

# **CBDA Mercury Projects Technical Review**

Summary Evaluation

CALFED CBDA Project Workshop

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# Acknowledgments

## Thanks to..

- Bay Delta Program (CBDA)
- Allen Barnes
- Carol Atkins, Mary Menconi, and Bellory Fong
- The investigators and presenters
- Attending managers and public

# Outline

- Project-level comments
- Integration and synthesis
- Future directions

# Scientific Progress on mercury issues in the Bay-Delta Ecosystem

Understanding of mercury transport, methylation, bioaccumulation, and ecotoxicology have all been greatly advanced since the beginning of mercury studies in the Bay-Delta Ecosystem in 1999.

Contract #S-03-ER-020

# **Programmatic Quality Assurance and Quality Control for CBDA Mercury Research and Monitoring Projects**

**B.H. Van Buuren**

**A.F. Vandervort**

**W. Hagan**

**M.V. Kilner**

**J. Parker**

**E.J. von der Geest**

# General comments

- Excellent effort by Van Buuren et al.
- QA process is essential to program synthesis and peer review.
  - QA report shows that the projects are producing data of high analytical reliability and comparability for THg and MeHg in water and sediment.
- A continued commitment to QA/QC oversight is strongly recommended for future Hg assessments pertaining to restoration projects.

# Specific outcomes of this project

- All matrix and analyte combinations were included in the second lab inter-comparison (total and methyl mercury in water, sediment and tissues), and THg in freshwater and MeHg in sediment were included in the third inter-comparison
- Both reference materials and sample material were analyzed by all laboratories
- These inter-comparisons were completed in March 06 and January 07, respectively
- Most results were rated as “good” or “very good” by the QA Oversight Group
- Evaluation of methodology for methyl mercury in sediment confirmed that methylene chloride extraction is better than distillation, which produces artefacts in sediments with high total Hg.

## Specific outcomes (cont.)

- 5% of all samples are designated for participation in the sample splits program, in which one half of each sample is analyzed by a referee laboratory. Two problems were encountered in this program. 1) Not all projects participated in the sample splits due to contracting delays. These delays were related to agency policies, not to individuals. 2) There was some confusion over the definition of “sample split”, which means one sample split in half, not a duplicate sample taken at the same time.
- An important supplement to the lab inter-comparisons and split sample programs is the reporting of each laboratory’s internal QA procedures



## **Specific comments (cont.)**

- On-site audits have taken place at all labs except the U. of Connecticut lab, which is pending
- An important supplement to the lab intercomparisons and split sample programs in the reporting of each laboratory's internal QA procedures
- Report recommends improvements in data transparency

Project #ERP=02D-P62

**Evaluation of Mercury Transformations  
and Trophic Transfer in the San  
Francisco Bay/Delta: Identifying Critical  
Processes for Ecosystem Restoration**

M. Marvin-DiPasquale, R. Stewart, N.S. Fisher,  
P. Pickhardt, R.P. Mason, A. Heyes,  
L. Windham-Myers

## **Are results used to test clearly stated hypotheses?**

- Yes
- Best job of following hypothesis based format
- Clear statement of hypotheses and results made it easy to understand significance of results.

## What new knowledge has this project produced?

- Transfer of MeHg up the food web occurred in a similar manner at both sites. Therefore, the difference in rate of production of MeHg at the two sites was the deciding factor in determining MeHg concentrations in the biota
- No single factor was predictive for rates of MeHg production; multiple factors had to be considered
- Methylation potential varied substantially among wetland types
- Flooding of the Cosumnes River resulted in elevated MeHg concentrations in the floodplain area
- This work has begun to put together methylation, THg trapping, and Hg<sup>0</sup> emissions for vegetated wetland sites, to give a better picture of the net effect of wetland creation

## **Are there ways in which data interpretation could be improved?**

- Compare biosentinel results with methylation potentials.
- Test whether reactive mercury improves the ability to predict methylation, compared to using only methylation rate constant ( $k_{\text{meth}}$ )
- Reconcile algal uptake laboratory experiments with field measurements of trophic transfer

## **Applicability of results to ecosystem restoration and management**

- Results single out mercury methylation as likely the most important process to understand and to minimize, where possible, in order to minimize MeHg contamination of resident biota
- Management of floodplain hydrology may provide opportunities to minimize MeHg production, compared to unmanaged flooding.

