Annual report: Mercury Release from Delta Wetlands: facilitation and fluxes; an amendment to existing CALFED Projects #2000-G01

Project Coordinator: Brian Bergamaschi
Project Researchers: Brian Bergamaschi, Jacob Fleck, Bryan Downing, David Schoellhamer, Megan Lionberger, Emmanuel Boss, George Aiken, Roger Fujii
Project Collaborators: Mark Stephenson, Kenneth Coale, Gary Gill, Chris Foe; Mark Marvin-DiPasquale, Robin Stewart, Nicholas S. Fisher, and Robert P. Mason

INTRODUCTION

Background

Mercury (Hg) contamination in the Sacramento-San Joaquin Delta is a complex mixture of elemental Hg (Hg^0) derived from gold mining operations in the Sierra Nevada and sulfidic Hg (HgS) derived from the Hg mines in Coast Ranges. Due to mining activities, more than 800,000,000 cubic yards of Hg-laden sediment has been washed into the Sacramento River and Delta and continues today (Thompson, 1959; Alpers and Hunerlach, 1999). These sediments will pose an environmental hazard if they are (1) solubilized and (2) methylated in Delta and Estuary wetlands (See conceptual model, Figure 1; Bloom, 2002; Alpers and Hunerlach, 1999).

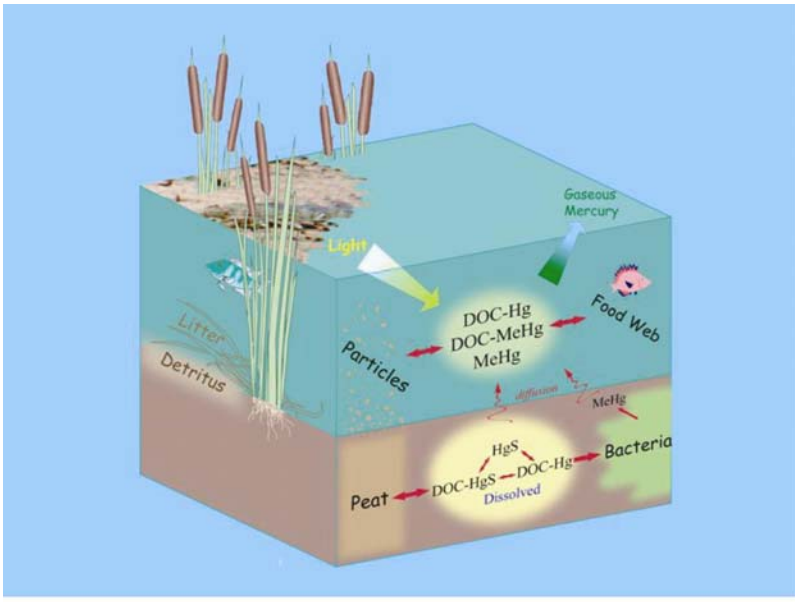

Fig. 1. Conceptual model of mercury-DOM interaction in peat sediments

Dissolved organic matter (DOM) plays an important role in mercury cycling and transport. Like mercury, DOM in the Delta is a complex mixture of different sources, with each source supplying DOM of different character and properties affecting the mercury interactions and cycling. This project focuses on evidence that tidal wetlands in

the Delta convert insoluble forms of sedimentary mercury into methylmercury (MeHg) with the objectives of quantifying the capacity of DOM from representative Delta wetlands to solubilize the major sedimentary forms of mercury in the Delta – cinnabar, metacinnabar, and elemental mercury – and determining the dissolved and particulate fluxes of mercury and methylmercury at selected, representative wetland sites in the Delta.

The approach of the study is to 1) to expand the current work of the USGS on chemical composition of DOM from different sources within the Delta to include parameters related to mercury solubilization, binding, and partitioning; and 2) to expand current measurement of tidal fluxes of DOM to include mercury species by identifying correlates measured in situ to predict real time fluxes of mercury and methylmercury in the complex hydrodynamic exchange of the tidal wetland environment.

