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

Calfed Mercury Project Annual Report

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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 fish eating 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

The work proposed for this project is based upon findings obtained in our previous work funded by CALFED. Our prior work to characterize the major pools and fluxes of Hg and MMHg in the Delta has led us to propose the following working hypotheses as guidelines for our current research.

1. *River borne MMHg is a major source of MMHg introduced to the Delta, especially under high river flow conditions*.
2. *Atmospheric Hg deposition is a minor, but significant source of total Hg loading to the Delta*.
3. *Methylmercury concentrations in Delta sediments increase during late spring through early summer as a result of increased Hg methylation in the sediment.*
4. *Mercury and MMHg concentrations in Delta sediments are spatially variable relative to habitat type and the distribution remains relatively constant year to year.*
5. *Within the Delta, wetland and marsh regions are major sites of MMHg production and enhanced sediment-water exchange flux*.
6. *MMHg is lost from the water column within the Delta ecosystem by an unknown removal mechanism as water flows from the Sacramento River to the Delta*.

Management Goals and Objectives addressed by this Project.

Develop an understanding of the transport, cycling, and fate of Hg and MMHg in the San Francisco Delta and tributary watersheds on both a temporal and spatial basis using a biogeochemical mass-balance framework as an integrating tool to assess sources, sinks and biogeochemical processes.

Project Timetable and Progress

All field work, except some follow up studies in task 2C, has been completed. An outline of the tasks conducted and a timeline of the field program is given in Table 1 below.

Table 1. Current project timetable showing project components, completed events (X's) and projected events (shaded squares).

Tasks	Sampling Program	2003								2004												2005												2006												2007												2008					
		J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J
Task 1 - Project Administration																																																															
	Quarterly Reports							X		X			X			X			X			X			X			X			X			X			X			X			X			X																	
	Annual Reports																					X																																										
	Quarterly Invoices							X		X			X			X			X			X			X			X			X			X			X			X			X																	
	Final Report																																																															
Task 2 - Mass Loading and Export																																																															
	A	Fixed Station Sampling													X			X	X	X	X	X	X	X	X	X			X	X	X	X	X	X	X	X	X	X	X	X																									
	B	Watershed Characterization													X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X																									
	C	Sub-watershed studies													X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X																									
Task 3 - Atmospheric Deposition												X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X																									
Task 4 - Delta Monitoring Program																																																													
	A	Surface Sediments					X					X			X					X						X					X																															
		Surface Sediments-4 sites	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X																													
	B	Benthic Flux Chamber													X					X			X			X			X					X																												
Task 5 - Process Oriented Studies																																																													
	A	Photo Demethylation													X					X				X					X					X			X			X																						
	B	Transect/Cross Channel Studies							X			X					X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X	X	X			X	X			X																	
	C1	Wetland Loading Studies		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X		X	X		X	X		X		X																
	C2	Sediment Biogeochemistry													X					X				X					X																																		
	D	Air-Water Studies													X					X				X					X																																	
Task 6 - GIS Integration																																																															

Mass Balance Geochemical Cycling Framework

The relative significance of all MMHg and Hg sources, sinks and cycling processes may be evaluated and constrained using a mass balance geochemical cycling framework. Given in Figure 1a and 2a below are our original mass balance assessments at the start of the project for MMHg and Total Hg for the San Francisco Bay Delta region under average river flow conditions.

Figure 1b and 2b is our revised conceptual model based on information obtained as part of this current work effort. The dominant MMHg sources to the Delta are riverine inputs and *in situ* production in marshes and farmed Delta Islands . The major sink for MMHg within the Delta occurs via photo-degredation. MMHg export from Delta Islands and uptake by aquatic biota may be quantitatively important processes and remain to be determined. For total Hg, rivers are a dominant source (1151 g/day) with sediment water exchange being the next biggest input (190 g/day). A major export for total Hg is estuarine transport (- 546 g/day). A significant amount of mercury is also removed by dredging (- 150 g/day). However, to balance the Total Hg budget, an additional sink of - 619 g/day is needed. We hypothesize that deposition of mercury enriched particles in Delta marshes and backwaters accounts for this additional sink.

Figure 1. Mass Balances Assessments for Monomethylmercury in the Bay-Delta Estuary. Original Assessment at Start of Project, 2004 (left panel); Current Assessment, April 2007 (right panel).

