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

Project Information

1. **Proposal Title:**

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

2. **Proposal applicants:**

   Mark Stephenson, California Department of Fish and Game
   Kenneth Coale, Moss Landing Marine Labs (San Jose State University)
   Gary Gill, Texas A&M University
   Max Puckett, Department of Fish and Game

3. **Corresponding Contact Person:**

   Kenneth Coale
   Moss Landing Marine Labs
   8272 Moss Landing Road Moss Landing, Calif. 95039
   831 632-4406
   coale@mlml.calstate.edu

4. **Project Keywords:**

   Contaminants
   Heavy Metals (mercury, selenium, etc.)
   Water Quality Assessment & Monitoring

5. **Type of project:**

   Research

6. **Does the project involve land acquisition, either in fee or through a conservation easement?**

   No

7. **Topic Area**:

   Ecosystem Water and Sediment Quality

8. **Type of applicant:**

   University

9. **Location - GIS coordinates:**

Latitude: 38.052

Longitude: 121.609

Datum:

Describe project location using information such as water bodies, river miles, road intersections, landmarks, and size in acres.

Study area encompasses the entire CALFED study area including all watersheds emptying into the Delta, Suison, and San Pablo Bays

10. **Location - Ecozone:**

3.1 Keswick Dam to Red Bluff Diversion Dam, 3.2 Red Bluff Diversion Dam to Chico Landing, 3.3 Chico Landing to Colusa, 3.4 Colusa to Verona, 3.5 Verona to Sacramento, 4.1 Clear Creek, 4.2 Cow Creek, 4.3 Bear Creek, 4.4 Battle Creek, 5.1 Upper Cottonwood Creek, 5.2 Lower Cottonwood Creek, 6.1 Stony Creek, 6.2 Elder Creek, 6.3 Thomas Creek, 6.4 Colusa Basin, 7.1 Paynes Creek, 7.2 Antelope Creek, 7.3 Mill Creek, 7.4 Deer Creek, 7.5 Big Chico Creek, 7.6 Butte Creek, 7.7 Butte Sink, 8.1 Feather River, 8.2 Yuba River, 8.3 Bear River and Honcut Creek, 8.4 Sutter Bypass, 9.1 American Basin, 9.2 Lower American River, 10.1 Cache Creek, 10.2 Putah Creek, 10.3 Solano, 10.4 Willow Slough, 12.1 Vernalis to Merced River, 12.2 Merced River to Mendota Pool, 12.3 Mendota Pool to Gravelly Ford, 12.4 Gravelly Ford to Friant Dam, 13.1 Stanislaus River, 13.2 Tuolumne River, 13.3 Merced River, West San Joaquin Basin, 1.1 North Delta, 1.2 East Delta, 1.3 South Delta, 1.4 Central and West Delta, 11.1 Cosumnes River, 11.2 Mokelumne River, 11.3 Calaveras River, 2.1 Suisun Bay & Marsh, 2.2 Napa River, 2.5 San Pablo Bay, Code 15: Landscape

11. **Location - County:**

Amador, Butte, Calaveras, Colusa, Contra Costa, El Dorado, Glenn, Lake, Lassen, Madera, Mariposa, Merced, Modoc, Napa, Placer, Plumas, Sacramento, San Joaquin, Shasta, Sierra, Siskiyou, Solano, Sonoma, Stanislaus, Sutter, Tehama, Tuolumne, Yuba

12. **Location - City:**

Does your project fall within a city jurisdiction?

No

13. **Location - Tribal Lands:**

Does your project fall on or adjacent to tribal lands?

Yes **If yes, please list the tribal lands:** Alturas, Redding, Big Bend, Roaring Creek, Lookout, Montgomery Creek, Susanville, Greenmile, Enterprise, Berry Creek, Moretown, Colusa, Sulfur Bank, Cortina, Rumsey, Shingle Springs, Jackson, Buenavista, Sheepranch, Chicken Ranch, Toulomne, Picayune, Big Sandy, Table Mountain, Cold Springs, and Santa Rosa Rancherias

14. **Location - Congressional District:**

3,4,5,11,18,20,10,19

15. **Location:**

    California State Senate District Number: 1,2,4,5,6,7,9,10,16,12,14

    California Assembly District Number: 1,2,3,4,6,7,8,11,15,10,26,25,17,31,29, 26, 30

16. **How many years of funding are you requesting?**

    3

17. **Requested Funds:**
    a) Are your overhead rates different depending on whether funds are state or federal?

    Yes

    If yes, list the different overhead rates and total requested funds:

State Overhead Rate:	26
Total State Funds:	$3,881,215.46
Federal Overhead Rate:	47
Total Federal Funds:	0

    b) Do you have cost share partners already identified?

    No

    c) Do you have potential cost share partners?

    No

    d) Are you specifically seeking non-federal cost share funds through this solicitation?

    No

    If the total non-federal cost share funds requested above does not match the total state funds requested in 17a, please explain the difference:

18. **Is this proposal for next-phase funding of an ongoing project funded by CALFED?**

    Yes

    If yes, identify project number(s), title(s) and CALFED program (e.g., ERP, Watershed, WUE, Drinking Water):

99FC200241	**Assessment of Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed**	**ERP**

Have you previously received funding from CALFED for other projects not listed above?

No

19. **Is this proposal for next-phase funding of an ongoing project funded by CVPIA?**

No

Have you previously received funding from CVPIA for other projects not listed above?

No

20. **Is this proposal for next-phase funding of an ongoing project funded by an entity other than CALFED or CVPIA?**

No

Please list suggested reviewers for your proposal. (optional)

Dr. James Wiener	**University of Wisconsin-La Crosse**	**608-785-6454**	**wiener.jame@uwlax.edu**
Dr. David Krabbenhoft	**U.S. Geological Survey**	**608-821-3843**	**dpkrabbe@usgs.gov**
Dr. Cynthia Gilmour	**The Academy of Natural Sciences, Estuarine Research Center**	**410-586-9713**	**gilmour@acnatsci.org**
Dr. William Landing	**Florida State University**	**409-740-4710**	**wlanding@mailer.fsu.edu**

21. **Comments:**

Environmental Compliance Checklist

<u>Transport, Cycling, and Fate of Mercury and Monomethyl Mercury in the San Francisco Delta and Tributaries--An Integrated Mass Balance Assessment Approach</u>

1. **CEQA or NEPA Compliance**
   a) Will this project require compliance with CEQA?

      No
   b) Will this project require compliance with NEPA?

      No
   c) If neither CEQA or NEPA compliance is required, please explain why compliance is not required for the actions in this proposal.

      This project is strictly a monitoring and research project for mercury.

2. **If the project will require CEQA and/or NEPA compliance, identify the lead agency(ies).** *If not applicable, put "None".*

   <u>CEQA Lead Agency:</u>
   <u>NEPA Lead Agency (or co-lead:)</u>
   <u>NEPA Co-Lead Agency (if applicable):</u>

3. **Please check which type of CEQA/NEPA documentation is anticipated.**

   CEQA
   -Categorical Exemption
   -Negative Declaration or Mitigated Negative Declaration
   -EIR
   Xnone

   NEPA
   -Categorical Exclusion
   -Environmental Assessment/FONSI
   -EIS
   Xnone

   If you anticipate relying on either the Categorical Exemption or Categorical Exclusion for this project, please specifically identify the exemption and/or exclusion that you believe covers this project.

4. **CEQA/NEPA Process**
   a) Is the CEQA/NEPA process complete?

      None

   b) If the CEQA/NEPA document has been completed, please list document name(s):

5. **Environmental Permitting and Approvals** (*If a permit is not required, leave both Required? and Obtained? check boxes blank.*)

LOCAL PERMITS AND APPROVALS

Conditional use permit

Variance

Subdivision Map Act

Grading Permit

General Plan Amendment

Specific Plan Approval

Rezone

Williamson Act Contract Cancellation

Other

STATE PERMITS AND APPROVALS

Scientific Collecting Permit

CESA Compliance: 2081

CESA Compliance: NCCP

1601/03

CWA 401 certification

Coastal Development Permit

Reclamation Board Approval

Notification of DPC or BCDC

Other

FEDERAL PERMITS AND APPROVALS

ESA Compliance Section 7 Consultation

ESA Compliance Section 10 Permit

Rivers and Harbors Act

CWA 404

Other

PERMISSION TO ACCESS PROPERTY

Permission to access city, county or other local agency land.
Agency Name:

Permission to access state land.
Agency Name:

Permission to access federal land.
Agency Name:

Permission to access private land.
Landowner Name:

6. **Comments.**

Mark Stephenson and staff are Department of Fish and Game employees and as such do not need a scientific collecting permit to collect sport fish (as long as they are not listed as threatened or endangered--which our target species are not).

Land Use Checklist

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

1. **Does the project involve land acquisition, either in fee or through a conservation easement?**

   No

2. **Will the applicant require access across public or private property that the applicant does not own to accomplish the activities in the proposal?**

   No

3. **Do the actions in the proposal involve physical changes in the land use?**

   No

   If you answered no to #3, explain what type of actions are involved in the proposal (i.e., research only, planning only).

   research and monitoring only

4. **Comments.**

Conflict of Interest Checklist

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

Please list below the full names and organizations of all individuals in the following categories:

- Applicants listed in the proposal who wrote the proposal, will be performing the tasks listed in the proposal or who will benefit financially if the proposal is funded.
- Subcontractors listed in the proposal who will perform some tasks listed in the proposal and will benefit financially if the proposal is funded.
- Individuals not listed in the proposal who helped with proposal development, for example by reviewing drafts, or by providing critical suggestions or ideas contained within the proposal.

The information provided on this form will be used to select appropriate and unbiased reviewers for your proposal.

Applicant(s):

Mark Stephenson, California Department of Fish and Game
Kenneth Coale, Moss Landing Marine Labs (San Jose State University)
Gary Gill, Texas A&M University
Max Puckett, Department of Fish and Game

Subcontractor(s):

Are specific subcontractors identified in this proposal? Yes

If yes, please list the name(s) and organization(s):

Mark Stephenson and Max Puckett	Department of Fish and Game
Gary Gill	Texas A&M University Galveston
Chris Foe	California Regional Water Quality Control Board--Sacramento
Brenda Lasorsa	Battelle Northwest
Joe Domagalski	U.S. Geological Survey
Kenneth Coale	Moss Landing Marine Labs (San Jose State University)
None	None
None	None
None	None
None	None

Helped with proposal development:

Are there persons who helped with proposal development?

No

Comments:

Budget Summary

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

Please provide a detailed budget for each year of requested funds, indicating on the form whether the indirect costs are based on the Federal overhead rate, State overhead rate, or are independent of fund source.

Independent of Fund Source

Year 1													
Task No.	**Task Description**	**Direct Labor Hours**	**Salary** ***(per year)***	**Benefits** ***(per year)***	**Travel**	**Supplies & Expendables**	**Services or Consultants**	**Equipment**	**Other Direct Costs**	**Total Direct Costs**	**Indirect Costs**	**Total Cost**
1	Administrative Support	519	10899	2833.74			32800			46532.74	10070.51	56603.25
2	Mass Loading, Riverine Characterization and Export Studies, sub-watershed studies	7038	110921.77	24415.39		37520.50	346267.00			519124.66	64442.99	583567.65
3	Atmospheric Mercury Deposition Studies	600.00	9600.00	2496.00	8000.00		198422.00			218518.0	11724.96	230242.96
4	Delta Wide Monitoring and Characterization Program: Determine Hg and MMHg; Benthic Flux Chamber Studies	2533	40643.78	10567.38	19000.00	7000.00	158765.00	8000.00		243976.16	20074.90	264051.06
5	Process Oriented Studies: Monomethyl Mercury Photo Demethylation, Delta Transects, Wetland Mass Loading,MMHg Loading, Sediment Biochemistry Conduct Air and Water Exchange	5616	89019.20	19942.70	16000.00	15000.00	262148.00	25000.00		427109.9	36390.09	463499.99

6	Process Oriented Studies: Monomethyl Mercury Photo Demethylation, Delta Transects, Wetland Mass Loading,MMHg Loading, Sediment Biochemistry Conduct Air and Water Exchange	1040	15600.00	468.00		500.00				16568.0	4307.68	20875.68
		17346	276683.75	60723.21	43000.00	60020.50	998402.00	33000.00	0.00	1471829.46	147011.13	1618840.59

Year 2												
Task No.	**Task Description**	**Direct Labor Hours**	**Salary** ***(per year)***	**Benefits** ***(per year)***	**Travel**	**Supplies & Expendables**	**Services or Consultants**	**Equipment**	**Other Direct Costs**	**Total Direct Costs**	**Indirect Costs**	**Total Cost**
1	Administrative Support	519.00	11443.95	2975.43			32800.00			47219.38	3749.04	50968.42
2	Mass Loading, Riverine Characterization and Export Studies, sub-watershed studies	6697.80	110539.79	24797.37		37520.50	346267.00			519124.66	44942.99	564067.65
3	Atmospheric Mercury Deposition Studies	600	10710.00	2784.60	8000.00		95057.00			116551.6	5588.60	122140.20
4	Delta Wide Monitoring and Characterization Program: Determine Hg and MMHg; Benthic Flux Chamber Studies	2533	42675.97	11095.75	19000.00	7000.00	116001.00			195772.72	20740.65	216513.37

5	Process Oriented Studies: Monomethyl Mercury Photo Demethylation, Delta Transects, Wetland Mass Loading,MMHg Loading, Sediment Biochemistry Conduct Air and Water Exchange	5616	98873.78	25707.18	16000.00	15000.00	233413.00			388993.96	40451.05	429445.01
6	Process Oriented Studies: Monomethyl Mercury Photo Demethylation, Delta Transects, Wetland Mass Loading,MMHg Loading, Sediment Biochemistry Conduct Air and Water Exchange	1040	16380.00	491.40		500.00				17371.4	4516.56	21887.96
		17005	290623.49	67851.73	43000.00	60020.50	823538.00	0.00	0.00	1285033.72	119988.89	1405022.61

Year 3												
Task No.	**Task Description**	**Direct Labor Hours**	**Salary** ***(per year)***	**Benefits** ***(per year)***	**Travel**	**Supplies & Expendables**	**Services or Consultants**	**Equipment**	**Other Direct Costs**	**Total Direct Costs**	**Indirect Costs**	**Total Cost**
1	Administrative Support	519	11988.90	3237.00			26000.00			41225.9	3958.73	45184.63
2	Mass Loading, Riverine Characterization and Export Studies, sub-watershed studies						65487			65487.0		65487.00

3	Atmospheric Mercury Deposition Studies	300	4950.00	1336.50	4000.00		96731.00			107017.5	2674.49	109691.99
4	Delta Wide Monitoring and Characterization Program: Determine Hg and MMHg; Benthic Flux Chamber Studies	2533	44708.16	12071.20	9500.00	7000.00	105476.00			178755.36	19052.63	197807.99
5	Process Oriented Studies: Monomethyl Mercury Photo Demethylation, Delta Transects, Wetland Mass Loading,MMHg Loading, Sediment Biochemistry Conduct Air and Water Exchange	5616	97921.12	26438.70	12000.00	15000.00	225567.00			376926.82	39353.55	416280.37
6	Process Oriented Studies: Monomethyl Mercury Photo Demethylation, Delta Transects, Wetland Mass Loading,MMHg Loading, Sediment Biochemistry Conduct Air and Water Exchange	1040	17160.00	514.80		500.00				18174.8	4725.45	22900.25
		10008	176728.18	43598.20	25500.00	22500.00	519261.00	0.00	0.00	787587.38	69764.85	857352.23

Grand Total=3881215.43

Comments.

Budget Justification

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

Direct Labor Hours. Provide estimated hours proposed for each individual.

Salary Information SJSUF Wes Heimfull time three years Lauri Park25%--three years Amy Byingtonfull time three years Tam Vossfull time three years Bettina Sohsthalf time three years Mya Gunnhalf time three years Wendy Wang25% time three years

Salary. Provide estimated rate of compensation proposed for each individual.

Salary Information SJSUF Wes Heim17-19/hrfull time three years Lauri Park20-22/hr25%--three years Amy Byington16-18/hrfull time three years Tam Voss16-18/hrfull time three years Bettina Sohst16-19/hrhalf time three years Mya Gunn16-18/hrhalf time three years Wendy Wang16-18/hr25% time three years

Benefits. Provide the overall benefit rate applicable to each category of employee proposed in the project.

All employees at SJSUF have a 26% benefit rate except for graduate students which have a 3%.

Travel. Provide purpose and estimate costs for all non-local travel.

All travel will be local (within study area), principly to collect samples and attend meetings

Supplies & Expendables. Indicate separately the amounts proposed for office, laboratory, computing, and field supplies.

The total amount proposed for supplies is $171,469 The percentage spent for types of supplies is: Mileage 0.50% Field Supplies 53.00% Laboratory 39.51% Office 1.00% Publications 1.00% Subscriptions 1.00% Telecommunications 1.00% Printing & Duplicating 0.49% Miscellaneous (Miscellaneous) 2.50%

Services or Consultants. Identify the specific tasks for which these services would be used. Estimate amount of time required and the hourly or daily rate.

Department of Fish and Game Contract Task 1--Management--Department of Fish and Game 41% time @26/hr for managing contract and coordinating= $32,800/year for three years Regional Water Quality Control Board, Sacramento--Chris Foe and co-workers Task 2--Collecting samples and writing reports--California Regional Water Quality Control Board--Sacramento--one and a half PYs for years 1 and 2, one half PYs for year three @ $26/hour= $458,423 for all three years combined. Battelle Contract Task 2 and 5B--analysis of methyl mercury--Battelle Northwest--cost base of $127 per water sample/2512 samples=$319,000 for all 3 yrs. Scientist $51,800-105,600/year; Science and Engineering assistant--$44,200-66,200/year Technician--$3,024-4,000/year Clerical--$2040-2856/year Texas A&M Contract--Gary Gill and Co-workers Task 3--Atmospheric Deposition--$368,492 Task 4B--Benthic Flux--$335,242 Task 5C--Sediment Biogeochemistry--$252,062 Task 5D--Air-Water Exchange--$117,503 Total all tasks for three years--$1,216,239 Principal investigator--all tasks--total 7 months per year for 3 years@$82,333 per year base salary plus benefits Graduate Student--tasks 4B and 5A--12 months total at 50% time@ approximately 17.06/hour Research Associate--tasks 3,4B,and

5C--total of 10 months @100% time for three years@ 21.41/hour--$97,948 plus benefits for three years combined. Post Doctoral Investigator--tasks 4B,5A,5C,and 5D--12 man months per year for three years (36 months)@approx. $18.17/hour--$113,490 total for three years combined plus benefits.

Equipment. Identify non-expendable personal property having a useful life of more than one (1) year and an acquisition cost of more than $5,000 per unit. If fabrication of equipment is proposed, list parts and materials required for each, and show costs separately from the other items.

Equipment Budget Justification Moss Landing Marine Labs Moss Landing Marine Labs has requested 6 equipment items. The first for task 4A is a detector for a Hg analytical systemTekran #2500 for $8,000. The second is a computer and printer for conducting the modeling work in Task 5B for $5,000. The other pieces of equipment are for the cross Delta transect work described in Task 5B for a system that can measure and record real time chemical parameters that can be used to track water masses in the Delta. Real time data is needed so the MMHg samples can be taken at the right place at the right time. The system will be mounted on a boat that pumps water as the boat is in route through a series of chemical detectors. The equipment requested includes: 1. Turner Designs SCUFA submersible fluorescence and nephelometry detector for $6,000, Yellow Springs Instrument Temperature, Conductivity, Oxygen meter $6,000, Licor data logger $2,000, Laptop Computer for $2,500, GPS for $500, and software and software consulting to integrate and log the data $3000. Equipment Budget Justification TAMUG Texas A&M University at Galveston has requested 8 equipment items for this project totaling $137,000. A sputter coater ($7,500) is needed to prepare the gold-coated collection columns to be used in the mercury analytical systems (all tasks), for field work involving the collection of total gaseous mercury (task 3), and for the air-water exchange studies (task 5D). The microelectrode system ($17,000) is an in situ device used to determine high resolution profiles of oxygen, sulfide, and other redox sensitive parameters in interstitial pore water of sediments (task 5C2). A mercury analyzer ($7,000) will be necessary for field use in order to conduct the air-water exchange studies (Task 5D) since it is impractical to store these samples for later analysis. The elemental mercury calibration system ($5,500) is a field device for calibrating the mercury analyzer in the field; this item is required for task 5D, but will also be used for other tasks if available. A subcontract in the amount of $30,000 is requested to automate sampling with the benthic flux chambers. This will significantly increase sample resolution capabilities and throughput. The first $25,000 of this contract is subject to overhead. To conduct the dry deposition flux studies described in task 3, will require that we purchase three separate analytical items which will allow the simultaneous determination of total gaseous mercury, reactive gaseous mercury, and particulate atmospheric mercury. All these items interface together to determine these atmospheric mercury components. The items are a Tekran model 2537 total mercury analyzer ($35,000), a Tekran model 1130 Reactive Gaseous Mercury module ($40,000), and a Tekran model 1135 particulate Hg collection module ($20,000).

Project Management. Describe the specific costs associated with insuring accomplishment of a specific project, such as inspection of work in progress, validation of costs, report preparation, giving presentatons, reponse to project specific questions and necessary costs directly associated with specific project oversight.

San Jose State University Foundation is the prime contractor for this project. Kenneth Coale, acting Director of Moss Landing Marine Labs, and Mark Stephenson, will be the principal investigators responsible for the project at SJSUF.The administrative aspects of the proposed project will be managed by Max Puckett of the California Department of Fish and Game (CDFG) through the San Jose State University Foundation (SJSUF). The CDFG has a standing relationship with SJSUF. Coordination, oversight and contracting of this team of investigators will be the principal management task for CDFG and SJSUF. This includes the day to day work involved in preparing, processing, and managing the numerous subcontracts, as well as the reimbursable contract, for the project. It also includes all associated administrative management duties for overseeing the subcontracts, such as invoicing, purchasing, personnel, and accounting. The budget for this subtask includes the estimated overhead costs for the pass-through subcontracts, as well as the tasks described herein. The work performed in this subtask includes the preparation and submission of Quarterly Progress Reports to the CALFED contract manager; the planning and conducting of quarterly status meetings with all project investigators to review progress and issues from the previous quarter; the preparation and submission of the project Final Report; and the preparation and submission of other deliverable products as specified. The Final Report will include a synthesis chapter integrating the conclusions of the separate research project into a mercury mass balance for the Bay-Delta. The funds allocated for Management are $56,603,$ 50968, and $45184 for years 1, 2 and 3 respectively. Approximately 58% of funds are for Department of Fish and Game for management and 42% are for SJSUF for bookkeeping. The expenses for management are broken down by the following percentages: 1. Overseeing Contracts--10% 2. Oversight and coordination of PIs--20% 3. Preparing Contracts--10% 4. Invoicing--10% 5. Preparing Quarterly Reports--5% 6. Conducting Quarterly Status Meetings (Inspection of work in progress)--10% 7. Submission of Final Report--10% 8. Reviewing QA documents--5% 9. Preparing summary QA documents--12% 10. Updating QAPP--5% 11. Preparing for Scientific Review Meeting--3% 12. Validation of costs--2% 13. Presentations--3% 14. Response to project specific questions10%

Other Direct Costs. Provide any other direct costs not already covered.

There are no other Direct Costs

Indirect Costs. Explain what is encompassed in the overhead rate (indirect costs). Overhead should include costs associated with general office requirements such as rent, phones, furniture, general office staff, etc., generally distributed by a predetermined percentage (or surcharge) of specific costs.

Indirect costs include costs associated with general office requirements such as rent, phones, furniture, general office staff, copying charges, utilities.

Executive Summary

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

This current proposal represents a continued scientific research effort to understand environmental mercury and monomethyl mercury issues that was initiated with our currently on-going Calfed Mercury Research Project. The primary goal of this proposal is to develop an understanding of the transport, cycling, and fate of mercury (Hg) and monomethyl mercury (MMHg) in the San Francisco Delta and tributary watersheds using a biogeochemical mass-balance framework as an integrating and assessment tool. Among the more important hypotheses are: (1) River borne MMHg is a major source of MMHg introduced to the Delta; (2) Within the Delta, wetland and marsh regions are major sites of MMHg production; and (3) MMHg is lost from the water column within the central Delta by an unknown removal mechanism. We propose a series of interrelated tasks to address the goals described above: (1) Determine mass loading estimates for Hg and MMHg into, and freshwater export from, the Delta on watershed and sub-watershed basis; (2) Conduct atmospheric mercury deposition studies; (3) Conduct benthic flux chamber studies in wetlands; (4) Conduct process-oriented studies (e.g. photo-demethylation, air-water exchange studies, Delta transect, and wetlands biogeochemistry studies) within a framework of an integrated hydrodynamic transport model, to investigate MMHg production and cycling; (5) Contiune monitoring and characterization studies of sediments with a focus on wetlands. The study area for this project encompasses the entire Delta, its tributaries and watershed, focusing in particular on wetland study sites for biogeochemical investigations. The studies described above will directly address several CALFED priorities where mercury contamination is an issue, including Goal 6 (Sediment and Water Quality) of the Ecosystem Restoration Program Draft Stage 1 Implementation Plan; MR-5, (ensure that restoration is not threatened by degraded environmental water quality). SR-7 (develop conceptual models to support restoration efforts); DR-6 (restore shallow water habitats); DR-7 (optimize the use of Delta Cross Channel); and BR-5 (restore shallow water, local stream and riparian habitats).

Proposal

California Department of Fish and Game

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

Mark Stephenson, California Department of Fish and Game
Kenneth Coale, Moss Landing Marine Labs (San Jose State University)
Gary Gill, Texas A&M University
Max Puckett, Department of Fish and Game

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

Mark Stephenson, Kenneth Coale, Gary Gill, and Chris Foe (Principal Investigators)

A. Project Description: Project Goals and Scope of Work

1. Problem

Between 1850 and 1980 California was the nation's leading producer of mercury (Hg) at about 100 million kilograms (Churchill, 2000). Most of the Hg was mined in the Coast range. Early Hg processing was inefficient and about 35 million kilos of metal are estimated to have been lost in the coast range (Churchill, 2000). Another 6 million kilos are thought to have been lost in placer and lode gold mining in the Sierra Nevada (Churchill, 2000). As a result there is widespread Hg contamination in fish, sediment and water in the Central Valley and Bay-Delta Estuary. This Hg poses a human health risk principally through the consumption of mercury-contaminated fish. Health advisories and interim health advisories have been posted in the Bay-Delta Estuary recommending no consumption of large striped bass and limited consumption of other sport fish (OEHHA 1994; San Francisco Regional Board, 1995). Elevated concentrations of Hg in fish tissue may also represent a hazard to piscivorous wildlife. Species most at risk are fish eating birds and mammals. Mercury contamination in aquatic organisms results from the conversion of inorganic Hg to monomethyl mercury (MMHg), principally by sulfate-reducing bacteria in surficial sediments (Gilmour et al., 1998). A recent study by the U.S. Geological Survey in twenty basins across the U.S. demonstrated a strong positive correlation between aqueous MMHg concentrations and fish tissue levels (personal communication, Brumbaugh et al.). Therefore, an understanding of the sources and sinks of aqueous Hg and MMHg is essential both for the development of control programs to reduce fish tissue levels and also to insure that CALFED wetland restoration efforts do not exacerbate an already serious human and wildlife health problem.

