a potentially toxic (MeHg) form under certain conditions in wetlands.
- MeHg bioaccumulates "up" the food chain.
  - Sediments 90% inorganic
  - Top predators 95% MeHg
- MeHg crosses biological membranes and can accumulate to 10^6 to 10^7 that of surface waters.
- Primary human exposure to Hg (as MeHg) is through the consumption of fish
- Problem also to wildlife (advisories against ducks in Midwest)

Wetland Restoration and Mercury Methylation

- Methylation and demethylation both occur:
  - ± same time
  - ± same place
- Size of MeHg pool highly variable in sediment
- Methylation/demethylation rates mediated by bacteria related to:
  - Oxygen
  - Sulfur compounds
  - pH
  - Light
  - Other characteristics

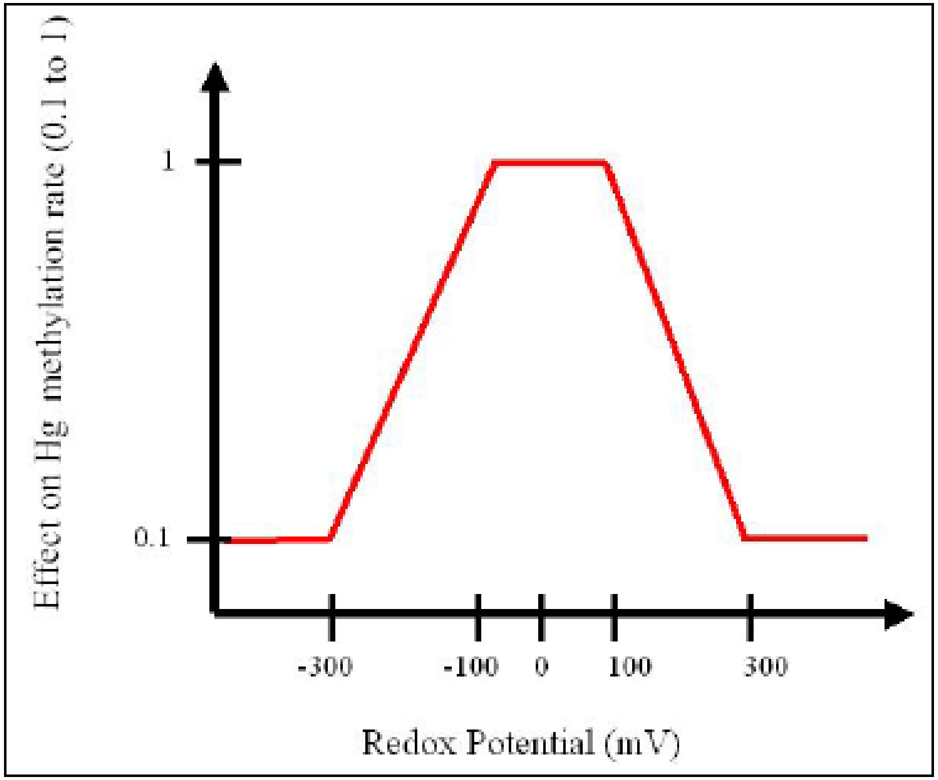


Figure B6. Effect of redox potential on Hg methylation rate (relative)

$$\text{THg} \underset{\textbf{demethylation}}{\overset{\textbf{methylation}}{\rightleftharpoons}} \text{MeHg}$$

("reactive Hg")

Wetland Restoration and Mercury Methylation: Dredging & Legacy Sources of Hg

- Relation between sediment sources of Hg from gold/mercury mining days and MeHg is poorly understood.
- Neither quantities of MeHg nor methylation rates are correlated to THg.
- However, near sources of Hg (i.e., very high concentrations) there is also higher MeHg.

