

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

Project Highlight Report

by

**Mark Stephenson
Dr. Chris Foe
Dr. Gary A. Gill
Dr. Kenneth H. Coale**

November 7, 2005

Submitted to:

**Dr. Carol Kelly
Chair of the Peer Review Panel**

and

**Donna Podger
CALIFORNIA BAY DELTA AUTHORITY**

Introduction:

Background. There is widespread mercury contamination in fish, sediment and water in the Central Valley and Bay-Delta Estuary. This mercury poses a human health risk principally through the consumption of mercury-contaminated fish. Health advisories and interim health advisories have been posted in the Bay-Delta Estuary recommending no consumption of large striped bass and limited consumption of other sport fish. Elevated concentrations of mercury in fish tissue may also represent a hazard to piscivorous wildlife. Mercury contamination in aquatic organisms results from the conversion of inorganic mercury (Hg) to monomethyl mercury (MMHg), principally by sulfate-reducing bacteria in surficial sediments. Statistically significant positive correlations have been observed in Cache and Guadalupe Creeks and the Sacramento-San Joaquin Bay-Delta Estuary between annual average unfiltered MMHg concentrations in water and in fish caught in fall. The relationship suggests that aqueous MMHg concentrations are an important factor controlling MMHg bioaccumulation in aquatic biota. Therefore, an understanding of the sources and sinks of aqueous Hg and MMHg is essential both for the development of control programs to reduce fish tissue levels and also to ensure that CALFED wetland restoration efforts do not exacerbate an already serious human and wildlife health problem.

Project Description, Investigative Approach, and Objectives. The primary goal of this project is to provide an integrated research project on sources and loads of mercury in the Bay Delta watershed, and the transport, cycling and transformation that occur to Hg and MMHg within the watershed. The relative significance of all Hg and MMHg sources, sinks and cycling processes will be evaluated and constrained using a mass balance geochemical cycling framework, which is based on our conceptual understand of Hg transport and cycling behavior in the Delta and its tributaries obtained in previous CALFED Mercury studies. This research program seeks to expand upon previous findings to:

1. Fill in data gaps in our current conceptual understanding of Hg and MMHg sources, sinks, and cycling in the Bay-Delta and its watershed.
2. Verify and quantify seasonal variations of MMHg in sediments and in the water column with respect to habitat type.
3. Accurately characterize the spatial distribution of total Hg and MMHg in the Delta;
4. Estimate the loadings of MMHg from wetlands and evaluate their importance relative to other sources.
5. Provide a foundation and framework for long term monitoring of Hg contamination issues in the Delta.

Working hypotheses have been developed and are given within the context of each task listed below in the highlights and results section of this Report.

Project Timetable and Progress. All work is on schedule with a few exceptions resulting from the delays inherent in the contract process. A timetable showing starting and target completion dates for the sampling program broken into each of the subtasks is given in Table 1. Tasks 1 target completion date is May 2007 (not shown in table).

The sampling period has been hydrologically similar to that monitored in the previous CALFED Mercury Study. Loads of total and MMHg entering the delta appear similar to measurements made in the earlier CALFED Mercury study. The mass loading continues to demonstrate a loss of MMHg as water travels across the Estuary. Much of the loading information collected to date has been used in the preparation of a Total Maximum Daily Load (TMDL) mercury report to the U.S. EPA. The draft report is available at <http://www.waterboards.ca.gov/centralvalley/programs/tmdl/delta/hg.html>. A poster will be prepared for the CBDA mercury workshop summarizing the mass balance of total mercury entering and leaving the Delta.

TASK 2B. Characterize tributary and regional input sources of MMHg and Hg in the Sacramento and San Joaquin Basins. Monthly river flow and mercury concentration data is being collected (initiated April, 2003¹) at key locations (27 gauged sites) down the Sacramento and San Joaquin Rivers and from all the major tributary inputs. The primary goal of the river monitoring will be to calculate mass balance estimates for Hg and MMHg for each river section. This information will be used to determine river reaches responsible for the major sources and sinks of mercury.

These results are the first comprehensive concentration and loading information for both the Sacramento and San Joaquin watersheds. An in depth description of MMHg patterns in the Sacramento and San Joaquin Rivers is being presented in poster format for the CBDA workshop.