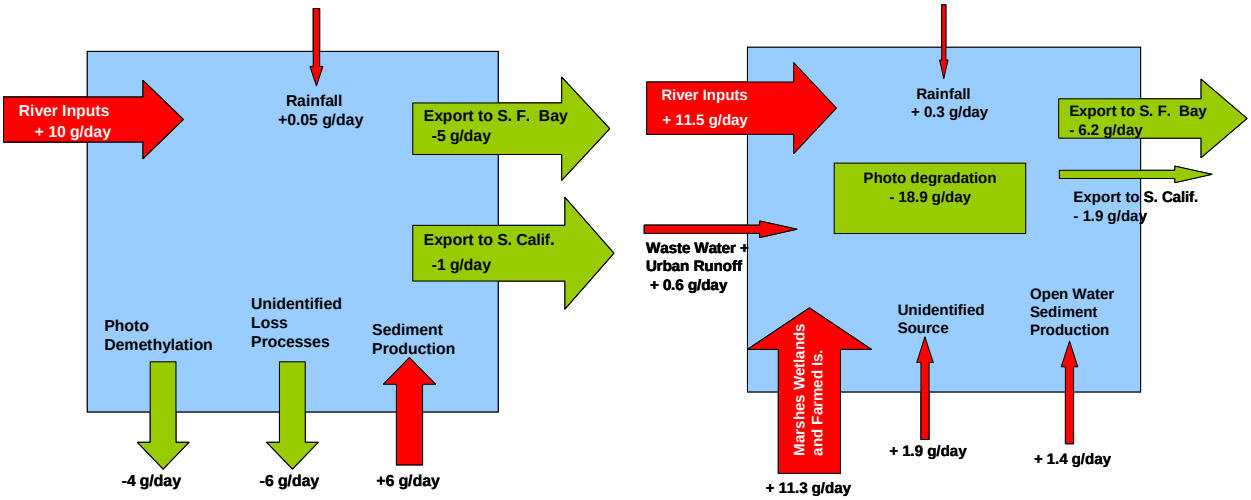
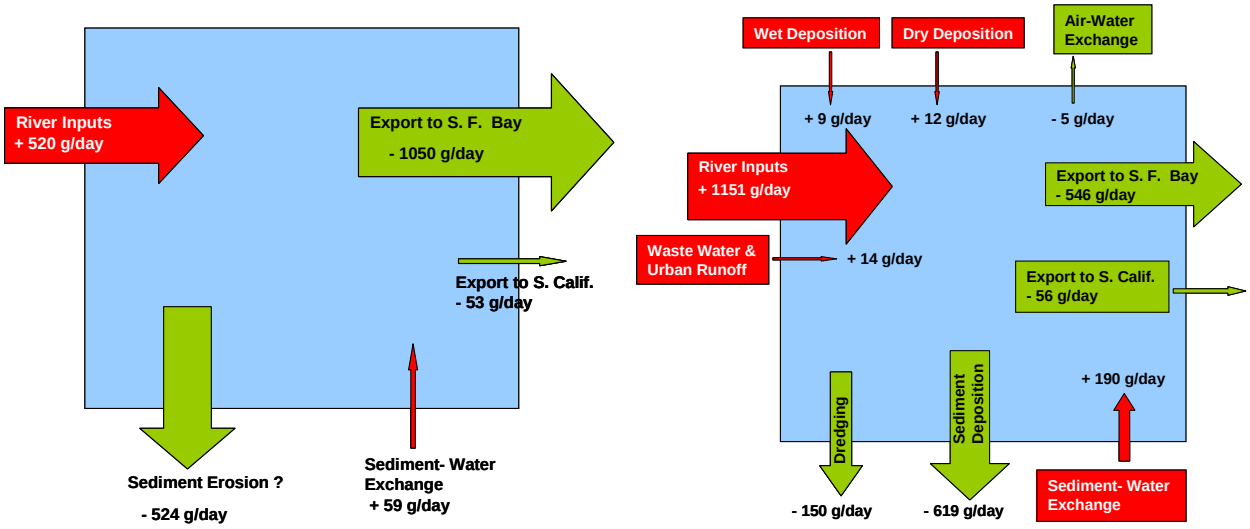


Figure 2. Mass Balances Assessments for Total Mercury in the Bay-Delta Estuary. Original Assessment at Start of Project, 2004 (left panel); Current Assessment, April 2007 (right panel).



Project Highlights and Results

A summary of major project highlights and results are presented in the following sections as evidence in support of (or rejection of) the working hypotheses described above. Additional details associated with this work are available in appendices and also from posters to be given at the review meeting. Additional new working hypotheses, generated as a result of this current work are also delineated at the end of the report.