## **Limitations on the applicability and transferability of results?**

- Still can not predict methylation as a function of individual site conditions; it appears that a suite of conditions characteristic of certain habitats might be more fruitful, but this is an ongoing challenge
- Some questions on bioconcentration factors between water and base of food web remain

## Responses to first review

- The recommendation to evaluate reactive mercury ( $\text{Hg(II)}_{\text{R}}$ ) as a measure of bioavailable mercury was followed in part, e.g., the session at the Global Mercury conference in Madison, but this measurement still remains unsubstantiated. If more recent work is available, this could be provided as an Appendix to the report.
- Methylation and demethylation rate data as predictors of MeHg concentrations were explored further using multivariate analysis, but a simple predictive model could also be developed.
- The recommendation to address biodilution as a possible factor was followed
- The recommendation to go to finer scale investigations was followed



Project #ERP-02-G01

# **Mercury Release from Delta Wetlands: Facilitation and Fluxes**

Brian Bergamaschi, Jacob Fleck, Bryan Downing,  
David Schoellhamer, Megan Lionberger, Neil  
Ganju, Roger Fujii (USGS Sacramento)

George Aiken, Doug Latch, Jarrod Gasper, Elke  
Suess, Chase Gerbig (USGS Boulder)

Emmanuel Boss (U. Maine)

Mark Stephenson, Wes Heim (Moss Landing  
Marine Laboratories)

## **Are results used to test clearly stated hypotheses?**

- Hypotheses are clear (H1: tidal fluxes lead to export; H2: DOM affects Hg binding; H3: DOM affects Hg mineral dissolution)
- Experimental work is driven by hypotheses; in the report, however, hypotheses were not explicitly accepted or rejected (based on reading of the report, H1: rejected; H2: accepted; H3: accepted, but other water chemistry also shown to be an important factor).

## What new knowledge has this project produced?

- Increasing DOM concentration/aromaticity +  $\text{Cl}^-$  enhances dissolution of Hg minerals.
- Polyvalent cations (from calcite) inhibit dissolution of Hg minerals.
- Use of continuous measurements of water quality parameters and other environmental measurements can be used to estimate high resolution time series of THg and MeHg fluxes and mass balances.
- The magnitude and direction of net MeHg and THg fluxes depend on time periods involved (e.g. spring neap), and were different from expected

## **Are there ways in which data interpretation could be improved?**

- The conclusion that the release of Hg due to DOM mediated dissolution will have a first order control on Hg methylation in the Bay-Delta needs further examination, since there are no data on the bioavailability of these Hg-DOM species.
- The statistical analyses used to derive the continuous Hg time series and fluxes are not documented. This, coupled to assumptions about water balance and flow path, must be approached carefully, given the scrutiny that this will receive in peer-review.
- Are there mechanistic explanations for the relationships that were observed between water quality parameters and other environmental measurements and Hg?

## **Are there limitations on the applicability and transferability of results? Are they clearly presented?**

- Recommendation in previous report to compare Browns Island with other sites was not pursued due to financial and time constraints. Instead, optical characterization of DOM from other locations is pending. Thus, limitations for transferral of results from Browns Island to other sites are unclear.
- Limitations and uncertainties associated with the current water balance estimates are acknowledged. Improvements in understanding of Browns Island topography and hydrology will improve transferability of results from this wetland study to other wetlands

# Applicability of results to ecosystem restoration and management

- The finding that a tidal wetland might not necessarily be a net source of Hg to surrounding areas is especially encouraging for the future of wetland restoration projects.
- Assessment of tidal transport of DOM and Hg species has important implications for restoration site selection and management (it could be Hg neutral, sink, or source depending on hydrologic regime). Uncertainty in water and sediment mass balances reduces confidence in this conclusion, and additional sites should be monitored using the methodology developed in this study.
- DOM-Hg binding/solubilization studies are directly relevant where wetland creation is planned in areas containing Hg-contaminated sediments. Knowledge of the type of DOM in overlying waters could help in predicting Hg release from the sediments. However, lack of Hg-DOM bioavailability data precludes a direct coupling to the contribution of this release to the methylation process.

