2003

Methyl and total mercury in surficial sediments of the San Francisco Bay-Delta

Wesley Alan Heim
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Heim, Wesley Alan, "Methyl and total mercury in surficial sediments of the San Francisco Bay-Delta" (2003). *Master's Theses*. 2443.
DOI: <https://doi.org/10.31979/etd.nrhx-z6xn>
https://scholarworks.sjsu.edu/etd_theses/2443

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

**METHYL AND TOTAL MERCURY IN SURFICIAL SEDIMENTS
OF THE SAN FRANCISCO BAY-DELTA**

A Thesis

Presented to

The Faculty of the Moss Landing Marine Laboratories

In Partial Fulfillment

of the Requirements for the Degree

Master of Marine Science

By

Wesley Alan Heim

August 2003

UMI Number: 1417479

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI Microform 1417479

Copyright 2004 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

© 2003

Wesley Alan Heim

ALL RIGHTS RESERVED

APPROVED FOR MOSS LANDING MARINE LABORATORIES

Dr. Kenneth H. Coale, Professor

Dr. William W. Broenkow, Professor

Dr. Ivano W. Aiello, Adjunct Professor

APPROVED FOR THE UNIVERSITY

ABSTRACT

METHYL AND TOTAL MERCURY IN SURFICIAL SEDIMENTS OF THE SAN FRANCISCO BAY-DELTA

by Wesley Alan Heim

Significant amounts of mercury are continually transported into the San Francisco Bay-Delta as a result of historic mining activities. In response to contamination of the Bay-Delta and potential risks to humans, health advisories limiting fish consumption have been posted. Broad scale surveys of Bay-Delta sediments revealed the greatest mercury methylation potential to be in the central Delta compared to the perimeter waterways and adjacent bays. Methyl mercury concentrations varied seasonally with highest concentrations found during summer. Changes in methyl mercury were likely the result of increased *in situ* production. Sediments originating from Coast range watersheds had higher total mercury concentrations compared to sediments with Sierra range origins. Methyl mercury concentrations were similar in sediments from both watersheds. Interior wetlands had consistently higher methyl mercury concentrations and methyl mercury/total mercury ratios than the adjacent channels. This information is used to form a basic conceptual model of Hg cycling in the Bay-Delta.

ACKNOWLEDGEMENTS

I am sincerely grateful to Dr. Kenneth Coale for the guidance and support he has given me from beginning through completion of my graduate work at Moss Landing Marine Laboratories. His faith and belief in my abilities have given me the opportunity to become the scientist I am today.

I also would like to express appreciation to Dr. William Broenkow and Dr. Ivano Aiello for their helpful edits and suggestions to this thesis and the timely manner in which they made them.

Thanks to Mark Stephenson who has given me many thoughtful discussions on mercury related problems and solutions as well as given me motivation, guidance, and most helpful of all, laughter during this arduous process.

I would also like to recognize Dr. Gary Gill for his generosity in allowing me the use of all his methyl mercury flux data and for guidance in the field of mercury geochemistry, and Dr. Chris Foe for providing the methyl mercury river loads and his invaluable knowledge of the Bay-Delta system.

Nicolas Bloom from Frontier Geosciences deserves recognition for the development of methodologies used in the determination of methyl mercury, supplying me with written step by step instruction for carrying out these procedures, and personal instruction and demonstrations of the procedures without which the analysis of methyl mercury would have been a much greater struggle.

The field work portion of this thesis was extensive and was achieved only by the combined efforts of many individuals from the MLML community. I would like to recognize all of their efforts and am extremely grateful for their help. Specifically, I would like to thank Sean Mundell for his efforts in collecting the seasonal samples, a task requiring long periods away from home on a regular basis.

The mercury laboratory group at MLML has my sincerest gratitude. Thank you Amy Byington, Myah Gunn, Lisa Berrios, Tam Voss, and Bettina Shost for all of your work and long hours analyzing mercury samples.

Thanks to Joan Parker and all of the MLML librarians, who assisted in providing the references for this research.

Thanks to Lynn McMasters for her artistic work in creating the “Mercury Cycling Conceptual Model” illustration.

I would like to thank my family for their support given to me throughout my graduate education. A special thanks to Myah Gunn for her understanding, commitment, strength, and sacrifices given to me throughout the entire process of writing this thesis.

This research was funded by a grant from CALFED (California Bay-Delta Authority) project number 99fc200241 and a grant from the Dr. Earl H. Myers and Ethel M. Myers Oceanographic and Marine Biology Trust.

PREFACE

This thesis presents results from the first comprehensive study of methyl mercury behavior in surficial sediments of the San Francisco Bay-Delta. The introduction gives a broad background of mercury cycling and toxicity as well as defines the purpose of this study. Five major studies are reported as parts of the entire thesis as follows:

Geographical survey, Seasonal study, Bioavailability study, Wetland study, and a Methyl Mercury budget. The Geographical survey describes the spatial variation in methyl and total mercury concentrations for a large number of locations in the Bay-Delta, while the Seasonal study looks at temporal changes in methyl mercury and total mercury concentrations at a select few locations. The Bioavailability study describes the methylation potential of mercury from Coastal and Sierra sources. The Wetland study looks at the methylation potential of the fringe wetland habitats in the Bay-Delta. The Methyl Mercury budget compares methyl mercury inputs from sediments and rivers to exports of methyl mercury to San Francisco Bay and southern California. The sediment input of methyl mercury is discussed in terms of habitat type and the contribution from each habitat type is summed for a total sediment contribution which is used in the budget. The thesis concludes with a working conceptual model of how mercury cycles within the Bay-Delta.

CONTENTS

ABSTRACT	iv
ACKNOWLEDGEMENTS	v
PREFACE	vii
LIST OF TABLES	x
LIST OF PICTURES	xi
LIST OF FIGURES	xii
INTRODUCTION	1
Overview	1
Biogeochemistry	1
Human and Wildlife Health	5
Mining in California	8
Purpose of Study	10
MATERIALS AND METHODS	12
Site Description	12
Sampling Designs	13
Geographical survey	13
Seasonal study	14
Bioavailability study	14
Wetland study	15
Proxy for MMHg flux	16
Geographical information system (GIS)	19
Sampling	20
Sediment sampler	20
Clean sample collection	21
Laboratory Analysis	22
Cleaning	22
<i>Apparatus and materials</i>	22
<i>Reagents</i>	22
<i>Cleaning for HgT</i>	23
<i>Cleaning for MMHg</i>	23
Determination of Total Mercury	24
<i>Scope of total mercury analysis</i>	24
<i>Materials</i>	25
<i>Reagents</i>	25
<i>Sediment digestion</i>	26

<i>Calibration and quality control</i>	27
<i>Analysis by flow injection mercury system (FIMS)</i>	28
Determination of Methyl Mercury	29
<i>Scope of methyl mercury analysis</i>	29
<i>Apparatus and materials</i>	30
<i>Reagents</i>	33
<i>Calibration and quality control</i>	35
<i>Sample preparation and extraction</i>	36
<i>Sample analysis</i>	38
<i>Calculations</i>	40
<i>Interferences</i>	41
RESULTS	43
Geographical Survey	43
Seasonal Study	45
Bioavailability Study	46
Wetland Study	48
MMHg Flux and Loads	49
DISCUSSION	50
Geographical Survey	50
Seasonal Study	53
Bioavailability Study	57
Wetland Study	60
Methyl Mercury Budget	62
CONCLUSION – CONCEPTUAL MODEL	68
REFERENCES	70
APPENDIXES	110
Appendix A Construction of the “Sludge O Matic”	111
Appendix B Raw Data	120

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Principle investigators of the CALFED mercury project in the Bay-Delta	77
2. Name, location, and habitat type of seasonal sampling sites	78
3. Name, location, and habitat type of wetland sampling sites	79
4. Site name, position, and description of flux chamber locations	80
5. A list of habitat types found in the Bay-Delta with the corresponding area, MMHg concentration, calculated flux (from proxy), and MMHg load. The sample size is in parenthesis. Dashed lines are given in categories where it was not possible to calculate flux and load (MMHg concentration below lower boundary limit of proxy)	81

LIST OF PICTURES

<u>Picture</u>	<u>Page</u>
1. A picture showing the fringe marsh habitat along rip-rap waterways at Mandeville Island located near Franks Tract in the central Bay-Delta. (Photo by W. Heim)	82
2. A picture of the area around Tower Park marina in the Bay-Delta, showing the subsidence of croplands and the necessity of levees for prevention of flooding. (Photo by W. Heim)	83
3. An assembled Sludge O Matic with attached shutter trigger line. The door is shown in the closed position. The attachment of the pulley system with plastic ties is clearly shown as is the handle configurations and aircraft pin. (Photo by W. Heim)	84
4. Close-up photo of the topmost 0.5 cm of sediment captured cleanly using the SOM. The trap door of the sampler is shown in the open position with sediment ready to be transferred into sample jars. (Photo by W. Heim)	85
5. Field team employing “clean hand techniques” at Sherman Island. Sediment is being sub-sampled from the SOM using a plastic scoop to transfer samples. “Clean hands” person is wearing clean room gloves during all sub-sampling. “Dirty hands” person never comes into contact with the sample but aids “clean hands” person as necessary. (Photo by R. Lehman)	86

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
<p>1. A simplified illustration of Hg cycling through the environment shows Hg converted from the inorganic to organic form (Hg methylation), processes that inhibit Hg methylation by altering the availability of inorganic Hg for methylation, and removal of MMHg by the formation of volatile di-methyl mercury (Modified from Winfrey and Rudd 1990)</p>	87
<p>2. A map showing locations of mercury mines (Δ) and gold mines (O) in both the California Coastal range and Sierra Nevada Mountains (Map modified from USGS CALFED-1 (Clear Lake to Delta) ArcView Project, contact Tom Suchanek, Feb 2002).....</p>	88
<p>3. Map of the Bay-Delta showing the spatial survey sampling locations ($\circ$)</p>	89
<p>4. Map of the San Francisco Bay-Delta showing the surrounding tributaries and bays. The six seasonal sampling stations are shown with asterisks and the following names: Prospect Slough, Cosumnes River, White Slough, Franks Tract, Connection Slough, and Sherman Island</p>	90
<p>5. Map showing the sampling sites for the Hg bioavailability study. The map key shows the symbol defining each sampling type</p>	91

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
<p>6. Map showing total mercury surficial sediment concentrations.</p> <p>The mercury concentrations are given as scale bars and the key is given in µg/g dry weight sediment. Locations with mercury values less than the method detection limit of 0.010 ug/g are represented by solid black circles</p>	92
<p>7. Map showing methyl mercury surficial sediment concentrations.</p> <p>The methyl mercury concentrations are given as scale bars and the key is given in ng/g dry weight sediment. Two sites are shown with the methyl mercury concentrations explicitly expressed (in ng/g). Locations with methyl mercury values less than the method detection limit of 0.019 ng/g are represented by solid black circles</p>	93
<p>8. Map showing methyl mercury to total mercury ratios (as a percent) in surficial sediment. Grey scale bars are indicative of an upper limit ratio, as the methyl mercury to total mercury ratio was calculated using the method detection limit for total mercury. Solid black circles were used to indicate locations with methyl mercury values and total mercury values less than method detection limits</p>	94
<p>9. Correlation between methyl mercury and percent loss on ignition in delta sediment samples collected during the winter of 1999 ($R^2 = 0.32$)</p>	95

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
10. Correlation between methyl mercury and total mercury in delta sediment samples collected during the winter of 1999 ($R^2 = 0.19$). The circled triangles were left out of the correlation analysis	96
11. Prospect Slough, Cosumnes River, and Sherman Island Seasonal changes in methyl mercury (▲), total mercury (■), and the methyl mercury to total mercury ratio (as a percent)(◆) in surficial sediment of the Bay-Delta. Methyl mercury (ppb) and methyl mercury to total mercury ratio (as %) share the primary y-axis. Total mercury is on the second y-axis (log scale). Error bars represent analytical uncertainty rather than field duplication	97
12. Methyl mercury and total mercury concentration of surficial sediment samples collected at Franks Tract (□), White Slough (Δ), Connection Slough (x), Prospect Slough (○), Cosumnes River (◇), and Sherman Island (●). A positive correlation between methyl mercury and total mercury is shown only for samples collected at Sherman Island (regression coefficient of $R^2 = 0.40$)	98

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
13. Three panels showing total mercury concentration, methyl mercury concentration, and the methyl mercury to total mercury ratio (as a percent) in unsieved surficial sediments collected from Coastal and Sierra lakes, mountain streams, and valley streams. Black bars are from the Coastal range and white bars are from the Sierra range. Each bar is the averaged value of many locations within a particular classification. The error bars are the standard error of samples within a particular classification	99
14. Three panels showing total mercury concentration, methyl mercury concentration, and the methyl mercury to total mercury ratio (as a percent) in sieved surficial sediments collected from Coastal and Sierra lakes, mountain streams, and valley streams. Black bars are from the Coastal range and white bars are from the Sierra range. Each bar is the averaged value of many locations within a particular classification. The error bars are the standard error of samples within a particular classification	100

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
<p>15. The upper figure gives MMHg as a percent of the total mercury for the micro-habitat types found along a cross channel transect. The y-axis is a log scale and a description of the habitat type is given along the x-axis. The lower figure is a cross channel water depth profile showing the depth from which each sample was collected</p>	101
<p>16. Methyl mercury concentrations in surficial sediments collected from three wetland areas and one control area outside the wetland area. Black bars are from the interior of the wetlands, grey bars are mid way between the interior and fringe of the wetland, and the white bars are from the outer fringe of the wetland areas. The bars represent the average of field duplicates and the error bars are the range of field duplicates</p>	102
<p>17. Concentration Methyl mercury to total mercury ratio as a percent in surficial sediments collected from three wetland areas and one control area outside the wetland area. Black bars are from the interior of the wetlands, grey bars are mid way between the interior and fringe of the wetland, and white bars are from the outer fringe of the wetland areas. The bars represent the average of field duplicates and the error bars are the range of field duplicates</p>	103

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
<p>18. Flux of MMHg from sediments plotted against MMHg sediment concentration. The black circles (●) are used in the regression and the black triangles (▲) from White Slough are not included in the regression. Error of MMHg concentration is calculated as the range of concentrations between field replicates. Error of MMHg flux is calculated from the error associated with the slope used to calculate flux for each measurement</p>	104
<p>19. Covariance of Chl a (-Δ-), sulfate (-◇-), temperature (-X-), and MMHg (-●-) from February through October, 2001 at the Cosumnes River station. Chl a, sulfate, and temperature data from Foe (2002)</p>	105
<p>20. A comparison of MMHg versus HgT for samples collected during the initial survey (○) and samples collected from the fringe marshes (◆) within the Bay-Delta. The R^2 value for the correlation between HgT and MMHg for the marsh samples is 0.52 compared to 0.02 for the initial survey.....</p>	106
<p>21. Map showing sampling sites of the Bay-Delta mercury budget study of Foe, 2001. These sites were used to quantify the major inputs (Yolo, Sacramento River, Mokelumne River, and San Joaquin River) and exports (X2, State Water Project, and Delta Mendota Canal) of mercury for the Bay-Delta</p>	107

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
22. MMHg budget for the Bay-Delta water shed. Major river inputs are the sum of the Sacramento River, San Joaquin River, Mokulumne and Cosumnes River, and Prospect Slough. Exports are to the ocean as measured at X2 and water export to southern California measured at the pump stations. Values are annual averages given in grams per day. Water input and export values are from Foe, 2001	108
23. A conceptual model of how Hg cycles in the Bay-Delta (illustration by Lynn McMasters)	109

INTRODUCTION

Overview

Mercury (Hg), as a chemical element, cannot be created or destroyed and the total amount on Earth remains unchanged. However, anthropogenic activities have altered the natural Hg cycle increasing the amount transferred from the lithosphere to the biosphere (Fitzgerald and Clarkson 1991, Mason et al. 1994, Fitzgerald et al. 1998). As the natural Hg cycle continues to be perturbed by anthropogenic activities, Hg contamination in aquatic and terrestrial ecosystems has become a global concern not always limited to locations with obvious sources of Hg (Fitzgerald and Clarkson 1991, Bodaly et al. 1993, Fitzgerald et al. 1998). Furthermore, certain locations have an additional burden of Hg from local sources, which often exceeds background levels. The potential for a variety of ecological and human health impacts increase as biota accumulate Hg as a result of routine exposure to the contaminated biosphere (Keating 1997).

Biogeochemistry

Elemental Hg is the only metal able to exist as a liquid at typical environmental temperatures and pressures. This unique property gives mercury a three phase nature; Hg is found as a liquid, solid, and vapor in the environment. The three phase nature of Hg makes its elemental biogeochemical cycle extremely complex and difficult to accurately characterize. In addition, Hg forms both inorganic and organic complexes that may occupy a solid, dissolved, true liquid, or gas phase. The transition of Hg between these compounds and phases is controlled by a multitude of environmental processes, including

photochemical reactions, chemical oxidation and reduction, microbial transformations, and physiological fractionation (Meili 1997).

The oxidation state of mercury determines its physical properties and chemical behavior. Hg exists in three oxidation states: elemental Hg (Hg^0), mercurous Hg (Hg^{+1}), and mercuric Hg (Hg^{+2}). Elemental Hg has a high vapor pressure, a low solubility, does not combine with inorganic or organic ligands, and is not available for reactions with organic compounds. At ambient conditions elemental Hg is readily vaporized and strongly partitions into the atmosphere as elemental Hg vapor. The mercurous ions and mercuric ions form many inorganic compounds. The mercurous ion is very unstable under normal conditions and combines only with inorganic compounds. The mercuric ion combines with both inorganic and organic ligands.

Unlike most metals, Hg tends to form covalent rather than ionic bonds. In water, sediments, and biota Hg is found primarily in the form of inorganic Hg salts and organomercurics. The organomercuric form of Hg is defined by a carbon-Hg (C-Hg) covalent bond. Inorganic Hg salts may associate with organics in the environment but lack the covalent C-Hg bond which differentiates the organomercuric. In the environment, organometallic compounds such as organomercuric, are more mobile, more toxic, and more readily bioaccumulated than compounds of the corresponding inorganic metal ions (or metalloids) (arsenic is an exception) (Weber 1993). Organometallic compounds are generally much more toxic than corresponding metalloids due to their ability to move across biological membranes, their greater solubility in lipid tissue, and their tendency to bioconcentrate (Weber 1993).

The organomercuric compound, mono methylmercury (MMHg) is formed by both abiotic and biotic methylation of inorganic mercury (Hg (II)) (Winfrey and Rudd 1990). MMHg is a potent neurotoxin and is one of the most toxic forms of Hg. In aquatic systems, MMHg is readily bioaccumulated into biota and biomagnified up the food web, ultimately posing a threat to fish consumers.

Although studies have shown abiotic methylation of mercury to be significant in some environments (Weber 1993), in aquatic systems it is generally accepted that MMHg production is mediated by microbial activities (Compeau and Bartha 1985, Berman and Bartha 1986, Kelly et al. 1997). The primary site of methylation occurs in sediments at the oxic/anoxic interface, which is often near the surface of marsh sediments (Gilmour et al. 1998). Sulfate reducing bacteria are thought to be the primary mediators of mercury methylation (Compeau and Bartha 1985, Gilmour et al. 1992, Choi et al. 1994). Enhanced activity of sulfur reducing bacteria and MMHg production is stimulated by sulfate (Gilmour et al. 1992), however, concomitant sulfide accumulation limits MMHg production as Hg is removed from solution via enhanced precipitation of mercury sulfide (HgS) (Gilmour et al. 1998). MMHg production is a function of both the activity of methylating bacteria and the availability of Hg for methylation (Benoit et al. 2001). It is thought that sulfide influences methylation by affecting the speciation of dissolved Hg and its uptake via passive diffusion into the microbe (Benoit et al. 2001). In anoxic fresh water sediment, mercury methylation occurs most rapidly when sulfide concentrations are at levels which favor the formation of neutral dissolved Hg-S species (HgS^0) (Benoit et al. 1999). Once Hg diffuses into the microbe, Hg methylation occurs in the cytoplasm

via a side reaction of the Acetyl-CoA pathway (Choi and Bartha 1993, Choi and Bartha 1994).

The amount of biologically available MMHg produced in sediment and water is governed not only by the rate of Hg methylation, but also the rates of processes altering the availability of inorganic Hg for methylation. A simplified illustration of the processes influencing the availability of Hg for methylation is shown in Figure 1. Inorganic Hg(II) has a large affinity for inorganic and organic particulates as well as dissolved organic carbon (DOC); the binding of Hg(II) to particulates will make it less available for methylation (Rudd and Turner 1983). The presence of hydrogen sulfide (H_2S) will readily precipitate Hg(II) as a highly insoluble Hg sulfide species (HgS), rendering the Hg unavailable for methylation. H_2S also may react with MMHg resulting in the formation of volatile di-methyl mercury (Craig and Moreton 1983). Finally, Hg (II) is made unavailable by bacterial mediated reduction to Hg^0 and subsequent volatilization to the atmosphere (Winfrey and Rudd 1990).

The net amount of MMHg in a given environment is a function of the concomitant processes of methylation and demethylation. Demethylation may occur both by biotic and abiotic pathways. Abiotic demethylation occurs mainly in the water column as a photodegradation process (Sellers et al. 2001). Biotic demethylation may occur by two pathways, oxidative demethylation (OD) and reductive degradation (mer-detoxification). Studies have shown that severely contaminated sediments tend to have microbial populations that actively degrade MMHg via mer-detoxification, whereas OD

is the most active pathway in less contaminated sediments (Marvin-Dipasquale et al. 2000).

Human and Wildlife Health

Historically, sources of occupational exposure to Hg came from mining of Hg, extracting Hg from ores, the extraction of silver and gold, and gilding (Magos 1997). Hg was also used in the felt industry. Hat making in particular required Hg for removing fur from pelts. A solution of mercury nitrate was brushed on the pelt. The Hg roughened the fiber and increased the wool's matting ability. After the pelt was dried the wool would be shaved off. Subsequent steps using heat would release Hg vapor. Poisoning of workers in this industry and their subsequent neurological deterioration led to the term "mad as a hatter."