The principal finding for the San Joaquin Basin is that Mud Slough contributes about 50% of the MMHg at Vernalis (legal boundary of the Delta) but only 10% of the water volume during the non-irrigation season (September to March). In contrast, the three east-side rivers—Merced, Tuolumne, and Stanislaus—discharge 60% of the water but only 38% of the MMHg. It is not possible to accurately estimate the contribution of Mud Slough to River MMHg concentrations during the irrigation season as about half the river volume is removed by multiple agricultural diversions located between Mud Slough and Vernalis and varying portions of the tail water returned after irrigation. Nonetheless, Mud Slough MMHg concentrations and loads are high during the irrigation season suggesting that the Slough continues to contribute a disproportionate part of the River load. Mean \pm 95% confidence limits of the annual MMHg concentration at four sites located in the 38 miles of River between Mud Slough and Vernalis are 0.25 ± 0.03 ng/l (N=59). The only exception was during June of 2005 when Friant Dam at the headwaters of the San Joaquin began spilling. Flow in the lower River doubled and methylmercury concentrations almost tripled (0.46 to 0.7-ng/l). The source of the MMHg is not known although a survey suggested it did not originate from Friant Dam. Follow up studies to determine the source(s) of the MMHg will be conducted should spilling resume. The Friant results are important as there is a proposal to increase Dam releases to insure that there is water in the upper River at its confluence with the lower San Joaquin. The added flow may significantly increase MMHg concentrations in the lower River.

The Sacramento watershed is the main source of water and MMHg to the Delta. Much of the precipitation in the Basin is captured in a series of large reservoirs in the foothills and released

¹ The first 11 months of data were collected with Regional Board TMDL funds and the remainder with CALFED money. MMHg loads have been calculated for the first 16-months of data (Mar 03 through Mar 05).

throughout the year to downstream water users. The four largest reservoirs—Shasta, Oroville, Englebright and Folsom discharged 75% of the water but only 25% of the MMHg load at Freeport (legal boundary of the Delta). This is because discharge from these reservoirs has a low MMHg concentration. For example, the mean and 95% confidence limits of MMHg concentrations from Shasta at Keswick is 0.03 ± 0.01 -ng/l (n=18). Average MMHg concentrations increase 2.8-fold in the 150-miles between Keswick and Colusa. The cause of the increase is unclear although some of the MMHg may originate from the discharge of 10 creeks located in this river reach. The mean and 95% confidence limit of MMHg concentrations at Freeport are 0.11 ± 0.02 -ng/l (N=18). Source(s) of the Freeport MMHg are the Sacramento River at Colusa (57%), Feather River (29%), American River (12%) and Colusa Basin Drain (10%). About 4% of the MMHg at Freeport is unaccounted for and may originate from Sacramento Slough and other small agricultural discharges.

TASK 2C. Conduct sub-watershed studies of tributaries or source regions to refine sources of MMHg and Hg within watershed. Four detailed follow-up studies to Task 2B have been undertaken on tributary inputs along key river reaches to ascertain sub watersheds responsible for the majority of the mercury load. Once these...have been identified, studies will follow in each tributary to identify actual sources.

First, MMHg loads from Mud Slough account for about 50% of the load at Vernalis. The source of the MMHg is not known but the Slough drains about 33,000 acres of seasonal and permanently flooded wetlands. Salt Slough, the next major drainage south of Mud Slough, also has a large wetland acreage but discharges lower MMHg concentrations. The U.S. Fish and Wildlife Service is the owner-operator of some of the largest wetlands in both basins. A cooperative study with the Service is underway to determine: (1) the geographic source of most of the MMHg load in Mud and Salt Sloughs, (2) ascertain net MMHg production rates (mg/acre/mo) of representative seasonal and permanent wetlands in both watersheds and (3) determine why MMHg concentrations are lower in Salt than Mud Sloughs.