Part 1 uses laboratory experiments to address the following:

- Binding of Hg to DOM
    - Equilibrium and binding site abundance experiments of the Delta's five main organic matter types
- Partitioning of Hg between particulate – colloidal and dissolved phases
    - Equilibrium experiments with five organic matter types and five particle types
- DOM enhanced dissolution of HgS
    - Release of mercury from mercury-rich endmember sediments (HgS and elemental Hg) upstream from Delta
- DOM-Hg photochemical reactivity
- Salinity effects on Hg geochemistry

Part 2 uses field studies consisting of:

- In-situ instrument deployment for high temporal resolution measurements of a suite of spectroscopic variables and water flux in tidal wetlands
- Intensive calibration sampling over tidal cycles
- Statistical determination of correlative relationships for accurate Hg and MeHg flux calculations
- Initial deployments identifying seasonal variability conducted at Browns Island (Figure 2), deployments identifying spatial variability after Browns Island work is completed

Figure 2. Primary site of the field study, Browns Island.

Goals and objectives

The project's primary objectives are:

OBJECTIVE 1: Quantify the capacity of DOM from representative Delta wetlands to solubilize the major sedimentary forms of mercury in the Delta, cinnabar (HgS), metacinnabar, and elemental Hg, as well as affect the partitioning of total Hg and MeHg between aqueous and particulate phases.

This part of the study will provide (1) a link between Hg binding and the environmental source of the DOM, as elucidated by the original DOM Sources study performed by the USGS; (2) a basis for evaluating the relationship between Hg binding and the chemical properties of the DOM; (3) potentially, a link to more readily measured chemical properties useful for predicting Hg binding at other sites; and (4) a means to evaluate, in conjunction with flux data, the role of DOM in Hg cycling in the Delta.

OBJECTIVE 2: Determine the fluxes of total Hg and monomethyl-Hg (MeHg) in dissolved and particulate phases at Browns Island and selected, representative wetland sites in the Delta.

This part of the study will provide (1) a means to evaluate the contribution of tidal wetlands to elevated dissolved and particulate Hg observed at various Delta locations; (2) a means to assess if process-level rates determined by other studies fully account for observed environmental fluxes; (3) a basis for estimating the likely Hg flux from future restored wetlands; and (4) demonstration of tools and correlates useful for assessing Hg fluxes in future studies.

With a better understanding of the role of wetland DOM in mobilizing Hg, provided by this study, CALFED managers will be better able to design wetlands restoration projects that minimize mobilization of Hg in the environment.

Hypotheses

I. Tidal advective and dispersive fluxes from wetlands within the Delta export significant quantities of mercury and methylmercury to Delta channels.

II. DOM from different environments will have significantly different rates and extents of mercury binding.

III. DOM from different Delta environments will have significantly different capacities to solubilize mineral forms of mercury.

Management goals

Effective management strategies for mitigating mercury contamination of the Sacramento-San Joaquin Delta and San Francisco Estuary will require a more thorough understanding of the factors and processes that solubilize and transport Hg, and affect its reactivity. The purpose of the work proposed here is to help guide wetland restoration efforts by quantifying specific physical and chemical characteristics of Sacramento-San Joaquin Delta wetlands not currently measured by other studies. The intent is to work with other ongoing studies to identify physical, chemical, and biological parameters associated with high *net* MeHg production and export, so that they may be minimized during implementation of restoration. We propose to focus our research on two aspects of Hg cycling not currently under study: 1) the role that DOM plays in the solubilization and facilitated transport of Hg species, and 2) the importance of physical processes in determining the net export of MeHg from tidal wetlands.

PROJECT TIMETABLE/PROGRESS

Starting and completion dates

Project funding was received in August 2004 and permission to begin work was granted in October 2004. Funding runs out in fiscal year 2007.