MMHg is a potent neurotoxin. In adults, the earliest signs of exposure are nonspecific symptoms from the central nervous system (CNS), including paresthesia and malaise (Mottet et al. 1997). With further exposure coordination problems, hearing impairment, and constriction of the visual field may develop (Mottet et al. 1997). The most severe cases of MMHg exposure may result in death. In adults, symptoms of MMHg exposure are derived from damage to specific areas of the CNS such as the visual cortex of the cerebrum and the granular cells of the cerebellum (Mottet et al. 1997). The damage is characterized by both the loss of neurons and gliosis (Mottet et al. 1997) and refs therein). Microtubule disruption in the neuronal cytoskeleton has been proposed as the biochemical mechanism of MMHg toxicity (NAS 1999 and references therein). Hg binds to thiol in the tubulin, the protein monomers that form microtubules, and blocks the

depolymerization and repolymerization of microtubules (NAS 1999 and references therein). The breakdown and assembly of microtubules are required for many cell functions, including cell division and migration; disruption of microtubule assembly would disrupt cellular processes and result in many of the symptoms associated with Hg poisoning (NAS 1999 and references therein).

The developing brain is extremely sensitive to MMHg, and the fetal brain may be affected even if the mother shows no signs of poisoning. MMHg exposure during gestation may produce degenerative as well as developmental deficits. The degree of each deficit is a function of the exposure level and the timing of the exposure event relative to gestation (Mottet et al. 1997 and refs therein). The mechanism of toxicity to developing brains may be different than mechanisms effecting adult brains. In developing brains MMHg may exert its adverse effects by inhibiting both cell proliferation and migration (Mottet et al. 1997).

In 1956 the first documented account of MMHg poisoning in humans (now called Minamata syndrome) occurred at Minamata, Japan, where a factory producing acetaldehyde and vinyl chloride had discharged a total of 4.1 tons of MMHg directly into the enclosed Minamata Bay (Baldi 1997). Because of its lipid solubility, MMHg readily bioaccumulated up the food chain contaminating marine fish stocks. Fishermen and their families fed on these fish resulting in 750 deaths and 1750 cases of Minamata syndrome (Baldi 1997). Between 1972 and 1973 a second epidemic of Minamata syndrome occurred in Iraq. Six thousand five hundred thirty people were hospitalized and official

figures puts the number of deaths at 459 after Hg was ingested from homemade bread prepared from wheat seed treated with MMHg fungicides (Boudou and Ribeyre 1997).

In addition to human health risks associated with MMHg, there are also wildlife problems. MMHg became widely used in agriculture, as fungicides and seed disinfectants, between the 1940s and 1966 in both Sweden and North America (Boudou and Ribeyre 1997). Bird populations were found to contain very high levels of MMHg due to their feeding on the scattered seeds and field studies revealed a severe bird population decline. After the banning of MMHg fungicides in Sweden MMHg levels in birds decreased (Boudou and Ribeyre 1997).

As a result of the Minimata and Iraq case studies the international community has recognized the hazards of MMHg and its commercial use and discharge are now banned globally. Present MMHg concentrations found in the environment are generally a result of “natural” methylation of Hg(II) rather than MMHg created by industrial processes. However, Hg(II) of anthropogenic origin, both historic and present, still is responsible for the contamination of many ecosystems by supplying a source of Hg to be methylated.

Today, human exposure to MMHg occurs primarily through the consumption of contaminated fish (Fitzgerald et al. 1998, Paterson et al. 1998). Virtually all (99%) Hg bioaccumulated in fish is in the form of MMHg (Bloom 1992). Following ingestion of MMHg, it is almost completely absorbed to the bloodstream and distributed to all tissues within approximately 4 days (Mottet et al. 1997). Mason and Lawrence (1999) reports that impacts from the accumulation of MMHg in piscivorous fish, birds, and mammals

are a current regulatory focus as levels in fish often exceed human health and environmental impact criteria in many states in the United States and elsewhere.

At this writing, Hg concentrations in large striped bass and other game fish residing in the San Francisco Bay-Delta (Bay-Delta) exceed the California Environmental Protection Agency safety guidelines for human consumption. In response to the Hg contamination of fish in the Bay-Delta and the potential risks to humans, health advisories and interim health advisories have been posted in the estuary, recommending the following: 1) Adults should limit consumption of Bay sport fish and striped bass and sturgeon from the Delta to, at most, two meals per month, 2) Adults should not eat any striped bass over 35 inches (89 cm), and 3) Pregnant women, or women that may become pregnant or are breast-feeding, and children under 6 should not eat more than one meal per month, and should not eat any meals of shark over 24 inches (61 cm) or striped bass over 27 inches (69 cm) (Office of Environmental Health Hazard Assessment 1994, San Francisco Bay Regional Water Quality Control Board 1995). Elevated concentrations of Hg in fish tissue may also represent a hazard to piscivorous wildlife in the Bay-Delta. Species most at risk are fish-eating birds and mammals.

Mining in California

The Bay-Delta suffers an additional Hg burden that exceeds background levels associated with the global Hg cycle. California has large natural deposits of Hg in the form of cinnabar, a highly insoluble Hg sulfide mineral. The majority of the cinnabar deposits are located in the California Coastal range (Figure 2). Cinnabar deposits formed as a result of processes occurring in association with the movements of transform faults.

For example, cinnabar is found along the San Andreas fault in serpentine intrusions (“leaky transform”) as a result of movements of mercury laden fluids moving through the hydrothermal system. The discovery of gold in the Sierra Nevada motivated the initial excavation of the cinnabar deposits. Gold mining was extensive throughout the Sierra Nevada (Figure 2). Both placer and lode gold mining operations required the use of Hg to efficiently extract and condense gold; Hg forms an amalgam with gold which is then easily separated with heat. The Coastal range cinnabar deposits were utilized as a local source of Hg for Sierra gold mining operations.

Between 1850 and 1980 California was the nation’s leading producer of Hg, contributing about 100 million kilograms to the world market (Churchill 2000). The processing and refining of cinnabar into elemental mercury was generally carried out at the Hg mine sites. Early Hg processing, using furnace volatilization of the cinnabar ore and cold surface condensation of elemental Hg, was inefficient. It is estimated that approximately 35 million kilos of the metal have been released into the Coastal range watersheds as a result of Hg mining operations (Churchill 2000). Hg mined in the Coastal range was transported across the central valley to the Sierra Nevada where it was used in gold mining activities. Six million kilos of Hg are thought to have been lost in placer and lode gold mining operations in the Sierra Nevada (Churchill 2000). Recent studies have determined that large amounts of Hg are still being transported annually into the Bay-Delta from both the Coastal range and the Sierra Nevada (Larry Walker and Associates 1997, Foe and Croyle 1998, Roth et al. 2001).

Purpose of Study

High loads of elemental or ionic Hg to an ecosystem may not be directly correlated to high levels of MMHg in fish and other biota. The rate of *in situ* MMHg production is a key factor in MMHg bioaccumulation and subsequent biomagnification in the food web (Gilmour et al. 1998). The degree to which Hg is transformed to MMHg is termed methylation efficiency. Methylation efficiency may be used to gauge an ecosystem's potential production and bioaccumulation of MMHg. Ecosystems that have low methylation efficiency may exhibit low or moderate bioaccumulation even under high Hg loads. If methylation efficiency is high, significant bioaccumulation of MMHg can result even when Hg loads are very low (Krabbenhoft et al. 1999). Methylation efficiency of aquatic sediments has been estimated successfully using the MMHg to total Hg (HgT) ratio (Krabbenhoft et al. 1999). When using the ratio as a proxy for methylation efficiency, higher MMHg concentrations found in the sediments per unit of HgT indicate higher methylation efficiency.

Past studies investigating Hg concentrations in fish (Fairey et al. 1997, Davis et al. 1998, Davis et al. 2002b) and HgT concentrations in sediment and water (Domagalski 1998) have improved the understanding of Hg cycling in the Bay-Delta by characterizing major reservoirs and movement of Hg into the food web; however, significant data gaps still exist with respect to bulk phase HgT and MMHg spatial and temporal distributions, primary locations and habitat types promoting Hg methylation, and sources of Hg to the Bay-Delta. The goal of this study was to: 1) Determine the spatial and temporal trends in HgT and MMHg concentrations in Bay-Delta sediments, 2) Identify potential "hot

spots” in MMHg production within the Bay-Delta using the MMHg to HgT ratio as a proxy for Hg methylation efficiency, 3) Identify differences in the methylation efficiency of Hg deposited in the Coastal watershed versus Sierra watershed, 4) Identify the primary habitat types promoting MMHg production in the Bay-Delta, and 5) Develop a proxy for MMHg flux from sediment using MMHg bulk sediment concentrations, and use the proxy to calculate MMHg loads from sediments within the Bay-Delta. This information is critical to a basic conceptual model of how Hg cycles in the Bay-Delta. Quantifying the potential reservoirs of HgT and MMHg and the spatial and temporal changes in these bulk concentrations is a first step towards understanding the movement of Hg into the biota of the Bay-Delta. This information may be used to aid future process oriented work aimed at lowering Hg levels in fish.

This work was conducted as part of a CALFED funded study titled “Assessment of Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed.” The long term goal of the program is to reduce mercury concentrations in fish tissue to levels that do not pose a threat to wildlife or human health. The CALFED Mercury Research Group consisted of 15 principal investigators from state and federal agencies, universities, private analytical laboratories, and non-profit agencies. The CALFED Mercury Research Group was composed of two sub groups, the Cache Creek group and the Bay-Delta group. The following study was conducted in close association with principle investigators within the Bay-Delta group resulting in a multidisciplinary view of the Bay-Delta mercury problem (Table 1), but reflects the emphasis of this thesis.

MATERIALS AND METHODS

Site Description

The San Francisco Bay and Sacramento-San Joaquin Delta (Bay-Delta) is the largest estuary on the west coast of the United States. The major rivers that feed the system are the Sacramento, Mokelumne, Cosumnes, and San Joaquin rivers. Of these rivers only the Cosumnes flows into the delta unobstructed by dams. The Bay-Delta receives the runoff from 40 percent (60,000 sq miles) of California's land. The Bay-Delta covers 738,000 acres with hundreds of miles of waterways within its boundaries. These waterways, originally formed from the natural meandering of rivers through the marshland, are now held in place with banks made up of rip-rap armor and extensive dikes. Historic seasonal wetlands, created by the annual flooding as a result of rivers overflowing natural levees, have all but disappeared from the Bay-Delta. Large acreages of marsh habitat are now only found at wildlife recreation areas and restoration sites such as the Cosumnes River Preserve (northeast delta), the Lower Sherman Island Wildlife Area (west delta), and the Yolo Bypass Wildlife Area (northwest delta). Historically, seasonal wetlands and marshes were the predominant habitat features in the central delta. Today, the majority of these seasonal wetlands have been reclaimed for agricultural uses (Nichols et al. 1986).

In the central delta marshes and wetlands are generally constrained to the fringes of channels along rip-rap banks and narrow islands in the center of waterways (Picture 1). The subsidence of reclaimed swamp land as a result of oxidation and mechanical compaction has left much of the Bay-Delta below sea level necessitating the more than

1,000 miles of levees for protection against flooding (Picture 2). Occasionally, severe levee breaches occur resulting in the flooding of a farmed tract and the creation of shallow open water habitat. These “lakes” are not uncoupled from tidal action and continue to mix with water from the surrounding channeled waterways. Currently the Bay-Delta has four open water habitats: Franks Tract, Mildred Island, Big Break, and Liberty Island. The diverse habitats within the Bay-Delta provide essential habitat for fish and wildlife as well as supporting communities, agriculture, and recreation.

Sampling Designs

Geographical survey

A broad scale survey of the Bay-Delta was conducted October 10, 1999 through December 1, 1999. Ninety-six sites within the Bay-Delta were sampled within a two-month period, however, the majority of the samples were collected within the first five days (Figure 3). Water temperatures in the Bay-Delta at this time averaged 15 °C, and the Sacramento River was flowing at 10,000-19,000 cfs. Sampling locations were selected using GIS base maps to generate a random sampling within each major habitat type found in the Bay-Delta. Once in the field, many locations were changed due to problems with access, as a result the sampling was semi-random. Sediment samples were collected remotely using the “Sludge O Matic” (SOM), a sampler designed and built at Moss Landing Marine Labs described below and in Appendix A. Samples were collected for the analysis of HgT, MMHg, Loss on Ignition (LOI), and grain size (percent fines = < 0.063 mm) using standard methods reported by Plumb (1981).

Seasonal study

Six sites within the Bay-Delta system were selected for monthly monitoring (Figure 4). The locations were selected to represent the variety of habitat types found in the Bay-Delta. The position and brief description of each location is given in Table 2. Sampling frequency was monthly beginning May 2000 and increased to twice-monthly June 2001. Stations were located with a hand held GPS to assure re-sampling to within a few meters. Sediment was collected using the SOM sampler. The samples were analyzed for HgT, MMHg, and LOI. Grain size (percent fines as described above) analysis was conducted on a selected sub-set of the samples.

Bioavailability study

Sediment collections were made during October, 2001 in the coastal mountain range (Cache Creek and other areas) and in the Sierra Nevada range (Cosumnes River and other areas)(Figure 5). Two seasonal lakes (Capay Dam and Cache Creek Settling Basin) were also sampled to be able to make a comparison between the permanent lakes and seasonal lakes of the coastal range. Samples were collected using a scoop to remove the top 1 cm of sediments from depositional areas in the streambeds. A scoop was used rather than the SOM as the sediment type was predominately coarse grained sand which prevents the shutter door on the sampler from sealing properly. Lake samples were collected using the 0-1 cm interval of sectioned cores. Both sieved (60 μ m) and unsieved samples were collected. Sieved samples were collected to prevent bias introduced by differences in grain size from confounding results. Sieves were made from 60 μ m plastic mesh. The MMHg to HgT ratio was used as a proxy for methylation efficiency of the

sediments; higher MMHg concentrations found in the sediments per unit of HgT indicate higher methylation potential and bioavailability.

Wetland study

East Colombia Cut (38.03081 N, 121.49147 W) was selected as a perfect site to conduct an across channel study designed to elucidate differences in methylation efficiency of differing micro-habitat types. The east shore was characterized by a sandy sediment type, floating aquatic vegetation (FAV) and submerged aquatic vegetation (SAV). Moving down the channel bank the sediment type fined and there was an absence of vegetation. With progression into deeper water some macro infauna (*Corbicula*) appeared in patches. The channel then shoaled toward the west into a peat bank, first peaty silt then a solid peat mat. The transect work was done September, 2000. The channel width at the site was ~150 meters and eleven samples were collected along the transect line every 13 meters. Samples were collected, by scuba divers using the SOM, for the analysis of HgT, MMHg, LOI, and grain size.

Further investigations between the methylation efficiency of wetland and non-wetland areas were conducted during May, 2001. Name, location, and a brief habitat description of the three wetland areas studied are listed in Table 3. At each area studied, sampling was conducted along a transect, one station furthest into the interior of the wetland (inner), one midway from the inner station to the outside of the wetland (middle), and one just outside of the wetland (outer). The Mandeville Island station had sediment containing peat, channels greater than 2 meters deep, and the water was well mixed and visually appeared to be equivalent to the adjacent San Joaquin River. Webber Point and

Fourteen Mile Slough had silty sediment free of peat, limited water circulation, and were close to agricultural areas. At each station 2 replicate cores were collected, the sediment from each core was extruded and the sediment sub-sampled at the interval of 0-2 cm. The control sites were located on the San Joaquin River away from the wetlands and the sediments were silty and similar in appearance to Webber Point and Fourteen Mile Slough sediments. Samples were analyzed for HgT, MMHg, and LOI.

Proxy for MMHg flux

Determining the magnitude of MMHg flux from sediments into water is a necessary part of a MMHg budget for the Bay-Delta. Two commonly used methods for determining flux involve the use of diffusional gradients of pore water to model flux or measuring flux directly using benthic flux chambers (Gill et al. 1999). Flux chambers allow the direct measurement of flux by isolating a portion of the sediments and overlying water within a chamber. Water samples are drawn from the chamber over a brief period of time (hourly for 4-5 hrs). Tracking changes in the concentration of the desired analyte over time, knowing the surface area of the sediment isolated, and the volume of the overlying water allows flux to be calculated. Both of these approaches are labor intensive and time consuming. As a result the number of flux measurements determined by these methods is generally limited. It was therefore desirable to identify a proxy for MMHg flux which would enable flux to be calculated for numerous locations within the Bay-Delta.

Solid phase MMHg concentration was used as a proxy for MMHg flux. Direct measurements of MMHg flux determined using benthic flux chambers were plotted

against the corresponding average MMHg sediment concentration for each sampling location. The linear regression of these data points gave an equation which may be used to solve for MMHg flux given a value for solid phase MMHg concentration within the Bay-Delta.

All flux chamber work was headed by Dr. Gary Gill at Texas A & M University at Galveston (TAMUG). TAMUG processed all samples and have generously made their data available for use in this study.

The MMHg sediment concentrations were determined from replicate field samples collected at a benthic flux chamber deployment site. All sediment samples were collected by SCUBA divers with the SOM. The samples were analyzed for MMHg as described above.

The flux chamber deployment sites were selected based on sediment concentration data and habitat information obtained from the initial survey. The sites encompassed a wide range of MMHg sediment concentrations and were representative of major habitat types found within the Bay-Delta. Table 4 lists name, position, and environmental conditions (water, depth, percent sand, and percent LOI) at each flux chamber location.

A total of 24 flux chamber deployments took place over a period of 1.5 years resulting in 31 direct measurements of MMHg flux. Analysis of the flux data identified some MMHg flux measurements to have a large degree of uncertainty, indicated by erratic behavior of the oxygen concentrations within the chambers. It may be possible that some of these flux measurements were made with a poor seal of the chamber over

the sediment surface as some locations had hard bottom substrates and/or strong currents making a proper placement of the chamber extremely difficult. A good seal of the chamber results in a linear decrease in oxygen concentration over time. The exception would be production of oxygen within the chamber, as a result of benthic photosynthesis, which would result in a linear increase in oxygen over time. Measurements with a fluctuating oxygen concentration over time were not used in calculating the proxy (9 measurements). Only flux chamber measurements with oxygen data having an $R^2 = 0.50$ after regression of the time series were used to calculate the MMHg flux proxy, because it was felt that only flux chamber deployment data that behaved in a predictable and well behaved manner should be used to calculate the proxy to eliminate potential complications due to measurements with a large degree of error associated with them.

Not all flux chamber deployments showed a flux of MMHg out of the sediments into the water column. There were some measurements made where MMHg flux was into the sediment. Flux into the sediment is driven by diagenetic processes, while flux from the sediment is driven primarily by diffusion and advection. MMHg sediment concentrations as a proxy for flux of MMHg is only for calculating flux from the sediments into the water, therefore, measurements of flux into the sediment were not included in this analysis (4 measurements). Porewater concentrations were always higher than overlying water suggesting that over longer periods of time the net flux of MMHg was from the sediments. This treatment, therefore, was assumed to introduce an insignificant error associated with the proxy when considered at monthly timescales.

Finally, two outlying measurements were not included in calculating the MMHg flux proxy. Both measurements were from White Slough, a location characterized by vast quantities of flocculant material covering the sediment surface and surfaces of the SAV. This increased organic material shoals the oxic/anoxic boundary layer and may promote the reduction of Mn and oxidation of Fe to insoluble Fe(III). The conversion of Fe(II) to Fe(III) has been shown to restrict the availability of MMHg to the overlying water (Gill et al. 1999). Porewater MMHg concentrations at White Slough were observed to be very high while the MMHg flux from the sediment was always very low (data not shown). The city of Lodi operates the White Slough Water Pollution Control Facility, a waste water collection and treatment facility which discharges indirectly into White Slough through adjacent farmlands which use the recycled water. The City utilizes a process called anaerobic digestion to convert the solids removed from the wastewater into a useful byproduct known as biosolids. The discharge from this facility and the presence of large amounts of flocculant material at the site make White Slough an anomalous location with respect to other locations sampled in the Bay-Delta. For these reasons the two measurements at White Slough were not included in the regression of MMHg concentration versus MMHg flux.

Geographic information system (GIS)

The computer program ArcView™ was the geographic information system used for all spatial analysis. Map layers describing habitat types found in the Bay-Delta were downloaded over the internet from the National Wetlands Inventory. The map layer was separated into nine pertinent habitat types as follows: Upland, Riparian woodland, Salt

ponds, Mudflats, Open water, Seasonal wetlands, Farmed wetlands, Lakes and ponds, and Marsh. The area of each of these habitat types was calculated and summed for a total area of the Bay-Delta. Sampling locations were imported into the map layers. A habitat type was assigned to each sample collected during the initial survey based on proximity to the given habitat feature.

Sampling

Sediment sampler

The upper portions of the sediment column are thought to be the most important in terms of trophic transfer and sediment/water flux. It is here that the sediment contacts the water, and the transition from oxic to anoxic usually occurs within a few millimeters. Thus the upper most portion of the sediments are where maximum rates of Hg methylation occur (Gilmour et al. 1992). In addition it is from this sedimentary layer that most diffusional flux originates (Gill et al. 1999), and it is here where most benthic infaunal invertebrates live. There are, however no commercially available samplers capable of reliably sampling this portion of the sediment column. A sampler was therefore designed and built to cleanly capture the top 0.5 centimeters of sediment. Picture 3 shows the SOM fully assembled with the trap door in the closed position and the trigger line attached ready for remote use. Picture 4 shows a close-up of SOM with the trap door open exposing the cleanly captured top 0.5 cm of sediment. Appendix A contains detailed instructions for the construction of the SOM sampler. The primary benefits of this sampler were the large sediment yield per deployment, the straight forward sub-sampling of the targeted surface sediment interval, and the consistency in

sampling the surface sediment interval. Unlike sectioning cores for a targeted sediment interval, where the sub-sampling is tedious and time consuming, this sampler required nothing more than scooping the sediment out of the sampler and into the sample container. The sampler is deployed remotely from a small boat by attaching a hand pole or line and weight depending on water column depth. In addition, the sampler may be used directly by a SCUBA diver.