The second special study is being conducted in Cache Creek. The Creek was a major focus of the first CALFED grant. An important finding was that MMHg concentrations are elevated in Bear Creek above the confluence with Sulfur Ck. The finding is important as the site is above the discharge of all known mercury mines. An additional year of monitoring has now been completed. The primary source of MMHg above Sulfur in Bear Creek was determined to be from the ephemeral Rathburn Creek. The Creek was found to contain waste from the Rathburn mercury mine. The Regional Board has issued the Bureau of Land Management a Cleanup and Abatement order to remove the waste. Groundwater was also found to be surfacing in Bear at the confluence with Rathburn Creek. The groundwater has elevated electrical conductivity (1-2 0/00 salinity), dissolved THg (up to 800 ng/l), and unfiltered MMHg (up to 6-ng/l). The groundwater is thought to be modified connate water surfacing because of tectonic compression of the Coast Range. The finding may be important as it was previously hypothesized that no new mercury deposits were forming this far north. Several water bodies exist in the Coast Range north of here with fish advisories but no known source of mercury. We hypothesize that groundwater may be the source of their mercury and will evaluate the hypothesis by sampling seeps and springs discharging to these water bodies next spring.

The third special study is being conducted in the Cache Creek Settling Basin. Cache Creek transports a lot of sediment and the U.S. Army Corps of Engineers constructed the Basin to trap sediment and insure no reduction in the flood carrying capacity of the Yolo Bypass. Cache Creek also exports about half of all THg entering the Delta. About half the Cache Creek THg is trapped with sediment in the Settling Basin and the remainder exported to the Yolo Bypass. A feasibility study is underway to evaluate increasing the settling capacity of the Basin. However, no information exists on MMHg production and fate in the Basin. The Settling Basin has a low flow channel rated for up to 400-cfs. Water backs up in the Basin at higher flows and discharges across the high flow weir. Paired sampling at the entrance and exit of the Settling Basin demonstrate that average MMHg concentrations increase 2.3 fold during low flow. The increase is significant ($P < 0.01$, two tailed paired T-Test). No relationship exists between production and low flow rates ($P > 0.1$, ANOVA). In contrast, MMHg production is inversely proportional to flow when the Basin is spilling across the weir. The compensation point is at about 4,000-cfs with production being positive at lower flows and negative at higher ones. The information may prove useful in redesigning the basin.

The final special study is being conducted in the Yolo Bypass. The Bypass is a 59,000-acre structure to carry Sacramento River flood flows around the City of Sacramento for discharge them into the Delta. Cache and Putah Creeks, two watersheds with mercury mines, also discharge into the Bypass. Land use in the top of the Bypass is a combination of agriculture and wetlands. About 4,500 acres of tidally flooded acreage is located at the bottom of the Bypass. The flooded islands were purchased by the State of California for passive restoration to marshland. The first CALFED study measured the highest annual average MMHg concentrations in the Delta in water leaving the Yolo Bypass at Prospect Slough (0.24-ng/l). The Bypass was also found to be the single largest source of MMHg to the Delta when flooded. However, no information exists on where the MMHg is produced or what its fate is upon passage through the flooded lower Bypass. The MMHg load of all water entering and leaving the Bypass was estimated on 6 occasions last winter and spring. Twenty-five to 66% of the MMHg leaving the Bypass is estimated to have been produced in it. The flooded tracts in the lower Bypass was found to be a net sink for MMHg. Unfortunately Sacramento River water only spilled into the Bypass for 3 days last winter and no mass balance was possible. However, the highest MMHg concentrations ever observed in the lower Bypass (up to 1.6-ng/l) occurred as this water exited. Additional studies will be conducted this winter if the Sacramento River spills into the Bypass.

Task 3. Atmospheric Mercury Deposition Studies

Currently, atmospheric mercury deposition is thought to be a minor but significant source of mercury to the Bay-Delta. The following studies will allow this source to be quantified and compared to other sources.

Rainfall Collections. Three atmospheric deposition monitoring stations were established in the Bay-Delta watershed to model the wet deposition flux of total Hg into the Bay-Delta. Sites were chosen to characterize background input off the Pacific ocean at a coastal site (Pt. Reyes), input into the central Delta region (Twitchell Is. and Woodland), and the Sierras (Big Bend). Sampling at all sites is being conducted on a bi-weekly basis, but only during the wet season

(October through April). The program is intended to be operated for approximately a 28 month period. Sampling is being conducted using an Aerochemetrics wet-dry deposition collector, modified for monitoring Hg. A summary of the results obtained to date are given in Table 2. To date, we obtained a total of 16 rainfall collections with sufficient volume (>25 mL's) to accurately quantify mercury concentrations. We had a significant number of sample deployments in which no rain was collected.