	USGS ABSTRACT OF TASKS, DELIVERABLES, AND SCHEDULE															
TASKS	DESCRIPTION		SCHEDULE													DELIVERABLE
		quarter	1	2	3	4	5	6	7	8	9	10	11	12	13	
Task 1.	Scientific Advisory Panel (to be coordinated with other															
	Hg studies and conducted by CALFED)															
Task 2.	Interactions between DOM and Hg															
	DOM-Hg binding studies															Quarterly Reports
	Effects of salinity on binding studies															Quarterly Reports
	Cinnabar dissolution studies															Quarterly Reports
	Partitioning of Hg species, soils and sediments															Quarterly Reports
	Hg speciation model															Quarterly Reports
	Presentations and Reports															Abstracts, Journal Articles
Task 3.	Mercury loads and correlations, tidal wetlands															
	Browns Island - field sampling & data collection															Quarterly Reports
	Browns Island - laboratory analysis of Hg species															Quarterly Reports
	Browns Island - data processing, analysis and interpretation															Quarterly Reports
	Other wetlands (3 total deployments)															Quarterly Reports
	Presentations and Report															Abstracts, Journal Articles
Task 4.	Project Management															
	Field and laboratory coordination															Quarterly Reports
	Other duties															Quarterly Reports

Project status

Lab Study

Work in the Aiken lab portion of the CALFED project is divided among three main areas: measuring the binding strength of Hg^{2+} with DOM, probing the distribution of Hg^{2+} between particulate and dissolved organic matter, and the role of DOM in the photochemical cycling of mercury. This area of work was initiated in the Aiken lab in February 2005. The early focus of this work has been to use well-defined organic matter isolates in order to elucidate the important factors controlling these processes, as well as to establish reliable analytical techniques. This work is ongoing, and will be followed by similar experiments with material taken from the CALFED study areas. A description of these research topics and a timetable for each is given below.

Recent work in the Aiken lab has centered on using different techniques to measure the strength of interactions between Hg^{2+} and various DOM isolates. During the course of these studies, a competitive ligand exchange solid phase extraction (CLE-SPE) procedure was found to be the most appropriate for measuring the strong binding of Hg^{2+} by reduced sulfur moieties contained in DOM (paper submitted for review). Continuing work with the CLE-SPE method involves modifying the ligands in competition with the DOM for Hg^{2+} in order to measure the much weaker binding that occurs under high Hg^{2+}:DOM concentration ratios. Under these conditions, all of the strong thiolate binding sites within the DOM become occupied, and the remaining Hg^{2+} is then bound by much weaker oxygen-containing ligands. Work in this area should be completed in the near future, and then DOM isolated from water collected at various sites within the Sacramento-San Joaquin Delta will be analyzed for the number and magnitude of strong binding sites. *These experiments will be conducted throughout the coming year (Jarrod Gasper).*

Characterization of sediments obtained from multiple sites in the CALFED study area began in February 2005 and is ongoing. These samples have been size-fractionated, freeze-dried, and measured for total carbon and mercury content. Work has just begun to determine the mineralogy of the sediments and to assess the distribution and availability of mercury contained within them. A powder X-ray diffraction protocol will be used to assess the mineralogy. This work was recently begun in November 2005. Initial studies on the distribution of mercury contained within the sediments were performed using a sequential extraction technique in the summer and fall of 2005. Further studies will be performed to assess how much mercury can be leached from these sediments by DOM isolated from different CALFED sites. Analysis of these data will also show from which sediment fractions the mercury is being leached, and what properties of the DOM are important in the redistribution of the Hg. *This work will be conducted over the next four months (Jarrod Gasper and Elke Suess, a graduate student on exchange from Germany).*

Beginning in the summer of 2005, the Aiken lab has begun to perform mechanistic studies on the photoreduction of Hg^{2+} in the presence of a relatively well-characterized DOM isolate. During the course of these studies, it has become apparent that DOM is intimately involved in this process, and that Hg^{2+} bound by thiolate constituents of the

DOM are the active species in the photoreduction. Ongoing work is designed to further elucidate the involvement of thiolate moieties in Hg^{2+} binding and subsequent photoreduction. These experiments will involve photolysis experiments with DOM that has been spiked with divalent cations or exogenous ligands that display an affinity for Hg^{2+}. The hypotheses in these experiments are that the added cations will block the thiolate sites from binding Hg^{2+} or the added ligands will pull the Hg^{2+} away from the free thiolate binding sites. In either case, the formation of the expected DOM thiolate-Hg complex is prevented, with subsequent consequences to the photochemical kinetics. *These experiments are currently being performed, and will continue over the course of the next year (Doug Latch). Future work regarding mercury photochemistry will involve performing the analyses with whole water samples and DOM isolated from various CALFED waterways, as well as conducting similar experiments regarding the photooxidation kinetics of* Hg^0.