Primary Project Goal. *Develop an understanding of the transport, cycling, and fate of mercury (Hg) and monomethyl mercury (MMHg) in the San Francisco Delta and tributary watersheds on both a temporal and spatial basis using a biogeochemical mass-balance framework as an integrating tool to assess sources, sinks and biogeochemical processes.* These results will be incorporated into a working hydrological transport model that will facilitate the prediction of Hg cycling and transport across the Delta and exported to San Francisco Bay or to Southern California.

Working Hypotheses and Investigative Approaches. The work proposed in this current proposal is based upon findings obtained in our currently on-going CALFED Mercury Program. Additional details and reports generated from this current program are attached in the appendices and are also available at the following web site: Http://loer.tamug.tamu.edu/calfed. Our work to characterize the major reservoir concentrations and flows of Hg and MMHg in the Delta to date has lead us to develop the following working hypotheses. Also given is a brief description of the proposed investigative approaches. Greater detail is provided with the descriptions given of individual tasks in section 3**.**

1. ***Riverborne MMHg is a major source of MMHg introduced to the Delta, especially under high river flow conditions***. We propose to continue to conduct monitoring of the major riverine inputs and water export losses to the Delta on a seasonal basis for multiple years in order to address concerns regarding temporal variability.
2. ***Atmospheric Hg deposition is a minor, but significant source of total Hg loading to the Delta***. We propose to set up a series of three atmospheric deposition monitoring stations in key regions around the Bay, Delta, and associated watersheds to characterize the atmospheric deposition flows of Hg and MMHg into the Delta for both wet deposition and dry deposition.
3. ***Methylmercury concentrations in Delta sediments increase during late spring through early summer as a result of increased Hg methylation in the sediment***. We propose to conduct monthly sediment sampling in the Delta at four locations for three years and increase the frequency of sampling to bimonthly during late spring and summer.
4. ***Mercury and MMHg concentrations in Delta sediments are spatially variable relative to habitat type and the distribution remains relatively constant year to year***. We propose to sample 28 locations, representative of the multiple habitat types found in the Delta. Sampling will occur twice a year (high flow season and low flow season) for two years.
5. ***Within the Delta, wetland and marsh regions are major sites of MMHg production and enhanced sediment-water exchange flux***. We propose to conduct a series of investigative studies to assess the importance of wetland or marsh habitats as sources of MMHg to the Delta. Investigative approaches include: benthic flux chamber deployments at marsh sites, monitoring of inflow and outflow Hg and MMHg concentrations to a marsh over a tidal cycle, and benthic sediment biogeochemical studies to try and understand controlling variables in surface sediments.
6. ***MMHg is lost from the water column within the Delta ecosystem by an unknown removal mechanism as water flows from the Sacramento River to the Delta***. We propose a series of synoptic Delta transects to examine MMHg concentrations along water transport pathways. This information will be used as input to a hydrodynamic model of water flow in the Delta to investigate where MMHg is being lost (non-conservatively) and to quantify the magnitude of the loss.

A Mass Balance Geochemical Framework. The relative significance of all Hg and MMHg sources, sinks and cycling processes will be evaluated and constrained using a mass balance geochemical cycling framework, which is based on our conceptual understand of Hg transport and cycling behavior in the Delta and its tributaries (see Appendix A). This investigative approach was highly successful in identifying major pathways and processes in a number of aquatic environmental Hg studies including the Mercury in Temperate Lakes (MTL) project in Wisconsin (Watras et al., 1994, 1996), the Lake Michigan Mass Balance Study (Mason and Sullivan, 1997), and at an EPA Hg superfund site (Gill et al., 1999, Mason, et al., 1998, Bloom et al., 1998). Moreover, information from studies based on mass balance modeling approaches can provide a fundamental starting point or conceptual model for use in the development of more sophisticated environmental modeling efforts (see for example Hudson et al., 1994). The geochemical processes quantified as part of this study will be used to inform a numerical model of solute transport so that quantitative budgets of Hg cycling can be produced.

Current Program Objectives. This current proposal represents a continued effort to understand environmental Hg issues that were initiated in our currently on-going CALFED Mercury Research Project. This currently proposed research program seeks to expand upon our current findings by: ***(1)*** *Filling in data gaps in our current conceptual understanding of Hg and MMHg sources, sinks, and cycling in the Bay-Delta and its watershed;* ***(2)*** *Verifying and quantifying seasonal variations of MMHg in sediments and in the water column with respect to habitat type;* ***(3)*** *Accurately* *characterizing the spatial distribution of total Hg and MMHg in the Delta;* (***4***) *Estimate the loadings of MMHg from wetlands and evaluate them as to their importance relative to other sources; and* (***5***) *Providing a foundation and framework for long term monitoring of Hg contamination issues in the Delta.*

2. Justification

The proposed work for this project has been separated into several highly integrated tasks. While each task may be conducted independently of each other, the overall strength of this proposal will only be achieved if all tasks are conducted concurrently. This is because our main goal is to develop a Hg mass balance with each task being a separate component of the mass balance equation. Only by summing all the sources and sinks and determining how close they balance will we eventually be able to determine the degree to which we understand Hg cycling in the system. The rationale, justification and approach for each task and sub-task are described individually in the following section. All the tasks are focused to achieve the primary project goals and objectives described above.

3. Approach

This proposal has been broken down into 6 tasks, some with subtasks. The principal investigator primarily responsible for each task is noted in parentheses.

Task 1. Administrative Support (Puckett)

The administrative aspects of the proposed project will be managed by Max Puckett of the California Department of Fish and Game (CDFG), through the San Jose State University Foundation (SJSUF). The CDFG has a standing relationship with SJSUF. Coordination, oversight and contracting of this team of investigators will be the principal management task for CDFG and SJSUF. This includes preparing, processing, and managing the subcontracts, as well as the reimbursable contract, for the project. The work performed in this subtask also includes the preparation and submission of Quarterly Progress Reports to the CALFED contract manager; the planning and conducting of quarterly status meetings with all project investigators to review progress and issues from the previous quarter; the preparation and submission of the project Final Report; and the preparation and submission of other deliverable products as specified. The Final Report will include a synthesis chapter integrating the conclusions of the separate research project into a mercury mass balance for the Bay-Delta.

Task 2. Mass Loading, Riverine Characterization and Export Studies (Foe)

The present CALFED sponsored Hg studies have demonstrated the importance of river inputs in controlling Hg loads and aqueous and biotic concentrations in the Bay-Delta estuary. Unfortunately, the present CALFED work was conducted during a normal to dry water year (March 2000 through September 2001) and no information exists on MMHg dynamics during wet years. The Central Valley Regional Water Quality Control Board (CVRWQCB) has requested and received funds to continue the Bay-Delta loading studies for an additional year. In addition, the Board requested and received funds to conduct a year of loading studies in the Sacramento and San Joaquin Rivers to determine the major sources of Hg to each. The total amount of the award is $200,000 and a person year of staff time. These studies will begin in the fall of 2001. We believe such multi-year loading studies are critical for understanding Hg processes and cycling in the system and for developing control programs to minimize the Hg hazard for people and wildlife. It is unlikely; however, that the Regional Board will be able to sustain the multi-year effort necessary to adequately understand the problem. Therefore, the Board is requesting funding to continue the loading studies in the Sacramento and San Joaquin watersheds and Bay-Delta Estuary for two additional years. The work will be closely coordinated with the much more limited sampling presently being conducted by the Sacramento Watershed Program. While the cost of this task is high, it must also be emphasized that the size of the watershed is also large, about 26 million acres. It is also important to note that ultimately no correction of the Hg problem is possible without an accurate identification of sources and the magnitude of their releases. This is precisely the information being collected in Task 2.

Task 2A. Determine Mass loading estimates for Hg and MMHg into, and freshwater export from, the Delta. The approach will be similar to that employed in the present CALFED grant. Raw and filtered aqueous total and MMHg concentrations will be determined monthly at all the major inputs to the Bay-Delta (Sacramento, San Joaquin, and Mokelumne Rivers and Prospect Slough in the Yolo Bypass) and at the major export sites (State and Federal pumps and Chipps Island to estimate exports to San Francisco Bay). These measurements will be coupled with flow estimates to calculate Hg loads and sinks (kilograms Hg/month).

Task 2B. Characterize tributary and regional input sources of MMHg and Hg in the Sacramento and San Joaquin Basins. In a similar fashion we propose collecting monthly river flow and Hg concentration data at key locations down the Sacramento and San Joaquin Rivers and from all the major tributary inputs. This will necessitate monitoring about 26 sites monthly in the two basins. The primary goal of the river monitoring will be to calculate mass balance estimates for raw and filtered total and MMHg for each river section. This information will be used to determine river reaches responsible for the major sources and sinks of Hg.

Task 2C. Conduct sub-watershed studies of tributaries or source regions to refine region of sources of MMHg and Hg within a watershed. We propose to follow up on the findings in Task 2B by conducting detailed studies on tributary inputs along key river reaches to ascertain sub watersheds responsible for the majority of the load. Once these have been identified then we will follow up on this information with studies in each tributary to identify actual sources. Flow information may or may not be available for the key sub watersheds. We will use all the flow data available to estimate loads. When unavailable, we will estimate flow with hand-held flow meters and measurements of stream cross section. The authors were able to identify the primary sources of Hg in Cache Creek using similar methods (Foe and Croyle, 1998). It is difficult to estimate how many sub watersheds will necessitate detailed investigative follow-up. Provisionally, we request funds for sampling about 10 sites monthly. Harley, Sulfur and Davis Creeks have been identified as major sources of Hg to both Cache Creek and the Bay-Delta Estuary. A U.S. Geological Survey gauging site has been constructed on each creek. However, only one year of source loading information has been obtained for each drainage. Mine remediation efforts are being planned based solely upon this limited information. We propose to continue to sample Hg discharges to determine background export rates (about 125 samples over a 2 year time frame). Funding is also requested to maintain the three gauging sites. The resulting new background information will be critical in evaluating the effectiveness of subsequent Hg control efforts.

Task 3. Atmospheric Mercury Deposition Studies (G. Gill, M. Stephenson and K. Coale)

It is now well accepted that atmospheric deposition plays a major role in the delivery of Hg to aquatic systems (Pirrone et al 1998; Mason et al., 1997; Lorey and Driscoll, 1999; Fitzgerald et al., 1997; Kang et al., 2000). We hypothesize that atmospheric Hg deposition is a minor, but not insignificant source of Hg loading to the Delta. Currently, there is only limited data on the atmospheric deposition of total Hg, and no information on the atmospheric deposition of MMHg in the central California region. This paucity of data limits our ability to develop a rigorous and well constrained mass balance for Hg and MMHg in the Delta (see Appendix A). An atmospheric deposition pilot study was recently conducted to examine deposition to San Francisco Bay (see http://www.sfei.org/rmp/reports/air_dep/mercury_airdep/ADHg_abstract.html). Volume weighted average Hg concentration in precipitation was 8.0 ng/L, ranging from 6.6 to 9.7 ng/L. Mercury flux from wet deposition to the entire estuary was estimated at 4.2 $\mu g/m^2/yr$, ranging from 3.5 $\mu g/m^2/yr$ at the South Bay site to 4.5 $\mu g/m^2/yr$ at the Central Bay site. The report concludes that atmospheric deposition contributes a sufficient enough load of Hg to the estuary to warrant further evaluation. A Mercury Deposition Network (MDN) site has also recently been established in San Jose California. The current mean Hg concentration in wet deposition from this MDN site is 12.7 ± 9.6 ng/L. These Hg concentration levels are not dramatically different from that observed at other areas of the U.S. (see e.g. Guentzel et al., 2001; Watras et al., 2000; Sorensen et al 1994; Poissant and Piolte, 1998; Pirrone et al., 1998; Mason et al., 1997; and references therein). However, the data available are very limited, and the sites where this data were collected are not necessarily representative of deposition conditions in the Delta or of watershed regions feeding into the Delta. In addition, atmospheric deposition modeling of Hg conducted using EPA's RELMAP model predicts that the Delta and Bay area is a region of rather enhanced localized Hg deposition in the Central California area (see Figure 1) (Bullock et al., 1997, 1998). Although the values reported here and shown in Figure 1 are not elevated compared to other areas, episodic inputs may account for significant but ephemeral loadings to this environment. Forest fires, in particular, are known to volatilize large amounts of Hg and both the coast range and the Sierra foothills are habitats characterized by seasonal conflagrations. As part of this program we hope to sample these natural inputs and utilize them to trace the subsequent fate of Hg in the system by adjusting our sampling intervals and stations in response to episodic events. We propose to set up a series of three atmospheric deposition monitoring stations in the Bay-Delta watershed to estimate the wet deposition of total Hg and also MMHg. Sites will be chosen to characterize input into the coastal mountain range focusing on the Cache Creek watershed, the central Delta region, and the Sierras, focusing on the Cosumnes watershed. Sampling will be conducted on a bi-weekly basis for approximately a 28-30 month period at all sites. Either an Aerochemetrics or a MIC-B wet-dry deposition collector, modified for monitoring Hg, will be used for sample collection. These samplers have been used successfully to monitor atmospheric deposition (Landis and Keeler, 1997; Landing et al., 1998). In addition, we will conduct some preliminary investigations to access the importance of the dry deposition flux of Hg by conducting measurements of reactive gaseous mercury (RGM). Initially, RGM measurements will be obtained using approaches developed during the FAMS project (Guentzel et al., 2001). If RGM appears a significant source, we will seek to acquire or borrow the instrumentation recently developed and made available by Tekran, Inc. (see: http://www.tekran.com/access/1130.html) for determining RGM simultaneously with total gaseous mercury (TGM) in the atmosphere.

Task 4. Delta Wide Monitoring and Characterization Program (Stephenson, Coale, Gill, and Foe)

Task 4A. Determine Hg and MMHg in surface sediments of different Delta ecosystems (i.e. habitat-based). After one year of sampling we observed an increase in MMHg in sediments at 2 of 6 stations during spring and summer. (Figure 2). Additional years of seasonal sampling will allow us to confirm these trends. Four sites will be sampled monthly for 30 months, with bimonthly sampling during late spring and summer. If a recurring elevation of MMHg is observed in the summer, ancillary data will be used to identify environmental conditions leading to summer increases of MMHg. After examination of data collected in year one, an adaptive strategy will be used to adjust sampling and ancillary measurements, as necessary to identify environmental conditions driving the summer increase of MMHg. In order to determine how MMHg distribution in sediments relates to habitat type, approximately 28 sites will be sampled twice each year in the three-year project. The chosen sampling locations will be representative of the broad range of habitat types found in the Delta that are incorporated into the National Wetlands Inventory Arc View GIS layers, and will also be located at the sites selected for the other tasks in this proposal, as well as sites from the fish bioaccumulation studies (proposals submitted concurrently by Jay Davis, San Francisco Estuary Institute). The goal is to accurately map the spatial distribution of Hg in the Delta. The sampling is designed to allow comparisons to be made between distinctly different hydrologic seasons (high and low flow), as well as possible changes caused by wet and dry year hydrology. Data will be continually evaluated over the three-year project, and adaptive strategies will be used to adjust sampling as needed to better address the hypotheses. The foundation for long-term monitoring of the Delta for Hg will be established with this study. This data will be invaluable to future remediation projects concerned with lowering MMHg levels in fish. Samples will be stored, processed, and analyzed using non-contaminating techniques, following protocols established for the CALFED Mercury Project. The following ancillary measurements and samples will be taken at each station: Temperature, conductivity, water depth, water flow rate, turbidity, chlorophyll, nutrients, oxygen, grain size, and total organic carbon. Each sampling station will be described and classified as a habitat type, based on dominant landscape feature.

Task 4B. Benthic Flux Chamber Studies (G. Gill). Benthic flux chamber studies have been a major part of our current CALFED Hg research program and we propose to continue this effort, but to work in different habitats where no information is currently available. Current estimates suggest that sediment-water exchange input of Hg and MMHg in the Delta (on an aerial basis) are roughly equivalent to that introduced by riverine flow, except during high flow periods. Admittedly, the number of measurements used to make this assessment is very limited and much more data is needed before a reliable assessment of the importance of benthic inputs can be reliably made. Especially lacking are assessments of different habitat types, which are many and varied in the Delta ecosystem. The current sampling program was intended to characterize major open water areas of the Delta, such as Frank's Tract. In particular, we will focus on investigating those areas which are of special importance to future CALFED restoration efforts, including Yolo Bypass, Suisun Marsh and the Cosumnes River. We have some preliminary evidence, collected during our May 2001 Field trip, which leads us to hypothesize that marsh sites are habitats of elevated MMHg fluxes compared to open water sites. MMHg concentrations in sediments in marsh habitats in Franks Track are approximately five-fold higher than in open water areas (Figure 3). Shown in Figure 4 are corresponding benthic flux chamber deployments in Franks Track (open water) and a marsh site on the north side of Frank's Track. The marsh site had approximately 50% higher flux than the open water site. We propose to focus much more effort on wetlands and marsh areas in the current proposal. We propose 6 field efforts spread out seasonally over approximately a 24-month period with monitoring at 4-6 sites. Field site locations will be integrated with the wetlands studies described in Task 5C. Benthic flux chamber deployments and sampling are currently conducted manually using SCUBA divers. This requires that a team of divers remain on-site during a deployment period for all sample collections, making the current sampling procedure very labor intensive and inefficient. To significantly improve our sampling capability we propose to automate the sample collection so that unattended sampling can be conducted. This will allow for much greater sampling interval flexibility (e.g. 24 hour and light/dark studies) and also will permit multiple chamber deployments at different sites. This will significantly increasing the information obtained during a given field effort.

Task 5. Process Oriented Studies (Stephenson, Coale, and Gill)

A series of process-oriented studies are proposed. The major purpose of these studies is to identify links between Hg and methylmercury production and destruction and to derive environmental rate dependencies with respect to major biogeochemical processes and constituent concentrations.

Task 5A. Monomethyl Mercury Photo Demethylation Studies (G. Gill). A recent study in the Experimental Lakes Area (ELA) of northwestern Ontario, Canada observed that MMHg in the water column can undergo destruction through a photodegredation process (Sellers et al., 1996). This is a relatively new finding in the aquatic cycle of Hg and one in which the relative importance is currently not understood. MMHg loss by photodemethylation was the major MMHg loss term in the ELA study; it was greater than that MMHg delivered to the lake via stream flow and run-off. If a photodemethylation of MMHg is occurring in the Delta, this process could easily be the mechanism for the loss of MMHg that we have hypothesized occurs within the Delta as water flows from the Sacramento River to the export pumps in the southern portion of the Delta. Loss of MMHg by photodemethylation is also one of the information gaps where we have no information. To investigate the possibility that photodemethylation is the mechanism responsible for loss of MMHg in the Delta, we propose to conduct bottle incubation experiments during different seasons of the year at the sites where other process oriented tasks and intensive studies are being conducted. This information will be assessed using the mass balance geochemical framework described previously. In addition, we will also compare the MMHg rate loss constants derived from this study to: (1) the non-conservative loss quantified from the hydrodynamic model efforts described in Task 4 and (2) the air-water exchange loss of elemental Hg proposed in task 5D. The combination of these two comparisons will provide constraints on the relative importance of photodemethylation as a MMHg loss mechanism in the Delta. These studies will be conducted in tight coordination with the air-water exchange studies of dissolved gaseous Hg described in Task 5D.

Task 5B. Delta Transects and Cross Channel Studies (K. Coale and M Stephenson). Work conducted to date on our CALFED Mercury Project has led us to hypothesize that there is an internal sink for MMHg in the Delta. The objective of this task is to thoroughly document the existence of the sink and relate it to hydrologic, chemical, and biological parameters. Evidence of this is shown in Figure 4, which shows that the concentration of MMHg imported into the Delta (Greens landing data) is always higher than the exports during low flow regimes in 2000. More recent data (not shown) indicates the same pattern has developed during summer 2001. The concentrations of MMHg represent a balance between sources and sinks that are likely sensitive to the hydrodynamics and water residence times in the system. Therefore, new studies should take into account hydraulic transport. The recently developed hydrologic forecast model developed by the DWR Delta Modeling Section provides a useful framework with which to test some of these assumptions and develop hypotheses. The hypotheses can be tested by combining forecasts of particle-tracking simulations with high-resolution field sampling. The model would allow for prediction of Hg transport and dilution in a conservative manner. Deviations from this predicted behavior will identify sources and sinks. There is some indication that Hg is not behaving conservatively, but the coupling of our water column measurements with the hydraulic transport model will allow for the quantification of this sink. Where this disagreement is significant, we will focus our studies to identify the mechanisms giving rise to the non-conservative behavior. The model will also allow us to test certain hypotheses now emerging from our first year's field data. For instance, we hypothesize that some of the loss of MMHg is driven by demethylation and subsequent air/water exchange. The magnitude of this loss term will be a function of hydraulic residence time. The numerical simulations of water flow in the DSM2 Forecast model can be used to characterize regions of the Delta system, in terms of hydraulic residence time at different times of the year. These areas can then be sampled in high resolution to test whether these regions loose or accumulate Hg. Based upon these results, further sampling will be conducted to identify the source and sink terms. Another potential loss of MMHg is via bioaccumulation. This may occur when MMHg is accumulated by phytoplankton blooms and subsequently removed via benthic or water column filtration. We can test for this loss by sampling dissolved and particulate phases of the water column, together with the MMHg in benthic macrofaunal invertebrate populations (most notably *Corbicula spp*.). This effort will involve the water sampling of Delta river segments as constrained, by gauging station or model grid point at both inflow and outflow stations. High resolution transects along the river stations using a geo-referenced flow-through sensor package (C, T, Transmissometry, Fluorescence, etc…) determined underway will enable us to quantify the basic water column parameters between these end-members. The magnitude of the influx or removal of methylmercury between the end-members can be quantified by the difference between predicted and observed mass flux. We have contacted researchers at DWR, and have confirmed that using their model as a starting point, such an analysis is feasible. Dr. Wendy Wang at MLML is an ocean modeler whose expertise is well suited to the task of modifying this model to allow for export, atmospheric exchange, diffusion, particle settling, bioaccumulation, and other processes that we intend to quantify as part of this study. The predictive capability that such a modeling component will offer will be of great value to many researchers in the CALFED program. Preliminary data from the CALFED Mercury Project revealed stations located in the South Mokelumne River Sloughs had significantly higher concentrations of MMHg in May 2001 than when initially surveyed in October 1999. Coincidentally, the Delta Cross Channel was closed in May 2001. The South Mokelumne River Sloughs are effectively cut off from influences of the Sacramento River by the closing of the Delta Cross Channel. While the Cutoff is closed, the Delta part of the Mokelumne is poorly flushed, providing opportunity for pollutants to accumulate in sediments (Figure 5) and water (Figure 6). We feel the existing data, although very sparse, is enough to initiate further investigation into the possible influence of closing the Cross Channel on methylmercury accumulation in sediments of the Northeast Delta. Samples will be collected from locations around the Cross Channel Cutoff immediately before the Cutoff is closed, a few weeks after it is closed, and again a few weeks after it is opened. Data generated from this study will be used to determine if additional investigations are warranted.

Task 5C. Wetland Mass Loading and Sediment Biogeochemistry Studies (G. Gill, K. Coale, and M. Stephenson). The production and bioaccumulation of MMHg in aquatic environments varies widely. Wetlands in particular are often considered to be regions of high MMHg production potential (St. Louis et al., 1994, 1995; Hurley et al. 1995, Krabbenhoft et al. 1999, Rudd 1995). Many Hg researchers have expressed their concern that CALFED's Ecosystem Restoration efforts could raise levels of MMHg in the Delta if wetlands are created. Although MMHg production has been associated with wetlands in other areas, it is not known on a quantitative basis how much

MMHg in the Delta is created by wetlands, and which types of wetlands create the most MMHg. The wetland loading studies (task 5C1) will attempt to provide this information. The biogeochemical studies (Task 5C2) will try and relate MMHg in both sediment pore water and sediments to major biogeochemical features occurring in the sediments, to see if a causal link can be established which influences MMHg concentrations.

Task 5C1. MMHg Loading Studies in Delta Wetlands. The objective of the wetlands loading section of this task will be to determine loadings of MMHg from different types of habitats (salt marsh, fresh water tule marsh, ponds with tules, and the Cache Creek Catchment Basin), and to compare the loadings from these wetlands to loadings from Delta tributaries, atmospheric deposition, and Delta sediment. Using this approach all the sources of MMHg can be put into perspective so their relative importance can be assessed. We propose to conduct wetland MMHg loading studies and sediment biogeochemistry studies at many of the same sites where intensive studies will occur for the other project tasks. In addition, this work will be tightly integrated with the sampling plan proposed for surface sediments in Task 4A. The wetland loading studies will use an approach that determines the net mass export/import of MMHg, and will be the difference between what goes in and what comes out of the wetlands. The on-going CALFED Mercury Project has completed one study at a tidally-influenced marsh near Frank's Tract using this method, and another study in a non-tidally influenced area in Cache Creek and the Yolo Bypass area. In both studies, loadings were determined successfully. This technique has also been used successfully in the Experimental Lake area in Canada (Rudd 1995). The loadings estimates will be expressed as mass of MMHg exported per acre, which can then be scaled up to a watershed basis by multiplying loadings by the total amount of acres per wetland type in the watershed. Fresh water marsh habitats to be studied include sites at Sherman Island, one in the Central Delta near Franks Tract, and one in the Yolo Bypass. Salt-water habitat sites will be selected from Suisun Marsh and North San Pablo Bay. Freshwater ponds with tule habitats include two sites in the Yolo Bypass Wildlife area and one site yet to be determined in the Delta. Three replicate wetland sites from saltwater marshes, freshwater marshes and tule ponds will be studied, enabling a statistical comparison among types. Loadings will be determined from each site three times per year during the summer for at least two years. In addition, two sites will be studied intensively 9 times per year for two years. Ancillary water column measurements will be made at each site, and include: Total suspended solids, chlorophyll- a, temperature, conductivity (or salinity), depth, dissolved oxygen, and sulfate. Sediments will be analyzed for organic carbon, MMHg, and total Hg at each of these sites. We will conduct correlation analysis between these measurements and MMHg production to identify potential controlling factors of MMHg production.

Task 5C2. Sediment Biogeochemistry Studies in Delta Wetlands. The primary site of MMHg production within an aquatic ecosystem is often found to occur in near-surface anoxic sediments mediated by sulfate-reducing bacteria (Compeau and Bartha, 1985; Gilmour et al., 1998). Hence, there are a number of environmental variables, characteristics or conditions that could influence the net production of MMHg and its ultimate release into the water column. The proposed work for this task will directly address a number of the hypotheses outlined previously, including our contention that within the Delta, wetland and marsh regions are major sites of MMHg production and that MMHg production in the Delta follows seasonal cycles which vary geographically, possibly due to habitat type. Gilmour et al. (1998) were able to demonstrate that MMHg concentration and production in the Everglades were inversely related to sulfate reduction rate and pore water sulfide concentrations. This controlling relationship was manifest in a north-south gradient in MMHg concentration and production in the Everglades. The eutrophic northern reaches had elevated sulfide levels, which inhibited MMHg production. The biogeochemical studies will seek to relate MMHg concentrations in both sediment pore water and sediments to major biogeochemical features occurring in the sediments to see if a causal link can be established which influences MMHg concentrations. These studies will be conducted on a subset of those sites from the wetlands loading studies (Task 5C1). Specifically, we propose to examine the depth distribution of MMHg in porewater and sediments relative to other potentially important controlling parameters such as oxygen, sulfate/sulfide, DOC and OC content, Fe and Mn. High resolution near-surface profiles of oxygen, sulfide, and other parameters in interstitial pore waters will be obtained using an in situ microelectrode profiler system from Unisense (http://www.unisense.com/products/products.html) (Gunderson and Jorgensen, 1990, 1991, Gunderson et al., 1992). Depth profiles of MMHg, total Hg and selected other trace elements (e.g. Mn and Fe) will be obtained using either whole-core squeezing techniques (Gill, et al., 1999) or by extrusion of intact cores under the protection of an anoxic environment in a glove bag. Pore water will be isolated using centrifugation. We have experimented with this approach during recent field efforts and find we can get up to 25 mL of pore water from surficial sediments which will permit a number of chemical analyses. Determination of trace lements will be conducted using ICP-MS techniques developed at Texas A&M University at Galveston (Warnken et al, 2000).