Table 2. Calfed Mercury Atmospheric Deposition (4/2005 to 3/2005).

Site	[Hg], ng/L ^a				
	Range	Average	Std	RSD	N
Pt. Reyes	1.1 - 8.0	4.7	2.6	55%	7
Twitchell Is.	1.0 - 4.1	2.7	1.6	58%	5
Woodland, CA	1.3 - 2.1	1.67	0.67	40%	3
Big Bend		10.2	1.76	17%	1
Field Blank	0 - 0.18	0.07	0.06	94%	15
Deploy Blank ^b	0 - 0.22	0.06	0.07	117%	17

^a Data not corrected for field blank

^b Deploy Blank = a sample collection in which no rain occurred.

Atmospheric Mercury Collections and Speciation. Modelling of the atmospheric dry deposition input flux to the Bay-Delta is being assessed based on measurements of total gaseous mercury (TGM), particulate Hg (Hg_p) and reactive gaseous mercury (RGM) at selected sites in the study area using Tekran instrumentation. The sampler has been operated for various lengths of time at Pt. Reyes, Woodland (Near Davis), Moss Landing Marine Laboratories, and at two field sites near Rio Vista California. Shown in Table 3 is a comparison of atmospheric mercury speciation information at Moss Landing Marine Laboratories (MLML) and at Woodland (near Davis), CA. Note that PGM and RGM concentrations found at Davis were much higher than those monitored at Moss Landing.

Table 3. A comparison of atmospheric mercury species measurements at MLML with Woodland, CA.

	Moss Landing, CA (17 Dec. 2004 – 14 Jun. 2005)			Woodland, CA (9 Jul. 2005 – 28 Jul. 2005)		
	EGM (ng/m ³)	PGM (pg/m ³)	RGM (pg/m ³)	EGM (ng/m ³)	PGM (pg/m ³)	RGM (pg/m ³)
<i>n</i>	12152	789	1164	2109	115	115
Average	1.75	1.44	0.83	1.84	7.12	23.31
St Dev	0.71	2.65	1.46	0.30	4.75	36.70
Max	22.04	35.61	22.07	3.45	37.13	189.68
Min	1.03	0.00	0.00	1.10	1.09	0.00
Median	1.63	0.53	0.41	1.81	6.22	4.54

Task 4. Delta Wide Monitoring and Characterization Program

The following studies were conducted to look at mercury behavior in Bay-Delta sediments. It has been previously observed that MMHg sediment concentrations vary seasonally and concentrations are variable relative to habitat type. Additionally, MMHg flux in/out of sediments has been shown to be an important vector during low flow periods and it is important to better constrain this component in the mercury budget of the Bay-Delta.

Subtask 4.1 Determine Hg and MMHg in surface sediments of different Delta ecosystems (i.e. habitat-based). In order to determine how MMHg distribution in sediments relates to habitat type, twenty-six locations within the Bay-Delta were classified to fall into one of six identified landscape features in one of seven distinct geographic areas (Table 4). Not all landscape features were found in all geographic areas. Replicate surficial sediment samples (top 0-1 cm) were collected from each of these locations to identify locations and habitat types with elevated MMHg. A comparison of sediment MMHg concentrations for both geographic areas and landscape features identifies locations within the Bay-Delta which are “hot spots” for mercury methylation. The upper wetlands and salt ponds of San Pablo Bay had a greater efficiency of converting inorganic mercury to methyl mercury than the open water sites. The same is true for the marsh sites in Suisun Bay, West and South Delta. The Northwest Delta (Prospect Slough area) showed the least efficiency at inorganic to organic mercury conversion with all landscape features sampled less than 1% methyl mercury (data not shown).