Clean sample collection

Sediment samples were collected into 60 mL wide-mouth borosilicate glass jars, with Teflon™ lined polyethylene caps (I-CHEM™ EPA-clean, or equivalent, acid-cleaned) using standard clean techniques. Clean techniques briefly described are as follows: sampling crews consisted of at least two persons, one wearing fresh clean room gloves “clean hands” and the other holding the sampler “dirty hands” (Picture 5). The clean hands person was responsible for transferring sediment from the sampler into the sample jar. The dirty hands person assisted while not coming into direct contact with the sample until the sample was contained. The jars were filled to 60-80 % of the container capacity with sediment (to minimize head-space losses of volatile Hg, while allowing for expansion due to freezing). Samples were frozen at $< -10^{\circ}\text{C}$ (ordinary freezer at lowest setting) with a maximum holding time of 1 year. All homogenization and other handling of low-level samples ($< 100 \text{ ng/g}$) were performed by clean-room gloved personnel in an area known to be low in atmospheric Hg. It should be noted that the clean techniques employed here were developed in conjunction with the MLML trace metals laboratories

and Gary Gill of Texas A&M University at Galveston. These methods have been shown to be non-contaminating for mercury and methyl mercury at low environmental levels.

Laboratory Analysis

Cleaning

All containers used in the analysis of Hg and MMHg were thoroughly and rigorously cleaned prior to each use.

Apparatus and materials

Non-metal scrub brush

Non-metal bottle brush

Small and large plastic bags

5L acid bath bins

Hot water bath (75°C)

Reagents

6N hydrochloric acid (Baker)

Prepared with 1000mL concentrated HCl in 1000mL MilliQ

7.5N reagent grade Baker HNO₃

Prepared with 1000mL HNO₃ in 1000mL MilliQ

Micro Detergent (International Products)

Type II water (ASTM D1193, MilliQ)

NeutraAcid (Lab Safety)

Cleaning for HgT

50 mL Centrifuge tubes used in the analysis of HgT were cleaned by filling the tubes with micro and soaking in a micro bath for 3 days. The tubes were then triple rinsed with DI. Next, the tubes were filled with 7.5N reagent grade Baker HNO₃ acid by completely submerging the tubes in a bath and placing the caps on while the tubes were in acid. The acid bath was either heated in a hot water bath for 8 hours or left cold for 3 days. The acid bath was allowed to cool and the tubes were removed from the acid and triple rinsed with MilliQ. The tubes were left to dry on clean room Crew Wipers in a Hg free environment, then capped tubes were double bagged with micro cleaned inner bag and new outer bag. The tubes were then ready to be used in analysis.

Cleaning for MMHg

Centrifuge tubes (35 mL Oak-Ridge type all-Teflon™) used in the analysis of MMHg were cleaned by filling the tubes with micro and soaking in a micro bath for 3 days. The tubes were then triple rinsed with DI. Next, the tubes were completely submerged in 6N reagent grade Baker HCl acid bath to fill tubes with acid and the tubes were capped while submerged. The acid bath was heated (>40°C) in a hot water bath for 8 hours. The acid bath was allowed to cool and the tubes were removed from the acid and triple rinsed with MilliQ. The tubes were left to dry on clean room Crew Wipers in a Hg free environment, then capped tubes were double bagged with micro cleaned inner bag and new outer bag. The tubes were then ready to be used in analysis. The cleaning of 60 mL Teflon™ distillation tubes and caps from Savillex (Minnetonka, MN) and tubing were cleaned in the same manner as centrifuge tubes with the added step of

scrubbing thoroughly with an alkaline detergent (Formula 409™) to remove all visible organic deposits prior to soaking the micro bath.

Determination of Total Mercury

Samples are collected, using clean techniques, into 60 mL glass jars with Teflon lined lids. Samples may be stored frozen for up to one year prior to analysis. The analysis of HgT in sediment is done by transferring no more than 2 g sediment (wet weight) into digestion vials, digesting with aqua regia for 4 hours, and diluting the digestate with MQ water. The ionic Hg is reduced to elemental Hg by contact with stannous chloride (SnCl_2) in a dilute HCl solution. Hg is detected using cold vapor atomic absorption spectrophotometry (CVAAS) by a Perkin Elmer Flow Injection Mercury System (FIMS-100) with the software application AA WinLab.

Scope of total mercury analysis

The following method for the digestion of geological and carbon samples to be analyzed for total mercury is summarized from Bloom (1999). Prior to digestion, the sample should be homogenized as thoroughly as possible. When used on fine-grain or powdered samples, recovery by this digestion is complete, but if used on coarse materials such as sand, Hg contained within the mineral grains will not be completely recovered. This method involves leaching the sample overnight by aqua regia (4:1 HCl/ HNO_3) at room temperature. Recovery of mercury in a wide range of geological materials was found to be 90-110% (Bloom 1999).

Aqua regia is not simply a mixture of two acids, but rather, the oxidizing action of concentrated HNO_3 on HCl results in the formation of nitrosyl chloride (NOCl) and free

Cl_2 , which are particularly strong oxidizers. Aqua regia only exists as a concentrated acid species—dilution of aqua regia with water destroys its unique oxidizing capability, rendering it a simple mixture of HNO_3 and HCl . Furthermore, aqua regia loses its strength rapidly after preparation, by loss of Cl_2 to the atmosphere. Aqua regia must therefore always be prepared fresh at the time of use.

Materials

Digestion vials

The digestion is performed in pre-cleaned 40 mL borosilicate glass vials with Teflon lined silicone septa caps (I-Chem series 300™). The vials will contain 40 ± 0.5 mL when filled such that the liquid meniscus is just to the bottom of the vial neck.

Pipettors

Hydrochloric and nitric acids are conveniently dispensed separately from all-glass or glass and Teflon bottle-top repetitive pipettors (0-10 mL size; Re-Pipette™ or equivalent).

Reagents

MQH_2O

Eighteen megohm ultra pure deionized water was produced using a Millipore MilliQ system starting from a pre-purified (distilled, R.O., etc.) source.

Nitric acid (HNO_3) (Baker, reagent grade)

Concentrated (16.0 N) HNO_3 , known to be low in Hg

Hydrochloric acid (HCl) (Baker, reagent grade)

Concentrated (12.2N) HCl , known to be low in Hg.

0.2N Bromine monochloride (BrCl)

To a 2.5 L bottle of concentrated HCl (analyzed and found to be low in Hg (<5 ng/L)) is added 27 g of KBr (Baker, reagent grade). A clean Teflon™ coated magnetic stir bar is placed in the bottle, and stirred for 1 hour, in a fume hood. Next, 38 g of pre-analyzed, low Hg KBrO₃ are slowly added to the acid while stirring. When all of the KBrO₃ has been added, the solution should have gone from yellow to red to orange. Loosely cap the bottle, and allow to stir another hour before tightening the lid. Caution should be taken, as this process generates copious quantities of free halogens (Cl₂, Br₂, BrCl) which are released from the bottle. The KBrO₃ (Baker, reagent grade) must be added slowly and in a well operating fume hood. This solution is stable for one year at room temperature.

0.07 N Bromine monochloride

Dilute 0.33 L of the 0.2 N BrCl solution to 1.0 L with MQ water in a 1000 mL Teflon bottle. This solution is stored at room temperature and is stable for 6 months.

Sediment digestion

Into the 40 mL digestion vial 0.5-2 g of homogenized sample (± 0.001 g) is directly transferred. Eight milliliters of concentrated HCl is added and the sample is swirled to wet all particles. Next, 2.0 mL of concentrated HNO₃ is added and the sample is swirled, then the cap is loosely put on the vial. The samples are allowed to digest in the fume hood, loosely capped, at room temperature, at least 4 hours (typically, overnight) at a room temperature of 18-25°C. Tightening the caps, or heating the samples may cause the vials to explode. At temperatures cooler than 18°C, the reaction is less

vigorous, so that longer digestion times may be necessary. At temperatures higher than 25°C, the reaction can generate much free chlorine, causing some samples to foam over. After the digestion is complete the samples are diluted to 40 mL with deionized water ($\pm$ 0.5 mL; such that the meniscus is just at the bottom of the vial neck). Prior to analysis the samples are shaken vigorously, and allowed to settle until the supernatant is clear. This method will extract all cinnabar, organic, and surface bound Hg but will not solubilize Hg in Aluminosilicate sands.

Calibration and quality control

Working standards are prepared by diluting 1000 ppm mercury (II) oxide (VWR, 0.1% Hg⁰ in dilute nitric acid (w:v)) with blank water (0.5% HCl in MQ, (v:v)) to final concentrations from 50 ppt to 5 ppb by weight. Method blanks are drawn from the same batch of blank water used in the preparation of working standards. Peak height versus standard concentration are plotted and a regression coefficient of $>.980$ is required before sample analysis is initiated. The standard curve is blank corrected and forced through zero.

Aliquots are drawn from digested mercury samples and transferred into and diluted with blank water until sample concentrations fall within working standard end-member concentrations. During sample analysis instrument drift is checked by running a calibration standard and SRM after every 10th sample.

A minimum of three digestion blanks, one digestion duplicate, and a digestion matrix spike/matrix spike duplicate is prepared for each discrete sample set (8-20 samples). Matrix spikes are made at the point that aqua regia is added to the sample.

NIST 1944 certified standard sediment is also digested with each set of samples.

Analysis by flow injection mercury system (FIMS)

HgT Samples are analyzed by Atomic Absorbtion Spectroscopy using a Perkin Elmer Flow Injection Mercury System (FIMS-100) with the software application AA WinLab. A peristaltic pump set to 85 mL/min is used to transport various liquids through the system. The peristaltic pump, in conjunction with an auto-sampler (Perkin Elmer AS-90) draws a 4 mL aliquot of the sample solution into the mixing block. The reducing reagent (1.1 % Tin (II) chloride in 3 % HCl (v:v)) is pumped simultaneously mixing with the sample and a spontaneous reaction takes place, reducing the ionic mercury to elemental mercury. The carrier gas (argon) then carries the mercury vapor to the gas/liquid separator at a flow rate of 50 mL/min. The liquid is pumped to waste, the gas phase continues on to the FIMS-cell, which is the radiation beam of the spectrometer. The radiation source is a low pressure mercury lamp. The detector is a photcell with maximum sensitivity at 254 nm. The FIMS-cell has an inner diameter of 4 mm and an optical path length of 260mm. The cell is heated to 50°C.

The method detection limit for sediment using the above procedures is 10.5 ng Hg per gram dry weight sediment.

Determination of Methyl Mercury

Samples are collected, using clean techniques, into 60 mL glass jars with Teflon lined lids. Samples were stored cold (1-4 °C) and in the dark if analysis was to proceed immediately (within weeks) or frozen for up to one year prior to analysis. To a 0.5-1.0 gram sediment aliquot is added acidic KBr, CuSO₄, and CH₂Cl₂ sequentially. The MMHg in the sample is extracted from the acidic KBr slurry into CH₂Cl₂, and then back into pure water. The distillate is buffered at pH 5 and reacted with sodium tetraethyl borate. Volatile CH₃CH₂HgCH₃ formed from CH₃HgCl is separated from the aqueous matrix by purging onto a Carbotrap™. The trap is thermally desorbed into an isothermal GC column for peak separation, sent through a pyrolytic organomercury breakdown column for conversion to Hg⁰, and then quantified by cold vapor atomic fluorescence spectrometry (CVAFS).

Scope of methyl mercury analysis

The following method for the determination of MMHg in sediments at concentrations of 0.01 to 10 ng/g is directly paraphrased from Bloom (1997). Through the use of smaller aliquots (mL to µL range), contaminated sediments of up to 1,000 ng/g can be directly measured (Bloom 1997). Bloom (1997) reported this method creates a negligible positive bias due to the interaction of ambient inorganic Hg with organic matter, and so is recommended over the distillation procedure in cases where the fraction MMHg to total Hg is expected to be low (<0.1% MMHg). MMHg as defined by this method means all MMHg forms and species found in soils and sediments which are

amenable to complexation and extraction as the bromide. This includes, but is not limited to CH_3Hg^+ , CH_3HgCl , CH_3HgOH , $\text{CH}_3\text{HgS-R}$.

Apparatus and materials

Atomic fluorescence spectrophotometer

The low detection levels and small, interference-free sample aliquots claimed by this method are made possible in part by use of a very sensitive (instrument detection limit $< 1 \text{ pg Hg}$) Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS). The instrument used in this study was a Teckran CVAFS detector with the following components:

1. Low pressure mercury vapor lamp (253.7 nm light source).
2. Far UV quartz flow-through fluorescence cell: 12 mm x 12 mm x 45 mm long, with a 10 mm path length.
3. UV-visible photometer: Photomultiplier sensitive to 254 nm isolated from the outside light with a 254 nm interference filter.
4. Flow meter: Flow meter with needle valve capable of reproducibility keeping carrier gas flow at 30mL/min.

Isothermal GC unit

A 1.3 meter packed GC column is made to the following specification: The column is made of 6.4 mm OD, 4.8 mm ID FEP tubing (Cole-Parmer). The tubing is formed into a 8 cm diameter coil of 1.0 m length with two 15 cm arms extending in parallel up from the coil. The column is packed with 1 m (in the coil section only) of preconditioned 60/80 mesh 15 % OV-3 on Chromasorb™ WAW-DMSC, held in place

with silanized glass wool plugs. The column is held in a small temperature-controlled isothermal oven (Glas-Col™ TM-580) interfaced with a Chromalox™ model 3910-11108 temperature controller. The column is held at a constant temperature of $110 \pm 2^\circ\text{C}$.

Pyrolytic organomercury breakdown column

The pyrolytic column is made from a 20 cm length of 7 mm O.D. by 4.5 mm I.D. quartz tubing with the central 10 cm packed with quartz wool. The column is wrapped with 1.5 m of 22 ga Nichrome wire which is electrically heated to about 700°C (bright orange) with 30-34 volts from an variable auto-transformer (Staco, 120V input, 0-140 V output).

Flow meter/needle valve

Flow meters must be capable of controlling and measuring gas flow to the purge vessel at 200-500 mL/min.

Teflon™ fittings

All components and columns are connected using 6.4 mm O.D., 4.8 mm I.D. Teflon™ FEP tubing, and Teflon™ friction-fit or threaded tubing connectors. Some connections between components require mobility and for these cases 3.2 mm O.D., 1.6 mm I.D. Teflon™ tubing is used, due to its greater flexibility.

Ethylation reactor/purge vessel

A 125 mL Florence flask with standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit which extends to within 0.2 cm of the flask bottom is used as an ethylation reactor/purge vessel during all wet chemistry reactions.

Carbotrap™ columns

Carbon Traps are made from 10 cm lengths of silanized 6.5 mm O.D. x 4 mm I.D. quartz tubing, with a slight crimp 2.0 cm from one end (end "A"). First, a small plug of silanized glass wool is placed into the tube, from the non-crimped end, and compressed firmly against the crimped region for support. Next, the tube is filled with 3.4 cm of Carbotrap™ (30/40 mesh), and the end plugged with silanized glass wool. Carbotrap™ columns are heated to 400-450 °C with a coil consisting of 75 cm of 24 ga Nichrome wire at a potential of 10 VAC. Potential is applied and finely adjusted with an variable auto-transformer (Staco, 120V input, 0-140 V output).

Solvent evaporator system

A temperature controlled aluminum block heated to 45°C and a purge tube delivering N₂ at a rate of 100 ± mL/min is used to drive off CH₂Cl₂ during the extraction procedure. For best results, the purge tube must be pushed into the distillation tube until it is touching the bottom (Bloom 1997). Purging of CH₂Cl₂ must be done in a venting fume hood to avoid exposure to potentially carcinogenic fumes.

Gold coated sand trap

The trap is made from a 20 cm length of 7 mm O.D. by 4.5 mm I.D. quartz tubing with the central 3 cm filled with gold coated sand (Brooks Rand) held in place with quartz wool plugs.

Reagents

MQH₂O

Eighteen megohm ultra pure deionized water was produced using a Millipore MilliQ system starting from a pre-purified (distilled, R.O., etc.) source is used in all mercury analysis. Water should typically contain less than 0.2 ng/L total Hg, and remedial action should be taken if the total Hg exceeds 1 ng/L. MMHg should be undetectable in reagent water (Bloom 1997).

Potassium Bromide Extraction Solution

Fifty milliliters of H₂SO₄ is slowly added to ~750 mL of MQ water. To the mixture is added 180 grams of reagent grade KBr. The solution is brought up to 1000 mL by weight. To the solution is added 0.2 grams of reagent grade NH₂OH·HCl as a redox preservative. This solution must be stored refrigerated, and in the dark to avoid oxidation of bromide to free Br₂. This solution should be replaced monthly or if it appears to be developing a yellowish color.

1 M CuSO₄ Solution

To MQ water is added 25 grams of CuSO₄·5H₂O and the solution brought up to 100 mL by weight. This solution has an indefinite storage time at room temperature.

Methylene Chloride

HPLC grade CH_2Cl_2 is used and new lots of solvent are blank checked as they are sometimes contaminated with low levels of MMHg. Caution is used while handling CH_2Cl_2 as it is a suspected carcinogen!

Acetate buffer

Two moles of reagent grade sodium acetate (272 g) and two moles of reagent grade glacial acetic acid (118 mL) are dissolved in MQ water to give a final volume of 1.0 L. This solution is stored at room temperature in a Teflon™ bottle with an indefinite shelf life.

Sodium tetraethyl borate solution

One hundred milliliters of a 2% KOH solution is prepared in a Teflon™ bottle, and chilled to 0°C. A 1.0 g air-sealed bottle of NaBEt_4 is opened and 5 mL of the KOH solution is poured in. The reagent bottle is capped and shaken to dissolve the NaBEt_4 . The dissolved NaBEt_4 is then poured into the 2% KOH solution, and shaken to mix. Immediately, the 1% NaBEt_4 in 2% KOH is poured into fifteen 7 mL Teflon™ bottles, which are capped and kept frozen. For use, one of these bottles is removed and thawed until just forming a liquid layer. The reagent is then used until just before all of the ice is melted. This reagent must not be exposed to air for a prolonged period of time. The frozen bottles will keep for at least one week. If any doubt arises about the quality of the ethylating reagent, make a new batch, as the old material often gives good results for D.I. water spikes, but not for environmental samples. Do not use NaBEt_4 solid or solutions if they have a yellow color.

Methylmercury stock solution

A 1 ppm MMHgCl standard solution was purchased from BrooksRand Inc.

Methylmercury working solution

Dilute 0.250 mL of the 1 ppm standard into 250 mL of reagent water containing 0.4% HCl. This makes a 1.00 ppb working standard.

QC check sample (dogfish tissue SRM)

Certified dogfish tissue (DORM-2) from the National Research Council of Canada. This material contains $4,470 \pm 370$ ng/g, and is prepared by digesting 1.000 gram of material in 20 mL of 25% KOH in methanol, and then diluting to 1000.0 mL with methanol (Bloom 1989). Aliquots of 0.025 mL are analyzed, as described for standards in this method.

Nitrogen

Standard laboratory grade (Grade 4.5) nitrogen which has been further purified by the removal of Hg using a gold-coated sand trap.

Argon

Ultra-high purity (Grade 5, GC grade) argon which has been further purified by the removal of Hg using gold-coated sand trap prepared as above.

Calibration and quality control

Calibration data is composed of three system (bubbler) blanks and 5 standards (.002-.200 ng range) achieving a linear regression coefficient (r) greater than 0.995. The calibration is run initially each day, and verified with a mid-range check standard at least every 10 samples. The analytical day ends with a check standard.

Definitions

An “Analytical Set” is 20 or fewer samples with the same matrix/analyte combination.

An “Instrument Blank” is performed by the analysis of a blanked Carbotrap™ to which no mercury has been added.

The “Method Blank” is the blank that is obtained from the extraction of reagent water, using exactly the reagents and procedures as for sediment samples.

The Method Detection Limit (MDL) was determined as three times the standard deviation of 20 method blank replicates.

Calibration procedures

At the start of analytical set an instrument calibration curve is prepared using five standards and three blanks. The standards spanned 0.002-0.200 ng MMHg. The linear correlation for the calibration curve must be >0.995. A mid-level QC check standard was used every 10th sample for continuing calibration. The check standard must not differ by more than 25% from the initial check standard.

Quality control analysis

Each analytical set carried three method blanks, a duplicate, matrix spike, matrix spike duplicate, and QC Check sample initially, after every 10th sample, and at the end of each analytical day.

Sample preparation and extraction

Sediment samples were kept frozen prior to analysis. Samples were then thawed at 10°C overnight. The 60 mL sample jar was placed on a magnetic stirrer and a Teflon™

stir bar was placed gently in the jar to avoid splashing of the sediment slurry. The tip (~5 mm) was cut off of a 1 mL pipette and this was used to transfer sediment aliquots, up to 1.00 gram wet weight, into 35 mL centrifuge tubes(Oak-Ridge type all-Teflon™). To each sample is sequentially added 5.0 mL of acidic bromide solution, 1.0 mL of the 1 M CuSO₄ solution, and 10.0 mL of CH₂Cl₂. After the addition of the reagents the samples are allowed to sit undisturbed for 1 hour in the dark. Next, the samples are shaken vigorously for 1 hour using a mechanical wrist action shaker (Burrell, model 75). To prevent exposure to light the centrifuge tubes are placed in pairs into plastic bags wrapped with tape prior to loading into the wrist shaker. After shaking, the tubes are centrifuged at 3000 RPM for 20 minutes at 10°C to separate the organic and aqueous phases. After centrifugation the upper aqueous layer is removed and discarded using a 3 mL plastic disposable pipette. A glass syringe is used to transfer 2 mL of the CH₂Cl₂ solution (bottom layer) into a clean 60 mL Teflon™ distillation vial containing 40 mL of DI water. The syringe is triple rinsed with CH₂Cl₂ prior to working with samples and between each sample transfer. After all the samples have been similarly aliquoted Teflon™ lids are attached to the distillation vials. The lids are equipped with two 1/8" fittings at 90° angles (one upward one outward). Tubing (1/8") is cut to lengths of 1' and placed into the upward facing fitting of the lid and extended down to 0.5 cm above the bottom of the vial. The vials are placed in an aluminum heating block held at 45°C and purged with nitrogen until all the CH₂Cl₂ has been volatilized out of the samples. Forty minutes of purging at 45°C is usually sufficient to volatilize all of the solvent. The samples are removed from the heating block and diluted to the 57.6 mL line (molded into

Teflon™ vials) with MQ, and capped until analysis by aqueous phase ethylation. The samples are kept at room temperature in the dark for up to 48 hours prior to analysis.