1. River borne MMHg is a major source of MMHg introduced to the Delta, especially under high river flow conditions.

MMHg was monitored monthly in all major water input and export channels to the Delta to develop a mass balance for the freshwater side of the estuary (Task 2a). The data demonstrates that Rivers are a major source of MMHg to the Delta (Figure 1b). MMHg concentrations have now been measured on all major river inputs for 53 months. Water years 1999 and 2000 were classified as dry while the winter of 2005/2006 was very wet. Therefore, we believe we have characterized MMHg loads as a function of the major hydrologic variability in the system. Our revised best estimate of average river inputs is 11.5 g/day. The Sacramento River is the main source of water (80%) and MMHg (77%) for the estuary. A major change in the conceptual model is that local marshes in the Delta produce about as much MMHg as do the Rivers.

2. Atmospheric Hg deposition is a minor, but significant source of total Hg loading to the Delta.

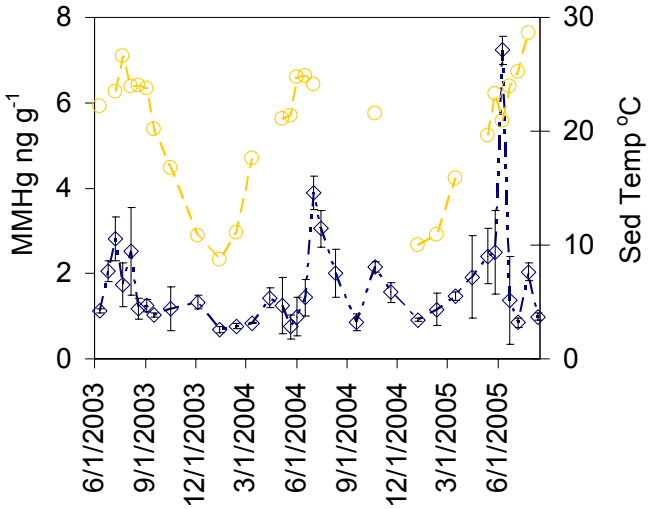
Sampling of atmospheric mercury species and wet deposition were conducted to assess the importance of the atmosphere as a source of Hg and MMHg to the Delta (Task 3). Wet deposition monitoring was conducted for 27 months at two sites in the central valley and one coastal location. Atmospheric mercury speciation monitoring was conducted at both and coastal and Delta locations. Direct atmospheric mercury deposition (wet + dry) to open water, mudflat, and marsh area habitats of the Bay-Delta is about 3.2 g/day. Hence, direct atmospheric deposition accounts for ~ 0.3 % of the total mercury input to open water areas of the Bay-Delta. If seasonal wetlands and farmed islands are included in the surface area receiving wet and dry deposition in the Delta, the input of atmospheric deposition (wet + dry) increases to 21 g/day (Figure 1). This is still a small input relative to riverine transport (1151 g/day) during normal river flow conditions, accounting for approximately 2 % of the total Hg input.

While the total Hg input from the atmosphere appears to be small, it is interesting to note that the daily mass balance budget of MMHg in the Bay-Delta is ~ 25 g/day (Figure 1b), which is roughly equivalent to the total atmospheric Hg deposition flux noted above for all habitat types in the Delta. Thus, if all the atmospherically derived mercury to all habitat types in the Delta were readily bioavailable and the deposition flux of total Hg was rapidly converted to MMHg, the majority of the MMHg budget of the Delta could be accounted for from rainfall related production alone.

3. *Methylmercury concentrations in Delta sediments increase during late spring through early summer as a result of increased Hg methylation in the sediment.*

Monthly measurements of MMHg in surficial sediments were conducted at 4 locations for a period of 27 months to assess temporal trends in MMHg production (Task 4). MMHg sediment concentrations increased from lows of around 1 ng g^{-1}, occurring mostly during winter periods, to highs of around 3-7 ng g^{-1} during mid to late summer periods (see Figure 3). Peak MMHg sediment concentrations occurred during peak sediment temperatures. Suspended particle MMHg concentration did not explain the seasonal increase observed in surficial sediments; providing further evidence that the MMHg production was *in situ*.