Field Study

The field study component has completed two of three deployments at Browns Island focusing on seasonal variability. A spring deployment was conducted in April and May of 2005 and a fall deployment was conducted in October 2005. The deployments involve two optical instrumentation packages, one package located at each of the two primary channels draining the center Brown's Island (Figure 2). The package at the main channel is the primary package consisting of a CDOM fluorescence spectrophotometer, ISUS UV spectrophotometer, optical DO probe, AC9 fluorescence spectrophotometer, Seabird CTD, and an optical backscattering sensor. The package at the side channel has the same components except that it does not have an ISUS unit. An acoustic Doppler current profiler (ADCP) unit was deployed at both locations to quantify water flux. *The final seasonal deployment at Browns Island, the winter deployment, is scheduled for late January 2006. Other deployments designed to determine spatial variability will be performed at 2-4 other wetland sites in spring 2006.*

Intensive calibration sampling efforts were conducted during each week of the deployment to calibrate *in situ* measurements with known laboratory measurements. During the spring deployment, total- and methyl-mercury samples were collected at the main channel site over one 12-hr period of the tidal cycle. The Hg effort was more than doubled in the fall deployment to include both sites and to extend the sampling to capture a greater portion of the tidal cycle (one 24-hr sampling at each site). *We will attempt to capture spring-neap variability in future deployments by collecting Hg samples throughout the deployment in addition to the current single tidal cycle sampling plan.*

The instrument packages performed well during the deployments. DOC values obtained in the laboratory were strongly correlated with CDOM measured *in situ* (r^2=0.98 in the main channel, 0.97 in the side channel) over both seasons. Suspended sediments and turbidity measured *in situ* were strongly correlated (r^2=0.99). The ISUS nitrate concentrations measured in situ were closely correlated with laboratory analyses of discrete samples (r^2=0.96). *Preliminary analyses of in situ time series data are currently underway and uncertainty analyses are being explored. Laboratory studies have begun*

to develop methods to determine nitrate and sulfide directly from UV data collected in situ. A great deal of work will be conducted over the next year to extract the raw spectra from the ISUS. Extracting the raw data will also provide us a greater ability to derive more DOC quality information that can be compared to our lab analyses. Once these tasks are completed, we will be able to back-calculate a wealth of information from all previous ISUS runs, greatly expanding the correlative power of the instrumentation package.

Complications

The project is about 6 months behind schedule due to contracting delays and unforeseen instrumentation development. The instrumentation difficulties are partly due to the need to double our efforts at Browns Island to capture a good water balance. The original assumption was that the main channel (B2, see Figure 2) on Browns Island was the dominant transport vector for tidal exchange on the island. After the proposal had been submitted, a side channel (B4, see Figure 2) was identified as a significant transport vector. It was determined that the side channel required similar instrumentation as the main channel to accurately measure fluxes on and off the island. The need for two instrumentation packages doubled our efforts and required an unplanned integration of borrowed instruments for a second *in situ* package. All instrumentation problems have been resolved and we currently have the instrumentation packages dedicated to our deployment schedule. As with any system that uses complex technological instrumentation, failures will undoubtedly occur. We have established protocols for identifying and addressing such issues as they arise. Our deployment schedule is designed to minimize fatal losses of time, effort, and data.