Rationale for study

- Variation not understood
- Management potential
  - Some flexibility in construction of wetland
  - Possibilities for adaptive management
- SF Estuary wetlands unique
- Dredging unique
- Regulatory issues?
  - MeHg TMDL
  - Mandated to monitor

MeHg Project Goals

- **Sponsored by San Francisco Bay Long Term Management Strategy (LTMS).**
- **Guidance for Hamilton Wetland Restoration Project (HWRP) & other restoration in SF Bay.**
  - Initial Design.
  - Basis for Monitoring and Adaptive Management Plan.

USACE Engineer Research and Development Center (ERDC) Vicksburg, MS

Dr. Vic McFarland – (Retired)

Dr. Herbert Fredrickson – (EPA) Project Management, Environmental Microbiologist

Dr. Elly Best – Project Management, Plant Ecophysiologist

Dr. Gui Lotufo – Aquatic Toxicologist

Dr. Rod Millward – Aquatic Toxicologist

Dr. Bobby Jones – Environmental Chemist

Mr. John Brezina – Field Support

Dr. Tony Bednar – Environmental Chemist

Others (Joan Clarke, Charlie Lutz, Gary Ray…)

University of Trent, Canada

Dr . Holger Hintelmann – Environmental Chemist

Dr. Olivier Clarisse – Environmental Chemist

Dr. Brian Dimock – Environmental Chemist

USACE San Francisco District

Mr. Frank Snitz (retired)

Al Paniccia -- Project Manager

ERDC Project Goal

- Mass Balance through food web
- Estimate net export of MeHg
- Develop tools
- Technical basis for management
  - Design and construct wetlands that minimize MeHg production
  - Balance wetland functions and values with MeHg production
- Many studies, multidisciplinary team

ERDC Project Objectives

- Site/habitat specific methylation/demythlation rates.
- Diffusive Gradient (DGT) thin film for monitoring methylmercury.
- Vegetation as a vector in mercury transport into the food web.
- Dynamics in decomposing macrophytes.
- Mercury dynamics in food webs.
- Bioavailability of sediment-associated mercury to macrobenthos.

(Most work at Hamilton, China Camp, etc. 2002 – present)

Site Specific Methylation/Demethylation Rates

- *Rationale*: Need to understand rates and controlling environmental factors in various subhabitats.
- Stable isotope *in situ* studies to simultaneously assess methylation & demethylation rates at several locations, seasons etc.

$$^{199}Hg^{2+} \rightarrow Me^{199}Hg$$

$$Me^{200}Hg \rightarrow {}^{200}Hg^{2+}$$

- Sites: Hamilton, China Camp, Sonoma Fringe Marsh, Sonoma Baylands, Petaluma River (salinity gradient).
- Sediment cores removed, spiked, incubated 5-72 hrs, returned to lab, sectioned, and analyzed.

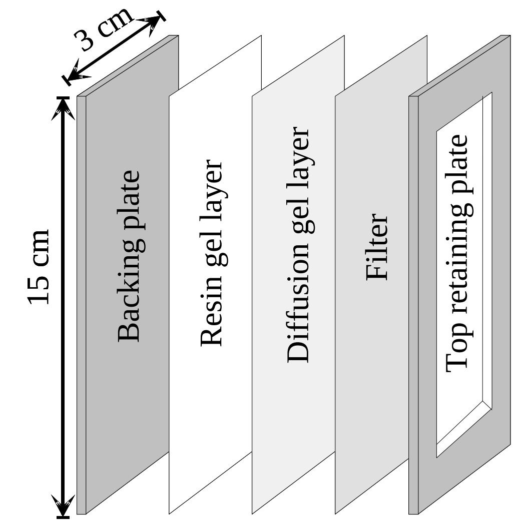
Site Specific Methylation/Demethylation Rates

- Methylation rates: MeHg would double daily if not for demythlation.
- Demythlation rates: MeHg would be depleted in ca. two days w/out methylation.