Sample analysis

Reaction vessels are filled with 50 mL MQ water (for standards, SRM's, and bubbler blanks) or a fraction of the aqueous extract brought up to 50 mL with MQ and 300 µL of acetate buffer followed by 35 µL of fresh sodium tetraethyl borate solution are added successively, with swirling after each addition. The cap of the bubbler is replaced and the contents swirled to mix. The bubblers are allowed to stand 20 minutes undisturbed to react. The Carbotrap™ column is placed on the output of the bubbler using a Teflon™ fitting, in such a way that the "A" end is facing the bubbler. The bubbler is connected to the nitrogen purge gas and the sample is purged for 17 minutes at a flow rate of 200-400 mL/min. Next, the trap is removed from the bubbler, and connected directly to the nitrogen purge gas, with the nitrogen entering the "A" side, for 10 minutes. The dried Carbotrap™ column is connected to the input side of the isothermal G.C. column with a Teflon™ fitting so that the "A" end of the Carbotrap™ column faces the G.C. column. This allows the mercury compounds to travel the shortest route to the G.C. column, minimizing on-trap thermal breakdown. A Nichrome wire coil wound to supply about 400°C (i.e. 0.85 m of 22 ga Nichrome wire, with 12 VAC current supplied via an auto transformer) is placed around the Carbotrap™, and argon carrier gas (25 mL/min; 10 psi) is connected to the open end of the Carbotrap™. The output side of the G.C. column passes via 3.2 mm O.D., 1.6 mm I.D. Teflon™ tubing first

through the pyrolytic breakdown column, then the CVAFS cell, and finally through a flowmeter.

Argon is allowed to flow through the column at least one minute before the Carbotrap™ column is heated with the Nichrome coil for a period of 30 seconds, transferring the mercury species to the G.C. column. According to (Bloom 1997), mercury species are eluted according to molecular weights, with the following peaks being typical:

- 1) A peak at about one minute corresponding to Hg^0 , usually a decomposition product of diethyl mercury, as Hg^0 is not trapped by Carbotrap™. A small Hg^0 peak is always present simply due to Hg released upon heating the Carbotrap™.
- 2) A peak at about 2.1 minutes corresponding to methyl ethyl mercury. This is the peak of interest, the ethylation product of methyl mercury.
- 3) A peak at about 4 minutes corresponding to diethyl mercury, resulting from the ethylation of Hg(II) -- inorganic in the reagents and sample. This is not quantitative for Hg(II) however, as most Hg(II) is excluded by the distillation procedure.
- 4) A small broad peak at approximately 7 minutes may sometimes be seen, especially in cases where a high diethyl Hg peak (i.e., high Hg(II) in the sample) is seen. This is monoethyl Hg, which occurs due to thermal breakdown of a small fraction of the diethyl Hg present. This peak should be ignored, although its presence suggests that new Carbotraps™ should be

prepared, as thermal breakdown of the organomercurials is the effect of degraded traps. The diethyl Hg will be seen to break down long before the methyl ethyl Hg (methyl Hg peak), giving sufficient warning to prepare new Carbotraps™.

Calculations

The following calculations are made to determine the amount of MMHg in a sediment sample:

1. The slope of the calibration curve A (chart units/ng) is calculated using a spreadsheet and the five initial calibration points. The calibration points are bubbler blank corrected and the regression line is forced through the origin (0,0).
2. The mean bubbler blank b (in chart units) is determined as the mean of at least three bubbler blanks analyzed with the same analytical set of samples.
3. The sample is S (in chart units).
4. The diluted volume V (mL) is generally 57.6 (using the molded-in line on the 60 mL distillation vials).
5. The aliquot volume v (mL) is from 0.1 to 57.6 mL depending on the concentration of MMHg in the samples.
6. The factor of 5 represents the 2/10 dilution of the methylene chloride extract taken back into the aqueous sample.

7. The mass m is the amount of sediment (to the nearest mg) weighed into the centrifuge tube.
8. The method blank B (ng/sample) is the mean of at least three blanks processed exactly as the samples.
9. The following formula is used to calculate the concentration of MMHg in a sample:

$$\text{MMHg(ng/g Hg)} = \{5 \cdot (V/v) \cdot (S-b)/A\}/m$$

Interferences

For best results doing low level mercury research, it is important that the laboratory air be low in both particulate and gaseous mercury. Many existing laboratories have permanently elevated room air levels (up to hundreds of ng/m³) due to broken thermometers, use of Hg salts as reagents, and Hg preserved paints on the walls. Ideally, mercury measurements should be conducted in a new laboratory with Hg-free paint on the walls. Outside air, which is very low in Hg, should be brought directly into the class-100 clean air station intakes. Also, atomic fluorescence intensity is strongly dependent upon the inertness of the carrier gas. High purity inert carrier gas and a leak-free train is essential to this method. In these studies, Argon was used as the carrier gas.

Sample containers should not be made from ordinary plastic (polyethylene, polypropylene or vinyl) as they are very permeable to Hg⁰ gas from the air. The best containers are made of hot-acid cleaned Teflon™, although Borosilicate or quartz glass bottles with Teflon™ lined lids are acceptable. In this study 60 mL Borosilicate jars with Teflon™ lined lids were used for all sediment collections. No HNO₃ or other oxidizing

agents (Cl_2 , BrCl , CrO_4^- , etc.) may be present in the sample, or MMHg may be destroyed. All acid washing of apparatus which may come into contact with the sample and sampling containers should be done with hot HCl only. Particular care must also be taken to eliminate the chlorine present in municipal water which feeds the deionized water system, by passing it through an activated carbon bed.

Positive interferences and poor baselines can result by water vapor condensing on the interior of the fluorescence cell. This problem is avoided by paying careful attention to the Carbotrap™ drying step.

Carbotrap™ columns must be kept track of by unique identifiers, so that any trap producing poor results can be quickly recognized and discarded. Occasionally, due to inadvertent contact with bubble solution, organic fumes, or overheating, a sampling column will become damaged, giving low and irreproducible results (Bloom 1997). Suspect columns should be checked with at least two consecutive standard runs before continued use.

The major cause of analytical problems with this method is from exhausted or poor quality sodium tetraethyl borate solution. This solution must be replaced weekly to minimize this likelihood. Also, the use of excess sodium tetraethyl borate results in an interference due to signal quenching by co-generated gaseous triethyl boron (Bloom 1997).

When performed correctly this methodology is virtually interference free (Bloom 1997).

RESULTS

Geographical Survey

HgT in the Bay-Delta decreased moving north to south from the northern tributaries of Prospect Slough and Cosumnes River into the central and southern Delta (Figure 6). HgT concentrations of sediments in the northern tributaries were as high as 0.5 ppm in contrast to the central Delta with mercury concentrations from 0.1-0.3 ppm. The southern Delta sediments typically had very low HgT concentration and the greatest cluster of samples below the method detection limit (MDL) were found in the southern portions of the Delta.

A second spatial trend observed was an increase in HgT, by a factor of two (0.15 to 0.30 ppm), moving east to west from the central Delta into Suisun Bay and Grizzly Bay (Figure 6). The Carquinez Straight, Suisun Bay, and Grizzly Bay areas had a large number of sites with high HgT concentrations. Generally, sediments in the bays averaged 0.3 ppm with some sites above 0.5 ppm HgT. The increase in HgT concentration moving out of the Delta was independent of changes in grain size as the normalized (data not shown) and un-normalized HgT concentration versus longitude yield similar correlation coefficients.

In contrast to the geographic patterns of HgT, MMHg generally increased from north to south moving into the central Delta from the northern tributaries (Prospect Slough and Cosumnes River) (Figure 7). The central Delta consistently had higher MMHg concentrations than the perimeter waterways and adjacent bays. MMHg concentrations were very low or non-detectable (MDL= 0.019 ppb) in the Sacramento

River and San Joaquin River channels moving west, out of the central Delta. At the convergence of the Sacramento and San Joaquin Rivers (Sherman Island area) MMHg concentrations increased to values as high as many of the central Delta sites (Figure 7). Joyce Island in Grizzly Bay had the highest MMHg sediment concentration (9.3 ppb) of all sites sampled in the North Bay and Delta.

The ratio of MMHg to HgT was used to identify locations within the Bay-Delta with high mercury methylation potential (Figure 8). The central Delta had the greatest potential for mercury methylation; many sites in the central Delta had greater than 2 % of the HgT as MMHg. Franks Tract had the largest measured ratio (2.6 %). In addition, a few sites within the central Delta appeared to have large methylation potentials as HgT concentrations were below the MDL and a considerable amount of MMHg was present (Figure 8- grey scale bars). However, the ratios at these sites were estimated using the MDL value of 10.5 ppb as a value for HgT and, therefore, must be considered only as estimated potentials. All of the tributaries surrounding the central Delta (e.g. Prospect Slough, Cosumnes River, Sherman Island, the upper San Joaquin River, and southern Delta) had very low mercury methylation potentials. Although Honker Bay had many sites with relatively high MMHg concentrations only one site (Joyce Island) showed a large potential for mercury methylation (2.3 % MMHg). A comparison of the methylation potential of the central Delta and the surrounding tributaries indicates the central Delta possesses environmental conditions favorable for mercury methylation.

Figure 9 shows MMHg concentration plotted against percent LOI for sediment samples collected during the survey. A positive relationship is shown between MMHg

and percent LOI (Pearson's $r^2 = 0.32$, $n = 61$, $p < 0.01$). LOI was found to be between 0- 5 percent. A limited number of samples had MMHg concentrations of 2 ng/g with the majority being below 1 ng/g.

Figure 10 shows MMHg concentration plotted against HgT for sediment samples collected during the survey. A weak positive relationship is shown between MMHg and HgT (Pearson's $r^2 = 0.19$, $n = 99$, $p < 0.01$). This relationship is dependent on excluding 4 points having the highest MMHg concentrations (1.5-2.0 ng/g). HgT concentrations were found to range between 15-500 ng/g. A tabular list of the ancillary and mercury data collected during the geographical survey is given in Appendix B, Table A2-1 & A2-2.

Seasonal Study

Solid phase MMHg showed distinct seasonal patterns at locations within the central Delta and Cosumnes River (Figure 11, panels c-f). MMHg concentrations at Franks Tract, Connection Slough, and Cosumnes River were elevated twice per year (Figure 11, panels c, d, f). The largest peak occurred during summer and the smaller peak occurred over winter. The winter peak, although lesser in magnitude (~2 ng/g), was generally a longer lasting feature (3-4 months) while the summer peak reached a maximum (~6 ng/g) and decreased within 1-2 months. MMHg in the sediments at Prospect Slough remained constant (~1 ng/g) over the length of the study (Figure 11, panel a). Sherman Island had an extended period of elevated solid phase MMHg concentration summer and fall of 2000, followed by a decrease in concentration throughout the remainder of the study (Figure 11, panel b).

HgT sediment concentrations showed no seasonal trends (Figure 11, panels a-f). However, at Sherman Island, HgT concentrations were higher during the first half of the study and generally decreased throughout the second half of the study; a similar trend was found for MMHg (Figure 11, panel b). HgT concentrations demonstrated increased variability at Prospect Slough and Sherman Island, as compared with the central Delta and Cosumnes River. The largely variable HgT concentrations at Prospect Slough and Sherman Island may be the result of bias due to changes in mean grain size, as high water flow and a scoured bottom characterize these locations. Within the central Delta, White Slough had the least variable HgT concentrations, and Cosumnes River consistently had the highest HgT concentrations (Figure 11, panel e, f).

A plot of MMHg versus HgT for the six seasonal locations is shown in Figure 12. No correlation between HgT and MMHg was found when data from all six locations was combined. However, if only the Sherman Island site is considered, there was a positive linear relationship between MMHg and HgT ($R^2 = 0.40$). See Appendix B, Table A2-3, for a tabular list of all the seasonal study data.

Bioavailability Study

The comparisons of Coastal versus Sierra range lakes, mountain streams, and valley streams HgT concentrations, MMHg concentrations, and the MMHg to HgT ratios in unsieved sediment samples are shown in Figure 13. Coastal and Sierra range lakes had equivalent levels of HgT, MMHg, and MMHg to HgT ratios. HgT concentrations were much higher (18,000 ng/g) in Coastal mountain streams, near mine sites, than Sierra mountain streams (49 ng/g) and slightly higher in Coastal valley streams (122 ng/g) than

Sierra valley streams (33 ng/g). MMHg concentrations were equivalent in Coastal and Sierra mountain and valley streams. The MMHg to HgT ratios in Sierra mountain and valley streams were significantly higher than coastal mountain streams. However, it is important to point out the large standard error associated with the Sierra valley stream data and the extremely high concentrations of HgT at many of the Coastal sites.

In an attempt to reduce any bias introduced by grain size variability and determine the methylation potential of only the fine-grained fraction, samples were sieved through a 60 μ m screen. Figure 14 shows comparisons between Coastal and Sierra range lakes, mountain streams, and valley streams HgT concentrations, MMHg concentrations, and the MMHg to HgT ratios in sieved sediment samples. Trends in HgT and MMHg of sieved samples are similar to unsieved samples (Figures 13 & 14). Both Coastal and Sierra range lakes had equivalent HgT, MMHg, and MMHg to HgT ratios (Figure 14). HgT concentrations were higher in Coastal mountain and valley streams than Sierra mountain and valley streams while MMHg concentrations were equivalent. The MMHg to HgT ratio in Sierra mountain streams was significantly higher than Coastal mountain streams but, unlike the unsieved results no difference was found in the MMHg to HgT ratios of Coastal and Sierra valley streams.

The permanent lakes were significantly lower (Least Significant Difference multiple comparison test, $p < 0.05$) in MMHg concentration and the MMHg to HgT ratio than valley or mountain streams (Figures 14). This is in contrast to the seasonal lakes (Capay Dam and Cache Creek Settling Basin) in which some of the highest concentrations of MMHg occurred (8 and 4 ng/g dry weight sediment respectively). A

tabular list of the mercury bioavailability study data is given in Appendix B, Table A2-4 & A2-5.

Wetland Study

Results from the across channel transect at Columbia Cut are shown in Figure 15. A depth profile of the channel is given in meters as is a brief description of the sediment type. Both the percent MMHg and HgT are given in a log scale for each station along the transect line. The percent MMHg is an order of magnitude higher in the fringe peat banks than any other habitat sampled along the transect line and is slightly higher in the vegetated shallow than in the deeper channel and sandy shallow. This indicates the fringes wetlands are most efficient at Hg methylation.

The results of wetland studies comparing MMHg concentrations in the interiors of the marshes, half way out of the marshes, and outside of the marshes at three locations are shown in Figure 16. In every case the MMHg concentrations at the interior of the wetlands were higher than at the exterior or adjacent waterways. Figure 17 shows the MMHg to HgT ratios for interior, halfway out, and adjacent waterways at the same locations. The methylation efficiencies were highest at the interior of all three marshes studied. The percent MMHg was as high as 3 % in the interior compared to less than 1 % in the adjacent waterways. The use of correlation analysis indicated that LOI was significantly correlated to both MMHg ($p < 0.001$) and the MMHg to HgT ratio ($p < 0.001$) (Data not shown). For a tabular list of all mercury wetland study data see Appendix B, Table A2-6 & A2-7.

MMHg Flux and Loads

A positive correlation between MMHg sediment concentration and MMHg flux from the sediment is shown in Figure 18. The upper boundary for converting MMHg concentration into MMHg flux is 5.3 ng/g and the lower boundary is 0.49 ng/g. Flux is calculated from MMHg sediment concentration using the equation:

$$\text{MMHg flux (ng m}^{-2} \text{ day}^{-1}) = 31.12 [\text{MMHg}]_{(\text{ng/g})} - 15.25$$

Using this proxy it was possible to convert MMHg sediment concentrations into MMHg flux numbers.

Table 5 shows the average MMHg sediment concentrations and standard errors for each habitat type sampled in the initial survey. The habitat type and corresponding area is also listed. The number of samples taken within each habitat type is shown in parenthesis within the habitat type column. Two habitat types had corresponding MMHg concentrations below the lower boundary set by the proxy and as a result the concentrations could not be converted in fluxes. No samples were collected from salt ponds but the area is shown to be insignificant when compared to other habitat types. MMHg concentrations for six habitat types were converted to MMHg flux and using the area of the habitat the flux values were converted to MMHg loads (Table 5). The flux of MMHg based on habitat fell out into two distinct groups. Marsh habitat, lakes and ponds, and farmed wetlands had higher MMHg flux than did seasonal wetlands, open water, and mudflats. The same trend occurred for MMHg loads. For a tabular list of all MMHg flux data see Appendix B, Table A2-8.

DISCUSSION

Geographical Survey

A survey of the Bay-Delta MMHg distribution indicated that sediments in the major tributaries are relatively low in mercury compared to the central delta (Figure 7). In addition, locations within the central delta were found to have the highest methylation potentials (Figure 8). Concurrent studies of Hg levels in game fish and prey items (small fish and invertebrates) found significantly higher mercury concentrations in biota collected in the tributaries than collections from the central delta (Davis et al. 2002a, Foe et al. 2002a, Slotten et al. 2002). An examination of the sediment and biota data leads to a working hypotheses that solid phase MMHg is decoupled from the processes driving Hg bioaccumulation on small spatial scales in the Bay-Delta. However, it is important to keep in mind that the sediment data presented in Figures 6-8 illustrates only a single sampling event which took place during a time when the Bay-Delta is characterized as having colder water temperatures, larger current velocities, and low primary production. A quite different MMHg spatial distribution may be found if the same survey were to be conducted during a time of warmer water temperatures, lower water flows, and higher primary production. Future work to investigate this paradigm is clearly justified and, if it holds true, sets the Bay-Delta apart from other studies of Hg cycling in the Chesapeake Bay and Florida Everglades. These studies have shown clear linkages between MMHg sediment concentration and MMHg in biota (Gilmour et al. 1998, Mason and Lawrence 1999).

The Hg distribution maps (Figures 6-8) produced from the initial survey are helpful in that they give a broad look at the region and identify both locations of more serious contamination as well as locations not severely impacted by pollution. They also show the large spatial variation Hg exhibits throughout the system. This information is useful for identifying general trends leading to the development of the paradigm described above. In addition a larger view can point to specific areas that may be in need of more detailed work. For example, if a study is interested in the process of Hg methylation it is desirable to go to a location with a large MMHg to HgT ratio, thus insuring a maximum signal of the process to be studied.

The relationship between MMHg and organic carbon (Figure 9) identifies organic carbon as a possible factor among several influencing the production of MMHg within the Bay-Delta. This is not a unique finding as numerous field-based studies have shown MMHg to be positively correlated with organic carbon in sediments as increases in organic carbon generally stimulate an increase in bacterial activities including sulfate reduction (Choi et al. 1994, Hurley et al. 1998, Krabbenhoft et al. 1999). In addition, lab based studies have shown that organic carbon is positively correlated to MMHg production (Olson and Cooper 1976, Furutani and Rudd 1980, Wright and Hamilton 1982, Lee and Hultberg 1990). An interesting point is the narrow range of LOI (0-5 %) found during the survey. This is lower than what was expected as other studies have reported values as high as 7 % for agricultural areas within the Bay-Delta (Krabbenhoft et al. 1999). Furthermore, other agricultural areas have been reported to have as much as ~20 % LOI (Krabbenhoft et al. 1999). Two factors may account for the low range in

LOI: 1) the data was collected during a period of very low productivity in the estuary, and 2) the sampling missed locations containing larger quantities of organic carbon such as interiors of marshes.

In addition to organic carbon, HgT was investigated as a possible factor influencing the production of MMHg. Regnell et al. (1997) indicated that HgT correlated positively with MMHg in surficial sediments of a seasonally stratified lake in southern Sweden. One of the reactants in the mercury methylation reaction is Hg^{2+} therefore the concentration of Hg^{2+} in a system might be expected to have an effect on the rate of formation and concentration of MMHg (Kelly et al. 1995). Rudd and Turner (1983) reported a linear relationship between amount of Hg^{2+} added to lake sediments and rate of formation of MMHg, demonstrating that in a system where all else remained constant, methylation was first order with respect to mercury concentration.

In data collected during this survey, a positive correlation was found between MMHg and HgT concentrations in sediments (see Figure 10). The correlation between MMHg and HgT indicates HgT may play a role in the production of MMHg, however, the correlation is weak and is only achieved by eliminating the outlying data points (4% of the data). The large range in HgT sediment concentrations with little production of MMHg was unexpected considering the extremely high levels of Hg in the biota. Concurrent studies looking at Hg levels in fish found that large mouth bass, striped bass, Sacramento pike minnow, channel catfish, and white catfish all had elevated Hg concentrations of a high potential human health concern (Foe et al. 2002a).

Two factors must be considered when examining the results of the correlation analysis between MMHg and HgT for the initial survey. First, the survey was done during a time that Hg methylation was likely inhibited due to temperature and microbial substrate availability. Second, while the survey was able to sample the majority of the habitat types found in the delta, it was largely weighted towards the channeled waterways, a portion of the delta which has been highly modified and likely does not represent more critical habitats, thought to be good methylators of Hg, such as the fringes and interiors of marshes.

In a study of the Florida Everglades, factors such as wetland density, low surface water pH, and sulfide were shown to be important in controlling MMHg production (Gilmour et al. 1998). It is possible that factors other than organic carbon and HgT may have a much stronger influence on the production of MMHg in the Bay-Delta. Strategies to control MMHg production in the Bay-Delta will need to consider the relative importance of HgT, organic carbon, as well as other factors mentioned above. Currently, the relative contribution to which each of these factors influences MMHg production in the Bay-Delta is unknown yet studies that will include pH, SO_4^{2-} , O_2 , DOC, TOC, and wetland density are being planned. These factors are thought to relate directly to the microbial activity of sulfate reducing bacteria, the primary methylators of Hg in these sediments.