In previous studies, increases in MMHg sediment concentrations occurred during spring and summer, and additional years of seasonal sampling allow confirmation of these trends. Surficial MMHg sediment concentrations varied greatly between the four sites sampled (Figure 1). A map of the sampling sites is shown in Figure 2 below. Browns Island had consistently higher MMHg concentrations than Franks Tract, Sycamore Slough, and Snodgrass Slough. A clear seasonality to MMHg sediment concentrations is visible in the data from Browns Island, Sycamore Slough, and Snodgrass Slough. MMHg concentrations were highest April, May and June at Browns Island and Snodgrass Slough while at Sycamore Slough it was slightly later (June, July and August). This is an important finding in that surficial sediment MMHg concentrations may influence dissolved MMHg concentrations and MMHg flux from the sediment in the Delta and the higher sediment concentrations occur during the time riverine inputs of MMHg are lowest.

Task 4.2 Benthic Flux Chamber Studies. Sediment-water exchange studies are being conducted using a benthic flux chamber and a newly developed approach using time series sampling to monitor the “whole-wetland”. The whole-wetland approach uses a time-series water sampler developed for this project and involves water sampling at the inlet of a marsh over a tidal cycle. The method involves monitoring the concentration of mercury and other biogeochemical parameters as water flows on and off the marsh during a tidal cycle. In addition, it is necessary to determine water flow rates and volume (with acoustic doppler instruments) to be able to determine the mass of mercury entering and leaving the marsh on each tidal cycle. We are sampling at two sites Mandeville Cut and Little Break (Figure 2 below). To date, we have conducted three 24-hour integrated sampling events and flux chamber deployments. Evidence of the effectiveness of the whole-wetland approach is shown in Figure 3. Note that during the low tide period MMHg levels were elevated as they drained water off the marsh. This information, along with exchange volume will be used to estimate export of MMHg from the wetland.

Table 4. Key to Spatial Study sampling plan. Dark grey is locations greater than ~5 ng/g MMHg, light grey equal ~2.5 ng/g, and no shade is less than 1 ng/g.

Geographic Area	Code	Landscape Features					
		Open Water (fine)	Open Water (sand)	Mudflat	Marsh	Seasonal Wetland	Salt Pond
San Pablo Bay	SPB	X	X	X	X	X	X
Suisun Bay	SB	X	X	X	X		
West Delta	WD	X	X	X	X		
Central Delta	CD	X	X		X		
Northwest Delta	NWD	X	X		X		
Cosumnes River	CR	X	X		X		
South Delta	SD	X	X		X		

Figure 1. Seasonal changes in methyl mercury sediment concentrations at Browns Island, Franks Tract, Sycamore Slough, and Snodgrass Slough.