Task 5D. Conduct Air-Water Exchange Studies of Dissolved Gaseous Mercury (G. Gill). The formation of volatile Hg species, particularly elemental Hg, in surface waters, and evasion to the atmosphere is an important component of the cycling of Hg in aquatic systems (Amyot et al., 1997a; 1997b; Fitzgerald et al., 1994; Mason et al., 1994). Fitzgerald et al. (1994) has hypothesized that dissolved gaseous mercury (DGM) is an end product of the biotic de-methylation of MMHg. DGM production has also been shown to be produced abiotically, mediated by photosensitive components in the presence of sunlight (Amyot, 1997a, 1997b; Zhang and Lindberg, 2001). There is also new evidence to suggest that the evasion of elemental Hg in aquatic systems with emergent aquatic vegetation can be considerably enhanced compared to open water areas (S. Lindberg, personal communication). The air-water exchange of gaseous Hg species represents another data gap in our overall understanding of the cycling of Hg in the Delta (See Appendix A). To the best of our knowledge, there have been no assessments of this process in the San Francisco Bay or Delta region to provide constraint of the cycling of Hg in these waters. We propose to conduct measurements of DGM with a goal of providing quantitative information on the air-water transfer of volatile Hg species for mass balance modeling purposes. These measurements will be conducted using two approaches: (1) bottle incubation studies such as those described by Amyot et al (1997a, b) and (2) we will build and utilize a flux chamber, similar to that described by Carpi and Lindberg (1998) for the determination of soil Hg flux. The latter approach will be used to determine whether air-water evasion flux of DGM at sites with aquatic vegetation have enhanced fluxes compared to open water sites. Measurements will be conducted during the 6 intensive field efforts, which span different seasons and habitats. These studies will be conducted in tight coordination with the Hg photodemethylation studies described in Task 5A.

Task 6. Integration of GIS into Program (M. Stephenson, K. Coale)

We propose to integrate GIS approaches into the current and proposed new program. The Hg data from this study will be overlaid on the National Wetlands Inventory ARCVIEW layers to estimate the area of MMHg in sediments in different types of habitats in the Delta. The types of habitats include open water, intertidal mud, tidal salt, seasonal wetlands, farmed wetlands, riparian wetlands, salt ponds, and lake ponds. We anticipate being able to statistically relate the MMHg concentrations in sediments to the flux of MMHg from sediments, and use this GIS approach to estimate the amount of MMHg released from sediments in the types of habitats listed above.

Study Sites. The sites for water collections are strategically located to track imports and exports of MMHg and total Hg in the Delta (Task 2A; see Figures 7 & 8 for maps of sampling sites). In addition, the stations on the tributaries to the Delta will be sampled for water to strategically assess the major sources to Cache Creek, the San Joaquin River, and the Sacramento River. To avoid duplication, sample locations will be determined after assessing studies conducted by other programs. Locations may be adjusted, in an adaptive way, taking advantage of the previous year's data (Task 2B and 2C). Sites for water collections for the Delta transects and cross channel studies (Task 5B) will be selected with the aid of the DWR hydrodynamic model, and will be located between the Delta import and export sites studied in Task 2A. The sediment stations for this project are strategically located to track trends from stations previously sampled since 1999. This would include the seasonal studies (Task 4A) and flux studies (Task 4B). Sediment stations will also target wetland types (Task 4A), wetland mass loading studies (Task 5C1), and intensive biogeochemical studies (Task 5C2). Two of the stations, Franks Tract and Sherman Island, will be used in all studies. A preference for site selection will be for habitats where CALFED has placed a high priority for restoration.

4. Feasibility

Many of the field sampling techniques and analytical methods discussed in this proposal have already been successfully used in the currently on-going CALFED Mercury Project over the past two years. No permits are required to complete this project

5. Performance Measures

The work proposed for this project is basic scientific research. As such, we propose as performance measures criteria that are often used to evaluate the performance of a research project or a researcher amongst the peer scientific community:

- Meet data quality objectives for chemical analysis
- Completion of field sampling program as outlined in the timeline
- Presentation of data and participation in external peer review on an annual basis
- Publication of interim and final project reports; disseminate on a project web site
- Publication of several papers in high quality peer-reviewed scientific journals

6. Data Handling and Storage

All data will be summarized in spreadsheet format (e.g. Excel) in a manner acceptable for posting to the IEP web page. Where feasible, data will be stored in an ARCVIEW compatible database. Annual reports will be prepared for review. All of these data sources will be maintained by project PI's and made available for public viewing and download for our CALFED mercury web site (http://loer.tamug.tamu.edu/calfed).

7. Expected Products/Outcomes

A major product of this work will be the development of a quantitative geochemical mass balance model which describes the major sources, sinks, and cycling of total Hg and MMHg in the Bay-Delta and its watershed. This model will be based on the conceptual model of Hg cycling in the Bay Delta ecosystem presented in Appendix A. Other products and outcomes of this project include:

- Quarterly and annual progress reports
- Participation in the annual scientific review of the all Hg programs funded by CALFED
- Presentations at scientific meetings
- Information transfer through participation in local workshops, seminars and a project web page
- Modifications to the hydrodynamic model of water movement in the Delta to predict non-conservative losses or sources of Hg and MMHg

8. Scientific Review and Quality Assurance.

The current CALFED Hg project has an extensive QA component and has an annual Scientific Review Meeting where leading national and international Hg researchers are brought in to review the research findings. Many of the analytical and field sampling procedures to be used for this project were described in detail as part of a Quality Assurance Project Plan (QAPP) prepared as part of our previous CALFED project. The QAPP is available for download and review from our Web site: http://loer.tamug.tamu.edu/calfed/QA.htm. The QAPP will be reviewed and updated, as necessary, prior to any field or analytical work. The CALFED Science Management team has discussed the desirability of having an external QA/QC program that all CALFED sponsored mercury research be required to participate in. We encourage CALFED to form such an effort because of the historical problems encountered in mercury analysis and the ultra trace levels of much of the present work. If such a program is formed, all participants in this proposal agree to participate fully. Since many of the participants conduct their own analysis, any additional QA/QC would be done at each individual participant's expense. Cost is unknown but may not be insignificant (perhaps as much as 5% of our entire program). Finally, the CALFED Science Management Team have discussed the desirability of having an annual mercury meeting where all researchers would be required to make oral and written presentations. Again, we agree that such an event would be very beneficial for advancing our understanding of mercury in the basin and agree to participate fully. The cost of participation is unknown but, again, may not be insignificant as it will involve a multi-day commitment by all principal investigators, possible writing of interim reports and cross country travel by one of the participants.

9. Work Schedule

The anticipated start date for this program is June 1, 2002. Field sampling will begin in the summer of 2002 and continue through the end of December 2004 (~30 months). A final report will be produced on or before June 30, 2005. The project will undergo external peer review on an annual basis. A detailed timeline of the various components of the project are given in Figure 9.

B. Applicability to CALFED ERP and Science Program Goals and Implementation Plan and CVPIA Priorities

1. ERP, Science Program and CVPIA Priorities

This proposal specifically addresses several CALFED priorities. Outlined below are the specific priorities addressed by this current proposal.

ERP Draft Stage 1 Implementation Plan Goal 6 (Water and Sediment Quality). Monomethyl mercury is specifically named in goal 6 as a persistent toxicant causing human health problems. In addition, it is noted that sediment disturbance and remediation efforts may exacerbate the toxicity problems. The research proposed in this study is designed to directly address this very issue, especially by targeting wetlands study sites and remediation sites where investigations will be conducted.

Multi-Regional Priority #5 (MR-5). MR-5 seeks to ensure that restoration is not threatened by degraded environmental water quality. Among the components cited as of particular concern is Hg. The major focus of our proposal is to directly address the need to asses Hg sources, loadings, and factors affecting transformations and bioaccumulation across the watershed, particular in wetland areas slated for restoration. In conducting this study, we will focus our efforts on sites where remediation is or will be occurring.

Sacramento Regional Priority #7 (SR-7). SR-7 seeks to develop conceptual models to support restoration efforts through more monitoring, better understanding of historic data, as well as greater knowledge of basic processes. Restoration at sites with Hg contaminated sediments is of particular concern since restoration may make Hg problems worse. Mercury evaluation and abatement work in the Sacramento River and tributaries is needed to determine and inventory sources of high levels of bioavailable Hg. Our proposed work will provide information directly applicable to this goal. Task 2 will yield information on watershed source strengths and task 4 will evaluate Hg and MMHg levels in proposed restoration areas.

Delta and Eastside Tributaries Regional Priority #6 (DR-6). The goal of DR-6 is to restore shallow water habitats in the Delta for the benefit of at-risk-species while minimizing potential adverse effects of contaminants. DR-6 specifically notes that Hg is a concern to water and sediment quality and that Hg issues may threaten the success of restoration efforts. DR-6 seeks information to better understand the processes that determine Hg methylation in the Delta and tributaries. Our proposed work directly addresses this exact need in several of the proposed tasks. We have proposed to conduct sediment biogeochemistry studies to investigate the environmental parameters which influence methylation in sediments; We have proposed to investigate the importance of wetland habitats as sites of methylmercury production; We have proposed to investigate the role of external versus internal sources of MMHg in the Delta. Further, we have proposed to work at several of the sites of particular interest to DR-6, including Yolo By-Pass and the Cosumnes River.

Delta and Eastside Tributaries Regional Priorities #7 (DR-7). DR-7 seeks to protect at-risk species in the Delta using water management and regulatory approaches. An item specifically mentioned in DR-7 is to optimize the use of Delta Cross Channel by addressing specific questions. The specific question that our proposal seeks to answer is how do operational manipulations of the Delta Cross Channel, the export pumps or barriers, independently or in combination, affect the transport of pollutants. The pollutant in question here is Hg. Our preliminary investigations under our current CALFED Mercury Program revealed that MMHg concentrations in Mokelumne sediments during Cross Channel closure can vary significantly (see Figure 6). We have proposed to follow-up on this preliminary observation in our currently proposed work.

Bay Region Priority # 5 (BR-5). BR-5 seeks to restore shallow water, local stream and riparian habitats for the benefit of at-risk species while minimizing potential constraints to successful restoration efforts. Within this framework there are three specific needs involving Hg: (1) Investigations of Hg inputs from Yolo Bypass and their implications in Suisun Marsh and Grizzly Bay; (2) Investigations of the effects of hydraulic mining debris and other Hg sources on wetlands development and production of methylmercury; and (3) Studies are needed to understand the implications of restoring Hg contaminated sediments for regional and local Hg production and food web accumulation. Tasks 4A, 4B, 5C, and 6 of this current proposal will directly address these issues. We propose to target our intensive studies, which will yield seasonal information on MMHg production, MMHg fluxes, and sediment biogeochemical characteristics relative to MMHg production and fluxes at sites of interest to priority BR-5. This information will be invaluable in assessing how habitat restoration efforts might influence MMHg production and bioaccumulation in these target areas.

2. Relationship to Other Ecosystem Restoration Projects

The work proposed in this project represents basic science, oriented around understanding how Hg and MMHg are transported and cycle within the San Francisco Bay, Delta, and tributaries, focusing on Hg contamination issues, and specifically MMHg production. Our proposed Hg project will benefit from, and be of benefit to, other proposed Hg research projects by providing a framework for assessing sources, sinks, and cycling; by providing Delta wide information on Hg and MMHg characterizations of different habitats; and through cooperative efforts where sampling sites are co-located. Three particularly important Hg proposal linkages are with the two proposal's by Dr. Jay Davis (PI) entitled "Delta Mercury Monitoring Network: Sport Fish" and "Mercury in Central Valley Sport Fish: Defining the Mercury Problem" and the proposal by Dr. Steve Schwarzbach (PI) entitled "Mercury in birds of the Bay/Delta Watershed - adverse effects to reproduction and patterns of bioaccumulation".

3. Request for Next Phase Funding

This current proposal is a collaborative effort between 4 principal investigators and 3 institutions to continue the scientific studies that were initiated by the CALFED Mercury Project (described in the next section). San Jose State University Foundation will be the prime contractor for this project (see budget justification forms for additional details).

4. Previous Recipients of CALFED Program or CVPIA Funding

The principal investigators who are part of this current proposal have received funding from CALFED for the project entitled: Assessment of Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed. We have referred to this project as the "CALFED Mercury Project". The principal investigator for this project is Dr. Mark Stephenson. The USBR award number for this project is 99FC200241, and the CALFED project number is 99-B06.

Current Project Status. The CALFED Mercury Project is a multi-investigator, multi-institution project, funded for a three-year period, which began on September 30, 1999 and will end on September 30, 2002. The project is quite broad in its scope. It has included investigations ranging from mine site characterization studies in the Cache Creek watershed, to studies of the impact of Hg on avian species, to characterization and quantification studies of Hg transport in the Bay and Delta regions. A summary of the progress made to date on this project is given in the executive summary for the first year annual report in Appendix B. The complete compendium of annual reports for this project by the various investigators can be obtained at our CALFED Mercury Project web site: http://loer.tamug.tamu.edu/calfed. The CALFED Mercury project underwent an external review in December of 2000 by outside scientists (the scientific review committee, SRC) who have expertise in environmental Hg studies. Their report is attached in Appendix C. Following is a quotation from this report which illustrates that significant progress has been made to date on the currently on-going project: *"The Scientific Review Committee (Committee) commends the CALFED Mercury Project investigators for their significant progress since the first project review in the collection of data, implementation of a QA/QC program, improvement of analytical capabilities, development of methods, and interpretation of initial results. This mercury project is a significant first step toward defining the sources, processes, and factors that control methylmercury (MeHg) exposure and associated ecological risks and health risks in the Bay-Delta watershed."*

Major findings of the current CALFED funded project, pertinent to this current proposal include:

- Tributaries appear to be a major source of MMHg to the Delta water column, especially during high flow periods.
- Mass balance studies suggest that there appears to be a net loss of MMHg from both unfiltered and filtered water in the Delta. The source of this is currently unknown.
- Recent data from the mass loading studies suggest that pulses of MMHg may occur in the spring.
- The range of sediment-water exchange fluxes of dissolved MMHg varies widely throughout the Delta (–19 ng/m^2/day to +22 ng/m^2/day) and is a major source of MMHg to the Delta, particularly during low flow periods.
- Both total Hg and MMHg exhibited non-conservative estuarine mixing profiles.
- Sediments in the central Delta tend to have higher MMHg values than those of the tributaries.
- Investigations of habitat types have indicated sediments from tule beds (peat-dominated), riverbank, and farmed-island habitats are significantly higher in MMHg than sediments from the main channels.
- MMHg to total Hg ratios in sediments are highest in the Delta, and lower in the tributaries. This suggests methylation efficiencies in the Delta are higher than in the tributaries.
- A comparison of MMHg to total Hg ratios in sediments from different tributary sources indicates there is no difference between Coast Range and Sierra Nevada sediments.
- MMHg levels in sediments are not predictive of MMHg levels in clams or fish.

5. System-Wide Ecosystem Benefits

Mercury contamination issues and fish consumption advisories are a system-wide problem in the Bay-Delta-tributaries system. In order to develop strategies to reduce Hg levels in fish, Hg transport cycling and behavior must be studied on a system wide basis – that is the approach taken with this project. We propose to examine Hg loads from several sources, including internal sources and sinks, and how different habitats respond to Hg and MMHg. Without information of this type, it will be impossible to know where and how to address any Hg remediation efforts or moreover, whether remediation efforts might exacerbate the Hg problem. For example, this study will be instrumental to the SWRCB efforts to develop a Total Maximum Daily Load (TMDL) for Hg in the Bay-Delta region.

C. Qualifications

The principal investigators involved with this project are currently principal investigators involved with the on-going CALFED Mercury Project.

Dr. Mark Stephenson is the current principle investigator for the CALFED mercury project. This is an inter-disciplinary effort with 13 investigators with the goal to study Hg cycling in the Sacramento San Joaquin Delta and Cache Creek and make recommendations to CALFED on how to lower the concentrations of mercury in sports fish. Recent environmental water quality projects in which he has been principal investigator include: California State Mussel Watch, Coastal Fish Contaminants, Impact of mercury on beneficial uses in San Francisco Bay and the Central Valley Region, Mercury monitoring in the Central Valley Region, and the Bay Protection and Toxic Cleanup Program.

Dr. Kenneth Coale is a biogeochemist with 25 years experience in trace metal biogeochemistry and currently serves as the Acting Director of Moss Landing Marine Laboratories. For the last 10 years, Dr. Coale has received funding from the National Science Foundation and the Office of Naval Research to study the processes which control the flux of toxic metals and nutrients between the sediments and overlying waters of the LA/Long Beach, San Francisco Bay, and continental coastal margin systems using benthic flux chambers and sediment porewater modeling. He has served as a panelist on the National Science Foundation's Chemical Oceanography review committee, is an Associate Editor of Marine Chemistry, Special Editor of a recent issue of Deep-Sea Research, has participated on over 50 oceanographic cruises, and has over 40 peer-reviewed publications on trace metals in marine and lacustrian environments. Dr. Coale is a PI on the on-going CALFED Mercury program.

Dr. Gary A. Gill is an Associate Professor of Oceanography at Texas A&M University in Galveston. Dr. Gill's area of research specialization is the biogeochemistry of Hg. Dr. Gill has more than 20 years of experience with a wide variety of environmental Hg studies and the analytical determination of ultra-trace levels of Hg in the environment. He has more than 25 peer-reviewed publications and has made numerous scientific presentations involving environmental Hg studies. Dr. Gill has most recently worked on environmental Hg problems at an EPA Superfund site in Lavaca Bay, Texas and in South Florida to address Hg problems in the Everglades. Dr. Gill is a PI on the currently on-going CALFED Mercury Program.

Dr. Chris Foe has worked for the regional board in a special studies section since 1987. Between 1993-95 he conducted an inorganic Hg load study to the bay-delta estuary and determined that cache creek in the coastal range was a major source of estuarine Hg. He is responsible for development of the mercury TMDL or control plan for the Bay-Delta Estuary. Dr. Foe is a PI on the currently on-going CALFED Mercury Program.

Mr. Max Puckett is an Environmental Specialist for the California Department of Fish and Game, and serves as the Director of the Granite Canyon Marine Pollution Studies Laboratory. In this capacity, Mr. Puckett has served as the day-to-day technical and administrative manager for numerous large-scale, long-term, multi-agency cooperative scientific projects, including most notably the Bay Protection and Toxic Cleanup Program, the statewide Surface Waters Ambient Monitoring Program (SWAMP), and the on-going CALFED mercury project. Mr. Puckett has over

24 years of experience in conducting as well as managing environmental studies, specializing in assessing aquatic pollution and its impacts on natural resources.

Dr. Xiujun (Wendy) Wang holds a Ph. D. in Soil Sciences (University of Melbourne) and a Ph. D. in Oceanography (University of Tasmania). The focus of her research is on the development of coupled physical/biogeochemical models of nutrient cycling in both terrestrial and aquatic ecosystems. More recently she developed a 1D bio-physical model to study nutrient utilization and resupply of nutrients to the upper ocean together with a 1D bio-geochemical model to simulate the carbon export and pCO_2 from the surface layers of the Southern Ocean.

D. Cost

1. Budget – see attached budget forms.

2. Cost-Sharing

The CVRWQCB's cost share for Task 2 is estimated at $340,000. In addition, the Regional Board will pay all expenses for ancillary measurements (TSS, sulfate, DOC, and chlorophyll) during the three years of the study. Estimated cost is about $10,000/year.

E. Local Involvement

The CALFED Mercury project website will continue to be used as a high visibility means for public dissemination of findings and other related information. In addition, all participating P.I.'s on this project will be making technical presentations on their respective project work at various public and scientific forums during the project period. Information sharing will continue with the Sacramento River Watershed program, as well as the Delta Tributaries Mercury Council (DTMC), both of which provide additional and significant outreach to interested parties. The Central Valley Regional Board will share all information on Hg sources and their loads with County Directors of Public Works and Public Health.

F. Compliance with Standard Terms and Conditions

The project will comply with State and Federal contract terms as outlined in application.

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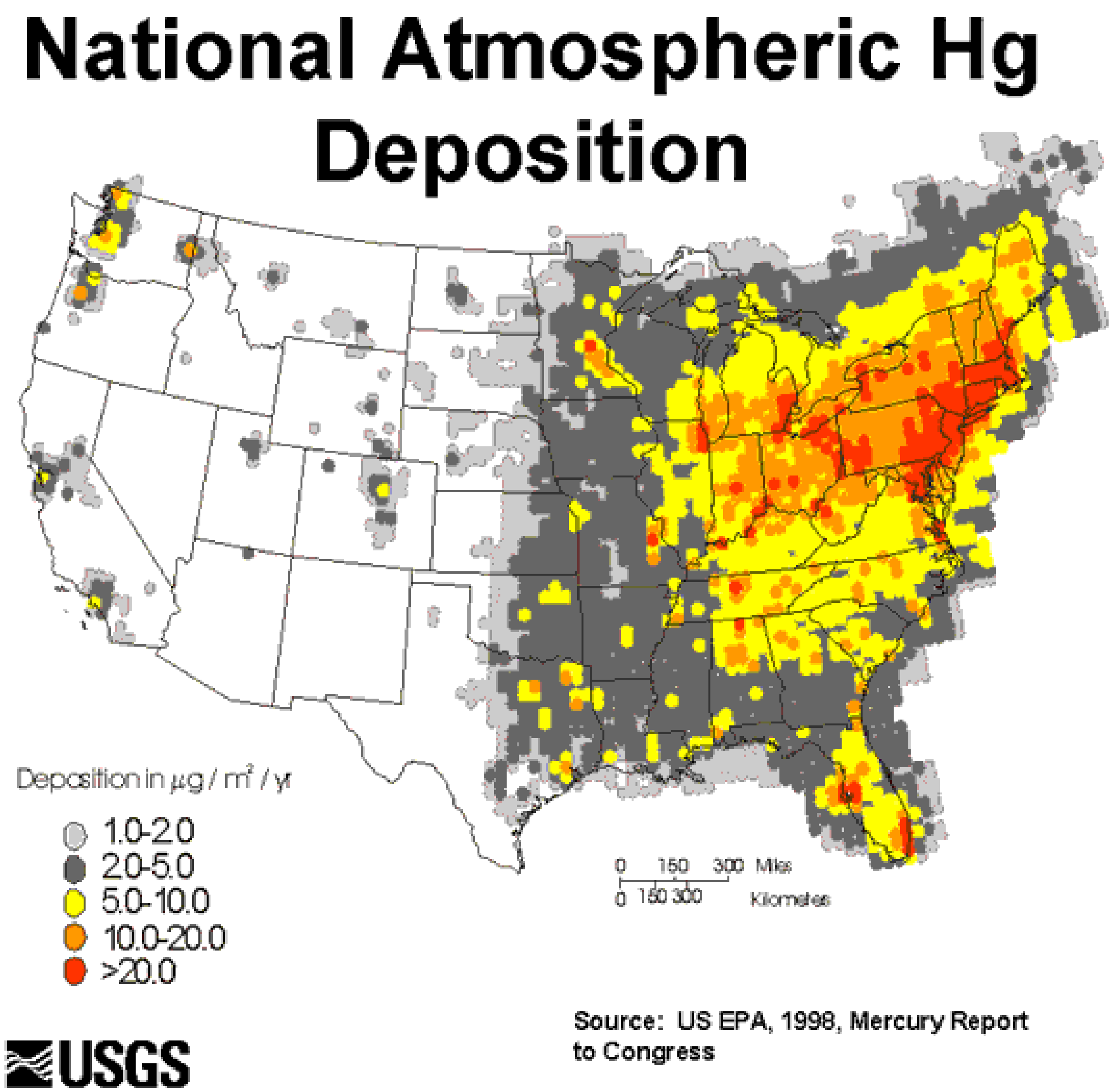
Figure 1. Summary of Atmospheric Mercury Deposition in the United States. Data were generated using the RELMAP program.



This figure was obtained from the USGS Mercury Studies Web Page
http://infotrek.er.usgs.gov/doc/mercury/lab_info.html

Figure 2. Monthly concentrations of monomethyl mercury in surface sediments at several sites in the Delta. These sites are representative of various habitat types found in the Delta. A seasonal spike in monomethyl mercury is observed at Sherman Island and Connection Slough. A Suison Bay winter spike in monomethyl mercury is not confirmed due to gaps in sampling caused by rough weather on the Bay prohibiting sampling efforts

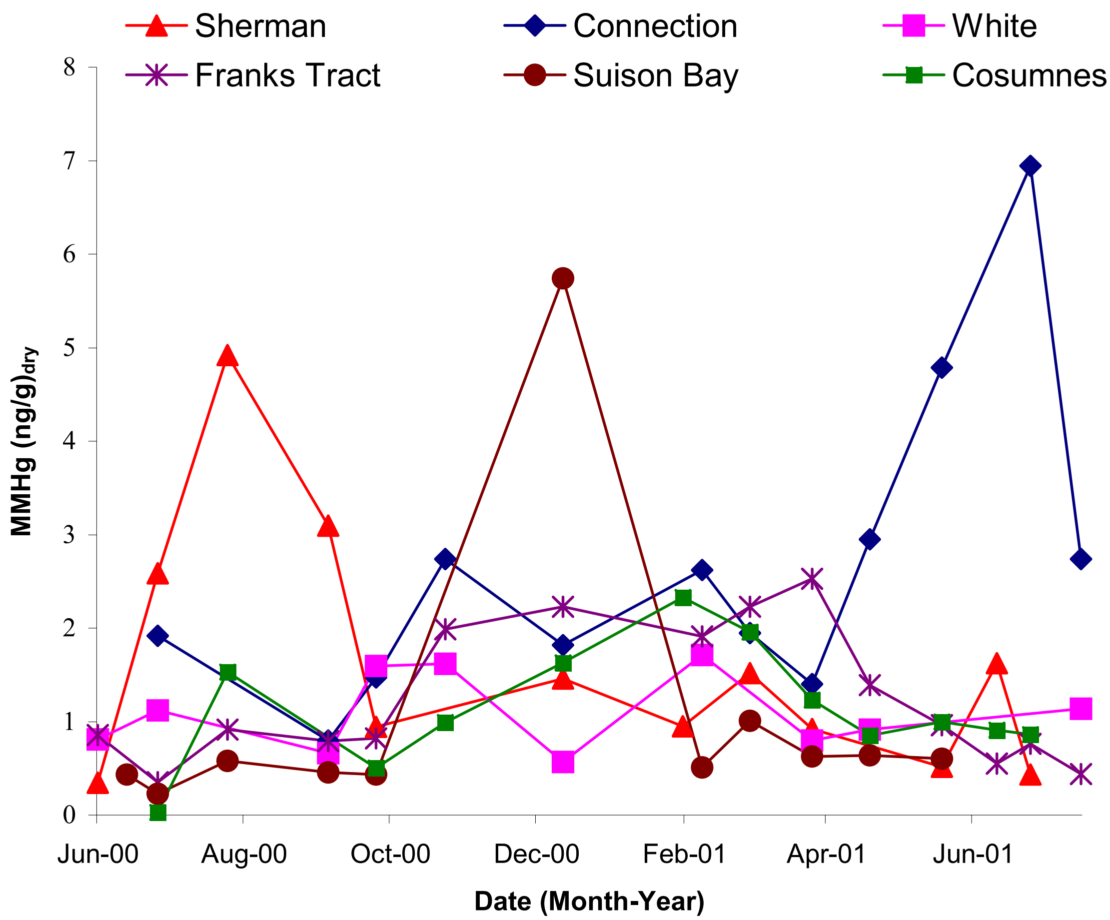


Figure 3. Comparison of monomethyl mercury concentrations in sediments from a wetlands and an open water site in Frank's Tract.