Seasonal Study

A clear seasonality to MMHg production was found at four of the six locations sampled (see Figure 11). For much of the year MMHg concentrations in the Bay-Delta

sediments are 2 ng/g or less, however, for a brief period concentrations may increase by as much as a factor of three. This finding further emphasizes the need for large scale surveys of the Bay-Delta in both warm and cold seasons, as the Hg concentrations and distributions may be quite different in summer versus winter. In addition, future work aimed at understanding processes of Hg methylation may benefit by conducting studies during the periods now known to have increased MMHg production.

One question that arises when looking at the seasonal data is the absence of an increase in MMHg during the summer of 2000 (exception is Connection Slough)(see Figure 11, panels c, e). This may be explained by the frequency of sampling during the summer of 2000. The sampling frequency was once per month at Franks Tract and White Slough during the summer of 2000, and it is probable that this interval allowed the summer peaks to go undetected. The 2001 summer peak at Franks Tract occurred very rapidly, and sampling twice per month was necessary to capture the event. Gill et al. (1999) also reported a rapid seasonal increase and decrease of MMHg, which necessitated frequent sampling during a study in Lavaca Bay, Texas. Sampling in higher temporal resolution will be necessary to substantiate this hypothesis.

Bloom et al. (1999) used the MMHg to HgT ratio in sediments to evaluate the seasonal variation of mercury methylation. Gilmour et al. (1998) found MMHg concentration was controlled by *in situ* production of MMHg in the Florida Everglades. The seasonal changes in sediment MMHg concentration observed in the Bay-Delta were likely the result of increased *in situ* production resulting from a stimulation of the microbial activity within the sediments rather than an external source of MMHg. The

MMHg to HgT ratio was driven by changes in MmHg and this is evidence of *in situ* production. Additional evidence for *in situ* production is found by looking at the pore water concentration gradients. MmHg concentration of pore water was always higher than the overlying water suggesting the production was occurring within the surficial sediments (Gill 2002).

Sulfate reducing bacteria are especially important methylators of mercury (Gilmour et al. 1992). Factors that increase sulfate reduction rates, such as high water temperature, high availability of organic carbon, and high sulfate concentrations are likely to increase the production of MmHg (Compeau and Bartha 1985, Gilmour et al. 1992).

Water temperature in the Delta fluctuates annually following a sinusoidal curve with maximum summer water temperatures of approximately 20 °C and winter minimum temperatures of approximately 10 °C. Consistent with the findings of Gilmour et al. (1998) in a study of the Florida Everglades, MmHg sediment concentrations in the Bay-Delta were elevated during periods of warm water temperatures.

Although results from the survey indicate percent LOI is a factor in MmHg production, seasonal increases in MmHg occur independent of changes in LOI (data not shown). A possible explanation is the insensitivity of the LOI determinations to the quality of the carbon present (C:N ratio, Protein: Carbohydrate, etc.). Stimulation of microbial activity and any resultant production of MmHg are dependent in part on the availability of labile carbon; LOI is a description of the total amount of material lost on ignition, both labile and refractory. Sediments containing a large fraction of refractory

material such as peat would give a high value for LOI with little benefit to the microbial community.

There was no relationship between HgT and MMHg concentrations at five of the six seasonal study sites (see Figure 12). The highest MMHg concentrations occurred over a broad range of HgT concentrations. In contrast to the overall picture, however, if only the Sherman Island site is considered, there was a positive linear relationship between MMHg and HgT ($R^2 = 0.40$). A predictive model of MMHg based on HgT concentrations determined from only the Sherman Island data may not be useful on a delta-basin wide scale as it appears changes in environmental conditions negate the first order relationship between HgT and MMHg.

Foe (2002) gives monthly chlorophyll a (Chl a), sulfate, and temperature values at Cosumnes River for February through October, 2001. Using the data of Foe (2002) and combining it with the coinciding monthly MMHg sediment concentrations it was possible to compare changes of these constituents during the summer increase in MMHg production (Figure 19). It is clearly shown that the summer increase in MMHg coincides with elevated water temperatures, increased primary production, and elevated sulfate concentrations. Sulfate concentrations are shown to be high with no elevations in MMHg during a time of very cold water temperatures. As water temperature rises sulfate concentrations fall. At the time of increased MMHg production water temperature is high, sulfate concentration is back up and chl a concentrations are high suggesting phytoplankton may, in part, play a role in the methylation of Hg, most likely as a source of labile carbon to the microbial community. This is a limited dataset and more samples

will be necessary to confirm the trends found at Cosumnes River. These findings illustrate the importance temperature plays in MMHg production in the Bay-Delta. The evaluation of this data also indicates that it is likely a combination of factors occurring simultaneously that control the production of MMHg.

Determining definitive primary factors responsible for the seasonal increase in production of MMHg for the Bay-Delta was beyond the scope of this study. This was the first seasonal study of HgT and MMHg in Bay-Delta sediments and initial results show increases in temperature, organic carbon, and sulfate promote MMHg production. The use of HgT concentration as a predictor of MMHg production was useful only in locations where seasonal changes in environmental conditions were minimal. Further research is needed to understand the processes and optimal combination of environmental factors that promote mercury methylation during spring and summer in the Bay-Delta.

Bioavailability Study

During the California gold rush era, mercury was mined in the Coastal mountains and transported to the Sierra Mountain Range for use in Gold mining. Mercury mined from the Coastal range was in the form of cinnabar (HgS) while the Sierra Range was contaminated exclusively with refined mercury (elemental). These forms of mercury have very different behaviors in terms of reactivity and solubility. The following discussion is aimed toward the question: Are the mercury species found in the Coastal and Sierra mountain ranges equally available for mercury methylation (bioavailable)? Finding dissimilar MMHg to HgT ratios in the Coastal and Sierra range watersheds

would be evidence that mercury in the Coastal and Sierra ranges are not equally available for methylation.

The most significant finding of the mercury bioavailability study was the higher methylation potentials (greater bioavailability) of sediments from the Sierra mountain streams compared to Coastal mountain streams (Figures 13-14). This is perhaps a problem of definition as the HgT concentrations near the mine site stations, in the Coast Range, are very high ($>10,000$ ng/g) resulting in very low MMHg to HgT ratios. However, the MMHg concentrations in the two watersheds were equivalent, indicating that the large pool of inorganic Hg in the Coastal range was largely unavailable for methylation. These findings suggest Hg in the upper watershed of the Coastal range is significantly less available for methylation than the mercury in the Sierra range.

As Coastal range Hg is transported through the watershed into the Bay-Delta it becomes more available for methylation. This working hypothesis is supported by the MMHg to HgT ratios of the Coastal and Sierra ranges being more similar moving down into the valley streams (Figure 13-14). Furthermore, significant Hg accumulation was found in the food webs of both the tributaries of the Coastal and Sierra watersheds, at their point of entry to Bay-Delta, indicating Hg from both watersheds was being methylated (Davis et al. 2002a, Foe et al. 2002a, Slotten et al. 2002).

Mercury at the mine sites is likely to start out as cinnabar and, through diagenetic processes in the sediment, is transformed to a more bioavailable Hg species. Paquette and Heltz (1995) showed that high concentrations of sulfide leading to the formation of soluble polysulfide complexes increase the solubility of cinnabar. In addition, it has been

demonstrated that organic rich sediments are capable of enhancing the dissolution of cinnabar (Ravichandran et al. 1998, Wallschlager et al. 1998). The Cache Creek watershed has high levels of sulfide as a result of thermal springs which could enhance cinnabar dissolution (Domagalski et al. 2002). The average LOI for Cache Creek is six percent (data not shown) making it unlikely that organic matter is responsible for the cinnabar dissolution. Clearly, additional studies directed towards further testing of this working hypothesis are needed. One question left unanswered is: What role if any does differing environmental conditions play in the methylation efficiency of Coastal versus Sierra range derived Hg?

The seasonal lakes (Capay Dam and Cache Creek Settling Basin) had significantly higher MMHg concentrations than the permanent lakes. These results are consistent with other studies showing newly flooded wetlands and reservoirs experience an increase in MMHg production (Bodaly et al. 1993, Kelly et al. 1995, Kelly et al. 1997). Kelly et al. (1997) concluded that the large increases in MMHg concentrations were a result of increased net production of MMHg rather than release of MMHg that was in the wetland prior to flooding. The increase in MMHg, at these newly flooded areas, is likely linked to increased microbial activity in response to a change in environmental conditions. Three changes in environmental conditions known to stimulate methylation of mercury are: 1) sudden death of vegetation supplying a large amount of organic carbon to become available for decomposition, 2) high decomposition leading to an increase in anaerobic habitat, and 3) mercury methylation stimulated by increased temperature (Kelly et al. 1997). Capay Dam and the Cache Creek Settling

Basin experience all three of these changes in environmental conditions on an annual basis allowing an increase in MMHg production to occur independent of an increase in HgT.

Wetland Study

Numerous studies have shown wetlands to be areas of high MMHg production (St. Louis et al. 1994, Hurley et al. 1995, Rudd 1995, St. Louis et al. 1995, Krabbenhoft et al. 1999). It was therefore, expected that the wetlands within the Bay-Delta would also be locations of high MMHg production. The common features of the areas studied were limited water circulation, close proximity to agricultural areas, and the presence of SAV and FAV. The LOI levels in the sediment in the interior of these wetlands was high (7-50%) relative to those in the main, well flushed, part of the Delta (usually <5%) as measured in the initial survey. Water circulation in the interior of the wetland areas was limited and led to increased water temperature (data not shown) and presumably increased residence time. The large amount of organic material present and the limited circulation of the water likely led to suboxic water conditions. This combination of environmental conditions is ideal for Hg methylation in the presence of reactive Hg (Kelly et al. 1997).

These fringe marsh areas make up a small percentage (3 %) of the overall area of the Bay-Delta and yet seem to be incredibly productive areas with respect to conversion of inorganic Hg to the more toxic and readily bioaccumulated form MMHg. The marshes and fringe marshes of the Bay-Delta also have a disproportional influence on the uptake of Hg into the biota as it is within these habitats that fish and birds forage. Time spent

foraging in the fringe marshes would likely result in a higher body burden of Hg than similar foraging in the more modified open water areas. A useful exercise is to compare the MMHg and HgT correlation of samples collected in the initial survey (Figure 10) to the MMHg and HgT correlation of samples specifically collected within the fringe marsh habitats to see if the same trends occur. Figure 20 shows the comparison of MMHg versus HgT for samples collected primarily from the modified open water areas of the delta (initial survey) to the MMHg versus HgT for samples collected explicitly from fringe marsh habitats. There is a striking difference in the behavior of Hg in the fringe marshes. For most of the Bay-Delta large changes in HgT result in little or no change in MMHg. However, for the fringe marshes a large increase in HgT generally results in a corresponding increase in MMHg. In addition the fringe marshes have much higher MMHg concentrations than any of the locations sampled in the initial survey. Although the correlation between MMHg and HgT for the wetlands is strong ($R^2 = 0.52$), caution must be used when considering this relationship as the sample size was small ($n=18$) and all of the samples were collected primarily from only three locations within the Bay-Delta. Also, the initial survey was done during cooler temperatures while the marsh survey was conducted during warmer temperatures. Still, this is a promising find as there is no doubt that the fringe marshes play an important role in the bioaccumulation of Hg into the biota, and if HgT is a dominate controlling factor of MMHg production at these locations, remediation strategies aimed at lowering the HgT load to these specific habitats may be the key to reducing Hg levels in fish.

Clearly the fringe marshes within the Bay-Delta have a high potential for production of MMHg. It is therefore, desirable to quantify the production of MMHg in the marsh habitats and determine the contribution these habitats make with respect to the MMHg budget for the entire Bay-Delta.

Methyl Mercury Budget

A major goal of CALFED is to reduce Hg in fish to levels that do not pose a threat to human and wildlife health. Remediation strategies directed towards achieving this goal must consider the important sources of Hg to the system. Sediments are a primary site of Hg methylation and likely are a major source of MMHg to the Bay-Delta. The current understanding of bioaccumulation of MMHg in game and forage fish of the Bay-Delta is that tissue concentration is correlated to clam tissue concentration (Foe et al. 2002a). In clams, MMHg uptake was positively related to aqueous methyl mercury divided by the square of the chlorophyll concentration giving an indirect link between MMHg in water and MMHg in fish (Foe et al. 2002b). The Bay-Delta receives runoff from 40% of California with some of this water traveling through Hg contaminated watersheds such as Cache Creek above the Sacramento (Domagalski et al. 2002). It is therefore, expected that river inputs of MMHg will also be a large source. Quantification of the sources and sinks of MMHg will give understanding to the role in which sediments and river loads play with respect to Hg cycling in the Bay-Delta.

A quantification of the amount of MMHg being delivered from the sediments into the water column is an integral component of producing a mass budget for the Bay-Delta. As described above a proxy was developed to relate MMHg sediment concentrations to

MMHg flux. Using the total area of a habitat type (calculated using GIS) and the flux of MMHg from the habitat type it was possible to calculate the MMHg load from a particular habitat type (Table 5). Summing the loads from all of the habitat types within the Bay-Delta gives a total MMHg load from the sediments of the Bay-Delta. As shown in Table 5, marsh habitat has the largest flux of MMHg, however, farmed wetlands contribute the largest total mass load of MMHg to the Bay-Delta, due to the large spatial coverage of this habitat type. It is important to point out the large potential for error in the “farmed wetlands” and “lakes and ponds” habitat types due to a small number of samples and a large spatial coverage. The sum of all loads from the six habitat types measured gives 13 g of MMHg per day delivered to the water in Bay-Delta.

Foe (2002) measured MMHg loads into the Bay-Delta at the Sacramento River, San Joaquin River, Mokelmne River, and Yolo Bypass as well as the loads going out of the Bay-Delta at X2 (the region defined as the location of the 2 ‰ isohaline), and the pump stations at the Delta Mendota Canal and State Water Project (Figure 21). The loads were calculated from total MMHg water concentrations and water flow. Samples were collected monthly over a two year period and the final load was calculated as the mean annual load. Large episodic flooding events may transport a greater amount of MMHg into the system on much smaller time scales than monthly monitoring. This is a potential source of error for the calculated loads. Averaging the data into annual loads integrates the loads over a much longer time scale and is a conservative approach for estimating the MMHg loads.

Figure 22 shows the MMHg budget for the Bay-Delta. All major river inputs of MMHg sum to 10 g/day while losses to San Francisco Bay and southern California sum to 6 g/day. The contribution from the sediments is calculated to be 13 g/day. This results in an imbalance of 17 g/day of MMHg.

Possible explanations as to why the mass budget is imbalanced include: 1) an unidentified loss process consuming 17 g/day MMHg is occurring within the Bay-Delta, 2) the uncertainties associated with all of the measurements made sum to 17 g/day of MMHg, 3) a combination of an unidentified loss process and uncertainties associated with the measurements sum to 17 g/day of MMHg. The third explanation is most likely.

Several processes could contribute to such a loss. Photomethylation may account for a substantial amount of MMHg conversion and subsequent removal. The Bay-Delta is tidally driven and water residence times can be quite large allowing the process of photodemethylation to remove MMHg efficiently. A second loss process may be the re-adsorption of MMHg to particles and resulting in a transfer back to the sediment. More information on the internal cycling of Hg is needed to answer these questions. With respect to the sediment data there is a large potential for error. Recalculating the sediment loads without the influence of the farmed wetlands would change the imbalance from 17 to 10 g/day. Conversely, work presented above clearly shows MMHg concentrations in the marsh habitats may be much higher than 1.46 ng/g used to calculate the load from this habitat type. Values as high as 8 ng/g have been measured. This would change the MMHg load of marshes from 1.5 to 12 g/day, a value that may be a more realistic contribution from these fringe marsh habitats. If this is a more

representative average for MMHg loads from fringe marshes it means an area comprising only three percent of the total Bay-Delta is responsible for the majority of the sediment load. Exchanging this higher value for marsh habitat and eliminating the farmed wetland contribution gives a load of 13.5 ng/day MMHg and an imbalance similar to the original scenario (see Figure 22). Also, all of the sediment concentrations for habitat types were calculated from winter values. Concentrations of MMHg for all habitat types are likely higher during summer months and the overall sediment contribution is probably more important than what has been calculated above.

Future work to further constrain the MMHg budget is warranted given that MMHg loads from sediments appear to be large and aqueous MMHg ultimately finds its way into the biota of the Bay-Delta. Additional sediment sampling of defined habitat types during warm and cold seasons will reduce the error and increase confidence in the sediment load value. Water sampling should consider hydrographic features such as the San Joaquin river and Sacramento river “out of phase” phenomenon which occurs right around X2. The fact that these rivers are out of phase tidally may result in the sampling of a different water mass than what is being targeted, thus confounding estimates of the San Francisco Bay export term. The hydrodynamics of the Bay-Delta are complicated by tidal forcing and mixing. Calculating loads by measuring MMHg concentration and multiplying by river flow at locations affected by tidal influences introduces complications as flow in not unilateral. The most certain value is the export to southern California as the water is isolated from tidal effects and measured by pumps.

This “first cut” budget shows that both the sediments and the rivers are major sources of MMHg to the Bay-Delta, export to San Francisco Bay is five times more than to southern California. The budget also indicates the presence of an as yet unidentified loss term that appears quite large. The true magnitude of this term should be better realized as river and sediment loads are constrained. This budget emphasizes the importance of both MMHg sediment flux and river load as sources to the system. Future work will be aimed at identifying the unidentified loss term and replacing it with more specific loss terms such as MMHg uptake into biota and photodemethylation.

The amount of Hg released into the environment as a result of the California gold and mercury mining legacy has been estimated at ~41 million Kg (Churchill 2000). Hydraulic mining during the late 1800’s facilitated the transport of large amounts of Hg contaminated sediments into the Bay-Delta. Furthermore, Hg continues to be transported into the Bay-Delta, adding to the large reservoir already present in the sediments. This source of Hg, anthropogenic in origin, may potentially be remobilized, methylated, bioaccumulated, and biomagnified with the end result a health threat to both humans and wildlife feeding on fish from the Bay-Delta. Remediation strategies aimed at reducing levels of Hg in fish are being discussed for the Bay-Delta. One suggested strategy is Hg remediation at mine sites to reduce river loads to the delta, the assumption being that cutting off the current supply of Hg will eventually decrease Hg levels in fish. This leads to the question: How long will it take to remove all of the Hg (anthropogenic in origin) from the Bay-Delta sediments if current loads were effectively cut off. First, it is necessary to know how much sediment has been introduced into the system. Hydraulic

mining activities were at a peak during the middle to late 1800's and banned completely in 1884. Subsequent water diversions led to a decrease in sediment load to the delta. Sediment accumulation for the Bay-Delta has been estimated at $1.87 \times 10^8 \text{ m}^3$ for the years 1870-1896, $8.39 \times 10^7 \text{ m}^3$ for 1897-1922, and $9.0 \times 10^7 \text{ m}^3$ between the years 1923-1950 (Krone 1979). The total sediment accumulation for the years 1870 to 1950 is $3.62 \times 10^8 \text{ m}^3$. The average Hg concentration in surficial sediments was 200 ng/g. From the total amount of sediment deposited into the delta, assuming the density of the sediment to be ~ 1 , and the average sediment Hg concentration the reservoir of Hg is calculated to be ~ 7 million Kg. Comparisons between historical and current data on striped bass indicate concentrations of Hg in the estuarine food web have changed little in 30 years (Davis et al. 2002a). Therefore, current measurements of Hg flux from the sediment are assumed to have changed little with respect to the recent past. Flux of Hg from the sediments was measured to be 59 g/day for the Bay-Delta system (Gill 2002). The ratio of the Hg reservoir to the Hg flux gives the amount of time required to remove all Hg from the delta. The Hg of anthropogenic origin would be removed from the system in ~ 3000 years if all new sources were effectively "cutoff." This is a conservative estimate and the actual time is much longer as this calculation only accounts for sediment brought in prior to 1951. If sediment loads post 1950 are comparable to those of 1923-1950, the time required to remove all Hg of anthropogenic origin from the delta is estimated to be ~ 5000 years. This cast some doubts on the effectiveness of mine site remediation at lowering Hg concentrations in fish within the delta.

CONCLUSION - CONCEPTUAL MODEL

The work from this project and work done by the principle investigators participating in the CALFED Mercury Project have greatly increased the understanding of how Hg cycles in the Bay-Delta watershed. Figure 23 is a conceptual model illustrating our current understanding of Hg cycling in the Bay-Delta as developed by this study. The Sacramento River is the major riverine source of Hg to the estuary (Foe 2002). Riverine inputs of Hg from both the coastal and Sierra watersheds is higher in the winter months as a result of increased flow. The major export of Hg is through the Golden Gate with a smaller fraction exported to southern California (Foe 2002). The bioavailability of Hg increases moving down the watershed of the coastal range but remains the same moving down the watershed of the Sierra (Heim et al. 2002, Heim et al. 2003). Once Hg reaches the valley it is equally available for methylation and this is reflected in both sediment data and the degree of Hg bioaccumulation in biota collected from tributaries of both the coastal and sierra ranges (Foe et al. 2002a, Gill et al. 2003). Hg undergoes a complicated biogeochemical cycle within the Bay-Delta. Sediment production and the resulting flux to the water is a significant source of MMHg (Gill 2002). Production of MMHg in sediments is at a maximum during warmer periods and varies substantially throughout the year (Heim et al. 2003). MMHg concentrations in several fish species were correlated with clams and MMHg uptake in clams was positively correlated to aqueous MMHg divided by the square of chlorophyll (Davis et al. 2002a, Foe et al. 2002b). MMHg in the water column may undergo photo demethylation and subsequent volatilization to the atmosphere. Demethylation may also occur within

the sediments and the net production of MMHg is a balance between the processes of methylation and demethylation. Hg is particle reactive and may repeatedly undergo adsorption and desorption at rates so far undetermined. Farmed wetlands account for 70 percent of the total area of the delta and appear to be net producers of MMHg. The large area of farmed wetlands may dictate the input of a substantial amount of MMHg even at relatively low sediment production. In contrast, fringe marsh makes up only 3 percent of the total area of the delta and yet contributes a substantial portion of the total MMHg sediment load (Gill et al. 2003). The current work indicates MMHg production in fringe marsh is controlled to some degree by the total amount of Hg present. The fringe marsh may have a disproportional influence over Hg bioaccumulation and biomagnification as this is the habitat most occupied by fish and foraging wildlife. Fish in the fringe marsh may experience a higher exposure to MMHg than out in the open water. Currently, Hg levels in many game fish and forage fish have Hg concentrations that pose a threat to piscivorous birds and wildlife as well as human fish consumers.