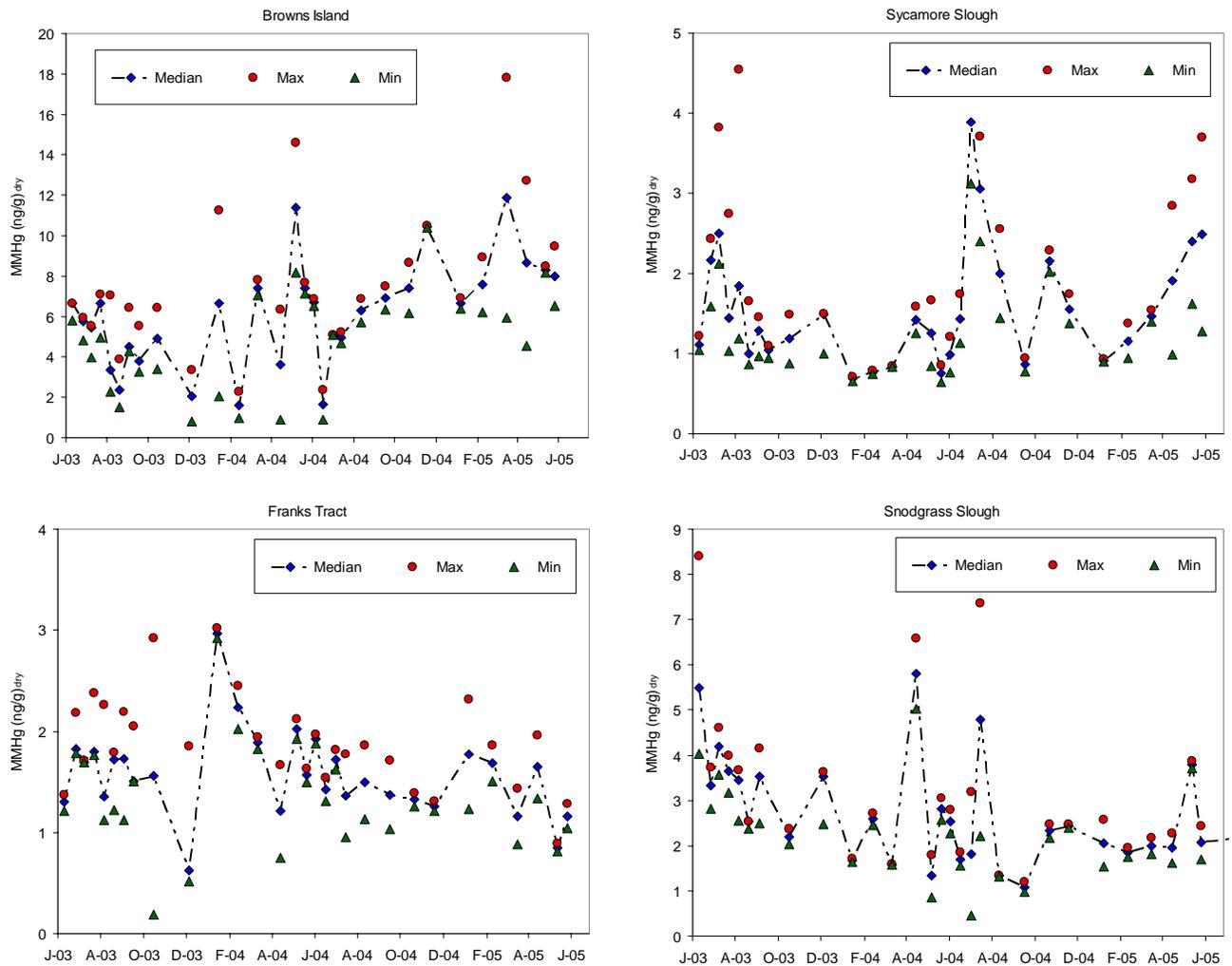


Figure 2. Map of Sampling sites for Task 4.1 and 4.2.

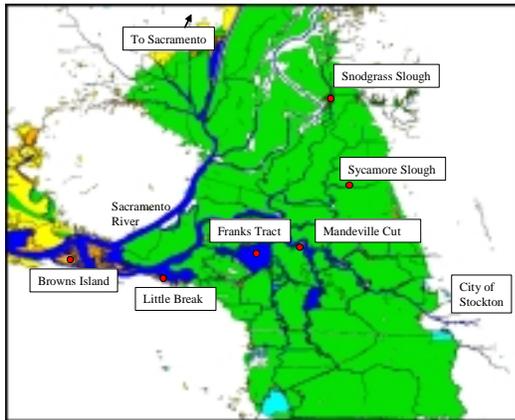
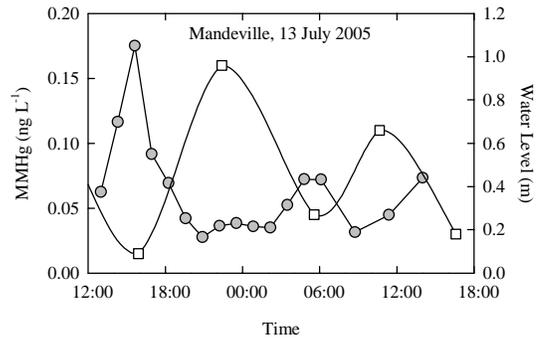


Figure 3. Time course measurements of MMHg at Mandeville Cut relative to tidal height.