Project #ERP-02D-P62

# **Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems**

Donald Yee, Joshua Collins, Letitia Grenier, San Francisco  
Estuary Institute

John Takekawa, Danika Tsao-Melcer, Isa Woo, Steven  
Schwarzbach, USGS BRD

Mark Marvin-DiPasquale, Lisamarie Windham, USGS Menlo  
Park

David Krabbenhoft, Shane Olund, USGS Middleton, WI.

Jules Evens, Avocet Research Associates

## **Are project results used to test clearly stated hypotheses?**

- “Current working hypotheses” are stated in the report as a set of factors that result in mercury contamination in wetland biota
  - Some of these factors/hypotheses are tested by the project or based upon previously established understanding
  - Other listed factors/hypotheses were not sufficiently tested by this project
- Hypotheses not highly project specific
- The report was not structured around the hypotheses



## New Knowledge

- Project showed that bioaccumulation in resident bird populations is correlated with sediment MeHg concentrations in their home ranges
- Project results show that interiors of high marshes have higher MeHg concentrations, higher  $\text{Hg(II)}_R$ , and higher  $k_{\text{meth}}$  than slough channels and channel edges
- MeHg production was correlated with live root density
- Experimental de-vegetation reduced rates of MeHg production
- Hg pools in plants, and Hg fluxes through plant uptake and decomposition, were not significant pools and fluxes of Hg and MeHg
- Linkage of natural history, biogeochemistry and ecology in a single project is impressive

## Limitations on Applicability and Transferability

- Limitations and transferability of findings were not discussed in detail
  - The report did not discuss variability of findings across marsh habitat gradients previously identified in 2005 report, e.g., elevation of marsh plain, salinity, marsh age
  - Uncertain if water Hg data is representative of average conditions due to sampling tending to occur at same tidal phase (high water = low MeHg)

## Suggestions for Improved Data Interpretation

- Reproductive risk for Black Rails not yet determined
  - Rely on Collins-Eagles et al. study for insight to potential reproductive risk
- Effects of salinity on MeHg production and bioaccumulation not discussed adequately
- Influence of marsh plain elevation, salinity and marsh age on MeHg production and bioaccumulation should be discussed
- Biosentinel work could confirm observed spatial and temporal trends in MeHg production and concentration in sediments
- Further interpretation of devegetation experiment is needed to determine if this is a potential remediation option, and if so under what circumstances

## **Applicability to Ecosystem Restoration**

- **Predictability:** Where conditions lead to high MeHg production in marshes, this will likely result in high MeHg in local, upper trophic level, biota
- **Monitoring:** Results show that there is a need to consider spatial variability of MeHg production, concentration and bioaccumulation within and among tidal marshes

Project # ERP-02D-C12

**Mercury in Birds of the San Francisco Bay-Delta: Trophic Pathways, Bioaccumulation, and Ecotoxicological Risk to Avian Reproduction**

Joshua Ackerman, Collin Eagles-Smith, Gary Heinz, Susan Wainwright-De La Cruz, John Takekawa, Terrence Adelsbach, Keith Miles, David Hoffman, Steven Schwarzbach, Thomas Suchanek, Thomas Maurer

## **Are results used to test clearly stated hypotheses?**

- Yes. Hypotheses were presented for each objective and task in null hypothesis form.

# New knowledge from this project

- *Definite evidence of a mercury pollution problem:* This study showed that exposure to methylmercury (via dietary uptake), could adversely affect certain aquatic birds that forage and nest in the Bay-Delta system.
- *Assessment of risk:* The species studied were at risk for MeHg toxicity, particularly for individuals foraging in North and South SF Bay. In Forster's tern, 58% of the adult birds breeding in SF Bay and 46% of eggs were at high risk for MeHg toxicity.
- *Mercury-selenium interactions :* In developing bird embryos, exposure to both methylmercury and selenium at certain concentrations resulted in greater effects than were seen than from exposure to either one of these alone.