The problem of Hg in the Bay-Delta is large. With these fluxes one may calculate that the sediments contaminated by gold and Hg mining may continue to impact food webs in the delta for thousands of years. This problem can only be mitigated if further studies of Hg cycling are undertaken to advance our knowledge of sources and sinks, rates of internal cycling, processes controlling the conversion of inorganic Hg to MMHg, and California is willing to take a critical look at state-wide water allocation and source mitigation in the watershed.

REFERENCES

- Baldi, F. 1997. Microbial Transformation of Mercury Species and Their Importance in the Biogeochemical Cycle of Mercury. Pages 213-257 in A. Siegel and H. Siegal, editors. *Metal Ions in Biological Systems; Mercury and its effects on environment and biology*. Marcel Dekker, New York.
- Benoit, J. M., C. C. Gilmour, and R. P. Mason. 2001. The influence of sulfide on solid-phase mercury bioavailability for methylation by pure cultures of *Desulfobulbus propionicus* (1pr3). *Environ. Sci. & Technol.* 35:127-132.
- Benoit, J. M., C. C. Gilmour, R. P. Mason, and A. Heyes. 1999. Sulfide Controls on Mercury Speciation and Bioavailability to Methylating Bacteria in Sediment Pore Waters. *Environmental Science and Technology* 33:951-957.
- Berman, M., and R. Bartha. 1986. Levels of chemical versus biological methylation of mercury in sediments. *Bull. of Environ. Contam. Toxicol.* 36:401-404.
- Bloom, N. 1989. Determination of Picogram Levels of Methylmercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapor Atomic Fluorescence Detection. *Can. J. Fish. Aquat. Sci.* 46:1131-1140.
- Bloom, N. S. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can. J. Fish. Aquat. Sci.* 49:1010-1017.
- Bloom, N. S. 1997. Methyl Mercury in Sediments by Acidic KBr Extraction in to Methylene Chloride. FGS 045, Frontier Geosciences Inc., Seattle.
- Bloom, N. S. 1999. Aqua Regia Digestion of Coal, Iodated Carbon Traps, Sediments, Soils, and Ores, for the Determination of Total Mercury by CVAFS. FGS 066, Frontier Geosciences Inc., Seattle.
- Bloom, N. S., G. A. Gill, S. Cappellino, C. Dobbs, L. McShea, C. Driscoll, R. Mason, and J. Rudd. 1999. Speciation and cycling of mercury in Lavaca, Bay, Texas, sediments. *Environ. Sci. & Technol.* 33:7-13.
- Bodaly, R. A., J. W. M. Rudd, and R. J. P. Fudge. 1993. Mercury concentrations in fish related to size of remote Canadian shield lakes. *Can. J. Fish. Aquat. Sci.* 50:980-987.
- Boudou, A., and F. Ribeyre. 1997. Mercury in the Food Web: Accumulation and Transfer Mechanisms. Pages 289-320 in A. Siegel and H. Siegal, editors. *Metal Ions in Biological Systems; Mercury and its effects on environment and biology*. Marcel Dekker, New York.

- Choi, S. C., and R. Bartha. 1993. Cobalamin-mediated mercury methylation by *Desulfovibrio desulfuricans* LS. *Appl. Environ. Microbiol.* 59:290-295.
- Choi, S. C., and R. Bartha. 1994. Environmental factors affecting mercury methylation in estuarine sediments. *Bull. Environ. Contam. Toxicol.* 53:805-812.
- Choi, S. C., T. Chase, and R. Bartha. 1994. Enzymatic catalysis of mercury methylation by *Desulfovibrio desulfuricans* LS. *Appl. Environ. Microbiol.* 60:1342-1346.
- Churchill, R. 2000. Contributions of Mercury to California's Environment from Mercury and Gold Mining Activities- Insights from the Historical Record. *in* Assessing and Managing Mercury from Historic and Current Mining Activities, San Francisco, Ca, USA.
- Compeau, G. C., and R. Bartha. 1985. Sulfate-reducing bacteria: Principal methylators of mercury in anoxic estuarine sediment. *Appl. Environ. Microbiol.* 50:498-502.
- Craig, P. J., and P. A. Moreton. 1983. Total mercury, methyl mercury and sulphide in river Carron sediments. *Marine Pollution Bulletin* 14:408-411.
- Davis, J. A., B. K. Greenfield, G. Ichikawa, and M. Stephenson. 2002a. Mercury in Sport Fish from the Delta Region. Draft Final Report to CALFED. San Francisco Estuary Institute.
- Davis, J. A., M. D. May, B. K. Greenfield, R. Fairey, C. Roberts, G. Ichikawa, M. S. Stoelting, J. S. Becker, and R. S. Tjeerdema. 2002b. Contaminant concentrations in sport fish from San Francisco Bay, 1997. *Mar. Pollut. Bulletin.* In press.
- Davis, J. A., M. D. May, G. Ichikawa, and D. Crane. 1998. Contaminant Concentrations in Fish from the Sacramento-San Joaquin Delta and Lower San Joaquin River. San Francisco Estuary Institute, Oakland, Ca.
- Domagalski, J. 1998. Occurrence and transport of total mercury and methyl mercury in the Sacramento River Basin, California. *Journal of Geochemical Exploration* 64:277-291.
- Domagalski, J. L., C. N. Alpers, D. G. Slotten, T. H. Suchanek, and S. H. Ayers. 2002. Mercury and Methylmercury Concentrations and Loads within the Cache Creek Watershed, California, January 2000 through May 2001. Draft Final Report to CALFED.

- Fairey, R., K. Taberski, S. Lamerdin, E. Johnson, R. P. Clark, J. W. Downing, J. Newman, and M. Petreas. 1997. Organochlorines and other environmental contaminants in muscle tissues of sportfish collected from San Francisco Bay. *Marine Pollution Bulletin* 34:1058-1071.
- Fitzgerald, W. F., and T. W. Clarkson. 1991. Mercury and monomethylmercury: present and future concerns. *Environmental Health Perspectives* 96:159-166.
- Fitzgerald, W. F., D. R. Engstrom, R. P. Mason, and E. A. Nater. 1998. The case for atmospheric mercury contamination in remote areas. *Environmental Science & Technology* 32:1-7.
- Foe, C. 2002. Mercury Mass Balance for the Freshwater Sacramento-San Joaquin Bay-Delta Estuary. Draft Final Report to CALFED.
- Foe, C., and W. Croyle. 1998. Mercury Concentrations and Loads from the Sacramento River and from Cache Creek to the Sacramento-San Joaquin Delta Estuary. Staff Report Central Valley Regional Water Quality Control Board, Sacramento.
- Foe, C., J. A. Davis, S. Schwarzbach, M. Stephenson, and D. G. Slotten. 2002a. Conceptual Model and Working Hypotheses of Mercury Bioaccumulation in the Bay-Delta Ecosystem and its Tributaries. Final Draft Report to CALFED.
- Foe, C., M. Stephenson, and S. Stanish. 2002b. Pilot Transplant Studies with the Introduced Asiatic Clam, *Corbicula fluminea*, to Measure Methyl Mercury Accumulation in the Sacramento-San Joaquin Delta Estuary. Draft Final Report to CALFED.
- Furutani, A., and J. W. M. Rudd. 1980. Measurement of mercury methylation in lake water and sediment samples. *Appl. Environ. Microbiol.* 40:770-776.
- Gill, G. 2002. An Assessment of Human Health and Ecological Impacts of Mercury in the Bay-Delta Watershed. Draft Final Report to CALFED. TAMUG.
- Gill, G., W. A. Heim, K. H. Coale, M. Stephenson, and C. Foe. 2003. Mercury cycling and transport in the San Francisco Bay-Delta Ecosystem and its tributaries: The Calfed Mercury Project. *in* American Society of Limnology and Oceanography Annual meeting, Salt Lake City, UT.
- Gill, G. A., N. S. Bloom, S. Cappellino, C. T. Driscoll, C. Dobbs, L. Mcshea, R. Mason, and J. W. M. Rudd. 1999. Sediment - water fluxes of mercury in Lavaca Bay, Texas. *Environ. Sci. & Technol.* 33:663-669.

- Gilmour, C. C., E. A. Henry, and R. Mitchell. 1992. Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Tech.* 26:2281-2287.
- Gilmour, C. C., G. S. Riedel, M. C. Ederington, J. T. Bell, J. M. Benoit, G. A. Gill, and M. C. Stordal. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry* 40:327-345.
- Heim, W. A., K. H. Coale, and M. Stephenson. 2002. An Assessment of Human Health and Ecological Impacts of Mercury in the Bay-Delta Watershed. Draft Final Report to CALFED. MLML.
- Heim, W. A., M. Stephenson, and K. H. Coale. 2003. Spatial and Temporal Trends of Solid Phase Methyl and Total Mercury in the San Francisco Bay-Delta. Pages 74 Abstract *in* CALFED Science Conference, Sacramento, Ca.
- Hurley, J. P., J. M. Benoit, C. L. Babiarz, M. M. Shafer, A. W. Andren, J. R. Sullivan, R. Hammond, and D. A. Webb. 1995. Influences of Watershed Characteristics on Mercury Levels in Wisconsin Rivers. *Environ. Sci. & Technol.* 29:1867-1875.
- Hurley, J. P., D. P. Krabbenhoft, L. B. Cleckner, M. L. Olson, G. R. Aiken, and P. S. Rawlik. 1998. System controls on the aqueous distribution of mercury in the northern Florida Everglades. *Biogeochemistry* 40:293-311.
- Keating, M. H. 1997. Mercury study report to congress Volume 1: Executive Summary. EPA-452/R-97-003, United States Environmental Protection Agency.
- Kelly, C. A., J. W. M. Rudd, R. A. Bodaly, N. P. Roulet, V. L. St. Louis, A. Heyes, T. R. Moore, S. Schiff, R. Aravena, K. J. Scott, B. Dyck, R. Harris, B. Warner, and G. Edwards. 1997. Increases in fluxes of greenhouse gases and methyl mercury following flooding of an experimental reservoir. *Environ. Sci. Technol.* 31:1334-1344.
- Kelly, C. A., J. W. M. Rudd, V. L. St. Louis, and A. Heyes. 1995. Is total mercury concentration a good predictor of methyl mercury concentration in aquatic systems. *Water, Air, and Soil Pollution* 80:715-724.
- Krabbenhoft, D. P., J. G. Wiener, W. G. Brumbaugh, M. L. Olson, J. F. DeWild, and T. J. Sabin. 1999. A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients. Pages 147-160 *in* D. W. Morganwalp and H. T. Buxton, editors. U.S. Geological Survey Toxic Substances Hydrology Program- Proceedings of the Technical Meeting, Charleston, South Carolina.

- Krone, R. B. 1979. Sedimentation in the San Francisco Bay System. Pages 85-96 *in* T. J. Conomos, editor. San Francisco Bay the Urbanized Estuary. Pacific Division of the American Association for the Advancement of Science, San Francisco.
- Larry Walker and Associates. 1997. Sacramento River Mercury Control Planning Project. Sacramento Regional County Sanitation District, Sacramento.
- Lee, Y. H., and H. Hultberg. 1990. Methylmercury in some Swedish Surface Waters. *Environ. Toxicol. Chem.* 9:833-841.
- Magos, L. 1997. Physiology and Toxicology of Mercury. Pages 321-370 *in* A. Siegel and H. Siegal, editors. Metal Ions in Biological Systems; Mercury and its effects on environment and biology. Marcel Dekker, New York.
- Marvin-Dipasquale, M., J. Agee, C. McGowan, R. S. Oremland, M. Thomas, D. Krabbenhoft, and C. C. Gilmour. 2000. Methyl-mercury degradation pathways: A comparison among three mercury-impacted ecosystems. *Environ. Sci. & Technol.* 34(23):4908-4916.
- Mason, R. P., W. F. Fitzgerald, and F. M. M. Morel. 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. *Geochim. Cosmochim. Acta* 58:3191-3198.
- Mason, R. P., and A. L. Lawrence. 1999. Concentration, Distribution, and Bioavailability of Mercury and Methylmercury in Sediments of Baltimore Harbor and Chesapeake Bay, Maryland, USA. *Environ. Toxicol. Chem.* 18:2438-2447.
- Meili, M. 1997. Mercury in Lakes and Rivers. Pages 21-51 *in* A. Siegel and H. Siegal, editors. Metal Ions in Biological Systems; Mercury and its effects on environment and biology. Marcel Dekker, New York.
- Mottet, N. K., M. E. Vahter, J. S. Charleston, and L. T. Firiberg. 1997. Metabolism of Methylmercury in the Brain and Its Toxicological Significance. Pages 371-403 *in* A. Siegel and H. Siegal, editors. Metal Ions in Biological Systems; Mercury and its effects on environment and biology. Marcel Dekker, New York.
- NAS. 1999. Toxicological Effects of Methylmercury. National Academy of Sciences, Washington, DC.
- Nichols, F. H., J. E. Cloern, S. N. Luoma, and D. H. Peterson. 1986. The Modification of an Estuary. *Science* 231:567-573.

- Office of Environmental Health Hazard Assessment. 1994. Health Advisory on Catching and Eating Fish: Interim Sport Fish Advisory for San Francisco Bay. California Environmental Protection Agency, Sacramento.
- Olson, B. H., and R. C. Cooper. 1976. Comparison of Aerobic and Anaerobic Methylation of Mercuric Chloride by San Francisco Bay Sediments. *Water Research* 10:113-116.
- Paquette, K., and G. Heltz. 1995. Solubility of Cinnabar (Red Hgs) and Implications for Mercury Speciation in Sulfidic Waters. *Water, Air and Soil Pollution* 80:1053-1056.
- Paterson, M. J., J. W. M. Rudd, and V. St. Louis. 1998. Increases in total and methylmercury in zooplankton following flooding of a peatland reservoir. *Environmental Science and Technology* 32:3868-3874.
- Plumb, R.H. 1981. Procedures for handling and chemical analysis of sediment and water samples. Tech. Rpt. EPA/CE-81-1.
- Ravichandran, M., G. R. Aiken, M. M. Reddy, and J. Ryan. 1998. Enhanced Dissolution of Cinnabar (Mercury Sulfide) by Dissolved Organic Matter Isolated from the Florida Everglades. *Environ. Sci. & Technol.* 32:3305-3311.
- Regnell, O., G. Ewald, and E. Lord. 1997. Factors controlling temporal variation in methyl mercury levels in sediment and water in a seasonally stratified lake. *Limnol. Oceanogr.* 42:1784-1795.
- Roth, D. A., H. E. Taylor, J. L. Domagalski, P. D. Dileanis, D. B. Peart, R. C. Antweiler, and C. N. Alpers. 2001. Distribution of Inorganic Mercury in Sacramento River Water and Suspended Colloidal Sediment Material. *Arch. Environ. Contam. Toxicol.* 40:161-142.
- Rudd, J. W. M. 1995. Sources of methylmercury to freshwater ecosystems. A review. *Water, Air, Soil, Pollution* 80:697-713.
- Rudd, J. W. M., and M. A. Turner. 1983. The English-Wabigoon River Ststem: II. Suppression of Mercury and Selenium Bioaccumulation by Suspended and Bottom Sediments. *Can. J. Fish. Aquat. Sci.* 40:2218-2227.
- San Francisco Bay Regional Water Quality Control Board. 1995. Contaminant Levels in Fish Tissue from San Francisco Bay. San Francisco Regional Board, State Water Resources, and California Department of Fish and Game, San Francisco.

- Sellers, P., C. A. Kelly, and J. W. M. Rudd. 2001. Fluxes of methylmercury to the water column of a drainage lake: The relative importance of internal and external sources. *Limnol. Oceanogr.* 46:623-631.
- Slotten, D. G., S. H. Ayers, T. H. Suchanek, R. D. Weyland, and A. M. Liston. 2002. Mercury Bioaccumulation and Trophic Transfer in the Cache Creek Watershed, California, in Relation to Diverse Aqueous Mercury Exposure Conditions. Draft Final Report to CALFED. U.C. Davis.
- St. Louis, V. L., J. W. M. Rudd, C. A. Kelly, and L. A. Barrie. 1995. Wet Deposition of Methyl Mercury in Northwestern Ontario Compared to other Geographic Locations. *Water, Air and Soil Pollution* 80:405-414.
- St. Louis, V. L., J. W. M. Rudd, C. A. Kelly, K. G. Beaty, N. S. Bloom, and R. J. Flett. 1994. Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. *Can. J. Fish. Aquat. Sci.* 51:1065-1076.
- Wallschlager, D., M. V. M. Desai, M. Spengler, and R. D. Wilken. 1998. Mercury Speciation in Floodplain Soils and Sediments Along a Contaminated River Transect. *J. Environ. Qual.* 27:1034-1044.
- Weber, J. H. 1993. Review of Possible Paths for Abiotic Methylation of Mercury (II) in the Aquatic Environment. *Chemosphere* 26:2063-2077.
- Winfrey, M. R., and J. W. M. Rudd. 1990. Environmental Factors Affecting the Formation of Methylmercury in Low pH Lakes. *Environmental Toxicology and Chemistry* 9:853-869.
- Wright, D. R., and R. D. Hamilton. 1982. Release of Methyl Mercury from Sediments: Effects of Mercury Concentration, Low Temperature, and Nutrient Addition. *Can. J. Fish. Aquat. Sci.* 39:1459-1466.

Table 1. Principle investigators of the CALFED mercury project in the Bay-Delta.

Investigator	Affiliation	Area of Study
Dr. Gary Gill	Texas A&M University Galveston	mercury flux across sediment/water
Dr. Chris Foe	State Water Quality Regional Control Board	Bay-Delta watershed mercury mass balance
Dr. Darell Slotten	University of California Davis	mercury in invertebrates and small fish
Dr. Jay Davis	San Francisco Estuary Institute	mercury in sport fish
Dr. Kenneth Coale	Moss Landing Marine Laboratories	mercury biogeochemistry and cycling
Mark Stephenson	Moss Landing Marine Laboratories	mercury biogeochemistry and cycling

Table 2. Name, location, and habitat type of seasonal sampling sites.

Name	Latitude	Longitude	Prevalent Habitat
Prospect Slough	38.28961	121.66239	Open water / fringe wetland
Sherman Island	38.04120	121.81930	Tidal wetland / riparian marshland
Franks Tract	38.05250	121.59191	Open water
Connection Slough	38.01250	121.55002	Rip-rap waterway /fringe wetland
Cosumnes River	38.25823	121.42618	Riparian marshland
White Slough	38.08723	121.47837	Fringe tule

Table 3. Name, location, and habitat type of wetland sampling sites.

Name	Latitude	Longitude	Habitat Classification
Mandeville Cut	38.06152	121.53774	Peaty sediment, Tule wetland
Fourteen Mile Slough	38.00659	121.39224	Silty sediment, Wetland, backwater
Webber Point	38.00965	121.44651	Silty sediment, Wetland, backwater
Control	38.00397	121.44416	San Joaquin River Channel

Table 4. Site name, position, and description of flux chamber locations.

Site Name	Latitude	Longitude	Water depth (ft)	Percent Sand	LOI %
Columbia Cut	38.03010	121.49054	24	22	7
Cosumnes River	38.25270	121.40602	5	34	8
Franks Tract	38.05280	121.59204	7	1	9
Franks Tract Marsh	38.05943	121.61162	3	---	23
Honker Bay	38.05848	121.93307	8	---	4
Little Holland	38.29043	121.66150	4	21	5
Prospect Slough	38.28621	121.66451	4	---	5
Sherman Island	38.04129	121.81944	4	46	4 - 24
White Slough	38.08731	121.47848	12	0.6	12

Table 5. A list of habitat types found in the Bay-Delta with the corresponding area, MMHg concentration, calculated flux (from proxy), and MMHg load. The sample size is in parenthesis. Dashed lines are given in categories where it was not possible to calculate flux and load (MMHg concentration below lower boundary limit of proxy).

Habitat Type	Area Km ²	[MMHg] (ng g ⁻¹)	MMHg Flux (ng m ⁻² day ⁻¹)	MMHg Load (g day ⁻¹)
Upland (2)	3751	.19 ± .03	---	---
Riparian Woodland (4)	41	.24 ± .08	---	---
Salt Ponds (0)	0.3	N/A	N/A	N/A
Mudflats (2)	3	.50 ± .32	.44	.001
Open Water (36)	238	.54 ± .06	1.55	.370
Seasonal Wetlands (3)	167	.55 ± .06	1.85	.308
Farmed Wetlands (8)	1447	.71 ± .20	6.70	9.70
Lakes and Ponds (2)	35	1.26 ± .43	23.96	.844
Marsh (7)	51	1.46 ± .35	30.19	1.55
Total	5733			13

Picture 1. A picture showing the fringe marsh habitat along rip-rap waterways at Mandeville Island located near Franks Tract in the central Bay-Delta. (Photo by W. Heim)

Picture 2. A picture of the area around Tower Park marina in the Bay-Delta, showing the subsidence of croplands and the necessity of levees for prevention of flooding. (Photo by W. Heim)

Picture 3. An assembled Sludge O Matic with attached shutter trigger line. The door is shown in the closed position. The attachment of the pulley system with plastic ties is clearly shown as is the handle configurations and aircraft pin. (Photo by W. Heim)

Picture 4. Close-up photo of the topmost 0.5 cm of sediment captured cleanly using the SOM. The trap door of the sampler is shown in the open position with sediment ready to be transferred into sample jars. (Photo by W. Heim)

Picture 5. Field team employing “clean hand techniques” at Sherman Island. Sediment is being sub-sampled from the SOM using a plastic scoop to transfer samples. “Clean hands” person is wearing clean room gloves during all sub-sampling. “Dirty hands” person never comes into contact with the sample but aids “clean hands” person as necessary. (Photo by R. Lehman)

Figure 1. A simplified illustration of Hg cycling through the environment shows Hg converted from the inorganic to organic form (Hg methylation), processes that inhibit Hg methylation by altering the availability of inorganic Hg for methylation, and removal of MMHg by the formation of volatile di-methyl mercury (Modified from Winfrey and Rudd 1990).