- No site-level differences.
- Lower MeHg production in vegetated than bare sediments.
- Seasonal differences.
- Significant relationship between microbial biomass and MeHg pool size.
- No significant difference between THg and other sediment characteristics.
- No relation between THg, MeHg, or estuarine gradients (salinity) and rates of methylation/demythlation.
- Used rates to produce some first-approximation estimates for site-level methylation rates and exports from HWRP to the Bay.

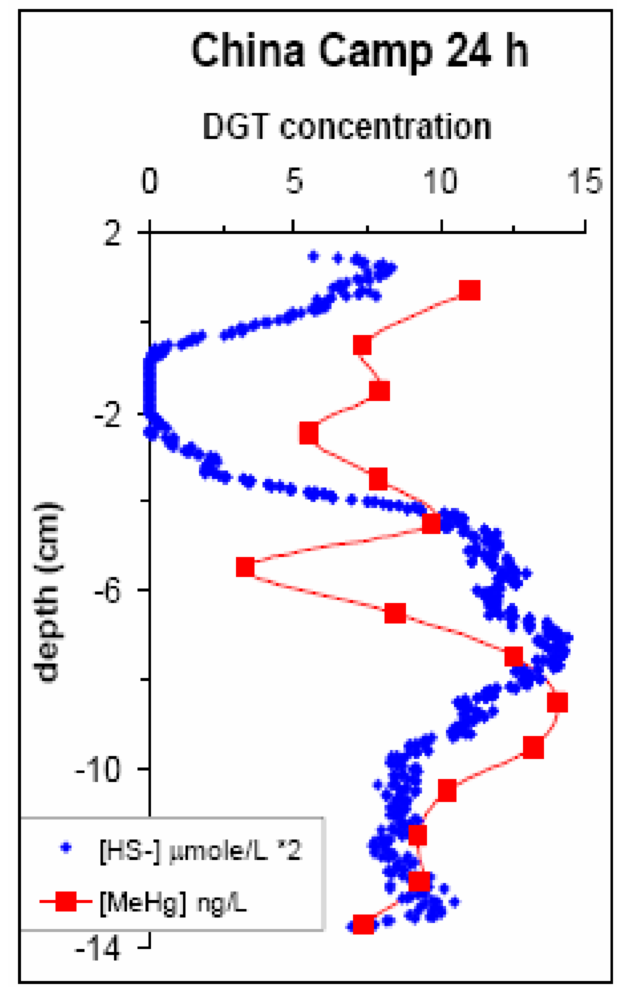
Diffusive Gradient Thin Film (DGT) for Monitoring Methylmercury

- *Rationale*: Develop cost-effective tool on which experiments could be specifically designed and monitoring conducted to supplement or replace "biosentinels"
  - Sediment/water quality: snapshot
  - Sentinel species – questionable precision, replication, etc.
- Ion exchange resin immobilized in a resin gel, separated from ambient environment by a diffusive gel.
- Field tests at China Camp and Petaluma River.



Diffusive Gradient Thin Film (DGT) for Monitoring Methylmercury

- Good correspondence with conventional analytical techniques.
- (Study on clams and fish still underway).
- Limit of detection 30 pg L^{-1} for 24 hr deployment (lower values require longer times).
- Advantages:
  - **Temporal integration (**Yields time-averaged values)
  - **Accurate results for porewater.**
  - **High spatial resolution (e.g., thin layers).**
  - **Used in tandem with other gel-based sampling techniques to look at sulfide, sulfate, manganese and iron.**
  - **Cost effective compared to "biosentinels"**



Vegetation as a Vector in Mercury Transport: Entry into the Aquatic Food Web

- *Rationale*: Design wetland with "optimal" proportion of *Salicornia*, *Spartina*, and unvegetated areas
- Objectives: Determine natural cycle of…
  - Uptake into *Spartina* and *Salicornia.*
  - From live plants to dead plant material.
  - Dead plant community to rest of ecosystem (fragmentation).
- HWRP & China Camp.
- Field collection over a year.