## New knowledge from this project

- *Rapid uptake and off-site exposure:* MeHg is rapidly (few weeks) accumulated by surf scoters while over-wintering in the SF Bay area. In reproducing hens, this MeHg is transferred to eggs, increasing *in ovo* exposure in embryos at the breeding grounds in northern Canada.
- *Substantial variation in sensitivity* to methylmercury among species.
- *Sensitive life stages:* Avian embryos and young hatchlings were the life stages most sensitive to MeHg exposure. This demonstrates the critical importance of *in ovo* exposure in the life cycle of birds.



## **New knowledge from this project**

- *Hotspots*: Identification of hotspots (foraging sites) and associated trophic pathways that cause bioaccumulation of MeHg in birds to toxicologically significant concentrations. MeHg exposures for some bird species at some sites are presently high enough to adversely affect embryos, young hatchlings, and adults.

## Applicability and transferability of results

- *Demonstrated complexity and interactions* of multiple factors, including foraging habitat, diet and trophic ecology, species and reproductive biology, that strongly influence methylmercury bioaccumulation and exposure for a given species.
- *Interspecific variation in sensitivity to methylmercury:* Toxicological test results are not readily transferable among bird species.
- *Species specific* data for mercury toxicology is transferable to other ecosystems but could be confounded by other contaminants.

## **Applicability and transferability of results**

- The results of this study lead the review panel to advise that the behavior of mercury in the Bay-Delta ecosystem merits careful scrutiny as ecosystem restoration and management proceed.

## **Responses to first review (November 2005)**

- *Responses were satisfactory.* In particular, the toxicological interaction between methylmercury and selenium, identified as a gap in the study design, has been examined in egg-injection experiments.

## Product Recommendation

- The investigators are encouraged to integrate the analysis of field data on methylmercury exposure in eggs with laboratory dose-response data on the effects of methylmercury on embryo survival. The review panel suggests that a journal manuscript be devoted to this topic.

## **Closing comment**

- This is the best investigation of the ecotoxicology of methylmercury in birds conducted anywhere to date. This project could serve as a model for investigations of the avian ecotoxicology of mercury in other contaminated ecosystems.

Project #ERP-002-C06 A/B

**Transport, Cycling, and Fate of  
Mercury and Monomethyl Mercury in  
the San Francisco Delta and  
Tributaries: An Integrated Mass  
Balance Assessment Approach**

Mark Stephenson

Chris Foe

Gary A. Gill

Kenneth H. Coale

## Clear Hypotheses?

- Focused goal of developing a complete mass balance of the Delta
- Objectives and hypotheses are clearly stated.
- Highly relevant to Ecosystem Restoration Program



## **New Knowledge-Total Mercury**

1. Tributaries are primary source of THg to Delta
2. Direct deposition is minor overall source to Delta (although bioavailability is a question)
3. Delta is a sink for THg

## **New Knowledge-Methylmercury**

1. Inundated floodplains can be major sources of MeHg
2. Short term studies suggest that wetlands may be either sources of or sinks for MeHg to surrounding waters
3. The tributaries are important sources of MeHg, as well as total Hg, to the Delta
4. Internal sources of MeHg within the Delta are also important
5. Removal processes (that decrease MeHg) are very important within the Delta, and overall, the Delta is a sink for MeHg
6. Photodegradation of MeHg is potentially a very important removal process

# Comments on interpretation

1. Refine analysis spatially and temporally (planned)
2. Tributaries:
  - Conservative transport of MeHg: The panel views this as a hypothesis, not as a conclusion.
  - What portions of tributary Hg loads to the Delta are ultimately atmospheric versus geologic?
3. Focus on big terms with large uncertainty (MeHg photodegradation, sediment/water exchange)
4. Further analysis of bioavailability of Hg in tributaries, deposition and Delta.
5. Continue efforts to refine estimates of wetland and floodplain MeHg fluxes
6. Currently all wetlands are treated the same in the mass balance calculation, but recent evidence suggests that some may export MeHg and others import MeHg. Thus, the wetland term may need to be divided into smaller categories.