Figure 2. A map showing locations of mercury mines (Δ) and gold mines (O) in both the California Coastal range and Sierra Nevada Mountains (Map modified from USGS CALFED-1 (Clear Lake to Delta) ArcView Project, contact Tom Suchanek, Feb 2002.).

Figure 3. Map of the Bay-Delta showing the spatial survey sampling locations (○).

Figure 4. Map of the San Francisco Bay-Delta showing the surrounding tributaries and bays. The six seasonal sampling stations are shown with asterisks and the following names: Prospect Slough, Cosumnes River, White Slough, Franks Tract, Connection Slough, and Sherman Island.

Figure 5. Map showing the sampling sites for the Hg bioavailability study. The map key shows the symbol defining each sampling type.

Figure 6. Map showing total mercury surficial sediment concentrations. The mercury concentrations are given as scale bars and the key is given in $\mu\text{g/g}$ dry weight sediment. Locations with mercury values less than the method detection limit of 0.010 $\mu\text{g/g}$ are represented by solid black circles.

Figure 7. Map showing methyl mercury surficial sediment concentrations. The methyl mercury concentrations are given as scale bars and the key is given in ng/g dry weight sediment. Two sites are shown with the methyl mercury concentrations explicitly expressed (in ng/g). Locations with methyl mercury values less than the method detection limit of 0.019 ng/g are represented by solid black circles.

Figure 8. Map showing methyl mercury to total mercury ratios (as a percent) in surficial sediment. Grey scale bars are indicative of an upper limit ratio, as the methyl mercury to total mercury ratio was calculated using the method detection limit for total mercury. Solid black circles were used to indicate locations with methyl mercury values and total mercury values less than method detection limits.

Figure 9. Correlation between methyl mercury and percent loss on ignition in delta sediment samples collected during the winter of 1999 ($R^2 = 0.32$).

Figure 10. Correlation between methyl mercury and total mercury in delta sediment samples collected during the winter of 1999 ($R^2 = 0.19$). The circled triangles were left out of the correlation analysis.

Figure 11. Seasonal changes in methyl mercury ($\blacktriangle$), total mercury ($\blacksquare$), and the methyl mercury to total mercury ratio (as a percent) ($\blacklozenge$) in surficial sediment of the Bay-Delta. Methyl mercury (ppb) and methyl mercury to total mercury ratio (as %) share the primary y-axis. Total mercury is on the second y-axis (log scale). Error bars represent analytical uncertainty rather than field duplication.

Figure 12. Methyl mercury and total mercury concentration of surficial sediment samples collected at Franks Tract ($\square$), White Slough (Δ), Connection Slough ($\times$), Prospect Slough ($\circ$), Cosumnes River ($\diamond$), and Sherman Island ($\bullet$). A positive correlation between methyl mercury and total mercury is shown only for samples collected at Sherman Island (regression coefficient of $R^2 = 0.40$).

Figure 13. Three panels showing total mercury concentration, methyl mercury concentration, and the methyl mercury to total mercury ratio (as a percent) in unsieved surficial sediments collected from Coastal and Sierra lakes, mountain streams, and valley streams. Black bars are from the Coastal range and white bars are from the Sierra range. Each bar is the averaged value of many locations within a particular classification. The error bars are the standard error of samples within a particular classification.

Figure 14. Three panels showing total mercury concentration, methyl mercury concentration, and the methyl mercury to total mercury ratio (as a percent) in sieved surficial sediments collected from Coastal and Sierra lakes, mountain streams, and valley streams. Black bars are from the Coastal range and white bars are from the Sierra range. Each bar is the averaged value of many locations within a particular classification. The error bars are the standard error of samples within a particular classification.

Figure 15. The upper figure gives MMHg as a percent of the total mercury for the micro-habitat types found along a cross channel transect. The y-axis is a log scale and a description of the habitat type is given along the x-axis. The lower figure is a cross channel water depth profile showing the depth from which each sample was collected.

Figure 16. Methyl mercury concentrations in surficial sediments collected from three wetland areas and one control area outside the wetland area. Black bars are from the interior of the wetlands, grey bars are mid way between the interior and fringe of the wetland, and the white bars are from the outer fringe of the wetland areas. The bars represent the average of field duplicates and the error bars are the range of field duplicates.

Figure 17. Methyl mercury to total mercury ratio as a percent in surficial sediments collected from three wetland areas and one control area outside the wetland area. Black bars are from the interior of the wetlands, grey bars are mid way between the interior and fringe of the wetland, and white bars are from the outer fringe of the wetland areas. The bars represent the average of field duplicates and the error bars are the range of field duplicates.

Figure 18. Flux of MMHg from sediments plotted against MMHg sediment concentration. The black circles (●) are used in the regression and the black triangles (▲) from White Slough are not included in the regression. Error of MMHg concentration is calculated as the range of concentrations between field replicates. Error of MMHg flux is calculated from the error associated with the slope used to calculate flux for each measurement.

Figure 19. Covariance of Chl a (Δ), sulfate ($\diamond$), temperature ($\times$), and MMHg ($\bullet$) from February through October, 2001 at the Cosumnes River station. Chl a, sulfate, and temperature data from Foe (2002).

Figure 20. A comparison of MMHg versus HgT for samples collected during the initial survey ($\circ$) and samples collected from the fringe marshes ($\blacklozenge$) within the Bay-Delta. The R^2 value for the correlation between HgT and MMHg for the marsh samples is 0.52 compared to 0.02 for the initial survey.

Figure 21. Map showing sampling sites of the Bay-Delta mercury budget study of Foe, 2001. These sites were used to quantify the major inputs (Yolo, Sacramento River, Mokelumne River, and San Joaquin River) and exports (X2, State Water Project, and Delta Mendota Canal) of mercury for the Bay-Delta.

Figure 22. MMHg budget for the Bay-Delta water shed. Major river inputs are the sum of the Sacramento River, San Joaquin River, Mokulumne and Cosumnes River, and Prospect Slough. Exports are to the ocean as measured at X2 and water export to southern California measured at the pump stations. Values are annual averages given in grams per day. Water input and export values are from Foe, 2001.

Figure 23. A conceptual model of how Hg cycles in the Bay-Delta (illustration by Lynn McMasters).

APPENDIXES

APPENDIX A. Construction of the “Sludge O Matic”

Picture 3 shows the “Sludge O Matic” (SOM) fully assembled with the trap door in the closed position and the trigger line attached ready for remote use. The SOM is constructed simply by following the instructions below and referring back to Picture 3 for clarification of the fitting together of various pieces. One 19 cm x 24 cm rectangular base plate (body) of polycarbonate 0.6 cm thick is cut from stock material. Holes are drilled into the body in 13 locations and these holes are tapped to accept flat-head Phillips, $\frac{1}{4}$ x 20 316 stainless steel screws used for holding the frame pieces and spacers together (Figure A1-1). The following lengths are cut, for framing material, from 2 cm wide strips of 0.6 cm polycarbonate: two at 24 cm, two at 22 cm, three at 15.2, one at 19 cm, and one at 11 cm (Figure A1-2). The following lengths are cut for spacing material from 1.3 cm wide strips of 0.6 cm polycarbonate: one at 16.5 cm, and two at 24 cm (Figure A1-2). Holes are drilled into the frame pieces and spacers with care given to match the hole configuration in the base as shown in Figure A1-1 and A1-2. The holes in all the top pieces of framing are countersunk to allow the flat-head screws to be seated flush into the framing. The pieces are assembled in the order shown in Figure A1-2. Screws are inserted and loosely tightened until all framing and spacing materials are in place. Piece “10” is glued in place 4 cm from the edge and acts as the sill when the shutter door is opened to sub-sample sediment (Figure A1-2). Piece “11” is the shutter stop and is not assembled until after the shutter door is slid in place. A shutter door is constructed by cutting 0.6 cm polycarbonate stock material into a 16.3 cm x 30 cm rectangle (Figure A1-3). One narrow side of the shutter is beveled to 45 degrees to act as

a cutting edge during closing of the door. The side of the shutter containing the sharp edge of the bevel has both edges rabbet down 0.5 mm by 0.6 cm length wise into the edge the entire 30 cm length (Figure A1-3). Handles are made using 1.25" (3.175 cm) polycarbonate round stock. One handle is cut to a length of 10 cm and a 0.5 cm x 0.5 cm groove is cut into the handle 1.5 cm from the base. Three holes are drilled and tapped into the base of the handle. This handle is fastened opposite the cutting edge side positioned 2.5 cm from the end and centered widthwise (Figure A1-3). Three stainless steel screws are used to attach the handle to the shutter and the screws are counter sunk into the shutter (Figure A1-3). A second handle is cut to a length of 29 cm and 26 cm of the shaft is taken down to a diameter of 2.6 cm on a lathe (Figure A1-4). A 0.5 cm x 0.5 cm groove is cut 2 cm from the base (non-lathed end) of the handle. A 1.0 cm wide notch is cut 2.5 cm deep into the narrow diameter end of the handle. A 6.0 mm diameter hole was drilled through the end of the handle across the center of the notch. The notch will accept the loop of a deployment line and the hole will accept a stainless steel aircraft pin used to lock off the deployment line or pole. A "handle attachment plate" is cut from 0.6 cm thick polycarbonate stock into a 10 cm x 19 cm piece to which the handle is fastened (Figure A1-4). Three holes are drilled then tapped in the base of the handle and stainless steel screws are used to attach the handle to the "handle attachment plate." The screws are counter sunk into the handle attachment plate allowing a flush fit when the plate is attached to the sampler body. Holes are drilled in the "handle attachment plate" to match the configuration of the tapped holes in the base (Figure A1-4 and A1-5). The holes in the "handle attachment plate" will align with and accept four of the screws used

to hold the framing and spacers together on the body (Figure A1-5). These four screws are long enough to extend through the framing, spacing, body, and handle attachment plate with enough threads left over to add lock washers and nuts. In this way the handle attachment plate and handle is securely fastened to the sampler body. The shutter door is slid into the grooves on the sampler body with the handle facing up in the same direction as the handle on the sampler body. The shutter stop is secured to the sampler body preventing the shutter door from being removed completely from the sampler. The sampler is now fully assembled and ready for use. If the sampler is going to be used remotely addition steps are as follows. A block system is rigged by attaching a double block to the shutter door handle using a plastic tie seated in the groove of the handle (Figure A1-6). A double block with becket is attached to the main handle on the sample body using a plastic tie seated in the groove of the handle. The desired length trigger line is rigged through the blocks and fastened securely to the becket giving a 4:1 pulling ratio. A pole or line may then be attached to the main handle and inserting a stainless steel pin through either the pole or line to lock it off. If a pole is used holes must be drilled in the pole to match the hole in the handle. If line is used prepared lead weights must be added to the sampler. Lead blocks are prepared at the desired weight simply by drilling a center hole in the lead and then painting the block to prevent contamination. The desired amount of weight is added to the sampler before attaching the deployment line.

Figure A1-1. Base plate (body) of sampler showing the locations of holes drilled and tapped to accept screws for holding the framing.

Figure A1-2. Framing pieces and spacing pieces are shown in their prospective position in relation to the base plate. The numbering in bold identifies the piece and order in which the piece should be assembled, with the lowest number assembled first. “Top pieces” 7-9 & 11 have counter sunk holes to accept counter sinking Philips head screws. Piece 10 is glued in place. Piece 11 is not installed until the shutter is slid in place.

Figure A1-3. Shutter door with a sharpened cutting edge on one end and handle on the other. The shutter body has a stop piece glued to it on the opposite side to which the handle is attached. The handle is attached with 3 stainless Philips head counter sinking screws. The shutter body has counter sunk holes to accept these screws. Rabbet edges 0.6 cm from the edge on the same side of the handle.

Figure A1-4. Handle attachment plate shown in two views, downward looking and side view. The screw hole pattern in the handle attachment plate matches the screw configuration of the sampler body. The notch to accept a deployment line is shown as is the hole to accept a locking pin. Note the hole is offset by 90 deg to the notch. Three countersunk Phillips head screws are used to attach the handle to the plate.

Figure A1-5. The handle attachment plate is shown securely fastened to the sampler body with four long screws, lock washers, and self locking nuts.

Figure A1-6. Downward view of sampler with shutter door installed. The block system positioning is shown with one block attached to each handle with a plastic tie seated in the groove of the handle.

APPENDIX B. Raw Data

Table A2-1 Initial Survey Ancillary Data

Station #	Station Name	Date	Latitude	Longitude	Fines (%)	LOI (%)
30	Sacramento R.	10/26/1999	38.3419	121.6453	88.69	2.7
35	Prospect Slough	10/27/1999	38.2583	121.6736	6.89	1.5
36	Cache Slough	10/27/1999	38.2883	121.7217	99.75	2.4
38	Prospect Slough	10/26/1999	38.2600	121.6711	44.79	1.4
39	Prospect Slough	10/26/1999	38.6373	121.6806	94.50	2.3
41	Sacramento R.	10/27/1999	38.4980	121.5591	0.17	0.4
43	Sacramento R.	10/27/1999	38.4272	121.5307	0.09	0.5
47	Sacramento R.	10/27/1999	38.3398	121.5636	23.57	0.6
50	Georgina Slough	10/27/1999	38.2157	121.5405	48.78	1.5
51	Sacramento R.	10/26/1999	38.2008	121.6583	71.89	2.5
53	Sacramento R.	10/27/1999	38.2560	121.5151	0.07	-
54	Snodgrass S.	10/27/1999	38.2535	121.4990	21.74	1.3
55	Sacramento R.	10/26/1999	38.0674	121.7712	94.60	2.1
56	Sacramento R.	10/26/1999	38.0907	121.7438	56.95	2.6
60	N Mokelumne R.	10/25/1999	38.1456	121.5553	97.18	1.6
61	N Mokelumne R.	10/25/1999	38.1589	121.5344	98.21	2.3
62	N Mokelumne R.	10/25/1999	38.1842	121.5244	93.28	0.8
64	Beaver Slough	10/25/1999	38.1947	121.4736	73.88	2.1
65	Hog Slough	10/25/1999	38.1686	121.4736	76.32	1.9
66	Sycamore S.	10/25/1999	38.1422	121.4744	96.43	4.7
67	Tower Park	10/25/1999	38.1044	121.4917	92.78	2.2
68	Potatoe Slough	10/25/1999	38.0831	121.5017	89.33	1.7
69	White Slough	10/25/1999	38.0878	121.4783	99.86	1.8
70	Disappointment	10/25/1999	38.0489	121.4861	99.55	2.0
71	Connection S	10/25/1999	38.0436	121.4972	32.63	1.9
72	Columbia Cut	10/26/1999	38.0286	121.4881	82.25	4.3
73	Headreach Cut	10/26/1999	38.0136	121.4561	97.21	4.7
74	Turner Cut	10/26/1999	37.9969	121.4522	42.97	2.1
76	Middle River	10/26/1999	37.9514	121.5328	28.23	0.6
77	Middle River	10/26/1999	37.9822	121.5300	87.84	1.9
78	Middle River	10/26/1999	38.0283	121.4881	34.14	4.6
79	Middle River	10/26/1999	38.0483	121.5336	96.53	2.5
80	Old River	10/26/1999	37.9542	121.5700	25.55	1.8
81	Old River	10/26/1999	37.9783	121.5808	93.27	3.9
82	Connection S.	10/26/1999	38.0133	121.5558	66.11	2.0
84	Franks Tract	10/26/1999	38.0517	121.5919	96.80	2.1
85	Franks Tract	10/26/1999	38.0583	121.6089	86.97	1.9
87	Old River Flats	10/26/1999	38.0942	121.5769	91.47	2.0
88	Fisherman's S.	10/26/1999	38.1058	121.6153	55.42	2.2

Table A2-1 cont. Initial Survey Ancillary Data

Station #	Station Name	Date	Latitude	Longitude	Fines (%)	LOI (%)
91	SJR Jersey Pt.	10/26/1999	38.0543	121.6922	11.16	1.2
93	Big Break	10/26/1999	38.0206	121.7237	67.22	1.0
94	Big Break	10/26/1999	38.0254	121.7490	1.39	0.4
95	San Joaquin River	10/26/1999	38.0201	121.7657	2.08	0.6
102	San Joaquin River	10/26/1999	38.0223	121.7573	0.42	0.5
103	Antioch Dunes	10/26/1999	38.0166	121.7931	40.02	1.5
104	Kimball Island	12/1/1999	38.0228	121.8094	79.34	2.0
105	San Joaquin River	12/1/1999	38.0253	121.8419	94.48	2.4
106	Sherman Lake	12/1/1999	38.0464	121.8042	99.94	1.9
107	Brown's Island	12/1/1999	38.0336	121.8697	98.86	6.8
108	Brown's Island	12/1/1999	38.0458	121.8631	98.87	2.4
109	Sac River	12/1/1999	38.0636	121.8067	99.97	2.5
110	San Joaquin River	12/1/1999	38.0739	121.8439	55.36	3.5
111	Mallard Island	12/1/1999	38.0423	121.9167	98.72	2.2
112	Suison Bay	12/1/1999	38.0559	121.9281	93.17	2.4
113	Van Sickel S.	12/1/1999	38.0698	121.9119	41.29	2.4
114	Montezuma S.	12/1/1999	38.0720	121.8711	98.32	3.0
115	Suison Bay	12/1/1999	38.0817	121.9206	91.56	2.5
116	Honker Bay	12/1/1999	38.0686	121.9195	3.48	1.2
117	Suison Bay	12/1/1999	38.0772	121.9447	99.88	2.3
118	Suison Bay Shore	11/30/1999	38.0539	121.9914	91.56	2.5
119	Suison Bay	11/18/1999	38.1059	122.0494	96.36	2.1
120	Suison Bay	11/30/1999	38.0875	122.0073	92.80	5.7
121	Roe Island Marsh	11/18/1999	38.0864	122.0500	54.47	2.0
123	Suison Bay Marsh	11/18/1999	38.1342	122.0425	99.54	2.0
124	Suison Bay Marsh	11/18/1999	38.1345	122.0509	80.56	3.1
125	Grizzly Island	11/18/1999	38.1369	122.0461	97.84	3.7
126	Joyce Island	11/18/1999	38.1286	122.0617	99.73	1.9
127	Montezuma S.	11/18/1999	38.1425	122.0595	99.59	1.7
128	Joyce Island	11/18/1999	38.1622	122.0478	99.96	3.2
129	Suison Slough	11/18/1999	38.1678	122.0672	99.89	1.3
130	Suison Bay	11/18/1999	38.1036	122.0645	97.34	2.1
131	Goodyear Slough	11/29/1999	38.0964	122.0769	99.29	3.0
132	Goodyear Slough	11/29/1999	38.0853	122.0897	98.74	2.3
134	S. Hampton Bay	11/16/1999	38.0656	122.1911	99.57	1.8
169	Smith canal	10/27/1999	37.9695	121.3136	80.31	2.2
171	San Joaquin River	10/27/1999	37.9286	121.3281	13.60	0.6
172	San Joaquin River	10/27/1999	37.8662	121.3269	15.80	1.0
200	Prospect Slough	10/27/1999	38.2740	121.6655	48.30	2.7

Table A2-1 cont. Initial Survey Ancillary Data

Station #	Station Name	Date	Latitude	Longitude	Fines (%)	LOI (%)
202	14 Mile Slough	10/29/1999	38.0105	121.3865	99.72	1.6
203	Port of Stockton	10/29/1999	37.9542	121.3164	94.06	1.7
211	Haas Slough	10/28/1999	38.2950	121.7258	38.50	-
212	Cache Slough	10/28/1999	38.2883	121.7217	94.51	3.3
213	Liberty island tule	10/28/1999	38.3133	121.6678	95.21	2.9
214	Liberty island	10/28/1999	38.3139	121.6672	99.97	2.8
215	Liberty Cut Marsh	10/28/1999	38.3294	121.6769	98.13	2.3
216	14 Mile Slough	10/29/1999	38.3136	121.6675	99.74	2.1
217	14 Mile Slough	10/29/1999	38.0056	121.3997	77.16	-
218	Middle River	10/29/1999	38.0136	121.4558	-	-
219	San Joaquin River	10/29/1999	38.0086	121.4469	98.36	2.6
220	Port of Stockton	10/29/1999	37.9514	121.3181	95.86	2.1
227	Sherman Island	11/9/1999	38.0856	121.6900	97.27	3.0
228	Brannon Island	11/9/1999	38.1230	121.6637	99.69	-
231	Consumnus River	11/10/1999	38.2705	121.4046	58.63	2.7
233	Consumnes R	11/10/1999	38.2527	121.4060	24.75	2.5
240	Consumnes R.	11/10/1999	38.2733	121.3922	56.19	2.8
250	CR at the "Beach"	11/10/1999	38.2579	121.4254	95.56	2.6