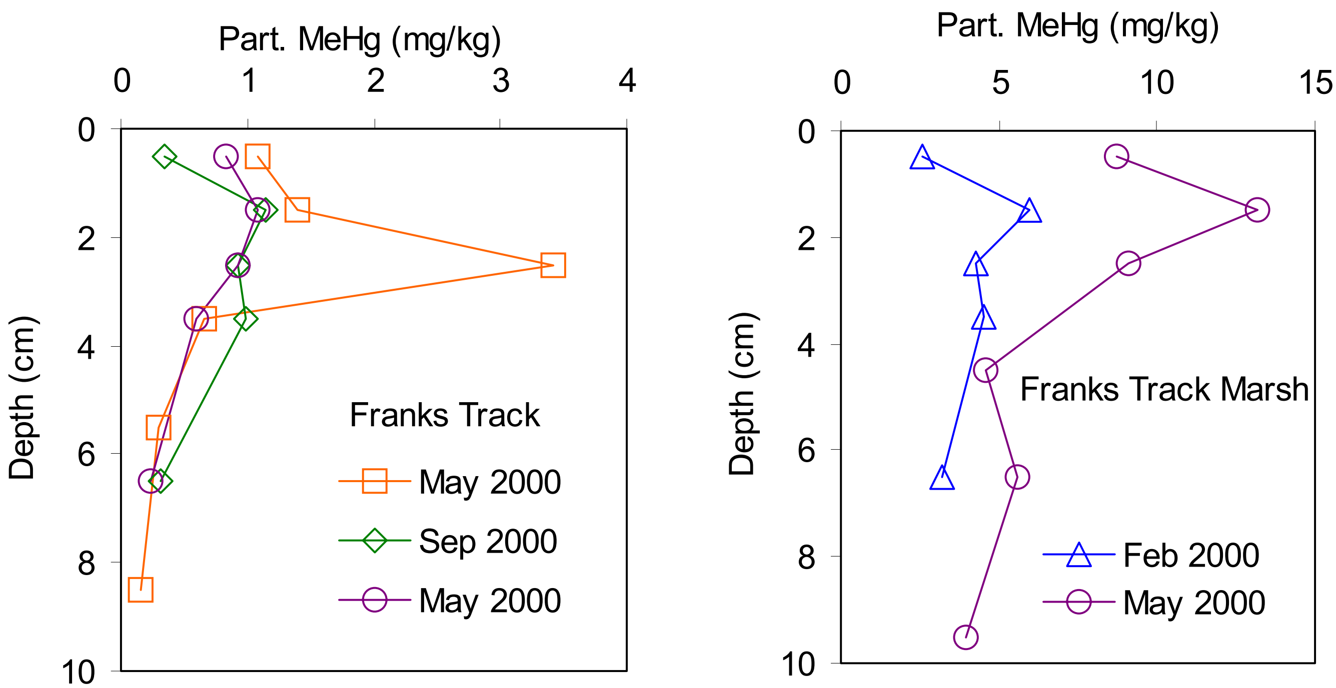
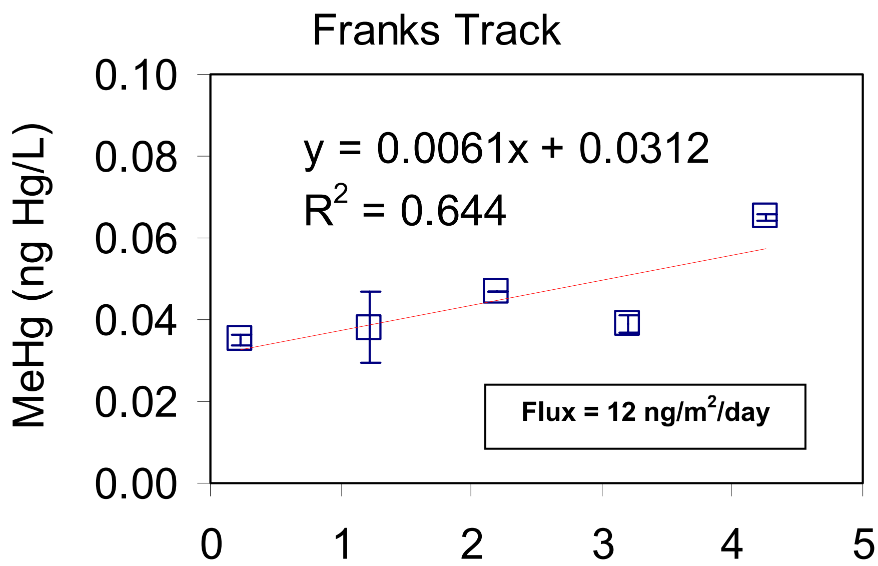


Figure 4 . Flux Chamber deployments in Franks Track in May 2001. The Franks Track site is in the open water and the marsh site is on the northern margins of Frank's Track within a shallow, highly vegetated marsh area.



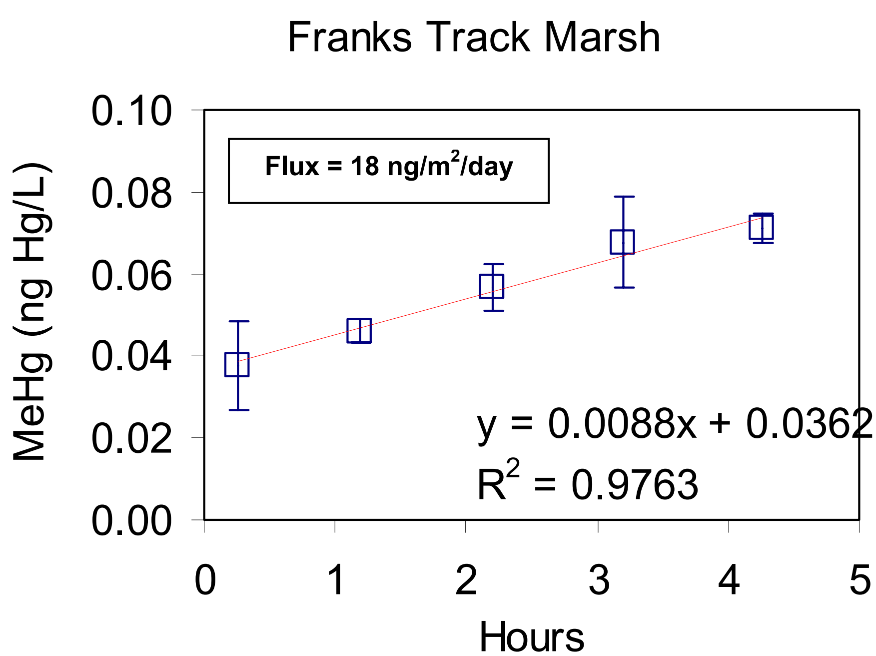
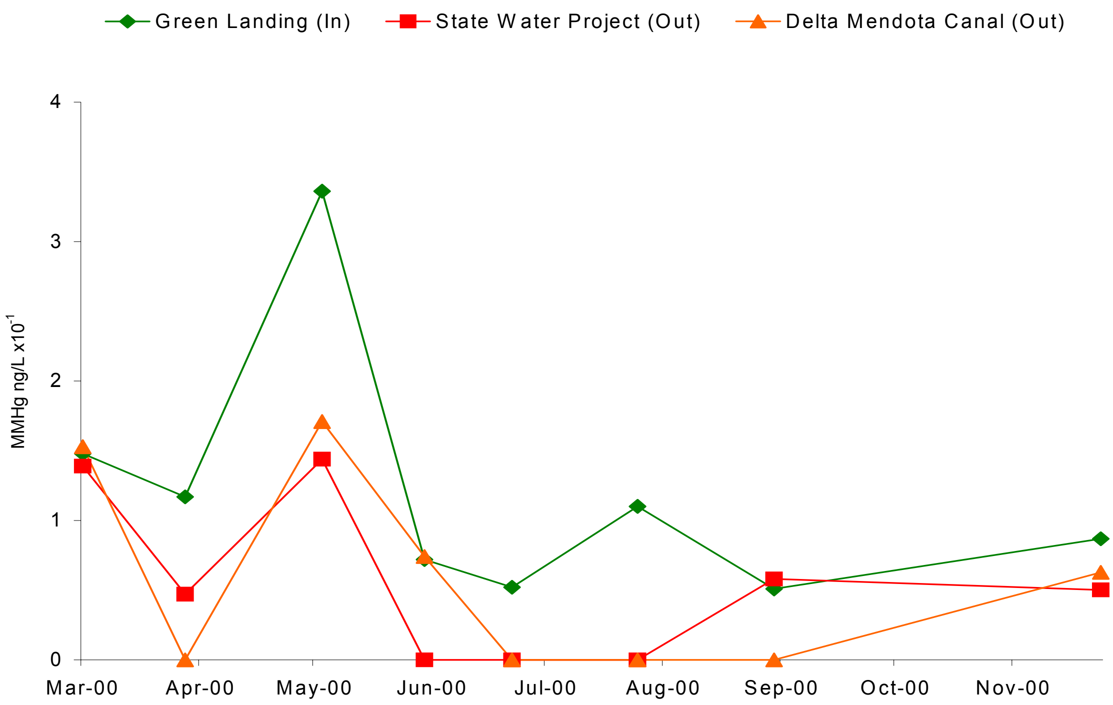


Figure 5. Monthly monomethyl mercury water concentrations at three locations in the Delta are shown for both unfiltered (top graph) and filtered (bottom graph) samples. Water from the Sacramento River flows into the Delta at Green Landing and out of the Delta at State Water Project and Delta Mendota Canal. Concentrations of monomethyl mercury in unfiltered samples were higher at the water import site compared to the export sites the majority of times sampled. Filtered water from the import site was higher than the export sites consistently for July through December of 2000.



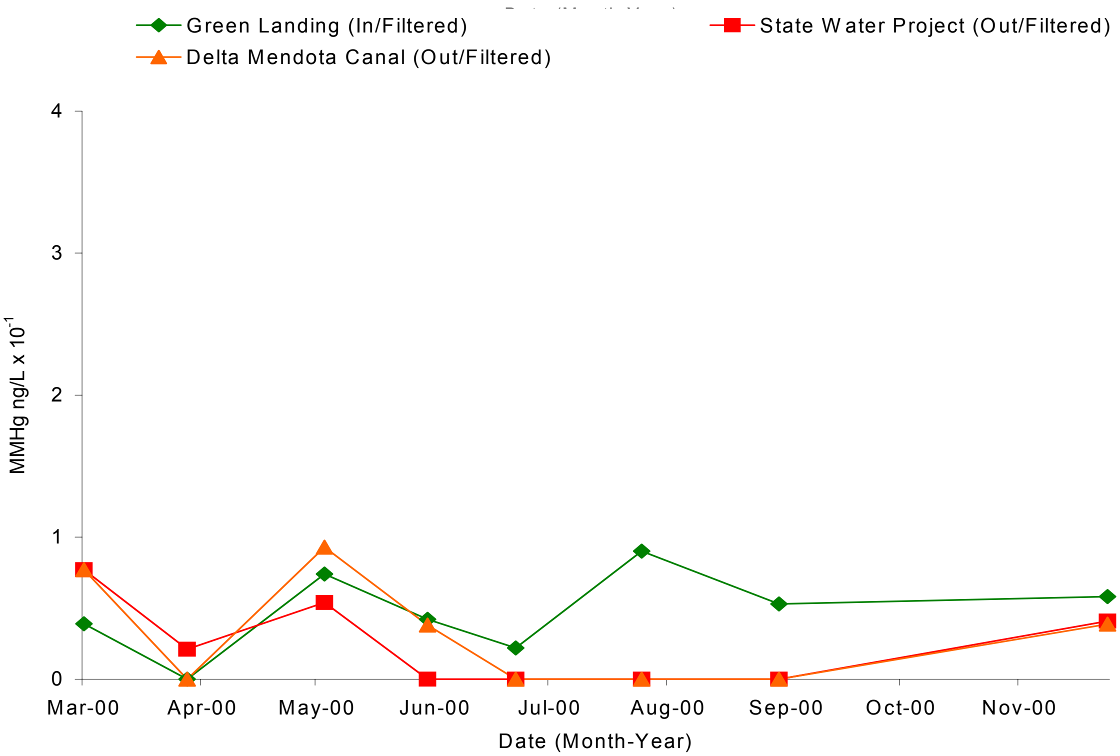


Figure 6. Monomethyl mercury concentrations in surficial sediment are shown for three sampling dates at four stations located off the Mokulumne River in the Northeast Delta. The October 1999 values are all less than 1 ppb. Revisiting the sites in May of 2001 revealed a significant increase in monomethyl mercury at three of the four sites. The sites were sampled again in September 2001 and the resulting monomethyl mercury values are shown to have fallen back down to values comparable to October 1999. Coincidently, the sampling in May 2001 took place during a time when the Mid Delta Cutoff was closed. The closing of the Mid Delta Cutoff stops all Sacramento River water from flushing the Mokulmne River areas. The changing of this hydrology may be having an influence on methyl mercury production in this portion of the Delta.

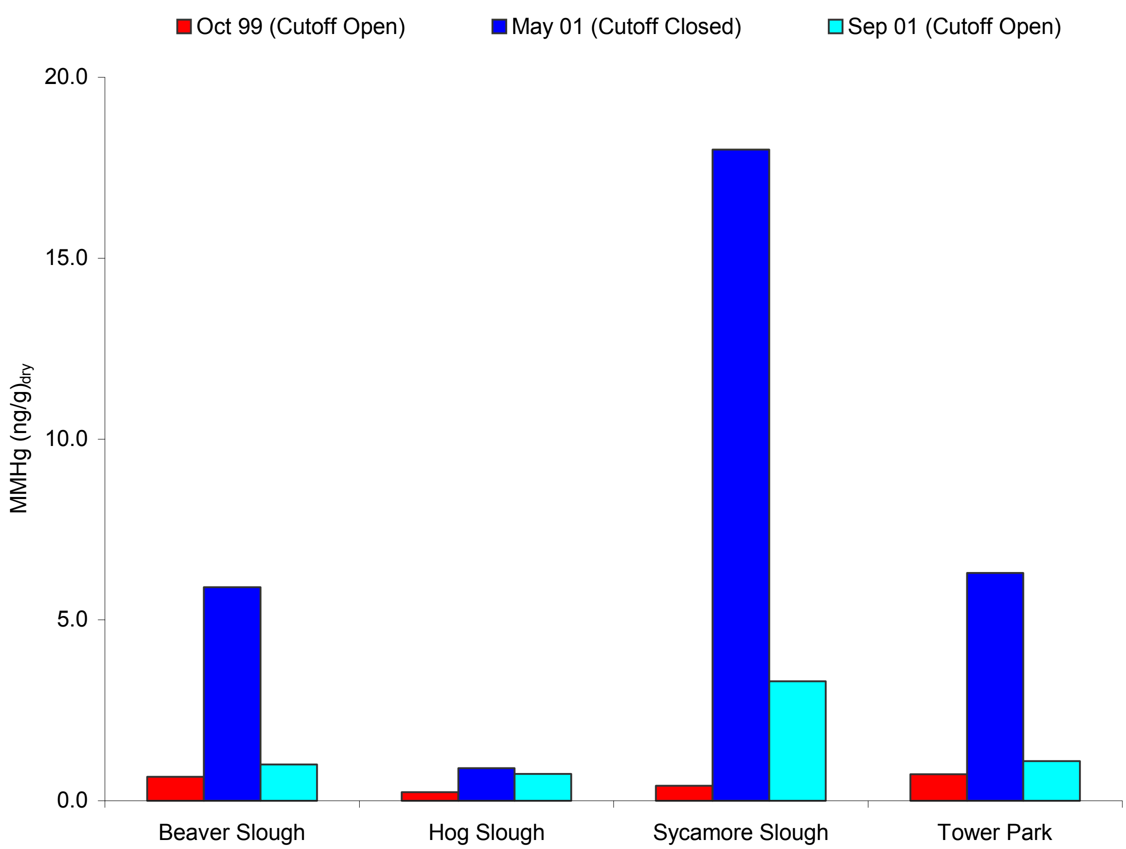


Figure 7. Map Showing Station Locations in the Delta for several proposed tasks. Some of the stations for other tasks are not shown and will be selected either randomly within habitat types, or after consultation with other researchers and local groups that have knowledge of the candidate sites.

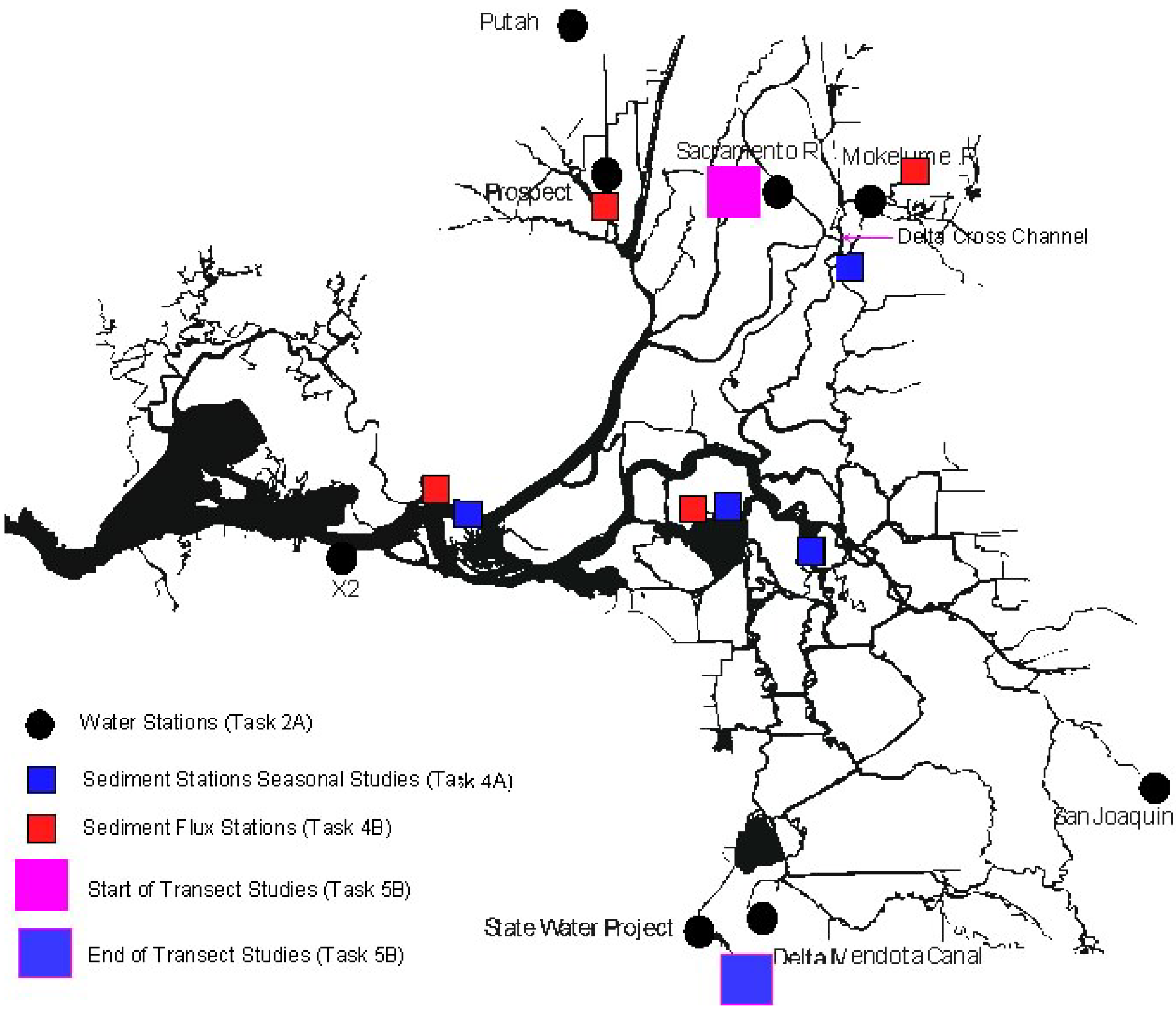


Figure 8. Map showing the proposed study areas for Tasks 2C and 5C. In the Cache Creek study area, Harley Gulch, Sulfur Creek and Davis Creek will be monitored. In the Saltwater Marsh study area, sites in North San Francisco Bay and Suison Marsh will be selected. In the Fresh Water Marsh Study Area sites in the Yolo Bypass and Central Delta will be selected.

Cache Creek Study Area (Task 2C)
and Marsh Wetland Study Areas(Task 5C)

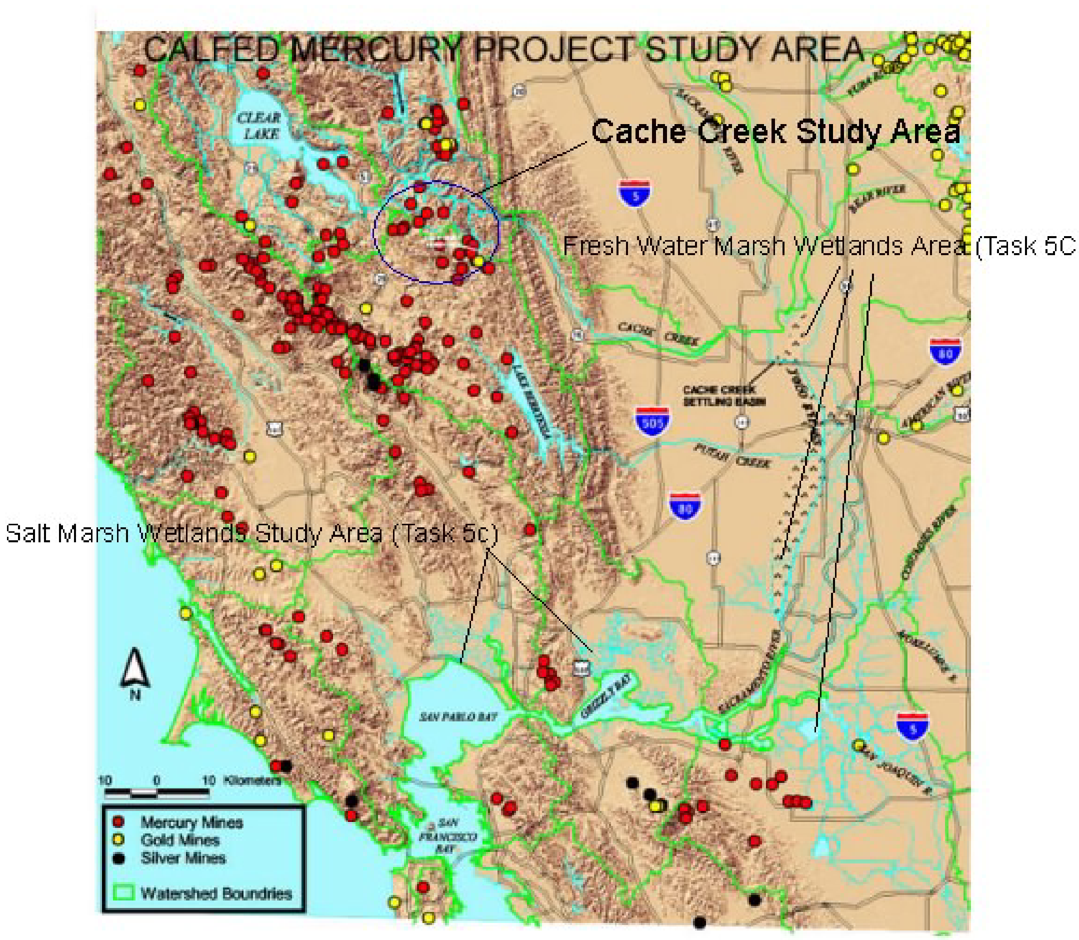


Figure 9. Project Timeline

Task	Sampling Effort	2002							2003												2004												2005					
		J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J
Task 1 - Project Administration																																						
Quarterly Reports					■			■			■						■			■			■						■			■			■			
Annual Reports														■												■												■
Task 2 - Mass Loading and Export																																						
A Fixed Station Sampling	Monthly at 6 sites		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■												
B Watershed Characterization	Monthly at 26 sites		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■												
C Sub-watershed studies	Monthly at 10 sites		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■												
Task 3 - Atmospheric Deposition	Bi-weekly at 3 sites				■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■						
Task 4 - Delta Monitoring Program																																						
A Surface Sediments	25 sites						■					■					■							■					■									
B Benthic Flux Chamber	6 trips; 6 sites						■					■					■				■					■					■							
Task 5 - Process Oriented Studies																										■												
A Demethylation	6 sites, 3 times/yr						■					■					■				■					■					■							
B Cross-channel studies	3 times/yr						■					■					■				■					■					■							
C1 Wetland Loading Studies	9 sites, 3 times/yr						■					■					■				■					■					■							
C1 Wetland Loading Studies	2 sites, 9 times/yr				■		■		■		■	■	■	■		■	■		■		■		■		■	■		■		■	■		■					
C2 Sediment Biogeochemistry	6 sites, 3 times/yr						■					■					■				■					■					■							
D Air-Water Studies	6 sites, 3 times/yr						■					■					■				■					■					■							
Task 6 - GIS Integration	Continuous						■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■				

APPENDICES

Appendix A. **Conceptual Overview of the Biogeochemical Cycling of Mercury in the Bay-Delta Ecosystem and its Watershed.**

Appendix B. **Executive Summary - An Assessment of Human Health and Ecological Impacts of Mercury in the Bay-Delta Watershed**

Appendix C. **Mid-Project Meeting of the Scientific Review Committee for the CALFED Project "An Assessment of Ecological and Human Health Impact of Mercury in the Bay-Delta Watershed", Moss Landing Marine Laboratories, Moss Landing, CA December 4-5, 2000**

Appendix D. **Proposal Executive Summary - Transport, Cycling, and Fate of Mercury and Monomethyl Mercury in the San Francisco Delta and Tributaries – An Integrated Mass Balance Assessment Approach.**

Appendix A

Conceptual Model of Mercury Cycling and Transport in the Bay-Delta Ecosystem and its Tributaries

Summary of Major Features

Figure 1 depicts a conceptual overview of the transport and biogeochemical cycling of mercury in the Bay-Delta ecosystem and its watersheds. This cycle is based upon recent environmental mercury research, particulary the findings from the Calfed Mercury Project entitled "*Assessment of Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed*". The cycle also includes current working hypotheses describing Hg behavior in the Bay-Delta ecosystem. The major sources, losses, internal cycling processes, and environmental impacts depicted in the figure are summarized below.