Vegetation as a Vector in Mercury Transport: Entry into the Aquatic Food Web

	Primary Production (g DW m^{-2} yr^{-1})	THg (ug m^{-2})	MeHg (ug m^{-2})
Spartina	1500	34.9	0.784
Salicornia	1360	9.42	0.018

Data analysis incomplete…

Dynamics in Decomposing Macrophytes

- *Rationale*: Document decomposition of macrophytes and relation to MeHg
- Laboratory study: plants incubated in litter bags with Bay water and incubated with sediment under aerobic and anaerobic conditions.
- Mass loss,THg and MeHg monitored for 150 days.

Dynamics in Decomposing Macrophytes

- *Salicornia* decayed slower than *Spartina*.
- Aerobic conditions accelerated decay of *Spartina* but delayed it in *Salicornia*.
- MeHg content increased during early phases of decomposition but then decreased (THg remained constant).
- Thus, plant litter can act as a transient source of MeHg.

Mercury Dynamics in Food Webs

- *Rationale*: Document flow of carbon (energy) through food chain. Design wetland with “optimal” proportion of *Salicornia*, *Spartina*, and unvegetated areas
- Stable isotopes (carbon, sulfur & nitrogen) used to examine food sources and trophic status of consumers.
- Particulate organic matter, producers (phytoplankton, microphytobenthos, macroalgae, *Spartina*, *Salicornia*), vascular plant litter and consumers (infaunal inverts, shrimp, crabs, fish; small mammals and birds provided by others) were collected from HWRP and China Camp.

Mercury Dynamics in Food Webs

- Bulk of primary production entering food web is from macroalgae, *Spartina*, microphytobenthos, and macroalgae.
- Little spatial partitioning of input.
- Minimal food web support from *Salicornia* and Bay phytoplankton.
- Data analysis still in progress.

Bioavailability of Sediment-Associated Mercury to Macrobenthos

- *Rationale*: How does MeHg in the sediment translate into MeHg in primary consumers?
- Objective: Describe uptake kinetics of THg and MeHg to the polychaete *Nereis virens* in natural vs. dredged material-restored marshes.
- Sediment from four sites (HWRP, China Camp, Sonoma Baylands natural and restored); *Nereis* from a commercial supply house.
- Laboratory incubation for 56 days.
- Highest uptake rate from natural marsh at Sonoma Baylands.
- (Tentative) conclusion: Marsh restoration does not provide evidence for increased bioavailability.

Small Studies

- Modeling
- MeHg sequestration

Completed and Anticipated

- Publicly available annual reports:
  - **Best, E. P. H., Fredrickson, H. L., McFarland, V. A., Hintelmann, H., Jones, R. P., Lutz, C. H., Kiker, G. A., Bednar, A. J., Millward, R. N., Price, R. A., Lotufo, G. R., and Ray, G. A. (2005). "Pre-Construction Biogeochemical Analysis of Mercury in Wetlands Bordering the Hamilton Army Airfield Wetlands Restoration Site," ERDC/EL TR-05-15, U.S. Army Engineer Research and Development Center, Vicksburg, MS.**
  - **http://el.erdc.usace.army.mil/elpubs/pdf/05-15.pdf**
  - **http://www.spn.usace.army.mil/ltms/200509Pre-ConstBiogeochemAnalysis.pdf**
- Peer-reviewed technical publications
  - (several submitted for 2007 publication)
- Professional conference presentation
  - Numerous
- Anticipated final annual report based on 2004-2005 work: Sept. 2007.
- Draft annual report for 2006 work: ?

Results of Technical Peer Review

- 2003 work reviewed by USACE/SF (wnb)
- 2004-2005 work reviewed by SFEI, MLML, USACE/SF
- Important contribution to understanding of MeHg biogeochemistry
  - Were able to do some things local researchers were not.
- Shortcomings
  - Large, multidisciplinary, expensive, study with no clear “road map”
  - Not firmly based on a clearly stated conceptual model
  - Not as tightly coupled to management decision ready information as might be desirable
  - “Administrative and editorial issues”

Do we need more work on MeHg & Wetlands in the San Francisco Estuary?