## Applicability

- This mass balance is a critical piece of the overall understanding of the contribution of historical mercury contamination to current mercury problems in the Bay-Delta system.
- A good understanding of wetland MeHg fluxes, as compared to other fluxes into the Delta, are critical to the predicting the effects of Ecosystem Restoration Program on MeHg levels in the Delta

# Comments on presentation/report

1. Add figures showing budgets in  $\mu\text{g}/\text{m}^2/\text{yr}$
2. Identify which fluxes are calculated by difference
3. Note that sediment Hg fluxes include diffusion and hydraulic gradient fluxes.

Project #ERP 02D-P67

**A Pilot Program for Monitoring,  
Stakeholder Involvement, and Risk  
Communication relating to Mercury in  
Fish in the Bay-Delta Watershed**

Jay Davis, Jennifer Hunt, Letitia Grenier,  
Mark Stephenson, Gary Ichikawa, Darrel  
Slotton, Shaun Ayers, Robert Brodberg,  
Mary Gassel, Alyce Ujihara, and Jessica  
Kaslow

# **Are project results used to test clearly stated hypotheses?**

- This project is not primarily hypothesis-driven, but is a monitoring project. The data are highly valuable as is, but the addition of stated hypotheses would add considerable value, and improve understanding of the effectiveness of the monitoring program.
- Suggested hypothesis for sport fish monitoring: “A monitoring and risk communication program will be effective in reducing human exposure to methyl mercury”
- The risk communication element could also be improved by clearly stating and potentially testing hypothesis such as “information dissemination by word of mouth at bait shops is more effective than advisories in newspaper articles.

# **Are project results used to test clearly stated hypotheses?**

The biosentinel monitoring data analysis could also be significantly improved by presenting the data in the context of simple, clear hypothesis such as:

- “MeHg levels in biosentinel organisms vary seasonally” or
- “MeHg levels are higher in areas with restored wetlands” or
- “MeHg in biosentinels are predictive of MeHg levels in larger sport fish in the same area.”



## **What new knowledge has this project produced?**

- Identifies fish species and geographic areas of high and low MeHg, and makes recommendations about which species are safer than others for consumption.
- Quantifies seasonal, interannual, and spatial differences in MeHg in fish tissue in Bay Delta system and tributaries, showing how these must be taken into account in any evaluation of fish mercury levels.

## **New knowledge (continued)**

- The sport fish species that were highest in MeHg concentrations were largemouth bass and pike minnows.
- Concentrations of MeHg in fish in the Sacramento, San Joaquin, and Cosumnes Rivers were often higher than in Delta. Bass in San Joaquin River are considered not safe for pregnant women.
- In the South Delta, all popular fish species were low enough in MeHg that they can be eaten regularly. The biosentinel data showed that increases in MeHg in young of the year silversides were often linked to flooding events.
- Not all wetland environments had high levels of MeHg in the biosentinel fish.

## **Are there ways in which data interpretation could be improved?**

- Integrate biosentinel data with sport fish data.
- Overlay regional scale biosentinel data over various environmental attributes data such as salinity, wetland area, restored wetland sites, etc.
- Use literature and findings from other Delta Hg research to explain or at least discuss the temporal and spatial variability (low levels in Delta, high levels in Petaluma relative to Napa, high levels in 2006 relative to 2005).

**Are there limitations on the applicability and transferability of results? Are they clearly presented?**

- Biosentinel and sport fish data very well presented in maps. It would be useful to present health advisory threshold information along with data tables and maps.
- Can the quality of stakeholder input regarding fish consumption be evaluated?

## **2005 recommendations still apply...**

The following recommendations were made at the last review and not addressed in the most recent report.