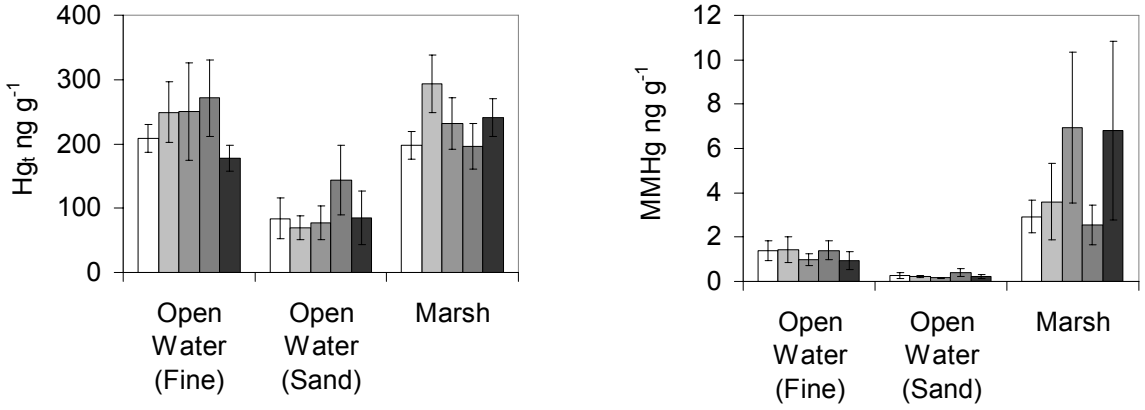
Figure 3 MMHg surficial sediment concentration (◊)(with standard error) and sediment temperature (○) measured at Sycamore Slough in the central Delta.



4. *Mercury and MMHg concentrations in Delta sediments are spatially variable relative to habitat type and the distribution remains relatively constant year to year.*

Total mercury concentrations in sediments remained relatively constant within a habitat types during this study, while MMHg concentrations varied more significantly with season, especially in marsh sediments (Figure 4). MMHg sediment concentration was higher in marsh habitat than open water habitat MMHg sediment concentration was higher in fine grain (<63 µm) dominated open water habitat than in sand (>63 µm) dominated open water habitat. Total Hg concentrations were also higher in marsh and fine grain (<63 µm) dominated open water habitat than in sand (>63 µm) dominated open water habitat. Similar seasonal pattern of MMHg sediment concentration was observed during this study.

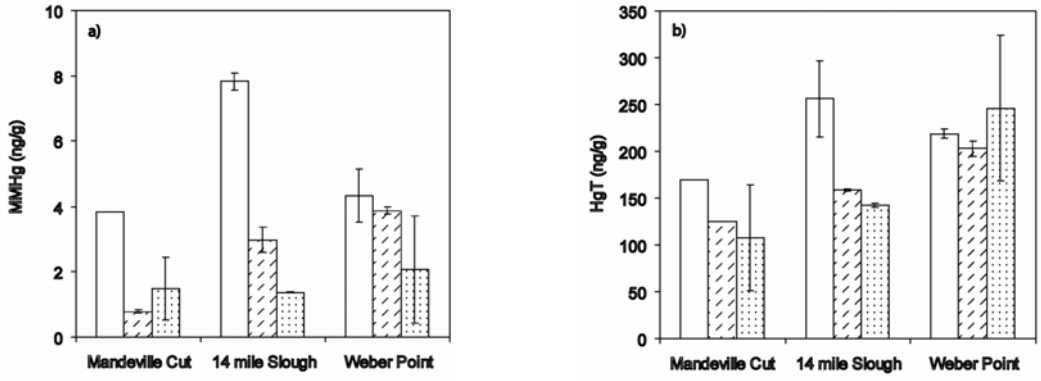
Figure 4. Average Total Hg and MMHg surficial sediment concentrations (with standard error) collected from three habitat types (Open Water Fine = sediment <63 µm, Open Water Sand = sediment >63 µm, and Marsh) across the Bay-Delta during five sampling events (left to right = Oct 03, April 04, July 04, Feb 05, Aug 05).



5. Within the Bay-Delta, wetland and marsh regions are major sites of MMHg production and enhanced sediment-water exchange flux.

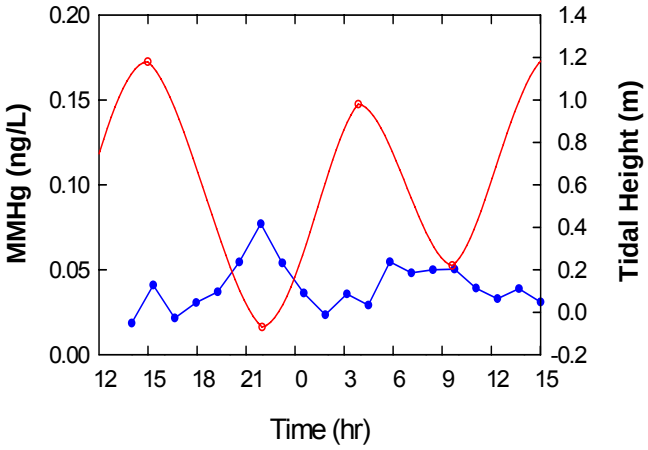
There are a number of lines of evidence in support of this hypothesis. The data given in Figure 4 above demonstrate that marshes have elevated concentrations of MMHg compared to open water areas. Moreover, the MMHg to total Hg ratio in marsh sediments is elevated, suggesting that marshes are sites of enhanced MMHg production. Illustrated in Figure 5 are measurements of total and MMHg in surficial sediments of three marshes (Heim et al., 2007). Note that the interior of the marshes have elevated levels of MMHg compared to the exterior of the marsh, implying a significant source. Within the Bay-Delta, Heim (2003) estimated that marsh habitat had the highest MMHg production rate (30 ng/m^2/day). Heim (2003) estimated that marshes and wetland areas in the Bay-Delta produce ~ 12.8 g/day of MMHg to the Bay-Delta estuary.