Milestones

Lab Study

- Sediments obtained for lab study February 2005
- Competitive ligand exchange solid phase extraction method successfully developed
- Sequential extraction performed to determine Hg speciation and distribution of sediments
- Photolysis methods established

Field study

- Successful integration of in-situ instrumentation, March 2005.
- Successful spring deployment, April 2005
- Successful fall deployment, October 2005

HIGHLIGHTS AND RESULTS

Lab Study

Our work to date has generated a number of important findings. First, the nature of the binding between DOM and Hg^{2+} has been elucidated. Our results show that the tremendous variability in reported Hg-DOM binding constants are likely the result of two factors: limitations of the various analytical techniques used in making the measurements and the ratio of concentrations of Hg^{2+} to DOM used in the studies. In the former case, each analytical method must be critically analyzed to determine whether it is capable of measuring the magnitude of the binding constants expected for a particular interaction. For any given analytical technique, only a certain range of binding constants can be measured. For this reason, each technique must be critiqued to determine whether it is capable of measuring the binding constant at the magnitude relevant for a particular system. For DOM-Hg interactions at typical environmental concentrations, we determined that the CLE-SPE method is effective at measuring the strong interactions between the Hg^{2+} ion and thiolate moieties, whereas liquid-liquid extraction and ion-exchange techniques had severe limitations in measuring these interactions. We also found that any measured Hg-DOM binding constant is reflective of the relative amount of Hg^{2+} bound by strong versus weak binding sites. Because the number of strong binding sites is limited, and measurements made at relatively high Hg^{2+} concentrations reflect binding with a larger fraction of weak binding sites that are typically less environmentally relevant, the concentration ratio of Hg^{2+} to DOM must be reported. In general, binding constants measured at high Hg^{2+} concentrations will be much lower than those made at the low Hg^{2+} concentrations relevant to natural waters. For this reason, reported binding constants made at relatively high Hg^{2+} concentrations are cast in doubt, and any future measurements must be made at low, explicitly reported ratios of Hg^{2+}:DOM concentrations.

It has been shown that DOM can enhance the dissolution of cinnabar and metacinnabar (paper published April 2005). During the course of these experiments, it became apparent that DOM isolates that were rich in aromatic carbon were particularly effective at dissolving cinnabar. In regards to the CALFED study, this result is important, because it implies that DOM from the different source waters may be more or less effective than others at adding new Hg^{2+} to the system. This is an area of particular significance in the watersheds above the Delta and in the Delta itself due to the large amount of cinnabar in the Coastal Range and the large amount of Hg transported downriver from Coastal range watersheds. We are continuing to study DOM-HgS interactions in the Delta.

In our studies of Hg photoreduction, we have discovered that Hg^{2+} bound to thiolate sites of DOM is rapidly reduced upon exposure to sunlight. The magnitude of this photoreduction process is similar to that of other Hg-thiolate species. During the course of our studies, it became apparent that at relatively low Hg^{2+} concentrations, the photoreduction of DOM-Hg complexes was dominated by these thiolate species. These results suggest that the reduction kinetics of Hg^{2+} in different natural waters are going to be similar and based on the cycling of Hg-thiols.

Field Study

Results of the field study indicate that we will be able to quantify mercury fluxes using *in situ* measurements and correlative techniques. Uncertainty will be assessed to quantify the power of our methods compared to traditional techniques. The following points support our current approach:

1. Instrumentation measurements show high temporal variability in constituents of interest over a number of timescales: tidal, spring-neap, seasonal and even episodic events. In Figures 3 and 4 below, the CDOM and conductivity measurements both show a distinct rise and fall with the tides, with peaks varying in magnitude over spring-neap cycles. The dropping baseline in the CDOM measurements reflects a seasonal shift in the river's character as it transitions to summer-like conditions at the site. Episodic events are noticed in the CDOM signal in Figure 4 late in the deployment and at the highest tides in the conductivity signal (Figure 3). The cause of the episodic events is thus far unknown. Similar time-series trends are apparent in nitrate, dissolved oxygen, pH, temperature, and carbon quality (data not shown). Turbidity data are more prone to episodic events than the other measurements, and some carbon quality measurements appear to possess unique trends (data not shown). Due to the multiple levels of temporal variability in constituent concentrations, the need for near real-time measurements in quantifying fluxes in tidal environments is apparent. Even well-planned traditional sampling protocols may lack the ability to accurately capture the dynamic nature of these systems, and may result in erroneous conclusions.