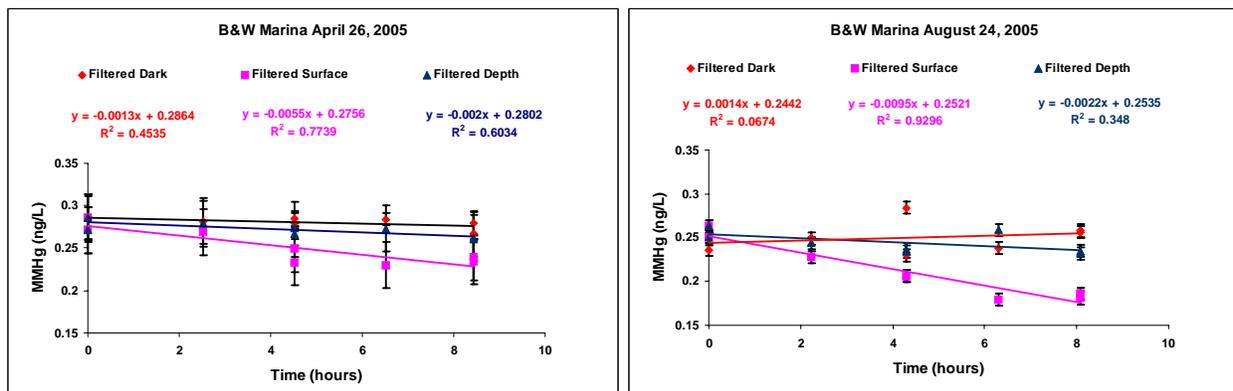


Task 5. Process Oriented Studies

A series of process-oriented studies are included in this research project to identify links between Hg and MMHg production and destruction and to derive environmental rate dependencies with respect to major biogeochemical processes and constituent concentrations.

Task 5.1 Monomethyl Mercury Photo Demethylation Studies. We have been conducting experiments to determine the relative significance of photo de-methylation as a loss term from MMHg in the Delta. This effort was spearheaded by Ms. Amy Byington of Moss Landing Marine Laboratories. To date, four experiments have been conducted using two different types of experiments. One type of experiment consisted of two point determinations, an initial and final value after a minimum of 6 hours of light exposure. These experiments were conducted using water obtained from several locations. The second type of experiment consisted of multiple time point determinations during the experiment period. Initial results suggest that photo-period and light intensity (cloud cover and water depth) are the most significant factors influencing photo demethylation (Figure 4). Using these preliminary results, photo-demethylation is a major loss term accounting for the destruction of 30% of the dissolved methyl mercury per day at the surface (upper 0.5 m). When averaged over a mean depth of the Delta (4 meters) this represents an integrated water column loss of about 4% per day. Extrapolated over the area of the delta (61,000 acres) this suggests a loss of 4 grams of MMHg per day, or about 40% of the "unidentified" loss term previously described by Foe (10 grams per day).

Figure 4. Photo-demethylation Experiments (April and August 2005).



Task 5.2 Transect Studies. Work conducted on the previous CALFED Mercury Project suggests that there is an internal sink for MMHg in the Delta (see Mass balance model - Figure 5). The objective of this task is to document the existence of the sink and relate it to hydrologic, chemical, and biological parameters. A 12 to 18 percent decrease in MMHg concentration was observed as water moved 2.4 miles downstream the San Joaquin River into the Stockton Deep Water Ship Channel. A concurrent loss of particles occurred indicating a possible removal mechanism. Particle loss as well as previously mentioned photo demethylation may account for much of the loss of MMHg as water moves across the estuary. Studies are continuing to quantify the loss due to particle settling.

Task 5.3a Methyl Mercury Loading Studies in Delta Wetlands. The objective of this task is to determine whether wetlands import or export methyl mercury during tidal exchanges. We are in the process of conducting studies at Suisun Marsh, Snodgrass Slough, Hog Slough, Sycamore Slough, Brown’s Island, and seasonal and permanent wetlands on Grizzly Island. Preliminary findings from one study at Suisun Marsh during the summer of 2004ⁱⁱ indicate MMHg was exported at a natural marsh (First Mallard Branch) while MMHg was imported at the mouth of Suisun Slough (Data not shown). We hypothesize the import at the mouth of Suisun Slough was caused by the import of high levels of MMHg on suspended sediments from Grizzly Bay during flood tide. We also hypothesize the export at First Mallard branch was caused by the export of high levels of methyl mercury in dissolved form from wetland areas that drain pore water during low tides into the tidal channels. This study illustrates the complexity of determining whether wetlands import or export methyl mercury.