Figure 5. Monomethylmercury (Panel a) and total mercury (Panel b) concentrations in surficial sediments (reported as dry weight sediment concentrations) collected from three marsh locations. Interior marsh sites are represented by bars with no fill, sites mid way between the interior and edge of the marsh are shown as hatched bars, and dotted bars are from the outer edge of the marsh. Measurements are an average of field duplicates and error bars are the range of field duplicates.



Studies of the transport of MMHg from tidal wetlands using *in situ* time series water column collections (task 4.2) show changes in MMHg concentrations related to tidal flushing (Figure 6). We hypothesize that this relationship results when marsh sediments are exposed during low tide and interstitial pore water with its elevated MMHg concentrations drains out of marsh sediments. Based on the *in situ* time series measurements and estimates of water flow rates using acoustic Doppler techniques, we estimate that tidal flushing ranged from -18 to 70 ng/m^2/day at Little Break, and from -8 to -19 ng/m^2/day at Mandeville Cut. These assessments are slightly lower than the estimates made by Heim (2003) based on MMHg/Total Hg ratios in sediments.

Figure 6. Time series measurements of MMHg relative to tidal height at Little Break, October 2005.



6. *MMHg is lost from the water column within the Delta ecosystem by an unknown removal mechanism as water flows from the Sacramento River to the Delta.*

Preliminary mass balance assessments at the time this project began indicated that there was an unidentified loss mechanism for MMHg in the Delta that had not been accounted for. When more refined assessments of various sources and sinks were made in this current project, the mass balance could be more tightly constrained (Figure 1b). The major loss term that helped to close the mass balance budget was photodegradation of MMHg. Photodegradation loss was assessed by conducting *in situ* bottle incubation experiments *(task 5.1)*. A series of six experiments were conducted in Teflon® bottles under *in situ* light conditions for lengths of time up to 12 hours. Dark bottle controls were also included. A summary of the experiments is given in Figure 7. These experiments predict that the photodegradation rate of MMHg in the Delta is 0.00296 ng of MMHg per liter of water, per square meter of surface water, for every mol of light hitting the surface (0.00296 ng m^2 L^{-1} mol^{-1}). To assess the degradation for the water column required that light penetration depths be taken into consideration. Assessments of the depth of light penetration were made using available secchi disk data as well as with hydrocasts using light sensors. Mean monthly light exposures were determined and light penetrations were assessed to estimate mean daily photdegradation losses of MMHg in the Delta (Figure 8). On an annual basis approximately 19 g of MMHg are lost daily in the Delta by the photodegradation processes. This is the most significant MMHg flux process we have identified for the Delta as a whole (see Figure 1b).

Figure 7. Relationship between the change in MMHg concentration as a function of total light exposure for individual bottle incubations.

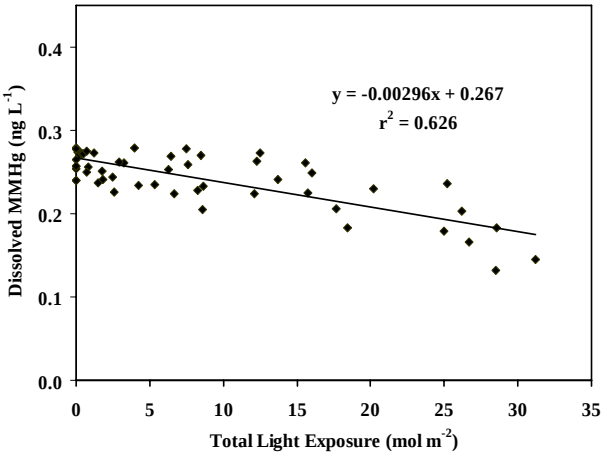
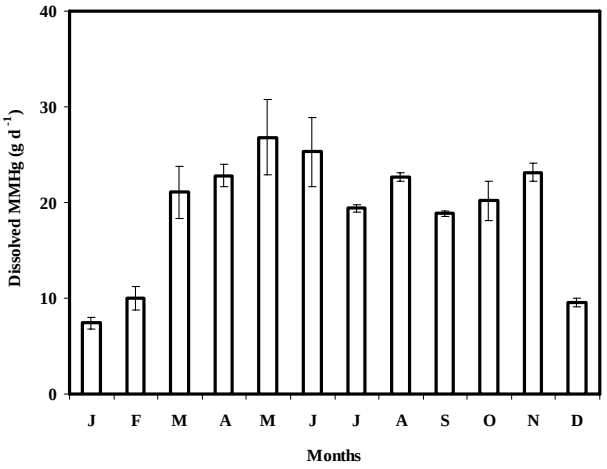


Figure 8. Mean daily photo-degradation losses of MMHg in the Delta for monthly periods. Error bars are the difference in estimates for years 2004 and 2005 total daily light exposure.