Major inputs to the Bay-Delta include:

- Riverine input from two distinct sources, the Sierra and Coastal mountain ranges
- Atmospheric deposition
- Irrigation return water

Major loss (or export) terms for mercury in the Bay-Delta include:

- Freshwater export to Southern California
- Evasion of volatile Hg species, especially elemental mercury
- Estuarine mixing and transport through the Bay
- Particle settling and burial in sediments

Major internal biogeochemical cycling processes include:

- Bioaccumulation of mercury (as monomethyl mercury) into the aquatic food chain
- Sediment-water exchange
- Production of monomethyl mercury in surficial sediments
- Destruction of monomethyl mercury via photo de-methylation

Primary environmental impacts include:

- Human health concerns from consumption of fish with elevated mercury content

- Birds which feed from the aquatic environment

Mass Balance Geochemical Modeling

Mass balance models provide a framework within which to focus research efforts, develop and test hypotheses, and describe the cycling of constituents in aquatic systems. Information from studies based on mass balance modeling approaches can provide a fundamental starting point or conceptual model for use in the development of more sophisticated environmental modeling efforts

Working Hypotheses

Our work to characterize the major reservoir and flows of mercury and MMHg in the Delta to date have lead us to develop the following working hypotheses.

1. River borne monomethyl mercury is the major source of monomethyl mercury found in Delta waters, especially under high river flow conditions.

2. Within the Delta, wetland and marsh regions are major sites of monomethyl mercury production.

3. Monomethyl mercury production in the Delta follows seasonal cycles which vary geographically, possibly due to habitat type.

4. Atmospheric mercury deposition is a minor, but significant source of mercury loading to the Delta.

5. Monomethyl mercury is removed from the water column along the transport pathway across the Delta as water flows from the Sacramento River to the export pumps in the southern Delta.

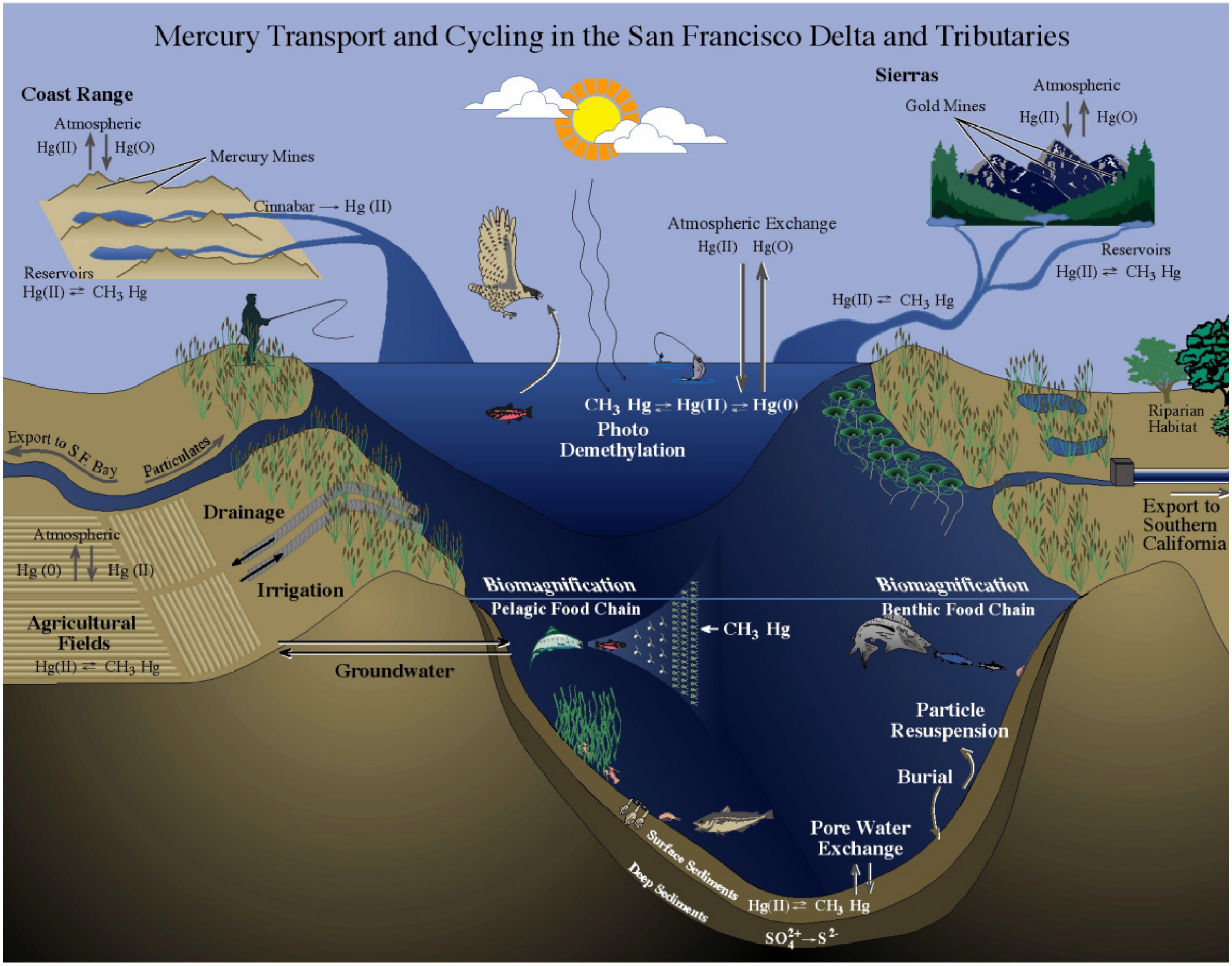


Figure 8. Mercury Transport and Cycling in the San Francisco Delta and Tributaries

Appendix B

EXECUTIVE SUMMARY

An Assessment of Human Health and Ecological Impacts of Mercury in the Bay-Delta Watershed

Introduction

Description of the Sacramento-San Joaquin River Delta

Historically, the Sacramento-San Joaquin River Delta (hereafter called "Delta") was a vast region of wetlands (Figure 1). The early settlers diked the wetlands to create extensive tracts of productive farmland. The Delta watershed drains more than 61,000 square miles, or roughly 37% of California's lands (Figure 2). Twenty four million acre-feet of water per year funnels into the Delta from the surrounding watersheds, ultimately ending up in San Francisco Bay. The Delta is much smaller in size than the watershed area, which flows into it, comprising only1,153 square miles (738,000 acres). Over 538,000 acres in the Delta region are utilized for production agriculture, with farm-gate income averaging about $500 million annually. The majority of the flow into the Delta comes from the Sacramento River. Most of the water exported from the Delta in the spring flows into San Francisco Bay (Delta outflow). During the summer, when flows are the lowest and the exports of water from the Delta are high (for irrigation and water supply for Southern California), about 57% of the flows from the Delta enter the San Francisco Bay, and 43% of the Delta flows travel in reverse up the San Joaquin River and smaller channels towards the export pumps (data from this report; and Figure 3).

The Delta islands, formed by the creation of dikes and subsequent filling of the diked areas, have an intricate network of irrigation diversions, including siphon pumps and floodgates (Figure 4), as well as irrigation return points where water is pumped back into the Delta (Figure 5). In the summer months, when irrigation is at a high and Delta flow inputs are at a low, approximately 20% of the Delta input is diverted to these islands.

It is estimated about 12 million people per year enjoy recreating in the Delta, where fishing is one of the most popular forms of recreation, as well as pleasure boating and other water sports.

About 90% of the mercury produced in the United States between 1850 and 1980 was mined in the Coast Range of California. There were 320 mercury mines at the peak, including several of the world's largest mercury mines. During the gold rush era in the mid to late 1800's, mercury was mined in the Coast Range and was shipped to gold mining operations in the Sierra-Nevada mountain range on the east side of the Sacramento and San Joaquin valley (Figure 6). The mercury was used to amalgamate the gold fractions, with much of the mercury lost to the environment in this process. Approximately 220 million pounds of mercury were produced from mines in the Coast Range, and about 26 million pounds of mercury were transported to gold mining operations in the Sierra-Nevada and Klamath-Trinity Mountains. As a result, widespread contamination occurred in mountain waterways in the Coast Range, Sierra-Nevada Range, and the Klamath-Trinity Range, as well as widespread contamination downstream in the rivers and Delta region of the Sacramento-San Joaquin Valleys.

Description of the CALFED Mercury Project

The CALFED Mercury Project was initiated in September 1999, at the request of various entities working with CALFED on water quality issues in the Delta region, including the Central Valley Regional Water Control Board. The Project is truly a collaboration among numerous scientists from federal, state, and regional governments, as well as Universities and other public and private entities. There are two main study areas: the Sacramento-San Joaquin Delta that receives flow from the Sacramento-San Joaquin watershed; and Cache Creek, a tributary to the Delta in the Coast Range which contains several major mercury mines. Research efforts include estimating mass loading of mercury, assessing the extent of bioaccumulation in various organisms, documenting potential human health and ecological effects (including avian reproductive impairments), and conducting extensive mercury speciation studies (Figure 7). A conceptual model of the CALFED Mercury Project is shown in Figure 8.

Primary goal of the CALFED Mercury Project

The CALFED Mercury Project's primary goal is to reduce mercury concentrations in fish tissue to levels that do not pose a human or wildlife health or ecological hazard. There are currently health advisories for fish consumption in thirteen water bodies in northern California, including San Francisco Bay and the Sacramento-San Joaquin Delta.

Studies of the Central Delta Area

Mercury mass loading results from the central Delta area

The mass loadings of mercury from June 2000 are discussed below, and typify the loadings in the low flow/high export period. The Delta has seven inputs and five outputs that were quantified for this report (Table 1). During this time period, the Sacramento River is the predominant source of water and methyl mercury to the Delta. The monthly balance calculations suggest several facts. First, there appears to be a net loss of raw and filtered methyl mercury in the Delta. The loss for raw and filtered methyl mercury is 35% and 51%, respectively, in June. The loss in the Delta observed during June was consistent with losses observed during sampling in the other summer months, also. Second, the concentrations of raw and filtered methyl mercury in water from the Sacramento River during summer months is always higher than the concentrations of those constituents downstream at the export pumps (State Water Project and Delta

Mendota Canal, Table 1). These two facts indicate there is a loss, especially during the summer, of methyl mercury in the estuary during the period studied.

Both total mercury and methyl mercury exhibited non-conservative estuarine mixing profiles. Methyl mercury concentrations are observed to be the highest in freshwater, at approximately 0.065 ng/L. At mid-salinities (ca. 5-22 parts per thousand, from Pittsburgh to Carquinez Straights area), the methyl mercury concentrations are observed to be minimal values, at approximately 0.015 mg/L (Suisun Bay). The values rise slightly at the saltwater end-member areas (ca. 24-33 parts per thousand), at approximately 0.02 ng/L . There appears to be a methyl mercury removal mechanism in the mid salinity area (Pittsburg to Carquinez Straights) that lowers the amount of methyl mercury that flows into San Francisco Bay.

The range of sediment-water exchange fluxes of dissolved methyl mercury varies widely throughout the Delta (–19 ng/m^2/day to +22 ng/ m^2/day). The Cosumnes River station and Little Holland station, near the mouths of two tributaries, as well as Franks Tract station, exhibited the highest flux rates observed in the study to date. The estimates on mass loadings of methyl mercury to the Delta from sediments can be calculated several ways. The main variables are the flux estimates and the surface area of the system. The flux measurements are variable and only preliminary estimates can be made. The surface estimates can vary depending on whether the Yolo Bypass, Grizzly Bay, and San Pablo Bay are included. During the winter months, the mass input of dissolved methyl mercury from the tributaries far exceeds fluxes from the sediments. During the summer months, however, the tributary and sediment flux input estimates are roughly equivalent based on assuming: 1) surface area is only the Sacramento River (from City of Sacramento to Grizzly Bay) and Delta (12.7×10^7 m^2), and 2) average sediment flux mass input is 5 ng/m^2/day. Even using this fairly conservative estimate of 5 ng/m^2/day, input from sediment remains an important factor in the overall mercury-loading picture.

The scientific community is in general agreement that sediments are of primary importance in mercury studies. This is due in large part because almost all the methyl mercury that bioaccumulates in fish is produced by sulfate-reducing bacteria that live in anaerobic sediments. For this reason, sediment studies were initiated to determine the specific details of methyl mercury production (where, when, and how much) and subsequent flux into the overlying water. Results from several hundred stations in this project indicate the sediments in the central Delta area tend to have higher methyl mercury values than those of the tributaries, however some of the stations in all areas in the Delta had significant levels of methyl mercury (Figure 9). Investigations of habitat types have indicated sediments from tule beds (peat-dominated), riverbank, and farmed-island habitats are significantly higher in methyl mercury than sediments from the main channels.

The studies done to date on seasonal trends in methyl mercury concentration in sediments have shown fairly consistent concentrations at most stations during the July to October period. Recent data from the mass loading studies suggest that pulses of methyl mercury may occur in the spring. No intensive sampling was conducted in spring 2000 to investigate this possible pulse, however, biweekly samples will be collected in spring 2001 for this purpose.

Some sediment is better than other sediment at converting total mercury to methyl mercury. One measure of this efficiency or potential is the methyl mercury to total mercury ratio in sediment. The higher the proportion of methyl mercury in the sediment is, relative to the total mercury in the sediment, the more efficient the methylation process. Agencies that regulate mercury discharges into waterways can use this information to promote regulations that reduce mercury levels in fish by requiring: 1) lower total mercury concentrations in the discharges, or 2) a decrease in the methylation efficiency in downstream sediment. Either of these two strategies should lead to lower methyl mercury concentrations in the environment. The methyl mercury to total mercury ratios are highest in the Delta, and lower in the tributaries. This indicates high methylation efficiencies in the Delta, and lower methylation efficiencies in the tributaries.

A comparison of methyl mercury to total mercury ratios in sediments from different tributary sources indicates there is no difference in efficiency between Coast Range sediment and Sierra Nevada sediments. These results indicate equal bioavailability of total mercury in sediments in these two areas, even though mercury in the Coast Range is derived from cinnabar (the mercuric sulfide ore from which mercury is derived), and mercury in the Sierra-Nevada Range is derived from elemental mercury.

From the data collected to date, the amount of methyl mercury fluxing from the sediments is positively correlated to the amount of methyl mercury in the surficial sediments. This is import because it will allow the use methyl mercury concentrations in sediments as a proxy for methyl mercury flux. We can then use the regression equation of flux vs. concentration to predict across habitat types the mass loading of mercury derived from sediments on a watershed scale. We can use this estimate in our mass balance models to estimate the importance of habitat types in fluxing mercury to the water column. This data will be presented in the final report.

Methyl mercury levels in sediments are not predictive of methyl mercury levels in clams or fish. This would indicate the methyl mercury in the fish is probably being derived from upstream sources of mercury, or that methyl mercury derived from the sediments is rapidly removed from the water column and is unavailable to the biota in the central Delta.

<u>Bioaccumulation studies from the central Delta area</u>

In this study, bioaccumulation data was obtained for striped bass, large mouth bass, and catfish. Data from another CALFED study in the Delta was obtained for clams and silversides (Slotton and Suchanek, University of California, Davis). The striped bass bioaccumulation data collected in this study show very similar mercury concentrations to data collected from 1970 to 1973 in a previous study, indicating mercury levels in the Delta have not declined over the past 30 years (Figure 10). Levels of mercury in water, clams, silversides, and large mouth bass all show a similar pattern of higher concentrations in the tributaries and lower concentrations in the center of the Delta (see Figure 11 as a typical example). Large mouth bass mercury concentration data is plotted versus the water, clam, silversides, and striped bass mercury concentration data in figures 12-15. The results show a consistent pattern in that all data sets are positively correlated to large mouth bass mercury concentrations, even though they ranged from samples of water, an obligate herbivore (clams), a zooplankton feeder (silversides), and a top level predator (striped bass). The fact that all the levels of the food chain are positively correlated to large mouth bass mercury concentrations would suggest that all components are ultimately receiving mercury from one source, presumably food (phytoplankton) or water imported from the tributaries. The fact that both the water and biota have lower concentrations of methyl mercury in the central Delta indicates the Delta is a sink for methyl mercury.

Studies on effects of mercury on aquatic birds in the central Delta area

The first phase of a field assessment of avian mercury/selenium exposure in San Francisco Bay, Suisun Bay and the Sacramento -San Joaquin Delta was completed with the goal of assessing the effect of mercury on aquatic birds.

This study has five objectives: 1. Assess mercury and selenium concentrations in randomly collected bird eggs of a range of species in different geographic regions of the Bay and Delta to determine if concentrations exceed established Lowest Observed Adverse Effect Concentrations (LOAEC's) for the avian egg. Currently, the LOAEC in bird eggs for mercury is 0.5-ppm fresh wet weight. Species-specific LOAEC's may ultimately be modified after review of work conducted in this project's Subtask 3B by USGS researchers in Patuxent, MD. 2. Assess mercury and selenium concentrations in fail-to-hatch bird eggs of endangered species nesting within the estuary to determine if concentrations exceed established LOAEC's in the avian egg. 3. Determine the proportion of methyl mercury in bird eggs in a subset of those eggs analyzed for total mercury for each species assessed. 4. Evaluate the species patterns and geographic patterns of mercury concentrations and determine if they track findings for mercury in other biota, water or sediment. 5. Evaluate correlations of selenium, mercury and methyl mercury in bird eggs of a range of species in different geographic regions of the Bay and Delta.

A review of data collected to date suggests that species classification appears more important than geographic location in determining the degree of mercury contamination in the 16 species of avian eggs sampled. Among randomly collected eggs, the greatest mercury concentrations were found in Caspian Terns, followed by Forster's Terns, and lastly followed by Double-crested Cormorants from Suisun Bay. Within-species comparisons of mercury concentrations in Caspian Terns eggs indicate the south Bay may be a hot spot for mercury. Within-species comparisons in Double-crested Cormorant eggs indicate Suisun Bay may be a hot spot for mercury in avian eggs, as compared with the central Bay.

Mercury concentrations in avian eggs are elevated high enough throughout the ecosystem in the study area to put one-third of the bird species sampled at risk of embryo mortality, if established egg mercury thresholds in mallards and pheasants can be applied to other species. Avian species at risk in Suisun/ San Francisco Bay include Caspian Terns, Forster's Terns, Double-crested Cormorants, California Clapper Rails, and Snowy Plovers. The latter two species are federally protected as endangered species (Table 2).

Degree of piscivory (avian diet that includes eating fish) was not the sole determinant of mercury concentrations in eggs, since benthic foragers like plovers, stilts and rails also accumulated significant amounts of mercury in their eggs.

We have confirmed that methyl mercury comprises most of the mercury found in avian eggs (Figure 16). Selenium concentrations in avian eggs from the 2000 field season were generally not elevated, with the exception of a few of the egret eggs. Selenium concentrations in eggs from the interior of the Delta have not been examined.

Laboratory studies on mercury injections into avian eggs

Elevated levels of mercury in the environment are especially dangerous to fish-eating birds because mercury accumulates in the food chains of these species. Not only are high concentrations of mercury found in fish, but nearly all of the mercury in fish is in the highly toxic methyl mercury form. Consequently, the tissues and eggs of fish-eating birds can contain dangerous levels of methyl mercury. Avian embryos are especially sensitive to methyl mercury. Laboratory studies with mallards (*Anas platyrhynchos)*, pheasants (*Phasianus colchicus)*, and chickens (*Gallus gallus)* have shown that reproductive success declines when mercury accumulates in eggs. Unfortunately, virtually nothing has been learned about the reproductive effects of mercury on fish-eating birds. Due to the difficulty and expense of breeding fish-eating birds in captivity, it is unlikely that feeding studies with mercury will be conducted in the near future.

As a practical substitute for captive breeding studies, we developed a technique for injecting the eggs of wild birds with methyl mercury and measuring the effects on embryo survival. The eggs of several fish-eating birds were collected in the field, shipped to us, and incubated in artificial incubators. Various doses of methyl mercury, dissolved in corn oil, were injected into the air cell of the egg and embryo survival was followed. Results for an experiment with double-crested cormorants (*Phalacrocorax auritus),* illustrating a dose response to increasing levels of mercury, are shown in Figure 17. In a recent experiment, when mallard eggs were injected with increasing concentrations of methyl mercury, hatching success was 76% for controls, and 56, 62, 53, 44, and 29% for eggs injected with 0.1, 0.2, 0.4, 0.8, and 1.6 ppm mercury, respectively. With white ibis (*Eudocimus albus*) eggs, hatching success was 62% for controls and 10, 25, and 20% for eggs injected with 0.2, 0.4, and 0.8 ppm mercury, respectively. For tricolored herons (*Egretta tricolor*) success was 60% for controls and 10% for eggs injected with 0.4 ppm mercury. For great egrets (*Casmerodius albus*) success was 60% for controls and 0% for eggs injected with either 0.4 or 1.3 ppm mercury.

Our results suggest that the embryos of some species of fish-eating birds may be more sensitive to methyl mercury than are the eggs of mallards and that estimates of harmful levels of mercury in eggs, which have been based on reproductive trials with mallards in the lab, may have to be re-evaluated.

Cache Creek Watershed Studies

Introduction

Description of the Cache Creek Watershed

The Cache Creek watershed, in the Coast Range, drains an area of 1,100 square miles and has the legacy of at least 40 abandoned mercury mines. The drainage from this watershed empties into the Sacramento-San Joaquin Delta after flowing through a steep mountain area, a gentle sloping agriculture area, the Cache Creek Catchment Basin (designed to catch suspended particles), and the Yolo Bypass--a flood control channel (Figure 18). In the winter, when flows are high, Cache Creek flows directly into the Delta through the main river channel and then out through the Yolo Bypass to the Delta. However, in the irrigation season from spring to fall, the waters of Cache Creek are mostly diverted into irrigation canals, and only intermittent flows reach the Yolo Bypass and Delta. Studies conducted between 1996 and 1998 by the Central Valley Regional Water Quality Control Board confirmed that Cache Creek was a major source of mercury. Bulk mercury loads from the Cache Creek watershed to the Cache Creek Catchment Basin were estimated at 980 Kg/yr for water year 1995. Similarly, export to the Yolo Bypass from the Catchment Basin was 495 Kg/yr, which is roughly equivalent to the bulk mercury loads from the Sacramento River.

The Cache Creek watershed was selected for study in this project because: 1. There were several major mercury mines located in the upper watershed, and 2. Previous studies showed the total mercury loadings from this watershed could be up to 47% of the total amount flowing into the Sacramento-San Joaquin Delta, and 3. Remediation of the mercury mines in the watershed is a possibility, which could ultimately result in a lowering of the mercury loads into the Delta.

The Cache Creek mercury research efforts consist of loading studies, mercury methylation potential studies, bioavailability studies, and mine remediation feasibility studies. These studies will allow us to evaluate the feasibility of effective remediation for materials that could be transported downstream and have adverse ecological impacts.

Cache Creek Loading Studies—Mine Sites

The goal of the mine site loading study was to evaluate mercury (Hg) loading from specific anthropogenic (mine-related) and natural (geothermal spring) sources.

Results: Hg concentrations in water influenced by abandoned mines and geothermal springs varied greatly among sites.

• Harley Gulch: Hg in water flowing into Harley Gulch ranged from 4 – 6,350 ng/L (ppt), typically with 84 – 99% of that in the particulate phase and the remainder in the dissolved phase (see Fig. 19). Water flowing through the Abbott Mine site had ca. 1,600-1,700 ng/L Hg, while water flowing through the Turkey Run site contained 6,350 ng/L Hg. Surprisingly, the geothermal spring on the Turkey Run Mine site contained the least amount of Hg (4.3 ng/L), but it is likely that high concentrations of sulfide strip out Hg in the spring before reaching the surface. A single sample (the Harley Gulch Index Station – see Task 5B) was analyzed for methyl Hg. Total Hg concentration at this site was 493 ng/L (91% particulate phase), while methyl Hg in unfiltered water was 0.35 ng/L. The estimated annual Hg loading from the Harley Gulch Creek was calculated at 0.1-35 kg/yr.

• Sulfur Creek: Hg in water flowing into Sulfur Creek ranged from 229 – 24,300 ng/L, typically with a greater proportion of that in the dissolved phase (10-67%), when compared with the Harley Gulch samples (see Fig. 20). The highest Hg concentration observed was from the Jones 'Fountain of Life' natural geothermal spring (24,300 ng/L), and the lowest observed was from a side stream originating from a region without any mines (229 ng/L). The highest Hg concentrations originating from a mine came from the stream flowing out of the Wide Awake Mine (2,450 ng/L). A single sample (the Sulfur Creek Index Station – see Task 5B) was analyzed for methyl Hg. Total Hg concentration at this site was 974 ng/L (90% particulate phase), while methyl Hg in unfiltered water was 0.48 ng/L. The estimated annual Hg loading from Sulfur Creek was calculated at 0.5-160 kg/yr.

Cache Creek Loading Studies—Cache Creek Watershed

The goal of the mine site loading study was to estimate mercury (Hg) loading from within the entire Cache Creek Watershed. Water samples were collected at 12 sites within the Cache Creek Basin during high water flow associated with storm water runoff (February and March 2000). The selected sites included those associated with anthropogenic (mining) and natural (geothermal) mercury sources, discharge from Clear Lake and Indian Valley Reservoir, and downstream receiving bodies of water including Cache Creek, the settling basin of Cache Creek ("Cache Creek Catchment Basin"), and the Yolo Bypass. The highest concentrations of mercury and methyl mercury were downstream of the mining and geothermal sources, but because of the relatively low discharge of water, those concentrations were diluted upon mixing with water from Clear Lake or Indian Valley Reservoir. Because of increases in discharge, loadings of mercury and methyl mercury increased downstream, with the greatest loading measured in the Yolo Bypass. Water samples were also collected during the summer irrigation season. Concentrations of mercury and methyl mercury, in samples collected downstream of the mines or geothermal sources, were similar to those measured in the winter, but the corresponding loads were low because of the low stream flow. The use of Cache Creek for irrigation water results in a decrease of flow in a downstream direction and corresponding low mercury loads during the growing season.

Studies of Cache Creek Methylation Potential

A microcosm experiment was conducted to quantify the potential of specific mine-derived source materials to produce methyl Hg. Preliminary (non-QCed) results for the microcosm experiment measuring the production of methyl Hg from Sulfur Creek floc yielded no detectable methyl Hg when incubated over 2.5 and 5.0 day periods. Additional methylation experiments will be conducted in the second year of the study.

Bioavailability Studies in the Cache Creek Watershed

The goals of the bioavailability studies were to: (1) develop and refine appropriate monitoring and interpretive protocols for use in Hg point source remediation assessment and TMDL regulatory work; (2) establish a baseline of existing aqueous and biotic Hg conditions in mine and non-mine site areas; and (3) assess temporal Hg patterns in the watershed.

First year results indicate dramatic differences in both aqueous Hg concentrations (Fig. 21) and biotic Hg accumulations (Fig. 22, 23) in different regions of the Cache Creek watershed. The mine sites had the highest methyl and total mercury in the biota and aqueous samples. Seasonal patterns are evident as well, particularly in the tributary streams (Fig. 22). While additional analyses and data processing are needed, initial results also indicate a general consistency in the Hg concentration relationships between co-occurring biota of different trophic levels and aqueous methyl and total mercury concentrations (Fig. 24).