Task 5.3b Sediment Biogeochemistry Studies in Delta Wetlands. This task is designed to investigate the relationship between major biogeochemical processes in sediments and the production of MMHg with a goal of developing conceptual and predictive models of methylmercury fluxes from open water and wetlands areas. The field work for this task involves measurements of mercury and MMHg in interstitial pore waters using the whole-core squeezing technique and also high resolution near-surface profiles of oxygen, sulfide, and other parameters in interstitial pore waters using a microelectrode profiler system (Unisense).

Task 5.4 Air-Water Exchange Studies of Dissolved Gaseous Mercury. The air-water exchange of gaseous Hg species represents another data gap in our overall understanding of the cycling of Hg in the Delta. We have conducted measurements of DGM at sites where other tasks are being conducted with a goal of providing quantitative information on the air-water transfer of volatile Hg species for mass balance modeling purposes. A summary of representative results for Mandeville Cut is shown in Table 5. Preliminary results suggest an efflux, primarily in summer months. However, the relative significance of this flux is uncertain due to low saturation values.

Table 5. DGM Measurements at Mandeville Cut

Date	Collection Time	DGM pg/L	% Saturation
7/19/2004	12:00	8.6	196
12/13/2004	13:35	8.5	150
12/14/2004	15:00	3.6	63
3/15/2005	12:30	2.2	39
3/16/2005	16:30	6.3	112
7/14/2005	18:30	4.5	103
Average		5.6	110.5
Std		2.6	57.1

ⁱⁱ This study was conducted with hydrological support from Chris Enright (DWR) and Jon Burau (USGS).

Mass Balance Geochemical Cycling Framework:

The relative significance of all MMHg (Figure 5) and Hg (Figure 6) sources, sinks and cycling processes may be evaluated and constrained using a mass balance geochemical cycling framework. This model is based on our current conceptual understanding of mercury transport and cycling behavior in the Delta and its tributaries. We continue to constrain previous estimates of mercury movement through the Bay-Delta system and add new vectors as results of ongoing studies are compiled and analyzed.

Figure 5. Monomethyl mercury fluxes in the Bay-Delta Estuary. The flux associated with the unidentified loss processes was determined by mass balance.

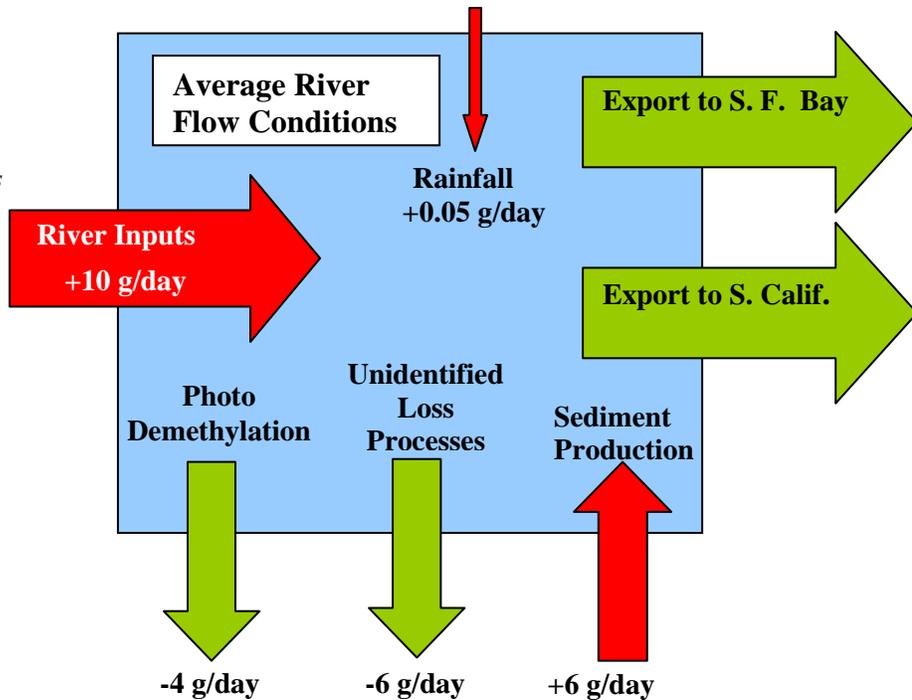


Figure 6. Total Hg fluxes in the Bay-Delta Estuary. The flux associated with the loss is assumed to be sediment erosion, but has not been identified.