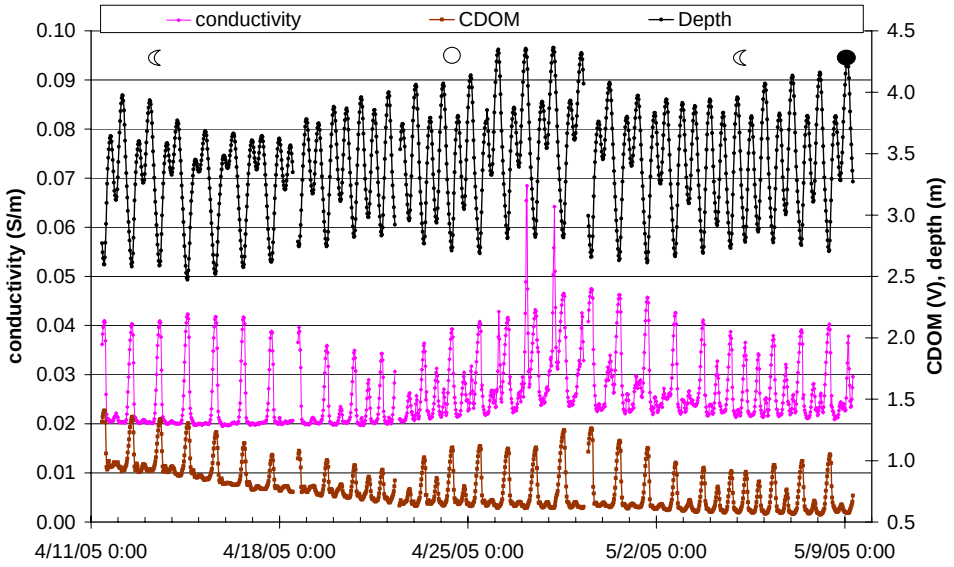

Figure 3. Time series of *in situ* data collected in the main channel (B2) of Brown's Island during the spring deployment 2005.

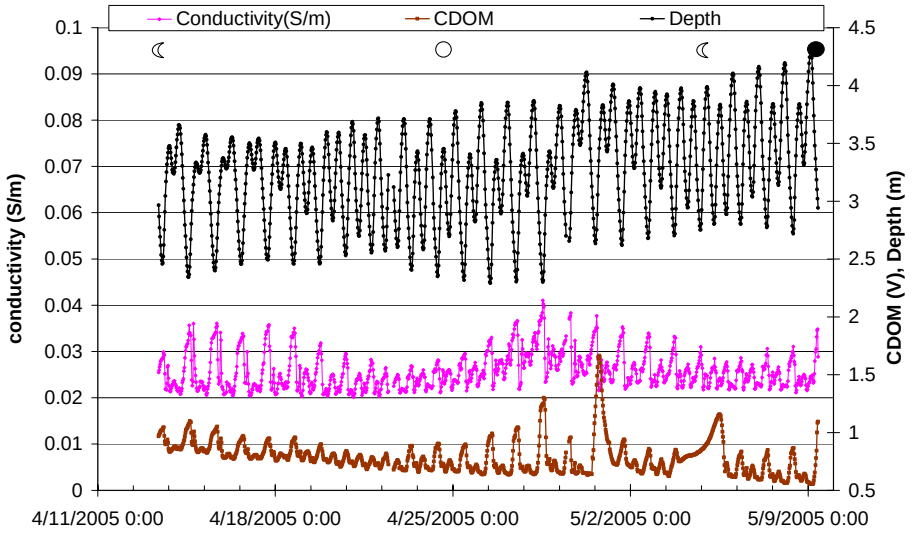

Figure 4. Time series of *in situ* data collected in the side channel (B4) of Brown's Island during the spring deployment 2005.

2. A strong, single variable correlation between instrumentation data and MeHg (filtered) concentrations has been observed. CDOM, a proxy for DOC (r^2=0.98), correlates strongly with the filtered fraction of MeHg during the spring deployment at Browns Island (Figure 5, r^2=0.94). This strong correlation should allow us to accurately estimate the flux of MeHg using near real time data. The generated MeHg concentrations in real-time are illustrated in Figure 6. We are currently working on merging these data with flow data and using the merged file to calculate real-time fluxes and error analysis of those fluxes at both sampling locations.