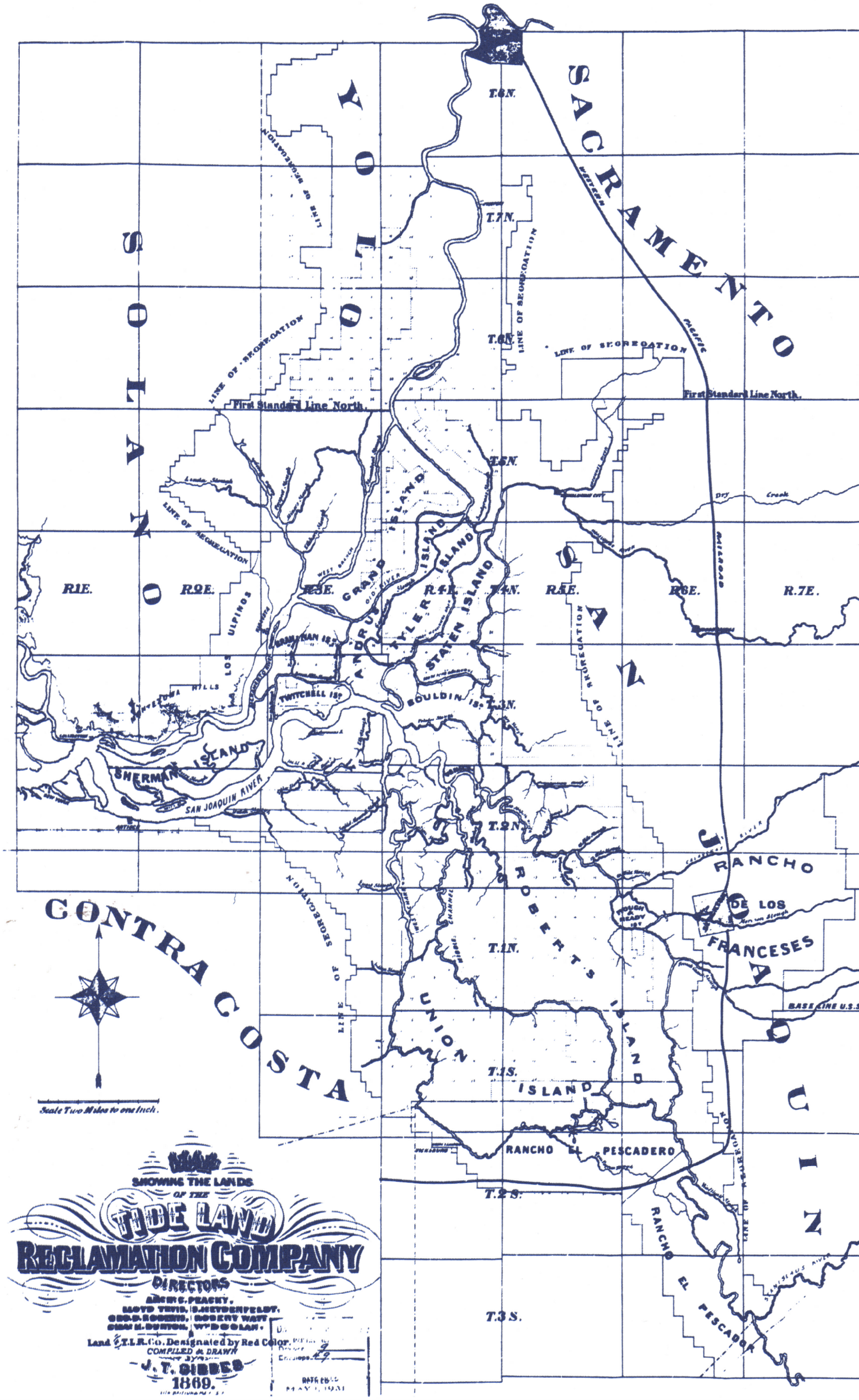
These results indicate that biota can be used to cost effectively monitor the effect of mercury remediation at the mine sites. The aqueous mercury loads should decrease after mine remediation, and the decrease should be reflected in the methyl and total mercury in invertebrates and fish in the watershed.

Ongoing work is directed at improving our understanding of these relationships and refining monitoring and interpretive strategies for use in point source remediation assessment and TMDL regulatory work.

Mine Remediation Feasibility Studies in the Cache Creek Watershed

As of December 2000, compilation and review of available published and unpublished geologic reports and historical information were completed for the twelve mine sites in the study area. The California Department of Conservation's Department of Mines and Geology (Abandoned Mine Land Unit--AMLU) has completed their reconnaissance examinations of all mercury and gold mine sites in the study area, except for the Abbott-Turkey Run site. Finally, a limited number of mine dump and soil samples, collected during the AMLU reconnaissance, have been submitted for total mercury determinations. Data compiled from historical records and reports have allowed preliminary estimation of the quantities of calcined tailings that are present at some of the mercury mine sites in the study area. Conclusions to date are: 1) The largest volume of calcined tailings in the study area are located on the Abbott-Turkey Run mine site; 2) Previous published work indicates the mercury in these tailings is present as cinnabar and metacinnabar; and 3) At least some of the mercury and gold mine sites in the study area have soils and rocks with anomalous mercury levels due to natural geologic processes, not mining activity. The AMLU will conduct additional detailed field examinations of the project area mine sites in the second year of the study. Digital (GIS) mine maps will be prepared and site data (physical and chemical) will be analyzed.

Figure 1. Map of Delta in 1869 (Sacramento San Joaquin Delta Atlas)



Courtesy of the State Lands Commission

Figure 2. Sacramento San Joaquin Watershed

Figure 3. Delta Circulation Patterns

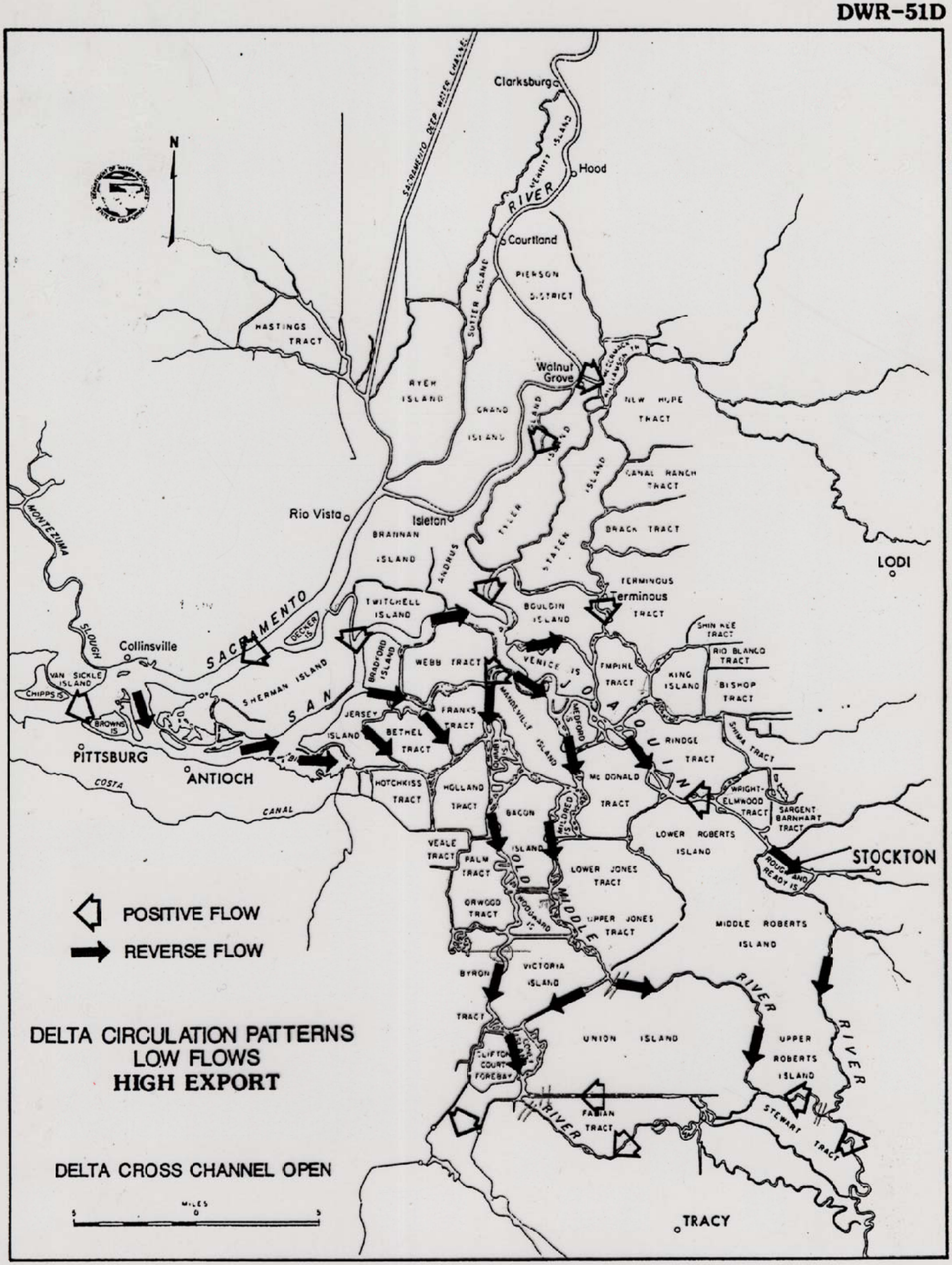


Figure 4. Agricultural Diversions (from Delta to Ag. Lands
(Sacramento San Joaquin Delta Atlas)

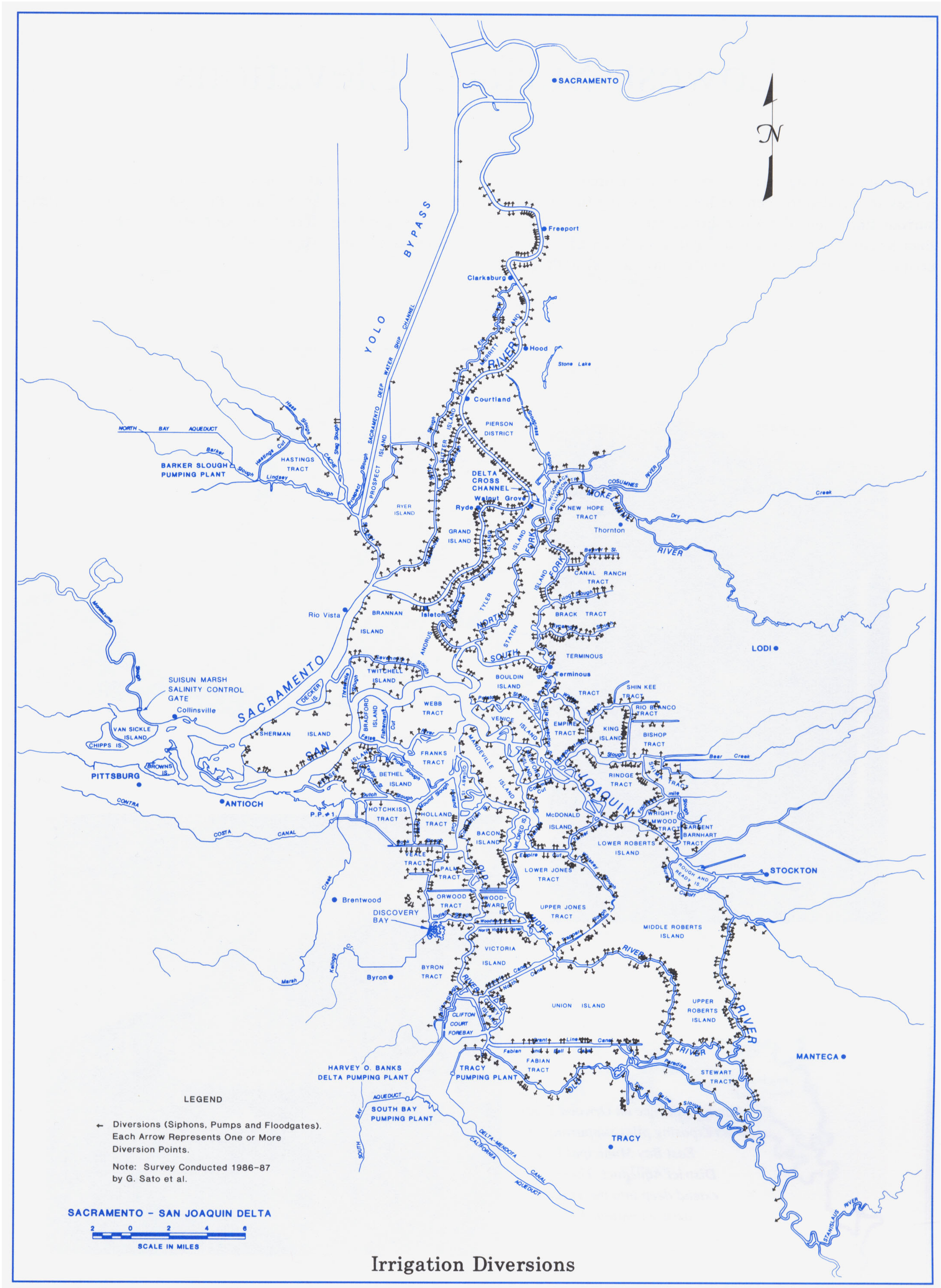


Figure 5. Agricultural Drainage Returns (Sacramento San Joaquin Delta Atlas)

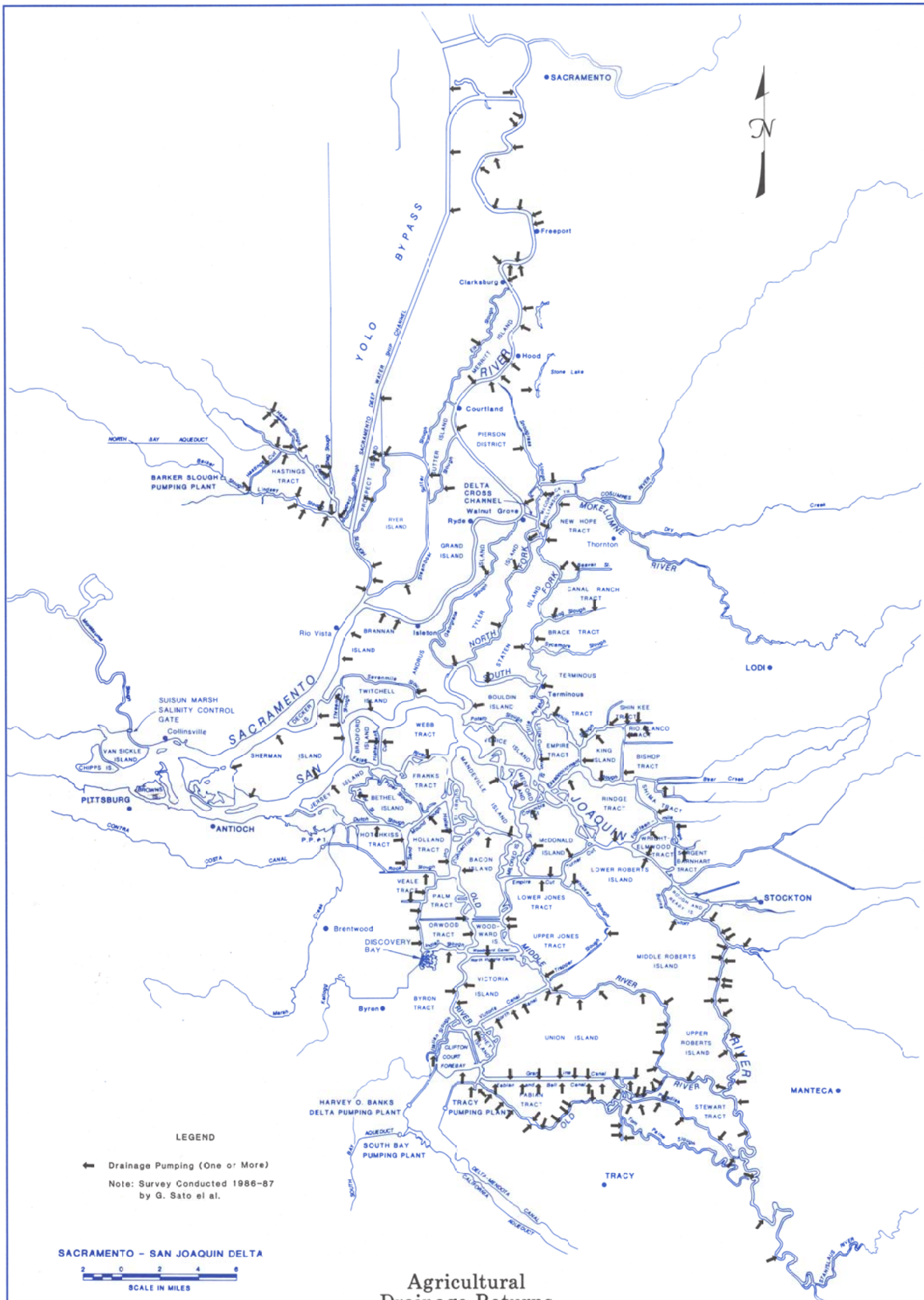
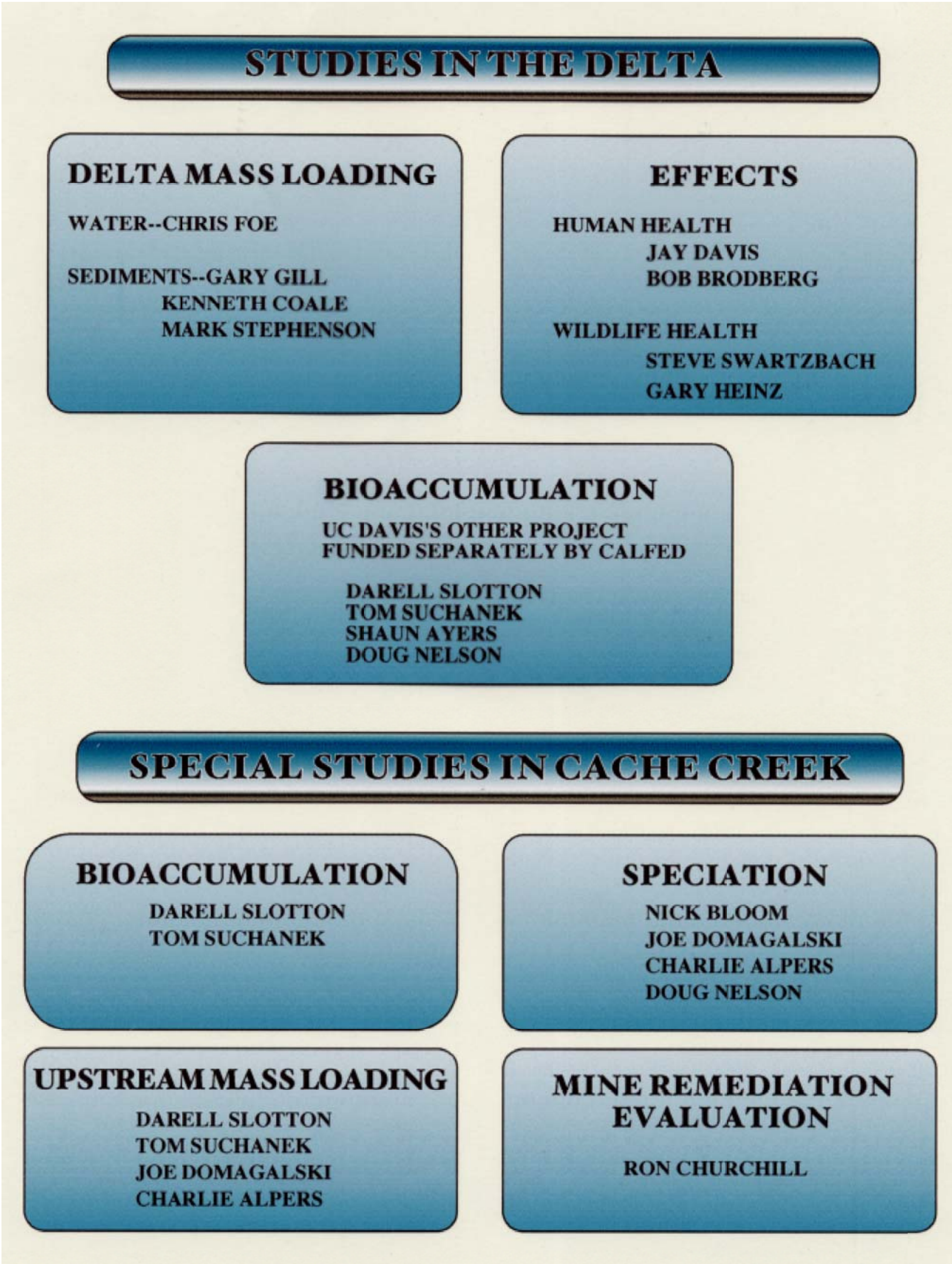


Figure 6. Mercury and Gold Mines in California

Figure 7. Calfed Mercury Project Organizational Structure



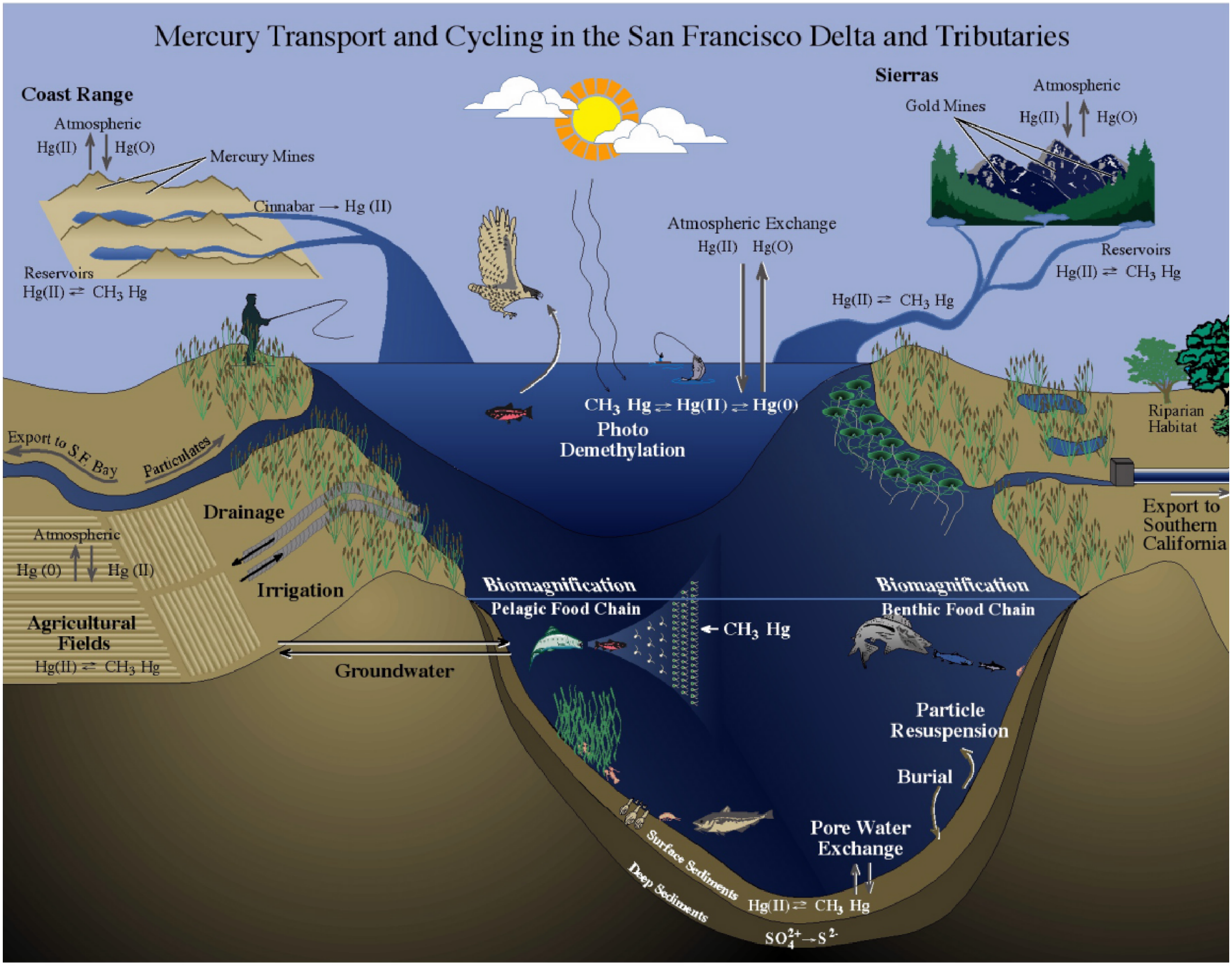


Figure 8. Mercury Transport and Cycling in the San Francisco Delta and Tributaries

Table 1. Summary of water and mercury inputs and exports from the Bay-Delta during June 2000. No rain fell during the month. The boxed values indicate that the mercury concentration used to estimate the load was below the detection limit. Half the detection limit (0.01 ng/l) was used to calculate loads

		Water	THg	DHg	TMMHg	DMMHg
INPUTS		Water	THg	DHg	TMMHg	DMMHg
		a-f	kg/mo	kg/mo	gm/mo	gm/mo
	Sacramento R.	975,312	4.1	0.7	86	51.0
	San Joaquin R.	175,483	1.8	0.2	48	2.2
	Mokelumne-Consumnes R.	51,143	0.3	0.1	7.2	3.6
	Prospect Slough	3,554	0.1	0	1.1	0.4
	Delta Island Return flows	92,485			40.6	12.1
	Atmospheric wet deposition					
	Sediment Flux					22
	TOTAL	1,297,977	6.3	1.0	182.9	91.3
EXPORTS						
	State Water Project	260,291	0.7	0.3	3.2	3.2
	Delta Mendota Canal	180,873	0.6	0.2	16.2	8.5
	Other Canal Diversions	18,739				
	Delta Island Diversions	282,470			20.9	10.5
	Delta Outflow	588,911	?	0.4	79.3	22.5
	TOTAL	1,331,284		0.9	119.6	44.7
	Inputs-Exports	-33,307		0.1	63.3	46.6
	Percent loss				35%	51%

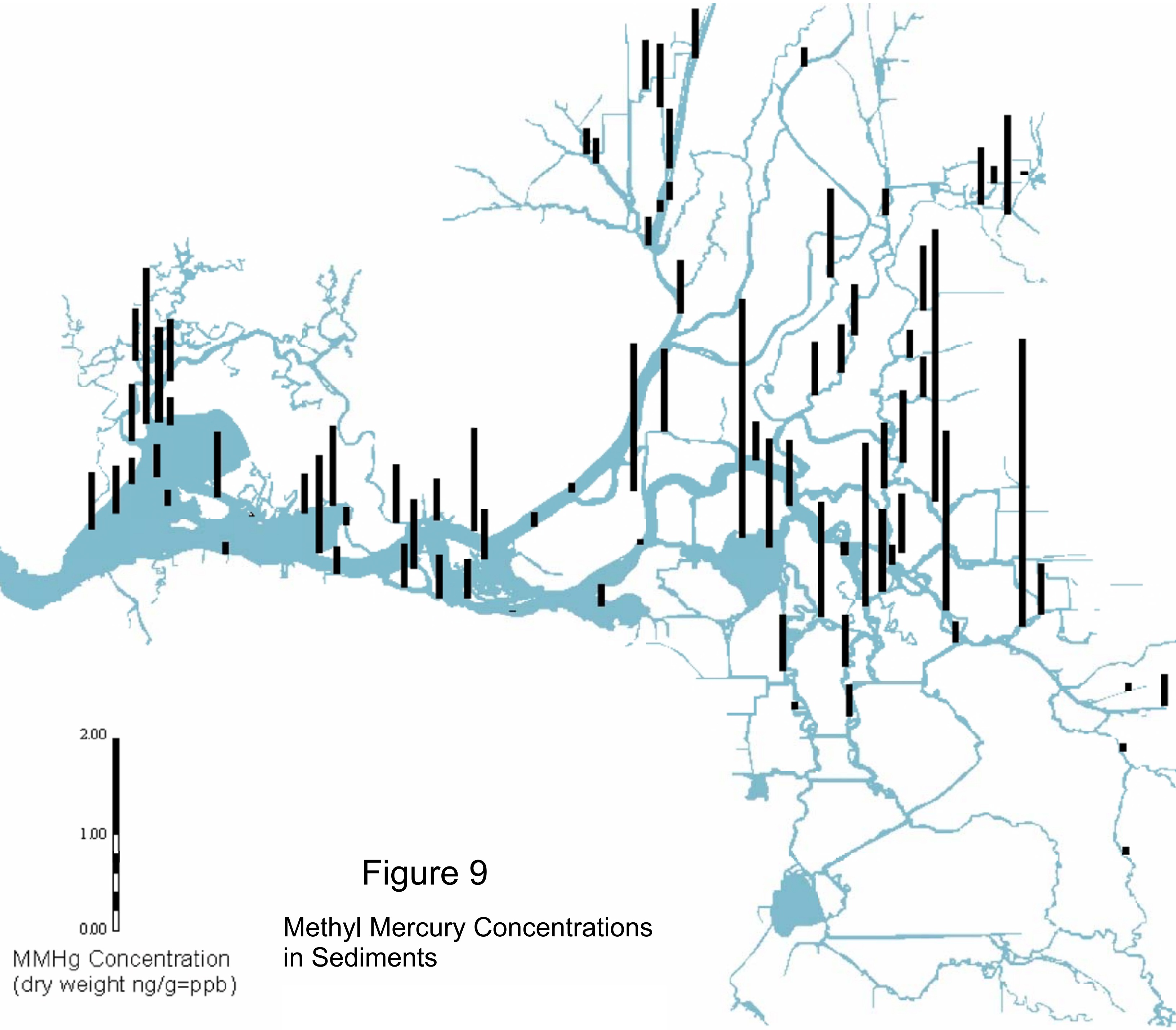


Figure 9

Methyl Mercury Concentrations in Sediments

Figure 10. Mercury concentrations versus length in striped bass in studies between 1970 and 1999.