New Questions/Hypotheses

7. MMHg concentrations increase in the Sacramento and San Joaquin Rivers as they flow downstream to the Delta.

Water was collected at key locations in the Sacramento and San Joaquin Rivers and their major tributaries to determine MMHg and total Hg concentrations and loads and to identify river reaches containing major sources and sinks of mercury (Task 2b). MMHg concentrations in the Sacramento increase 3-fold between Redding and Freeport (Figure 9, $P<0.0001$). The increase is because the upper river is dominated by releases from Shasta Reservoir with a low MMHg concentration (mean = 0.03 ng/L). Half the downstream increase in MMHg on the Sacramento River appears to be caused by many small creeks draining the Coast Range and Sierra Nevada mountains with higher concentrations. In contrast, MMHg concentrations in the San Joaquin River are higher in the upper River and decrease as it flows to the Delta (Figure 10, $P<0.01$). Concentrations are high in the upper River because of discharge from Mud Slough while the downstream decrease appears to result from dilution by the Tuolumne and Stanislaus Rivers.

Figure 9. Mean and 95% confidence limits of monthly non-storm MMHg concentrations down the Sacramento River between March 2003 and June 2006 (n=31). Redding is 240-river miles upstream of Freeport

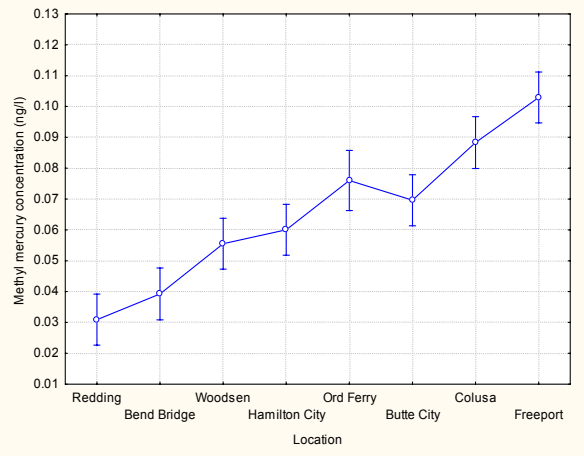
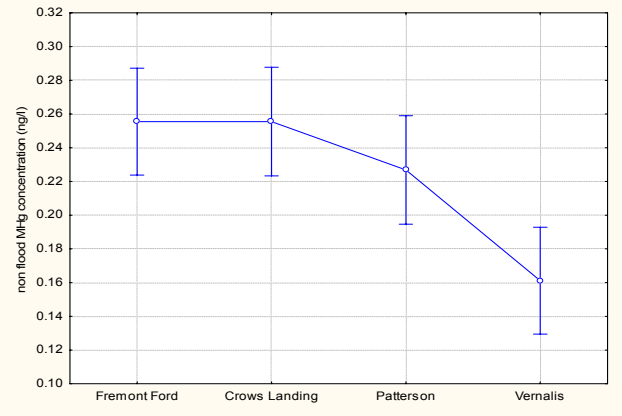


Figure 10. Mean and 95 % confidence limits for monthly non storm MMHg concentrations down the San Joaquin River between April 2003 and June 2006 (n=33). Fremont Ford is 55-river miles upstream of Vernalis.



8. Wetlands are important sites for MMHg production in the Central Valley

Studies are underway in sub watersheds discharging elevated concentrations and loads of MMHg to identify local sources (Task 2c). The sub watersheds studied include Mud Slough and the Yolo Bypass. These studies have identified seasonal marshes, agricultural tile drainage, and wetted floodplains as important sites for MMHg production.