- Specific hypotheses should be developed for the biosentinel component. For example:
  1. Formulate hypotheses pertaining to effects of different types of restoration projects on spatial and temporal patterns in methylmercury concentrations in biosentinel organisms.
  2. Evaluate the extent to which concentrations of methylmercury in biosentinel organisms can be used as an indicator of methylmercury in sport fishes.
- During the next year, the investigators should develop a publication plan for the project, identifying target manuscripts (by title), roles and responsibilities of contributing authors, target peer-reviewed journals, target dates for completion and submission of manuscripts.

## **Applicability of results to ecosystem restoration and management**

- Information from analyses of biosentinel organisms will be very applicable to assessing the effect of ecosystem restoration activities on methylmercury contamination of aquatic food webs.
- Methylmercury concentrations in aquatic biosentinel organisms can serve as a useful “performance measure” for management and restoration.

# Program level comments and recommendations

- GREAT WORK!
- Major advances in the understanding of Hg in Bay Delta system, and Hg cycling in general, as a result of this program.
- Value will be limited unless there is a concerted effort over the next year to synthesize and publish results.



# The Mercury Strategy: Core Components and Linkages

## Strategies for Reducing Exposure to Methylmercury (MeHg)

### Evaluate & Remediate Sources of Mercury

Characterize  
Prioritize  
Remediate  
Evaluate

### Monitor, Assess Risk, Advise, and Evaluate

Monitor mercury in fish  
Assess health risks  
Communicate advice  
Measure performance

### Manage Landscapes to Reduce MeHg

Identify factors controlling MeHg production that can be manipulated  
Evaluate responses to pilot-scale manipulation

### Assess Ecological Risk

Quantify MeHg exposure in field  
Experimentally examine effects of MeHg on reproduction  
Identify trophic pathways, areas, and habitats associated with high exposure to MeHg

### Ecosystem Restoration

### Assess Effects of Wetland Restoration on MeHg Exposure

Examine Hg cycling processes  
Identify controls on MeHg  
Evaluate effects on exposure

Black text = item largely accomplished  
Red text = item still not adequately addressed

# Research Highlights

- Mercury methylation is the key process.
- Strong evidence of adverse effects of MeHg exposure on certain bird species that forage at certain sites.
- Biosentinel results could be the vehicle for program level synthesis.
- Wetland MeHg fluxes can be highly variable over short periods. Over longer term, wetlands might not be large sources of MeHg to surrounding area (this does not mean that MeHg within the wetland is not a problem).
- Multiple lines of evidence suggest seasonal flooding is a concern for MeHg production and mobility.

# Predictions

We have learned much but still can not predict how MeHg production and bioaccumulation will change due to wetland restoration.

# Recommendations

1. Strongly endorse adaptive management
2. To make this happen, proponents need:
  - Hg science coordinator/liaison
  - The opportunity and resources to use restoration projects and field manipulations as experiments, to gather mercury data on a greater variety of systems
  - Manager/scientist interaction
3. Renewed commitment to Hg program needed as current studies reach completion

# Peer Review

1. This panel provides review comments, but it is not a complete critical assessment of the science.
2. The science is world-class but has low visibility
3. Peer-reviewed journal publications are essential for credibility and visibility

# Peer Review QA\*

Project	Peer Reviewed <sup>1</sup>	Non-peer reviewed <sup>1</sup>	Submitted <sup>2</sup>	In prep. <sup>2</sup>	(Scientific) Pres.
A	2	0	0	10	16
B	0	0	0	0	14
C	1	0	0	0	0
D	2	1	0	1	33
E	2	5	4	0	77
F	0	0	0	0	11
	7	6	4	11	151

<sup>1</sup> Published, in press, accepted.

<sup>2</sup> Peer-reviewed only.

(44 Principal Investigators)

**\*numbers in table taken from annual reports  
submitted to Review Panel**

## Dissemination of results, continued

- Project investigators are encouraged to develop a final publication plan for the project, identifying additional manuscripts (by title), roles and responsibilities of contributing authors, target peer-reviewed journals, and target dates for completion and submission.
- Consider CALFED post-doc program