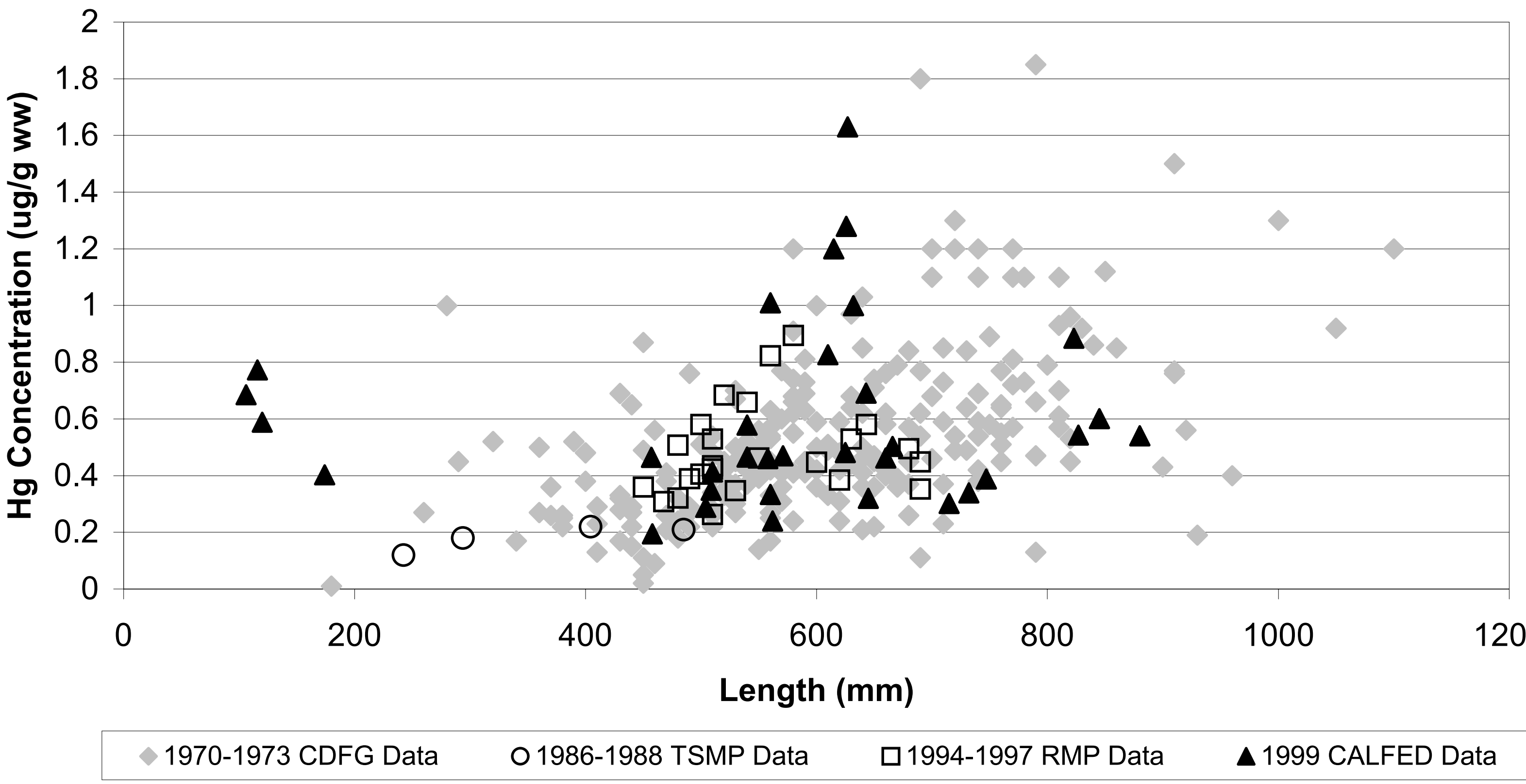


Figure 11. Average mercury concentrations in largemouth bass from each sampling location.

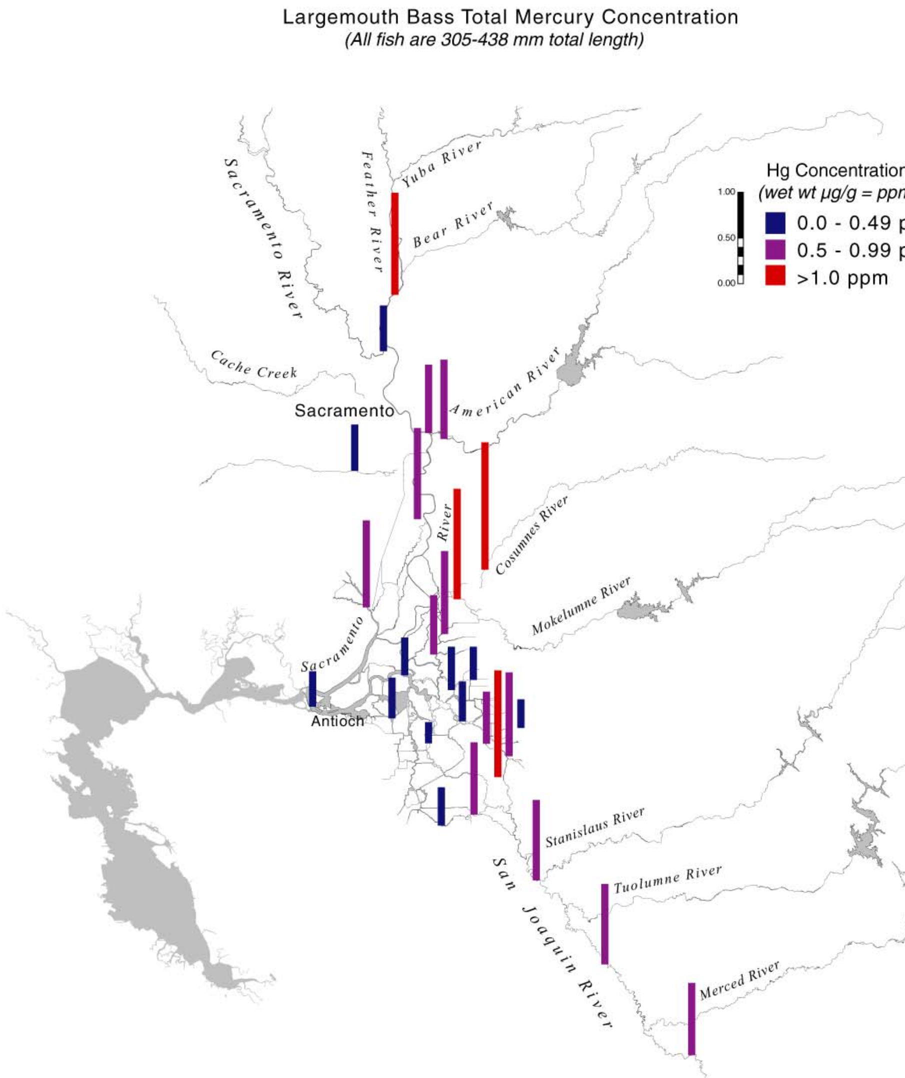


Figure 12. May Methyl Mercury in Water versus Largemouth Bass Mercury

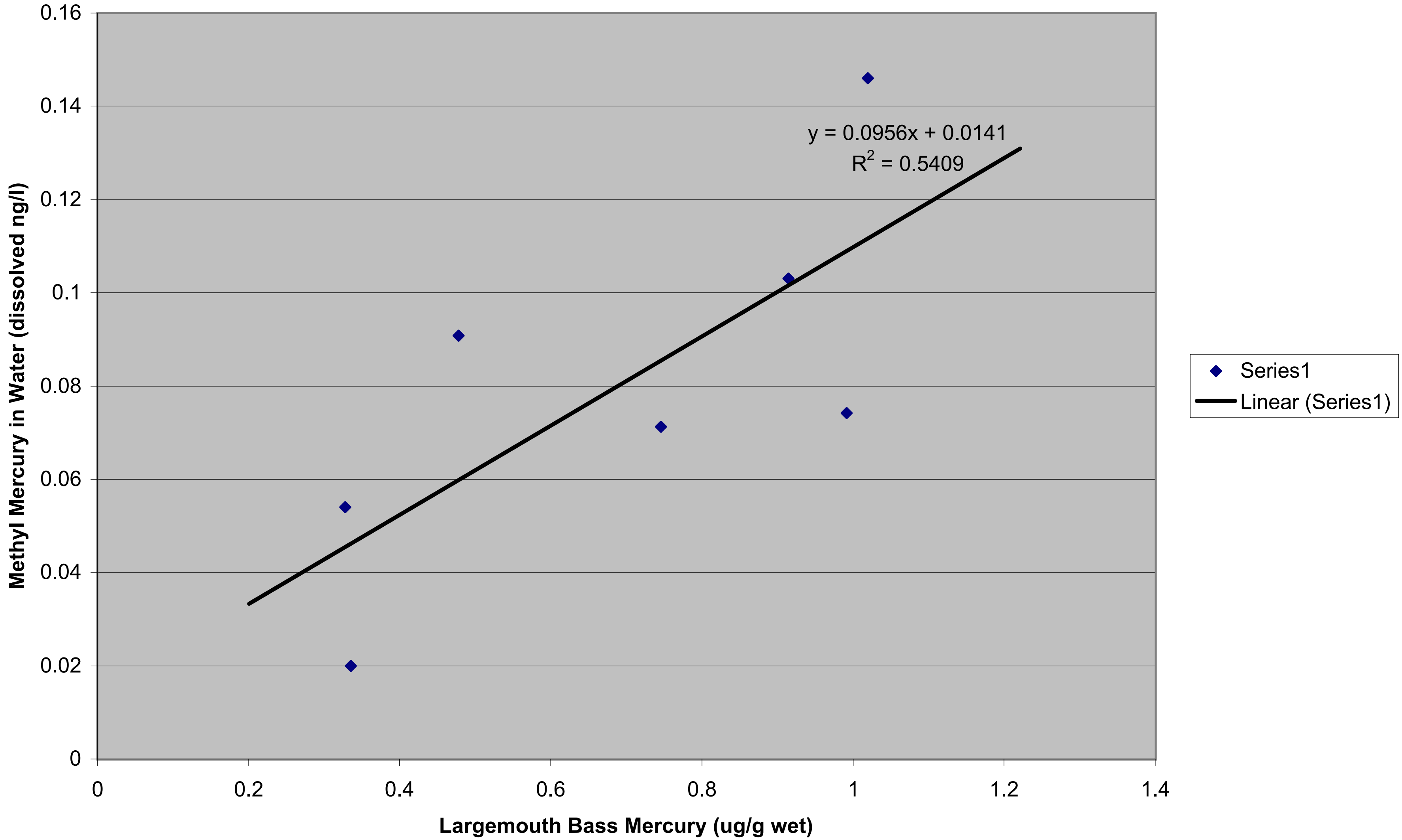
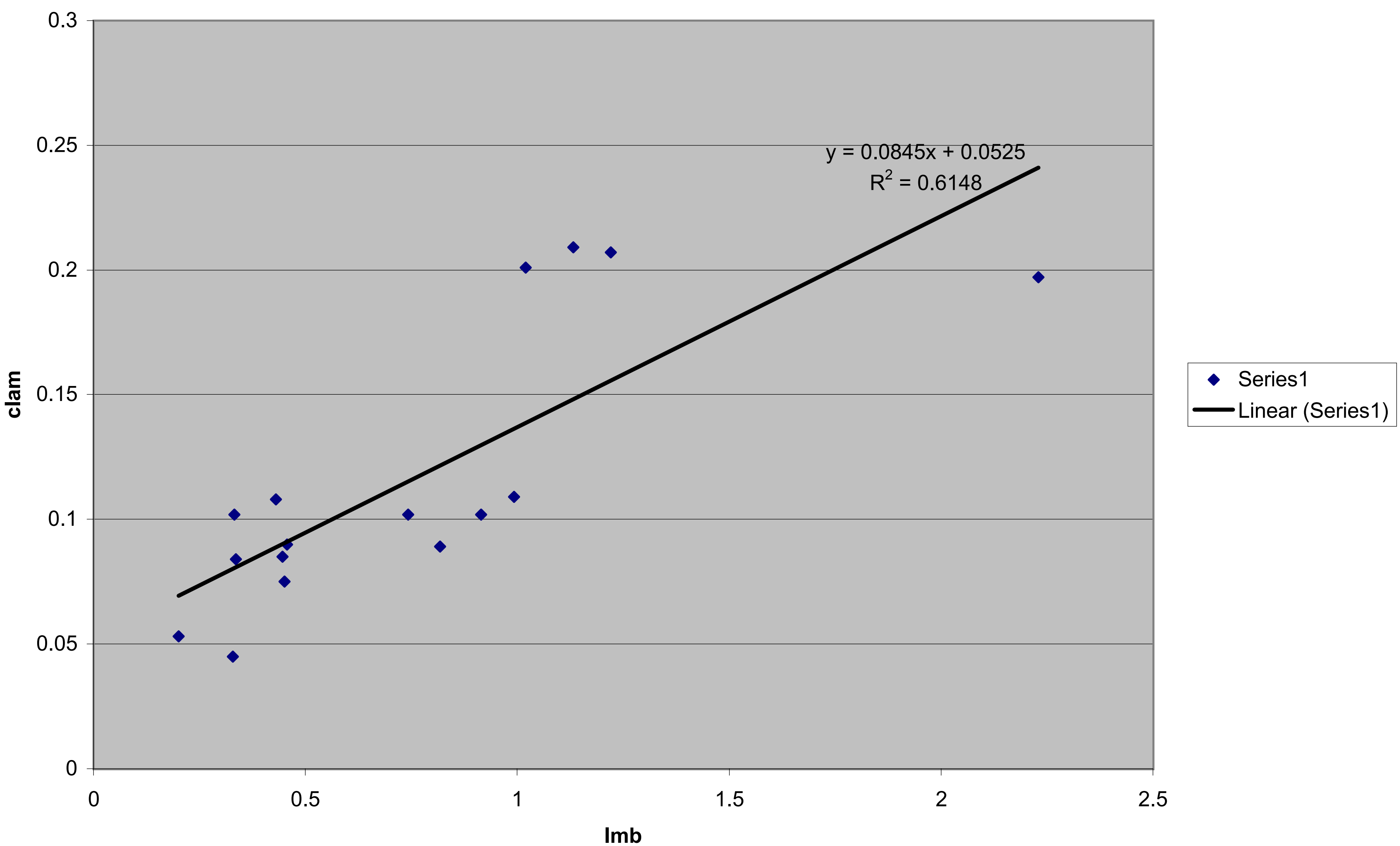


Figure 13. Largemouth Bass vs. clams



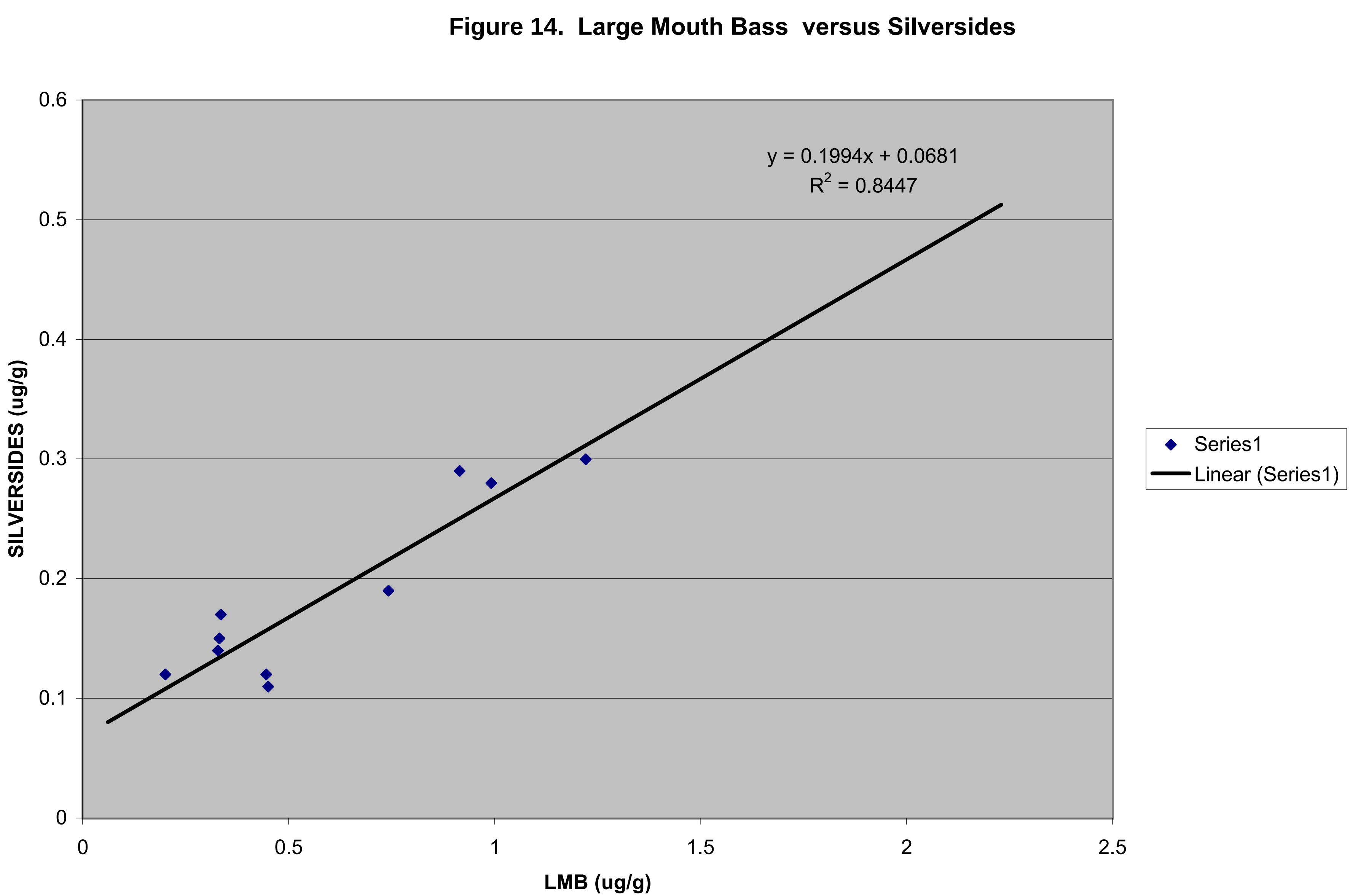


Figure 14. Large Mouth Bass versus Silversides
y = 0.1994x + 0.0681
R^2 = 0.8447
SILVERSIDES (ug/g)
LMB (ug/g)
0
0.1
0.2
0.3
0.4
0.5
0.6
0
0.5
1
1.5
2
2.5
Series1
Linear (Series1)

Figure 15. Large Mouth Bass versus Striped Bass

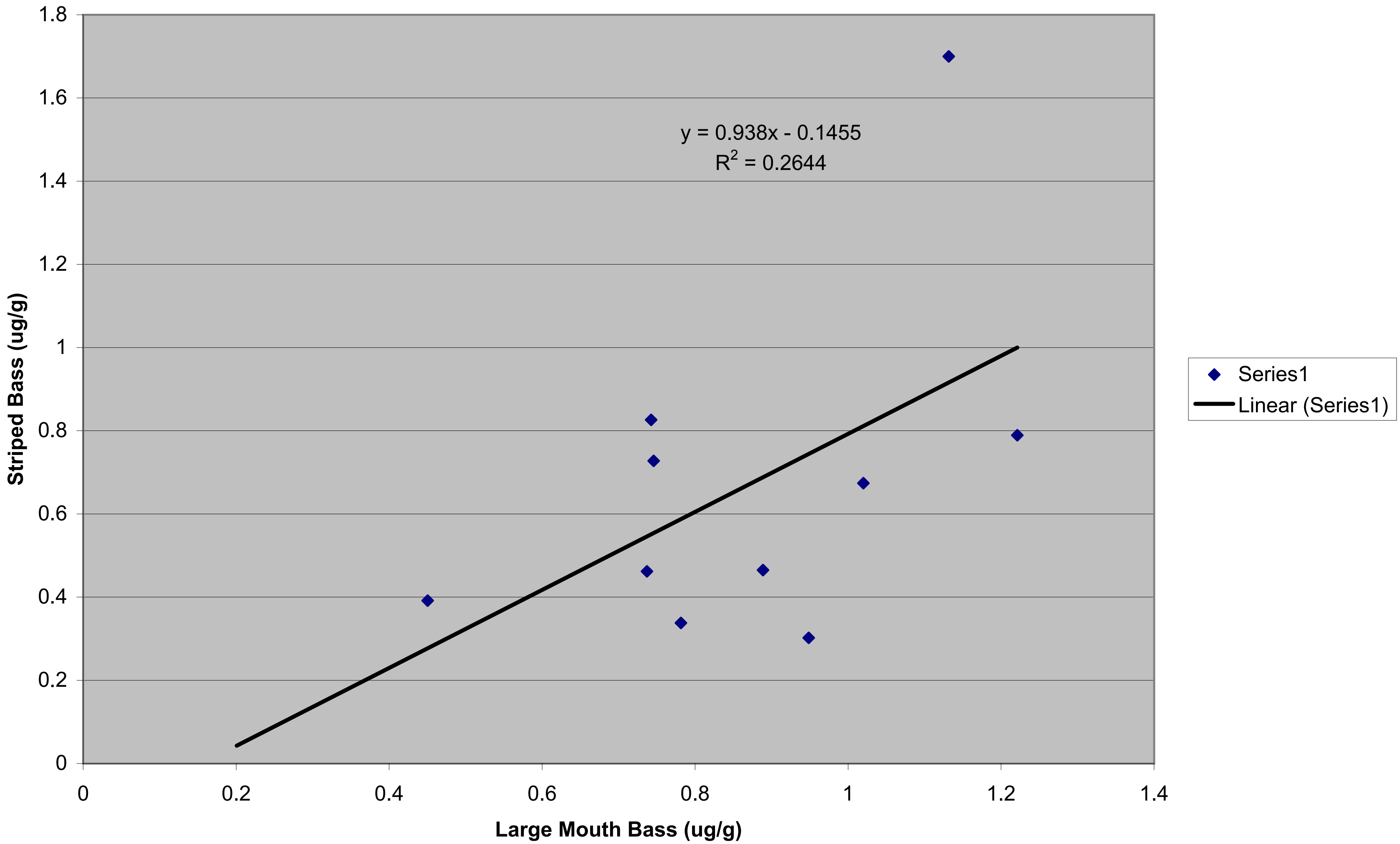


Table 2. Mean Mercury Concentrations (ppm wet weight) in Avian Eggs in San Francisco and Suisun Bays, Year 2000 Results. Means in excess of 0.5 ppm are bolded.