Mud Slough in the San Joaquin watershed discharges 26% of the MMHg but only 5% of the water at Vernalis during the non irrigation season. Concentrations in the Slough average about 0.5-ng/l with a peak in fall of 1.5 to 2-ng/l (Figure 11). In contrast, Salt Slough, the next coast range drainage downstream from Mud Slough, has a lower overall concentration and no seasonal peak. Major water sources to Mud Slough are the San Luis Drain, local agriculture, and about 30,000 acres of wetlands. The San Luis Drain discharges agricultural tile drainage water with elevated salt concentrations, including selenium. Tile drainage contributed about half the water and MMHg load in the Slough between May and September 2005. Water volumes and MMHg loads were lower during the non irrigation season. The major source of water in the Slough in fall and winter is discharge from wetlands. MMHg production was evaluated in six seasonal and two permanent wetlands on the San Luis Wildlife Refuge by measuring concentration in the incoming and discharge water. Concentrations were always higher in the discharge demonstrating that the seasonal marshes were net sources of MMHg (Figure 12). All seasonal marshes also showed an initial pulse of elevated MMHg immediately after flood up. The timing of this pulse appears to correspond to the elevated peak observed in Mud Slough in fall (Figure 11). In contrast, concentrations were similar in supply and discharge water from permanent marshes suggesting that they are not a large net source of MMHg.

The Yolo Bypass is a flood conveyance system designed to divert storm water from the Sacramento basin around the City of Sacramento. Flood water enters the Bypass through the Fremont and Sacramento Weirs and is discharged down Shag Slough and the Toe Drain to the Delta. The Yolo Bypass also receives water from Cache and Putah Creeks, two watersheds

with extensive historical mercury mining. The Bypass floods about every other year for two months. Water leaving the Bypass has the highest average annual MMHg concentration of any waterway in the Delta (0.27-ng/l), higher concentrations (0.70 to 1.37-ng/l, P<0.001) occur in storm water discharge. The winter and spring of 2005/2006 was very wet and the Yolo Bypass flooded repeatedly. MMHg loads were measured in all major source and export waters to determine whether the Bypass was a net source of MMHg and how production compared with export from the rest of the Sacramento Basin. MMHg exports were always greater than incoming loads (Figure 13a). The difference between the two curves is a measure of net production (Figure 13b). Bypass production increased as a function of increasing flow to at least 110,000-cfs, the highest discharge rate monitored. MMHg production in the Sacramento watershed was calculated for the same time period by summing the exports from the Bypass and from the Sacramento River at Isleton. MMHg production in the Bypass averaged 40 % of the rate for the entire Sacramento watershed. This is surprising as the Yolo Bypass is only 59,000 acres while the Sacramento watershed is 16,765,000 acres or 285 times larger.

Figure 11. Methyl mercury concentrations in Mud and Salt Sloughs

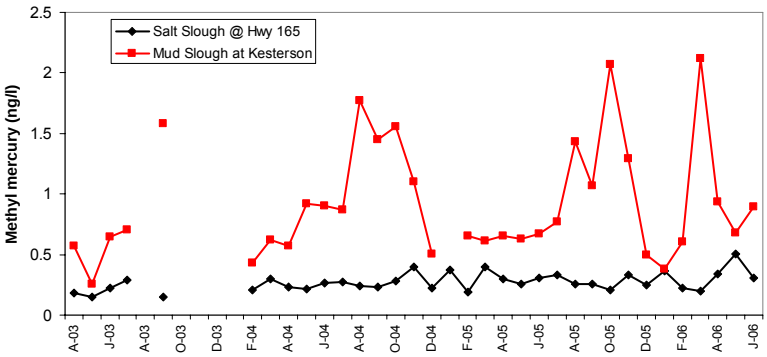


Figure 12. Methyl mercury concentrations (ng/L) in source and discharge water from two representative seasonal marshes in Mud Slough.