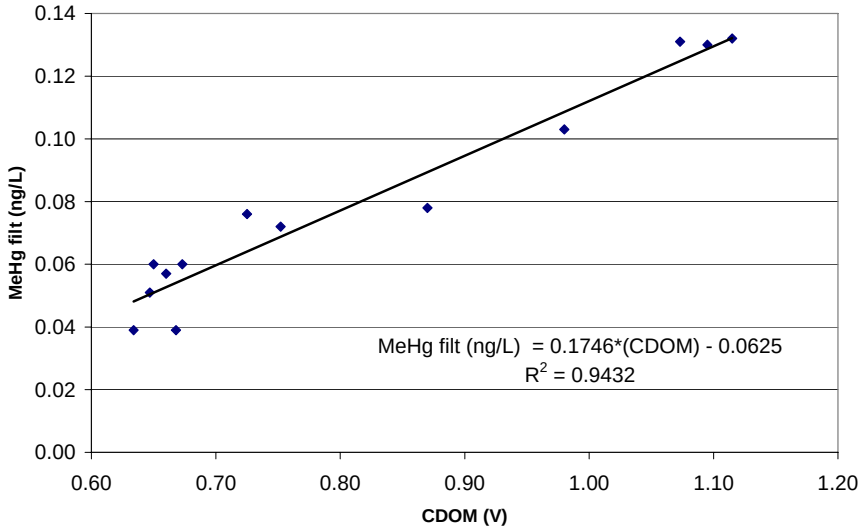

Figure 5. The correlation between CDOM and MeHg (filtered) during the Brown's Island spring deployment 2005.

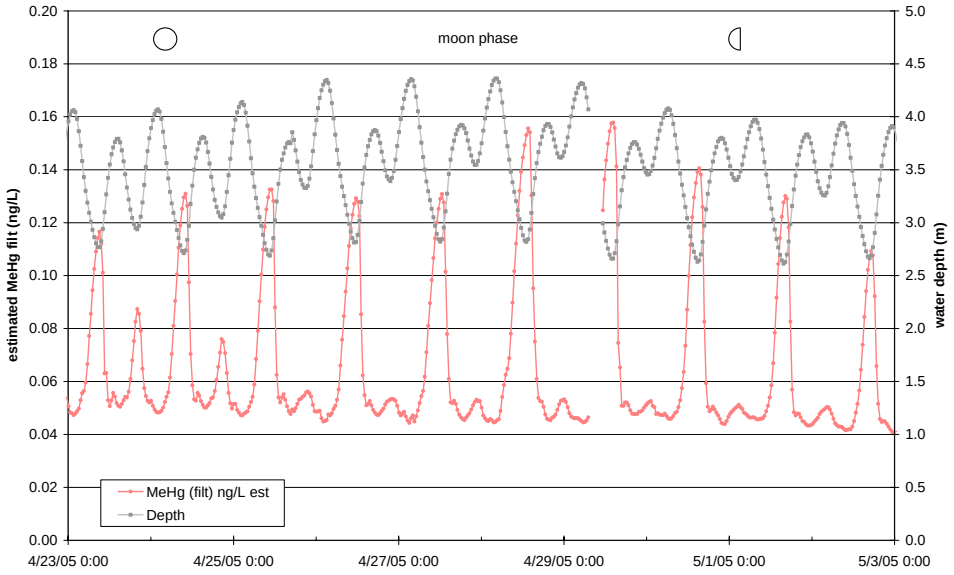

Figure 6. An example of MeHg time series data generated from *in situ* data and correlative calculation for a period in the deployment that has a stable CDOM baseline similar to the sampling period. The gap in data is due to instrument servicing.

3. A potential single variable correlation is present between instrumentation data and THg (unfiltered) and THg (particulate). However, more data are needed to validate the correlation (Figure 7). Real time data is not yet available for a time-series chart of THg. When real-time data are merged, they will be merged with flow data to calculate THg fluxes at both locations.