Table A2-2 Initial Survey Mercury Data

* = below detection limit

Station #	Station Name	Date	Latitude	Longitude	MMHg (ng/g)	HgT (ng/g)	Ratio (%)
30	Sacramento R	10/26/99	38.3419	121.6453	0.492	194.7	0.25
35	Prospect S.	10/27/99	38.2583	121.6736	0.119	113.3	0.11
36	Cache S.	10/27/99	38.2883	121.7217	0.259	130.7	0.20
38	Prospect S.	10/26/99	38.2600	121.6711	0.176	323.8	0.05
39	Prospect S.	10/26/99	38.6373	121.6806	0.277	124.6	0.22
41	Sacramento R	10/27/99	38.4980	121.5591	-	6.5*	-
43	Sacramento R	10/27/99	38.4272	121.5307	0.010*	9.5*	-
47	Sacramento R	10/27/99	38.3398	121.5636	0.181	61.1	0.30
50	Georgina S.	10/27/99	38.2157	121.5405	-	81.1	-
51	Sacramento R	10/26/99	38.2008	121.6583	0.536	208.5	0.26
53	Sacramento R	10/27/99	38.2560	121.5151	-	5.5*	-
54	Snodgrass R.	10/27/99	38.2535	121.4990	0.264	46.1	0.57
55	Sacramento R	10/26/99	38.0674	121.7712	-	224.7	-
56	Sacramento R	10/26/99	38.0907	121.7438	-	98.9	-
60	N.Mokelumne	10/25/99	38.1456	121.5553	0.537	279.8	0.19
61	N.Mokelumne	10/25/99	38.1589	121.5344	0.540	-	-
62	N Mokelumne	10/25/99	38.1842	121.5244	0.650	73.6	0.88
64	Beaver S	10/25/99	38.1947	121.4736	0.650	190.1	0.34
65	Hog S	10/25/99	38.1686	121.4736	0.238	112.5	0.21
66	Sycamore S	10/25/99	38.1422	121.4744	-	237.8	-
67	Tower Park	10/25/99	38.1044	121.4917	0.610	135.7	0.45
68	Little Potatoe	10/25/99	38.0831	121.5017	0.681	172.9	0.39
69	White S.	10/25/99	38.0878	121.4783	-	273.9	-
70	Disappoint S.	10/25/99	38.0489	121.4861	0.613	113.7	0.54
71	Connect S.	10/25/99	38.0436	121.4972	0.200	82.5	0.24
72	Columbia C.	10/26/99	38.0286	121.4881	0.827	145.1	0.57
73	Headreach	10/26/99	38.0136	121.4561	1.860	89.5	2.08
74	Turner Cut	10/26/99	37.9969	121.4522	0.206	110.2	0.19
76	Middle R.	10/26/99	37.9514	121.5328	0.313	33.6	0.93
77	Middle R.	10/26/99	37.9822	121.5300	0.940	139.1	0.68
78	Middle R.	10/26/99	38.0283	121.4881	1.687	125.6	1.34
79	Middle R.	10/26/99	38.0483	121.5336	0.134	162.7	0.08
80	Old River	10/26/99	37.9542	121.5700	0.077	84.1	0.09
81	Old River	10/26/99	37.9783	121.5808	0.573	57.5*	-
82	Connection S	10/26/99	38.0133	121.5558	1.810	125.8	1.44
84	Franks Tract	10/26/99	38.0517	121.5919	1.112	173.0	0.64
85	Franks Tract	10/26/99	38.0583	121.6089	2.070	78.5	2.64
87	Old River	10/26/99	38.0942	121.5769	0.655	108.0	0.61
88	Fisherman S	10/26/99	38.1058	121.6153	0.385	156.8	0.25

Table A2-2 cont. Initial Survey Mercury Data

* = below detection limit

Station #	Station Name	Date	Latitude	Longitude	MMHg (ng/g)	HgT (ng/g)	Ratio (%)
91	SJR	10/26/99	38.0543	121.6922	0.037	33.1	0.11
93	Big Break	10/26/99	38.0206	121.7237	-	151.5	-
94	Big Break	10/26/99	38.0254	121.7490	0.003*	10.99*	-
95	San Joaquin	10/26/99	38.0201	121.7657	0.009*	29.2	-
102	San Joaquin	10/26/99	38.0223	121.7573	0.006*	5.0*	-
103	Antioch	10/26/99	38.0166	121.7931	0.180	57.6	0.31
104	Kimball Is	12/01/99	38.0228	121.8094	0.395	235.7	0.17
105	San Joaquin	12/01/99	38.0253	121.8419	0.435	250.9	0.17
106	Sherman Is	12/01/99	38.0464	121.8042	0.510	226.6	0.23
107	Brown's Is	12/01/99	38.0336	121.8697	0.380	100.2	0.38
108	Brown's Is	12/01/99	38.0458	121.8631	0.705	270.5	0.26
109	Sac R	12/01/99	38.0636	121.8067	1.071	372.2	0.29
110	San Joaquin	12/01/99	38.0739	121.8439	0.422	266.8	0.16
111	Mallard Is	12/01/99	38.0423	121.9167	0.290	286.6	0.10
112	Suison Bay	12/01/99	38.0559	121.9281	1.005	245.1	0.41
113	Van Sickel	12/01/99	38.0698	121.9119	0.180	186.3	0.10
114	Montezuma	12/01/99	38.0720	121.8711	0.604	249.0	0.24
115	Suison Bay	12/01/99	38.0817	121.9206	0.829	483.3	0.17
116	Honker Bay	12/01/99	38.0686	121.9195	0.009*	69.6	-
117	Suison Bay	12/01/99	38.0772	121.9447	0.398	267.0	0.15
118	Suison Bay	11/30/99	38.0539	121.9914	0.111	252.5	0.04
119	Suison Bay	11/18/99	38.1059	122.0494	0.342	283.9	0.12
120	Suison Bay	11/30/99	38.0875	122.0073	0.679	66.3	1.02
121	Roe Island	11/18/99	38.0864	122.0500	0.164	189.6	0.09
123	Suison Bay	11/18/99	38.1342	122.0425	0.276	178.1	0.15
124	Suison Bay	11/18/99	38.1345	122.0509	-	347.0	-
125	Grizzly Is	11/18/99	38.1369	122.0461	0.977	574.5	0.17
126	Joyce Island	11/18/99	38.1286	122.0617	0.588	352.6	0.17
127	Montezuma	11/18/99	38.1425	122.0595	0.636	273.1	0.23
128	Joyce Island	11/18/99	38.1622	122.0478	9.338	414.4	2.25
129	Suison S	11/18/99	38.1678	122.0672	0.527	336.7	0.16
130	Suison Bay	11/18/99	38.1036	122.0645	0.261	334.8	0.08
131	Goodyear S	11/29/99	38.0964	122.0769	0.800	340.2	0.24
132	Goodyear S	11/29/99	38.0853	122.0897	0.579	393.5	0.15
134	Hampton	11/16/99	38.0656	122.1911	1.385	526.7	0.26
169	Smith canal	10/27/99	37.9695	121.3136	0.220	253.4	0.09
171	SJR	10/27/99	37.9286	121.3281	0.074	13.02*	-
172	SJR	10/27/99	37.8662	121.3269	0.070	21.0	0.33
200	Prospect S	10/27/99	38.2740	121.6655	0.628	223.5	0.28

Table A2-2 cont. Initial Survey Mercury Data

* = below detection limit

Station #	Station Name	Date	Latitude	Longitude	MMHg (ng/g)	HgT (ng/g)	Ratio (%)
200	Prospect S	10/27/99	38.2740	121.6655	0.628	223.5	0.28
202	14 Mile S	10/29/99	38.0105	121.3865	0.522	103.7	0.50
203	P Stockton	10/29/99	37.9542	121.3164	0.320	193.8	0.17
211	Haas S	10/28/99	38.2950	121.7258	0.259	142.6	0.18
212	Cache S	10/28/99	38.2883	121.7217	0.609	147.1	0.41
213	Liberty Is	10/28/99	38.3133	121.6678	0.470	103.8	0.45
214	Liberty Is	10/28/99	38.3139	121.6672	0.643	266.4	0.24
215	Liberty Cut	10/28/99	38.3294	121.6769	0.512	312.6	0.16
216	14 Mile S	10/29/99	38.3136	121.6675	0.338	107.3	0.32
217	14 Mile S	10/29/99	38.0056	121.3997	2.990	47.16*	-
218	Middle R	10/29/99	38.0136	121.4558	0.823	128.8*	-
219	SJR	10/29/99	38.0086	121.4469	2.040	157.0	1.30
220	P Stockton	10/29/99	37.9514	121.3181	0.320	130.3	0.25
227	Sherman Is	11/09/99	38.0856	121.6900	1.528	75.0	2.04
228	Brannon Is	11/09/99	38.1230	121.6637	0.847	49.36*	-
231	Cosumnes	11/10/99	38.2705	121.4046	0.169	52.7	0.32
233	Cosumnes	11/10/99	38.2527	121.4060	-	275.3	-
240	Cosumnes	11/10/99	38.2733	121.3922	0.024	15.75*	-
250	Cosumnes	11/10/99	38.2579	121.4254	-	344.2	-

Table A2-3 Seasonal Data

Station Name	Date	MMHg (ng/g)	HgT _{dry} (ng/g)	Ratio (%)
Prospect Slough	06/26/00	0.171	121.0	0.14
Prospect Slough	07/25/00	0.901	265.0	0.34
Prospect Slough	09/05/00	0.899	114.0	0.79
Prospect Slough	09/27/00	0.663	72.9	0.91
Prospect Slough	10/31/00	0.134	80.1	0.17
Prospect Slough	04/10/01	0.449	164.0	0.27
Prospect Slough	04/19/01	1.919	109.0	1.76
Prospect Slough	05/22/01	1.024	135.0	0.76
Prospect Slough	06/11/01	1.021	91.7	1.11
Prospect Slough	07/16/01	1.170	112.0	1.04
Prospect Slough	07/31/01	0.997	88.8	1.12
Prospect Slough	08/15/01	1.448	84.4	1.72
Prospect Slough	08/27/01	1.351	269.0	0.50
Sherman Island	06/01/00	0.345	48.2	0.72
Sherman Island	06/27/00	2.588	217.0	1.19
Sherman Island	07/26/00	4.920	240.0	2.05
Sherman Island	09/06/00	0.944	231.0	0.41
Sherman Island	09/26/00	3.099	170.0	1.82
Sherman Island	12/12/00	1.460	265.0	0.55
Sherman Island	01/31/01	0.950	161.0	0.59
Sherman Island	02/27/01	1.520	175.0	0.87
Sherman Island	03/27/01	0.919	146.0	0.63
Sherman Island	05/18/01	0.518	87.2	0.59
Sherman Island	06/11/01	1.626	239.0	0.68
Sherman Island	06/26/01	0.435	76.9	0.57
Sherman Island	07/31/01	0.592	76.4	0.77
Sherman Island	08/27/01	0.355	83.5	0.43
Sherman Island	10/16/01	0.375	122.0	0.31

Table A2-3 cont. Seasonal Data

Station Name	Date	MMHg (ng/g)	HgT (ng/g)	Ratio (%)
Franks Tract	05/28/00	0.856	172.0	0.50
Franks Tract	06/26/00	0.351	117.0	0.30
Franks Tract	07/25/00	0.913	157.0	0.58
Franks Tract	09/05/00	0.791	120.0	0.66
Franks Tract	09/23/00	0.822	196.0	0.42
Franks Tract	10/23/00	1.990	162.0	1.23
Franks Tract	12/12/00	2.230	196.0	1.14
Franks Tract	02/08/01	1.910	152.0	1.26
Franks Tract	02/28/01	2.230	146.0	1.53
Franks Tract	03/26/01	2.530	199.0	1.27
Franks Tract	04/19/01	1.390	161.0	0.86
Franks Tract	05/18/01	0.960	147.0	0.65
Franks Tract	06/11/01	0.550	157.0	0.35
Franks Tract	06/25/01	0.760	193.0	0.39
Franks Tract	07/16/01	0.440	157.0	0.28
Franks Tract	07/30/01	2.776	202.0	1.37
Franks Tract	08/15/01	5.814	143.0	4.07
Franks Tract	08/27/01	3.756	187.0	2.01
Franks Tract	10/19/01	0.510	189.0	0.27
Connection Slough	05/29/00	5.660	124.0	4.56
Connection Slough	06/26/00	1.915	167.0	1.15
Connection Slough	07/25/00	1.255	164.0	0.77
Connection Slough	09/05/00	0.797	185.0	0.43
Connection Slough	09/25/00	1.470	84.2	1.75
Connection Slough	10/24/00	2.740	205.0	1.34
Connection Slough	12/12/00	1.820	156.0	1.17
Connection Slough	02/08/01	2.620	128.0	2.05
Connection Slough	02/28/01	1.950	119.0	1.64
Connection Slough	03/26/01	1.400	81.1	1.73
Connection Slough	04/19/01	2.950	142.0	2.08
Connection Slough	05/19/01	4.785	159.0	3.01
Connection Slough	06/25/01	6.947	177.0	3.92
Connection Slough	07/16/01	2.741	170.0	1.61
Connection Slough	07/30/01	1.096	209.0	0.52
Connection Slough	08/27/01	0.761	161.0	0.47

Table A2-3 cont. Seasonal Data

Station Name	Date	MMHg (ng/g)	HgT (ng/g)	Ratio (%)
White Slough	06/01/00	0.808	222.0	0.36
White Slough	06/26/00	1.119	197.0	0.57
White Slough	07/25/00	1.161	193.0	0.60
White Slough	09/05/00	0.663	185.0	0.36
White Slough	09/23/00	1.596	199.0	0.80
White Slough	10/23/00	1.620	188.0	0.86
White Slough	12/12/00	0.566	155.0	0.37
White Slough	02/08/01	1.710	161.0	1.06
White Slough	03/26/01	0.800	157.0	0.51
White Slough	04/19/01	0.913	186.0	0.49
White Slough	05/24/01	1.727	185.0	0.93
White Slough	07/16/01	1.139	166.0	0.69
White Slough	08/27/01	7.552	167.0	4.52
White Slough	10/20/01	2.200	181.0	1.22
Cosumnes River	09/26/00	0.502	306.0	0.16
Cosumnes River	10/24/00	0.992	357.0	0.28
Cosumnes River	12/12/00	1.630	315.0	0.52
Cosumnes River	01/31/01	2.330	270.0	0.86
Cosumnes River	03/01/01	1.900	234.0	0.81
Cosumnes River	03/26/01	1.230	333.0	0.37
Cosumnes River	04/19/01	0.850	301.0	0.28
Cosumnes River	05/20/01	1.000	380.0	0.26
Cosumnes River	06/11/01	0.910	306.0	0.30
Cosumnes River	06/25/01	0.860	205.0	0.42
Cosumnes River	07/16/01	4.536	382.0	1.19
Cosumnes River	07/30/01	5.402	274.0	1.97
Cosumnes River	08/15/01	4.366	230.0	1.90
Cosumnes River	08/27/01	4.145	273.0	1.52
Cosumnes River	10/17/01	1.800	249.0	0.72

Table A2-4 Bioavailability Data Un-Sieved Samples

Station Name	Date/Time	Latitude	Longitude	MMHg (ng/g)	HgT (ng/g)
Don Pedro	10/16/2001	37.7069	120.4249	0.080	24.4
Caswell State Park	10/16/2001	37.6941	121.1808	0.120	21.7
Mokelumne River @ Lodi Lake	10/16/2001	38.1490	121.2934	0.588	75.0
Tuolumne River @ Robert's Ferry Bridge	10/16/2001	37.6358	120.6184	1.680	19.9
Comanche Reservoir	10/17/2001	38.2213	121.0106	0.091	101.0
Folsom Lake	10/17/2001	38.7141	121.1506	0.281	112.0
Mokelumne River	10/17/2001	38.3125	120.7207	0.047	12.0
North Fork Cosumnes @ Sandridge Rd & Hwy 49	10/17/2001	38.5886	120.8452	3.490	167.0
North Tuolumne @ Algerine Road	10/17/2001	37.8676	120.2947	0.013	4.5
Capay Dam	10/18/2001	38.7118	122.0851	7.760	376.0
Bear Creek @ Hwy 20	10/18/2001	39.0114	122.3610	3.520	2869.0
Bear Creek above Cache Creek	10/18/2001	38.9276	122.3335	1.810	10845.0
Cache Creek @ Rumsey Bridge	10/18/2001	38.8902	122.2387	0.311	75.0
Harley Gulch	10/18/2001	39.0140	122.4363	0.142	37923.0
Sulfur Creek	10/18/2001	39.0400	122.4085	1.900	38749.0
Cachement Basin	10/19/2001	38.6785	121.6736	1.100	382.0
Cache Creek @ Hwy 505	10/19/2001	38.6959	121.9550	0.484	134.0
Cache Creek @ Road 102	10/19/2001	38.7265	121.7299	0.216	109.0
Middle Fork Cosumnes R	10/19/2001	38.5534	120.8482	0.198	13.0
Cosumnes @ Dillard Road	10/19/2001	38.4911	121.1703	0.030	14.9
New Hogan	10/20/2001	38.1522	120.8081	0.158	135.0

Table A2-5 Bioavailability Data Sieved Samples

Station Name	Date	Latitude	Longitude	MMHg (ng/g)	HgT (ng/g)
Clear Lake		39.0803	122.8630	0.180	137.0
Lake Berryessa	10/18/2001	38.5155	122.1233	0.203	107.0
Harley Gulch	10/18/2001	39.0140	122.4363	0.142	37923.0
Sulfur Creek	10/18/2001	39.0400	122.4085	2.750	34170.0
Bear Creek @ Hwy 20	10/18/2001	39.0114	122.3610	2.900	4325.0
Bear Creek above Cache Creek	10/18/2001	38.9276	122.3335	3.850	1450.0
Cache Creek @ Rumsey Bridge	10/18/2001	38.8902	122.2387	1.480	345.0
Capay Dam	10/18/2001	38.7118	122.0851	7.760	376.0
Cache @ Esparto	10/25/2001	38.7146	122.0069	9.160	1086.0
Cache Creek @ Hwy 505	10/19/2001	38.6959	121.9550	4.400	172.0
Cache Creek @ Road 102	10/19/2001	38.7265	121.7299	0.216	109.0
Cachement Basin	10/19/2001	38.6785	121.6736	3.830	1157.0
Putah Creek @ E7	10/19/2001	38.5170	121.7601	0.464	789.0
Comanche Reservoir	10/17/2001	38.2213	121.0106	0.096	47.0
Don Pedro Reservoir	10/16/2001	37.7069	120.4249	0.255	554.0
Folsom Lake	10/17/2001	38.7141	121.1506	0.171	103.0
New Hogan MMHg	10/20/2001	38.1522	120.8081	0.158	135.0
Middle Fork Cosumnes R	10/19/2001	38.5534	120.8482	4.190	286.0
North Fork Cosumnes @ Sandridge Rd & Hwy 49	10/17/2001	38.5886	120.8452	2.400	127.0
North Tuolumne @ Algerine Road	10/17/2001	37.8676	120.2947	0.180	3.3
Mokelumne River @ Hwy 49	10/17/2001	38.3125	120.7207	0.762	139.0
Caswell State Park	10/16/2001	37.6941	121.1808	0.971	113.0
Cosumnes River @ Dillard Road	10/19/2001	38.4911	121.1703	2.540	140.0
Mokelumne River @ Lodi Lake	10/16/2001	38.1490	121.2934	1.440	175.0
Tuolumne River @ Robert's Ferry Bridge	10/16/2001	37.6358	120.6184	2.950	134.0

Table A2-6 Cross Channel Data

Station Name	Station #	Latitude	Longitude	MMHg (ng/g)	HgT (ng/g)
East Colombia Cut	T2	38.03081	121.49117	0.430	44.6
East Colombia Cut	T3	38.03078	121.49136	0.933	198.8
East Colombia Cut	T4	38.03081	121.49147	0.702	133.9
East Colombia Cut	T5	38.03078	121.49158	1.160	202
East Colombia Cut	T6	38.03075	121.49183	0.616	165.7
East Colombia Cut	T7	38.03072	121.49197	0.529	176.2
East Colombia Cut	T8	38.03069	121.49217	0.528	145.6
East Colombia Cut	T9	38.03066	121.49230	0.693	138.5
East Colombia Cut	T10	38.03061	121.49243	0.731	153.4
East Colombia Cut	T11	38.03059	121.49255	0.849	38.8*
East Colombia Cut	T12	38.03053	121.49270	3.580	23.9*

Table A2-7 Wetland Transect Data

Name	ID	Latitude	Longitude	MMHg (ng/g)	HgT (ng/g)
mandeville cut	under	38.06152	121.53774	3.84	170.0
mandeville cut	mid	-	-	0.785 ± .045	125.0
mandeville cut	channel	38.05840	121.54008	1.49 ± .91	164.0
14 mile slough	under	38.00659	121.39224	7.82 ± .26	256.0 ± 41.
14 mile slough	mid	-	-	2.99 ± .38	159.0 ± 1.0
14 mile slough	channel	-	-	1.37 ± .02	142.5 ± 2.5
weber point	under	38.00965	121.44651	4.34 ± .80	219.0 ± 5.0
weber point	mid	38.00977	121.44657	3.88 ± .10	203.0 ± 8.0
weber point	channel	38.00984	121.44635	2.06 ± 1.64	246.0 ± 78.0
sjr near hog	control	38.00397	121.44416	0.981	143.0
delta yacht club	control	38.02811	121.47695	0.202	96.3

Table A2-8 MMHg Flux Proxy Data

Name	Latitude	Longitude	Date	MMHg (ng/g)	SE	MMHg (ng/m2/day)	SE
Colombia Cut	38.03052	121.49203	05/30/00	0.653	0.11	12.1	5
Colombia Cut	38.03077	121.49116	05/30/00	1.239	0.43	11.7	28
Little Holland	38.29403	121.66144	05/29/00	0.801	0.27	21.6	4
Franks tract	38.05280	121.59204	09/23/00	0.822	-	2.0	3
Franks tract (dark)	38.05280	121.59204	09/23/00	0.822	-	12.1	2
Little Holland	38.28960	121.66228	09/27/00	0.663	-	2.8	8
Little Holland	38.28960	121.66228	09/27/00	0.663	-	6.1	4
Cosumnes River	38.25821	121.42641	03/01/01	1.926	0.27	31.9	30
Franks Tract Cosumnes River	38.05280	121.59204	05/18/01	0.778	0.18	14.7	11
Prospect Slough	38.25821	121.42641	05/20/01	1.233	0.23	18.4	8
Cosumnes River	38.28621	121.66451	05/22/01	0.705	0.32	16.0	4
Franks Tract Marsh	38.25821	121.42641	10/17/01	1.800	0.09	24.5	15
Franks Tract Marsh (dark)	38.05943	121.61162	10/18/01	5.312	0.63	169.5	22
Franks Tract Sherman Is (dark)	38.05943	121.61162	10/18/01	5.312	0.63	140.3	32
White S	38.05167	121.59181	10/19/01	0.499	0.01	1.6	3
White S	38.04128	121.81944	10/16/01	0.375	-	5.1	4
White S	38.08736	121.47834	10/20/01	2.16	0.61	6.06	-
White S	38.08736	121.47834	05/01/01	1.727	-	1.0	-
White S	38.08731	121.47848	06/01/00	0.808	0.03	-16.8	-
Sherman Is	38.04128	121.81944	09/26/00	3.099	-	-18.5	-
Sherman Is	38.04128	121.81944	05/01/01	1.820	-	-7.3	-
Cosumnes R	38.25821	121.42641	10/01/01	1.800	0.09	-6.1	-
Sherman Is	38.04128	121.81944	10/16/01	2.071	1.64	-0.6	-