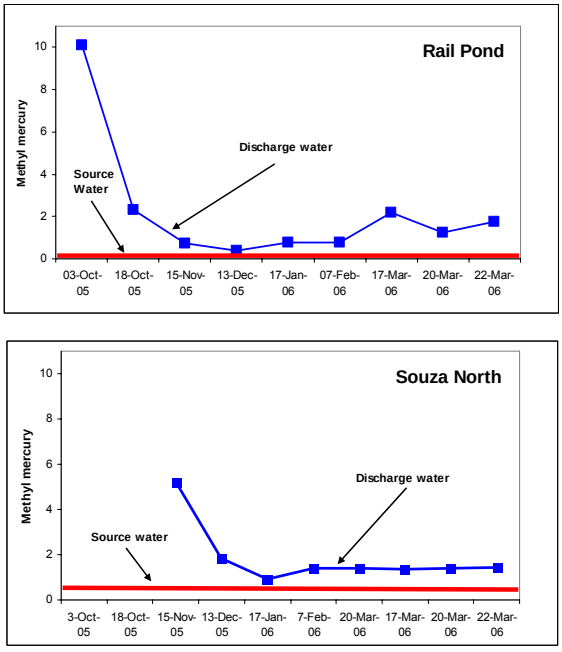
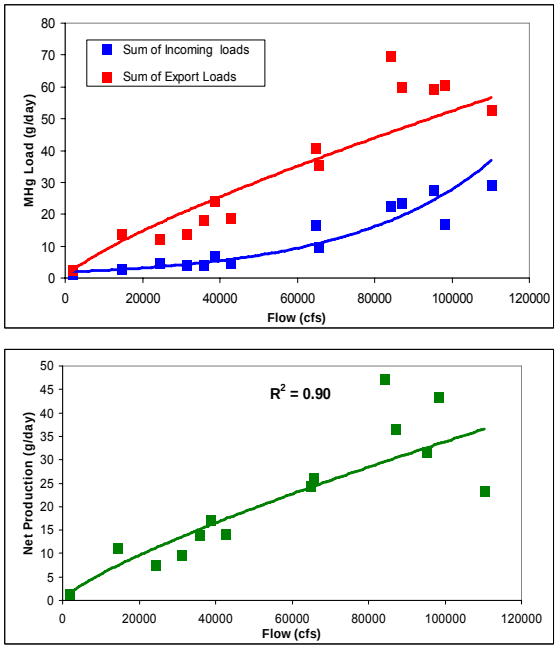


Figure 13. (a) Sum of MMHg loads entering and leaving the Yolo Bypass as a function of flow. (b) Net Bypass production as a function of flow



9. *Will upstream remediation to reduce MMHg discharges result in downstream reductions in concentrations and loads?*

Our results suggest that upstream MMHg controls may reduce downstream concentrations. The evidence comes from both the Sacramento and San Joaquin Rivers. The load of MMHg in the Sacramento River at Freeport (legal Delta boundary) is positively correlated to the sum of the contributions of upstream tributary inputs below Colusa (R^2=0.81, Figure 14). The distance between Colusa and Freeport is 90-river miles or 2-3 days travel time depending upon discharge rates. Similarly, loads in the San Joaquin River at Vernalis are positively correlated to upstream loads at Crows Landing (R^2= 0.98, Figure 15). If the data point representing the highest MMHg load is eliminated from Figure 15, then the R^2 is reduced to 0.91. The distance between Crows Landing and Vernalis is about 40-river miles or 1 to 2 days travel time. Both sets of correlations are most easily explained if MMHg is being transported in a conservative fashion downriver. An augment to this grant has been funded to test this hypothesis by measuring the rate of MMHg production and loss in a 20-mile reach of the Sacramento River in the summer and fall of 2007.

Figure 14. Correlation between MMHg load (g/mo) on the Sacramento River at Freeport and the sum of major upstream loads (Sacramento River at Colusa, Colusa Basin Drain, Feather and American Rivers). The correlation does not include storm events.

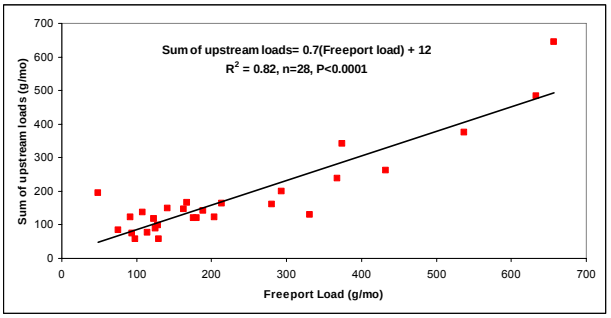
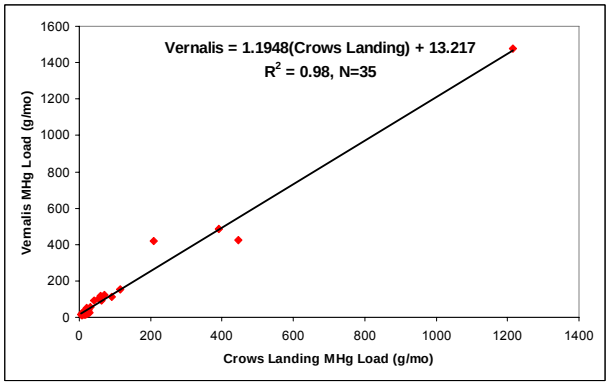


Figure 15. MMHg load (g/mo) on the San Joaquin River at Vernalis as a function of the upstream load at Crows Landing.



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Heim, Wesley A., Kenneth H. Coale, Mark Stephenson, Key-Young Choe, Gary A. Gill and Chris Foe (2007). Spatial and habitat-based variations in total and methyl mercury concentrations in surficial sediments in the San Francisco Bay-Delta. *Environmental Science and Technology* (in press).