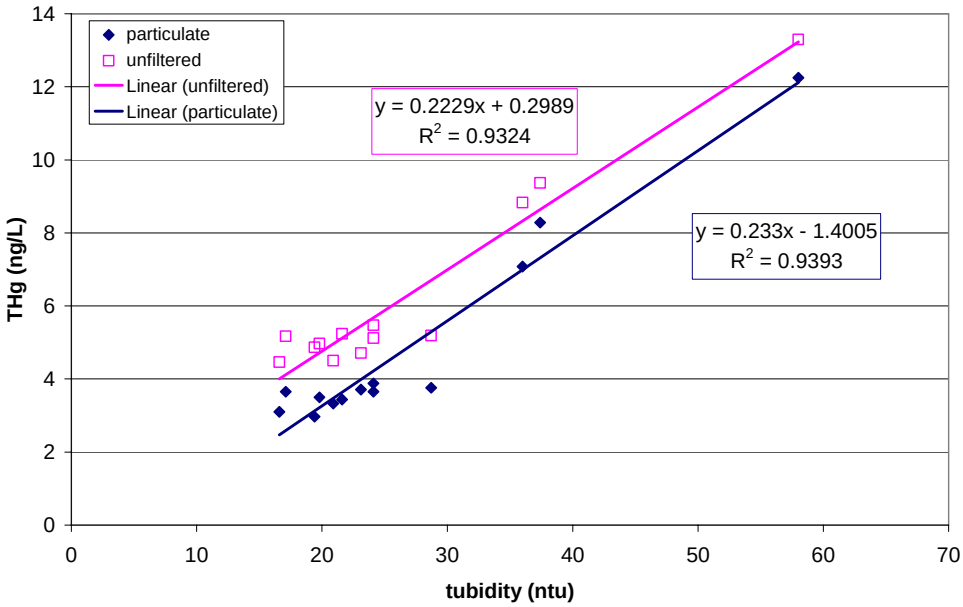

Figure 7. Correlation between total mercury (unfiltered and particulate) and turbidity measured *in situ* at Brown's Island during the spring deployment 2005.

4. Ratios of methylmercury to total mercury in filtered water are higher in water draining the island (8%) than in the surrounding ambient river

waters (4%). This result confirms that Browns Island is a site of methylation and a potential contributor to bioaccumulation rates in the Delta.

POTENTIAL IMPLICATIONS OF FINDINGS TO DATE

As work continues and uncertainties addressed, conclusions and implications will be offered regarding the study's hypotheses.

PRODUCTS TO DATE

Papers

Waples, J.S., Nagy, K.L., Aiken, G.R., and Ryan, J.N., 2005, Dissolution of cinnabar (HgS) in the presence of natural organic matter, Geochimica et Cosmochimica Acta, v. 69, pp. 1575-1588.

Gasper, J.D., Aiken, G.R., Ryan, J.N., submitted, A Critical Review of Methods Used for the Measurement of Mercury (Hg^{2+})-Dissolved Organic Matter Stability Constants, J of Applied Geochemistry, submitted 11/05

Abstracts/Presentations

Aiken, G., 2004, Carbon, Sulfur and Mercury - A Biogeochemical Axis of Evil, Keynote Address, 2004 CALFED Science Conference, October 4-6, 2004

Aiken, G., 2004, Mercury and Dissolved Organic Matter in the Florida Everglades, National Conference on Ecosystem Restoration, Orlando, FL, Dec 2004.

Aiken, G.R. and Ryan, J.N., 2005, Interactions of mercury with dissolved organic matter in the Florida, Everglades: Evidence for stabilization of colloidal mercuric sulfide, Humic Science and Technology VIII Conference, March 16-18, 2005, Boston, MA.

Nagy, K.L., Waples, J.S., Aiken, G.R., and Ryan, J.N., 2005, Dissolution of cinnabar in the presence of dissolved organic matter, 15th Annual V.M. Goldschmidt Conference, May 20-25, 2005, Moscow, Idaho

Aiken, G.R., Ryan, J.N., and Nagy, K.L., 2005, Interactions between dissolved organic matter and mercury in aquatic environments, 15th Annual V.M. Goldschmidt Conference, May 20-25, 2005, Moscow, Idaho