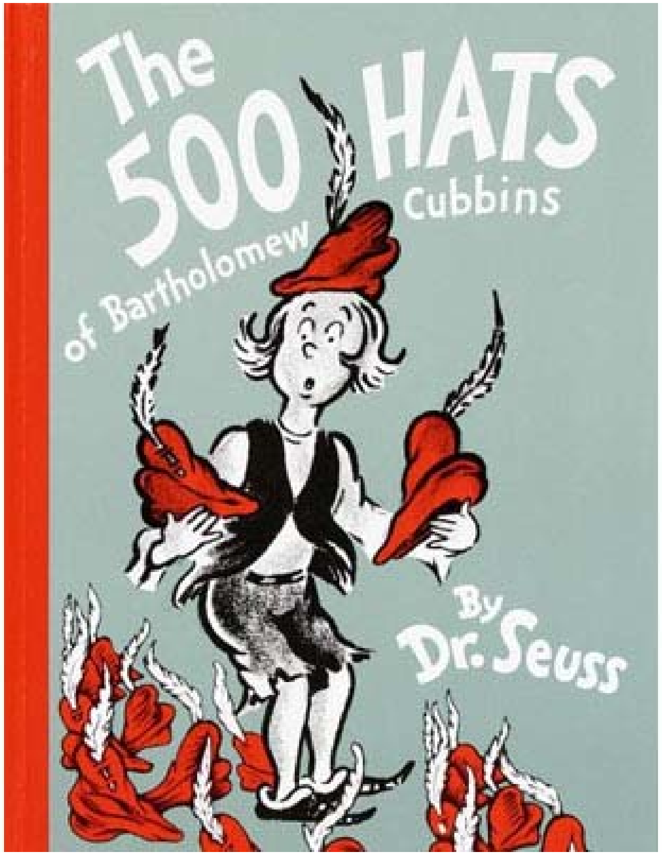
- Status of LTMS Corps
  - Interim suggestion DGT work in collaboration with “biosentinels”
- Possible work beyond this (contingent on consideration of peer review)
  - Regional significance?
  - Site specificity of research?
  - Specificity to dredged material placement?
  - Including monitoring/adaptive management.
- What pieces of the puzzle are missing?
  - Algal mats

Do we need more work on MeHg & Wetlands in the San Francisco Estuary?

- Requirement by several resource agencies to implement a monitoring and adaptive management plan for MeHg at HWRP.
- Science-based approach:
  - Involves pilot studies, calculation of optimal sample size, controls, reference sites, integration of mid-course corrections, technical advisory committee, data sharing, etc
  - Draft SOW to prepare developed by the USACE.
  - Advantages:
  - Disadvantages:
- Administrative approach involves:
  - Paying into RMP or adapting existing monitoring schemes for other wetland projects.
  - Advantages:
  - Disadvantages:

Impressions of a Researcher Turned Environmental Manager/Planner

- Expectations of project? Not really tuned to "using science to inform policy"
  - Evidence to support use of dredged material for restoring/establishing wetlands
    - Legacy sources not a major problem
    - Supports concept that wetlands can be designed to minimize MeHg
- Information transfer?
- Precision of results?
- Sample design (replicates, documenting variation, reference sites)?
- Extent of peer review?
- Interaction with other/local resource or permitting agencies and researchers?
- Interaction with existing salt marsh work?



Impressions of a researcher turned environmental manager

- Better and more frequent communication and coordination
- Better “education” of both managers and researchers (in progress: symposia like this)
- More levels of peer review *(in progress)*
- Initial phase of work will include literature review/white paper making the proposal accessible to a wider audience

Turning Science into Policy (or at least management decisions)

San Francisco Bay LTMS Environmental Windows Science Assessment and Data Gaps Work Group

– Refining peer review process
– Developing a protocol for turning studies into policy
– Next meeting: July 10