Species	Suisun Bay	North Bay	Central Bay	South Bay
Caspian Tern random		**0.97** (5)	**0.77** (5)	**1.36** (5)
Forsters Tern random		**0.76** (6)		**0.77** (15)
D-C Cormorant random	**0.66** (3)	0.39 (5)	0.36 (11)	
Brandt's Cormorant random			0.23 (5)	
Least Tern fail-to-hatch			0.41 (6)	
Clapper Rail fail-to-hatch			**1.04** (6)	
Snowy Plover fail-to-hatch				**0.55** (3)
Great Egrets random	0.22 (14)		0.28 (5)	0.45 (1)
Great Blue Heron random	0.42 (1)			
Snowy Egret random			.18 (6)	.13 (8)
Black -Crowned Night Heron random			.19 (15)	.07 (4)
Black-Necked Stilt random			.42 (2)	.34 (11)
California Gull random				.12 (2)
Western Gull random			.07 (3)	
American Bittern (Davis) random	.14 (2)			
Mallard (Davis) random	.05 (2)			

Figure 16. Percent Methyl Mercury in Avian Eggs
by species

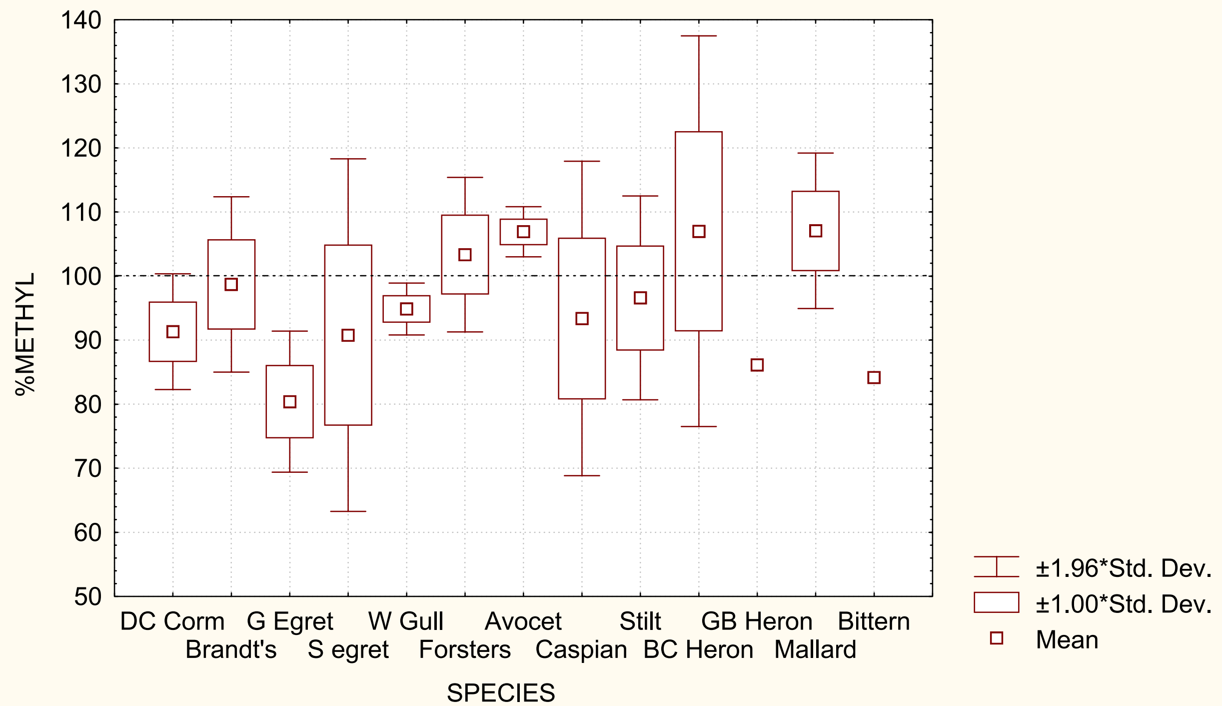


Fig 17. **Survival of embryos in cormorant eggs whose air cells were injected with various levels of mercury (as methylmercury) dissolved in corn oil**

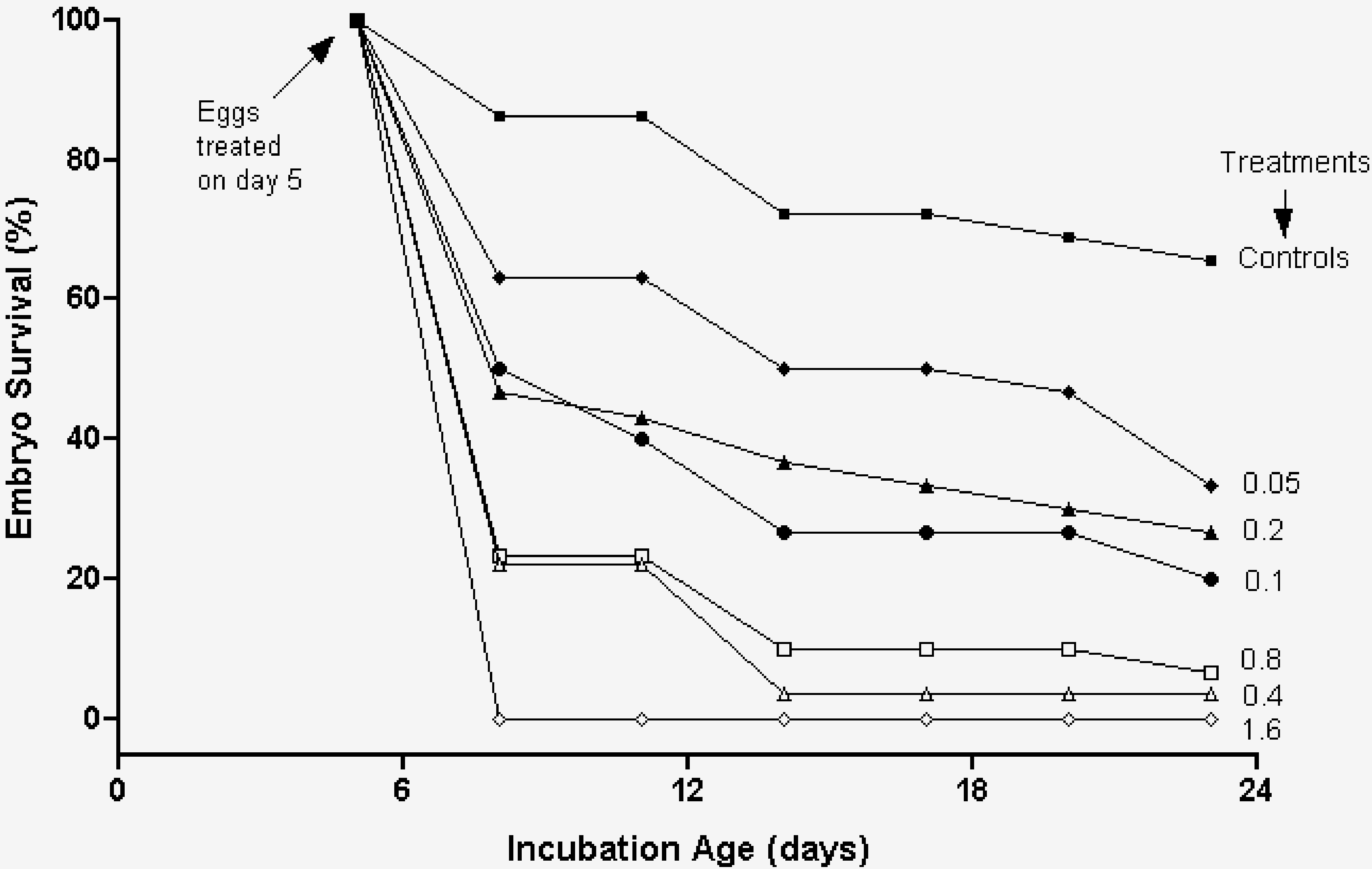


Figure 18. Cache Creek Watershed

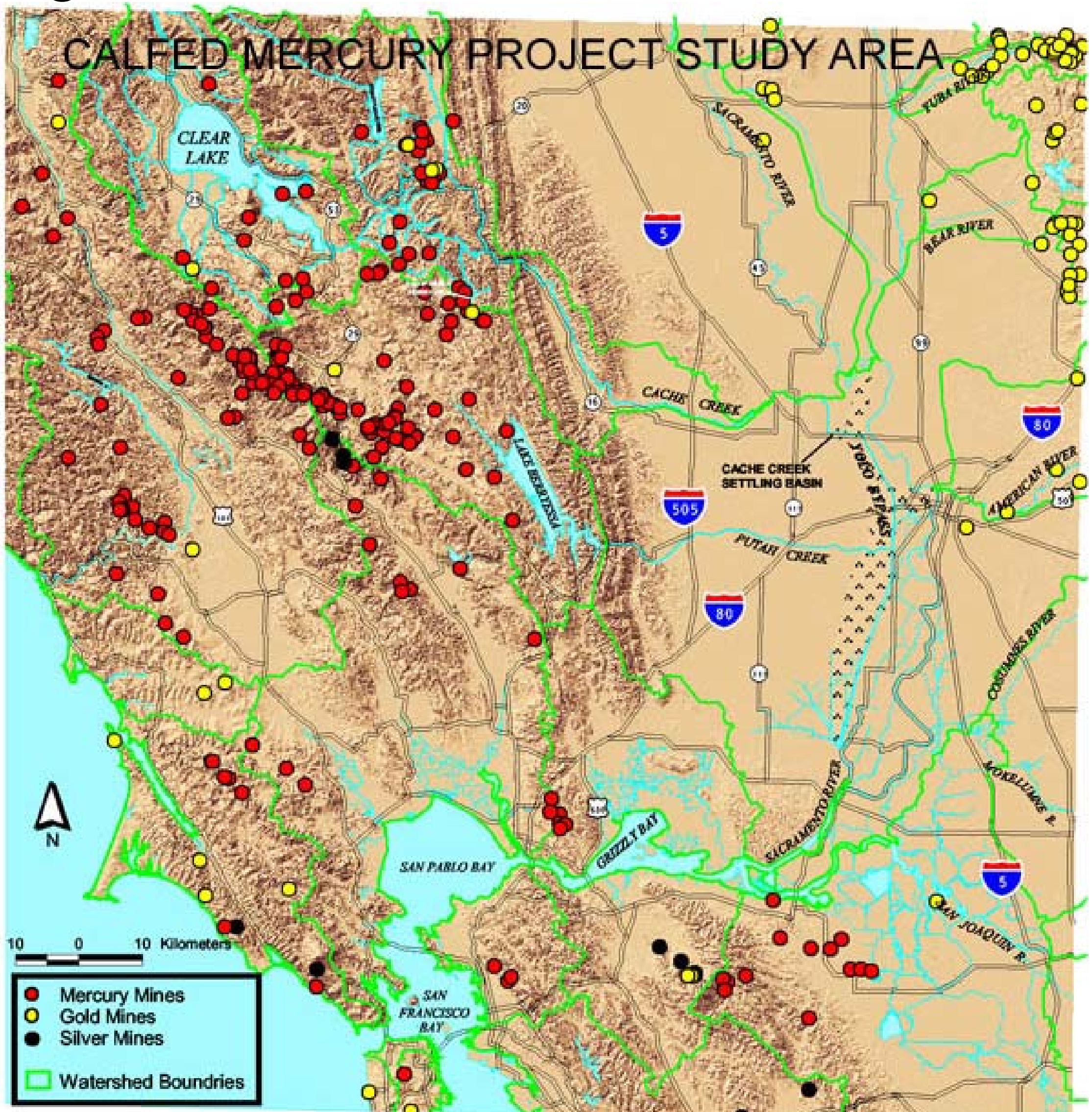


Figure 19. Hg in water from the Harley Gulch Mining Region Sites

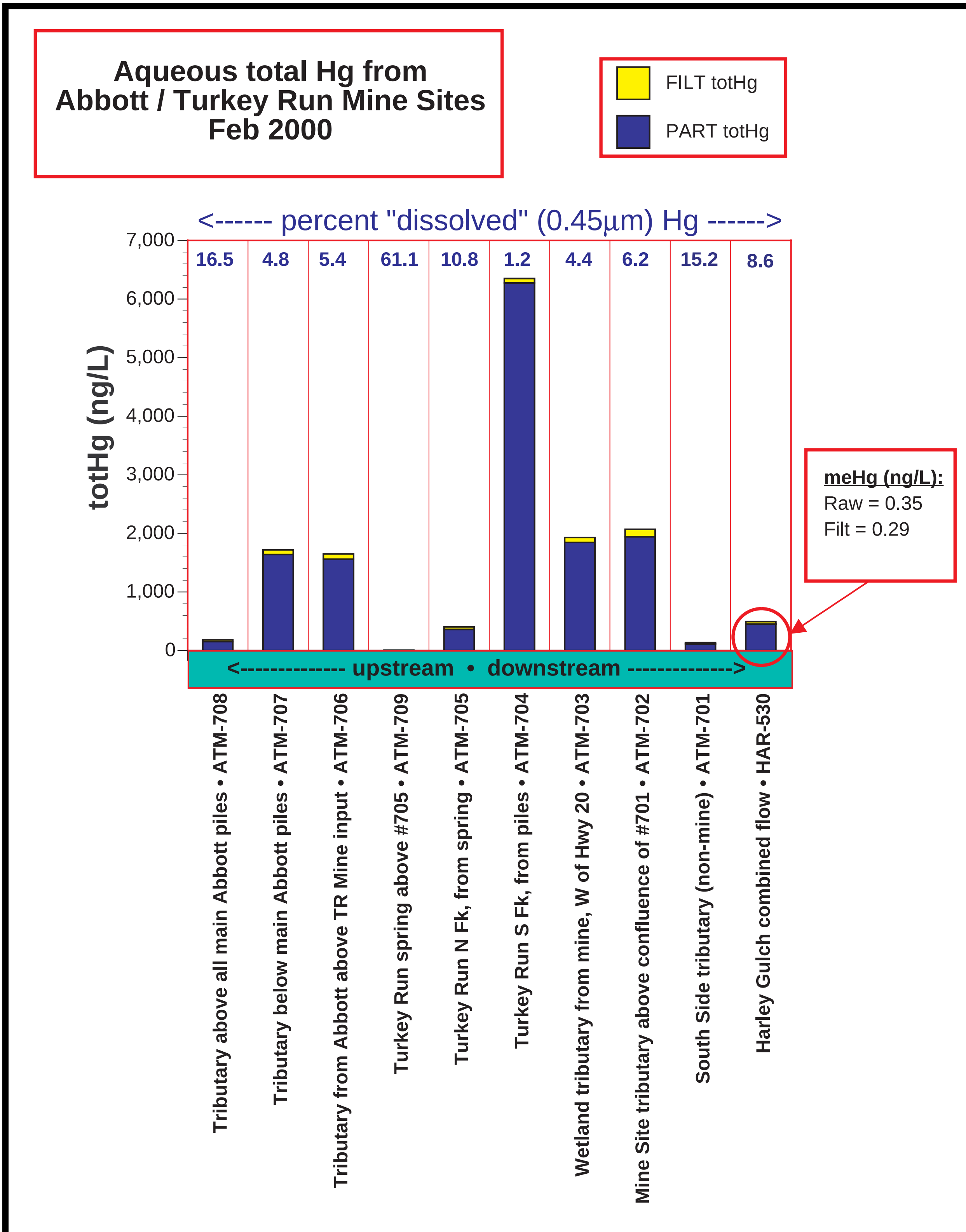


Figure 20. Hg in water from the Sulfur Creek Mining Region Sites

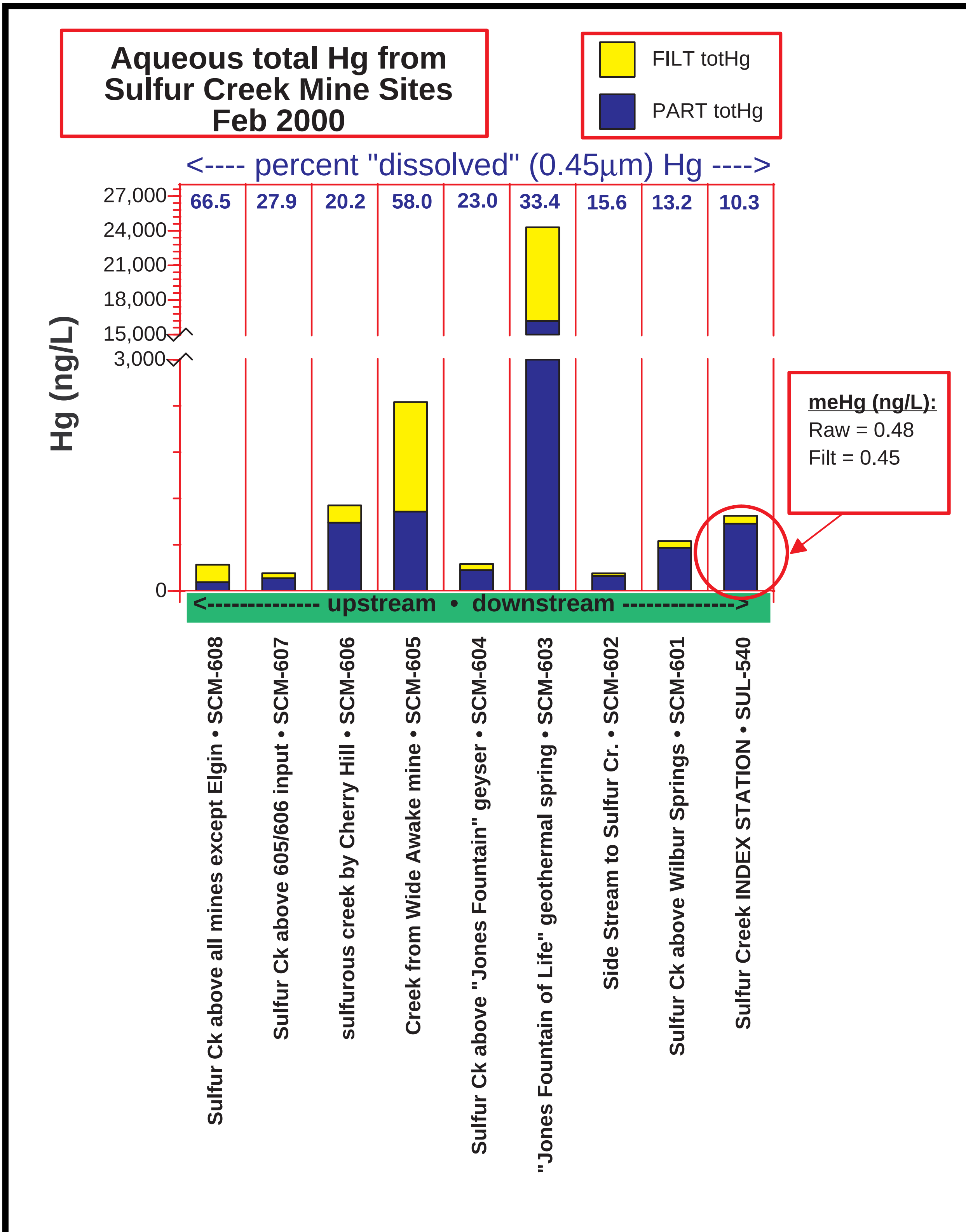


Figure 21.
Summary aqueous Hg speciation data from study sites in the Cache Ck. watershed.
Data from Jan. 2000 - Feb. 2001
(bars show range of concentration data with line at median value)

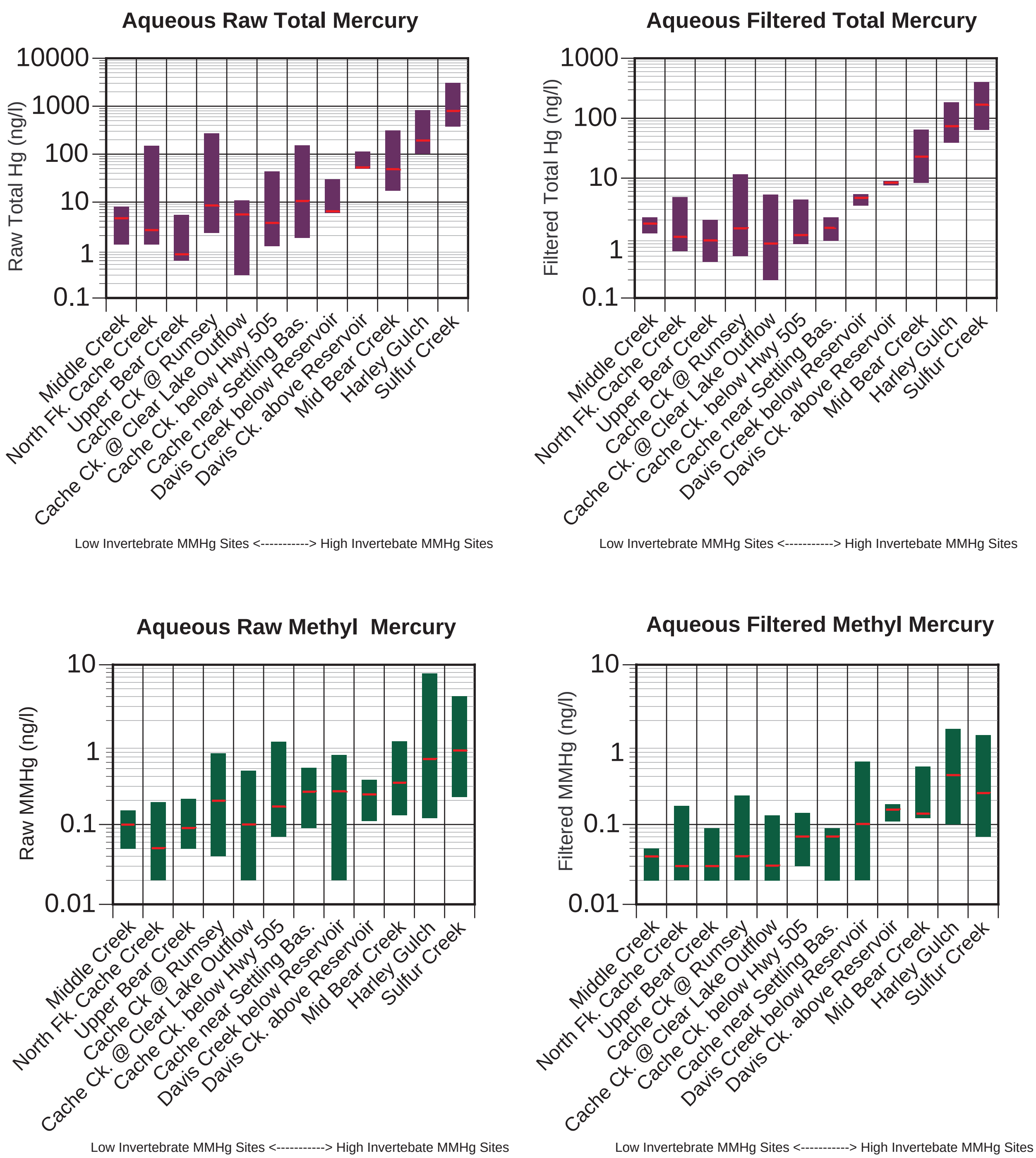


Figure 22.
Condensed mean invertebrate methyl mercury concentration vs. site and date.
(composite invertebrate MMHg = mean site-sampling MMHg of Hydropsyche and predatory taxa)

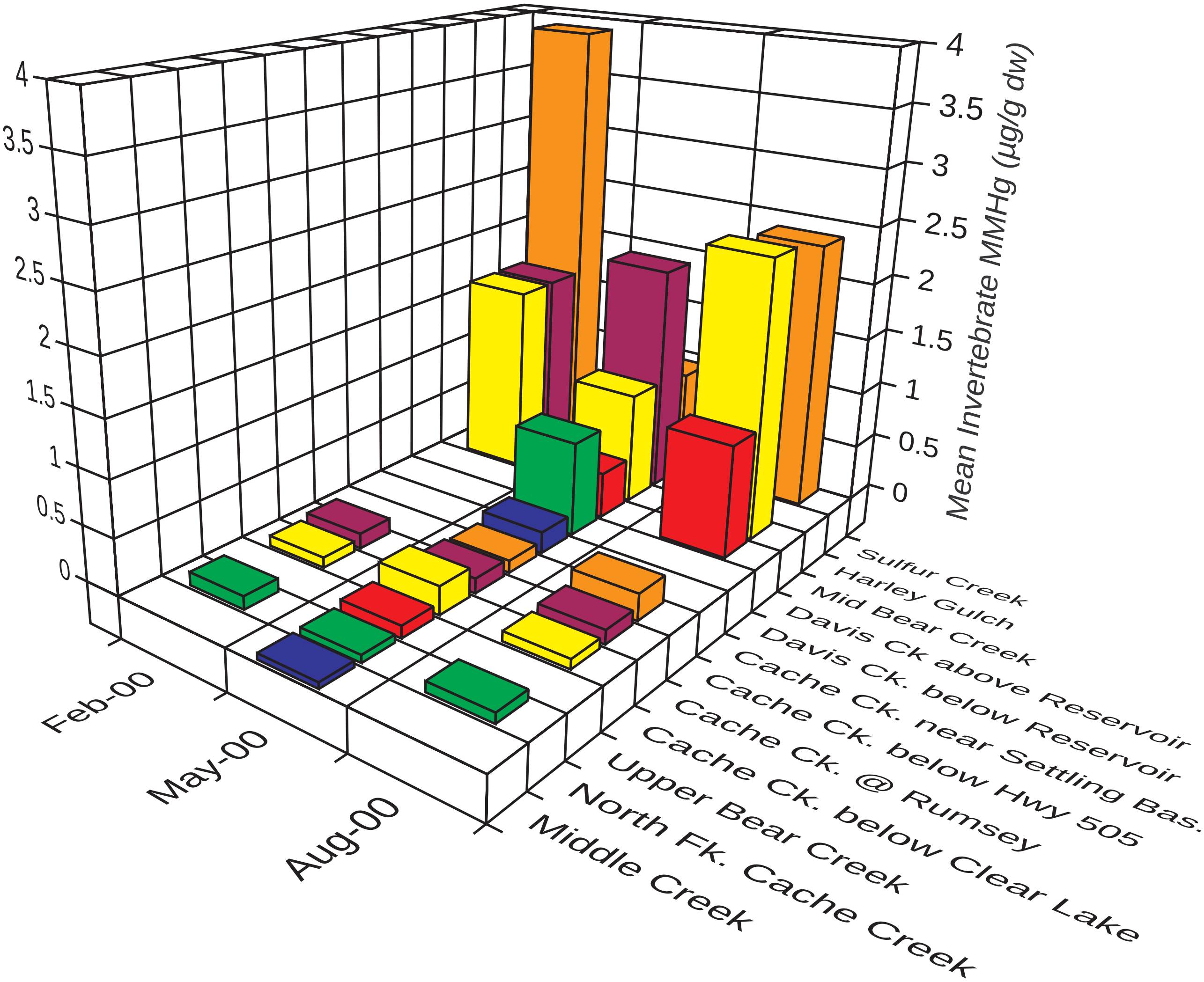


Figure 23.
Muscle mercury in piscivorous fish from four diverse stream locations in the Cache Creek watershed.

(fish weight vs muscle Hg)
(Sacramento pikeminnow, smallmouth bass, largemouth bass)
(sampling conducted December 2000)

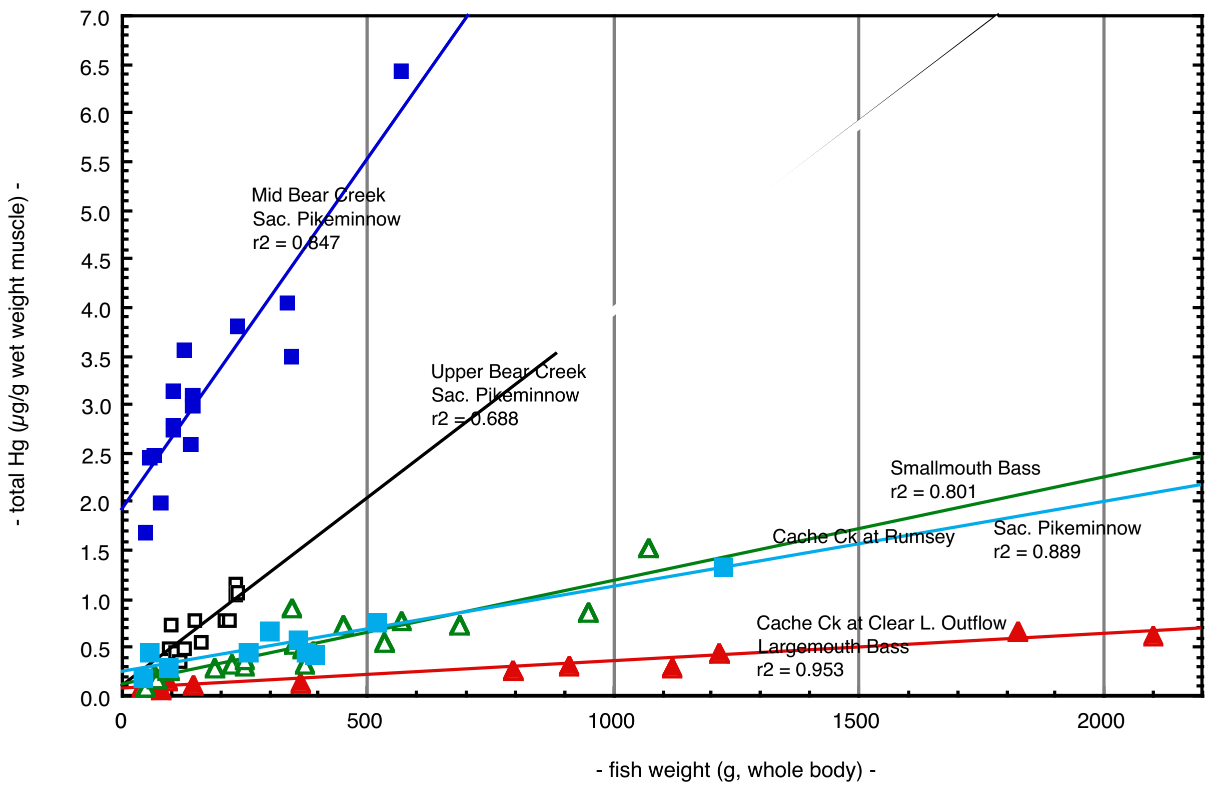
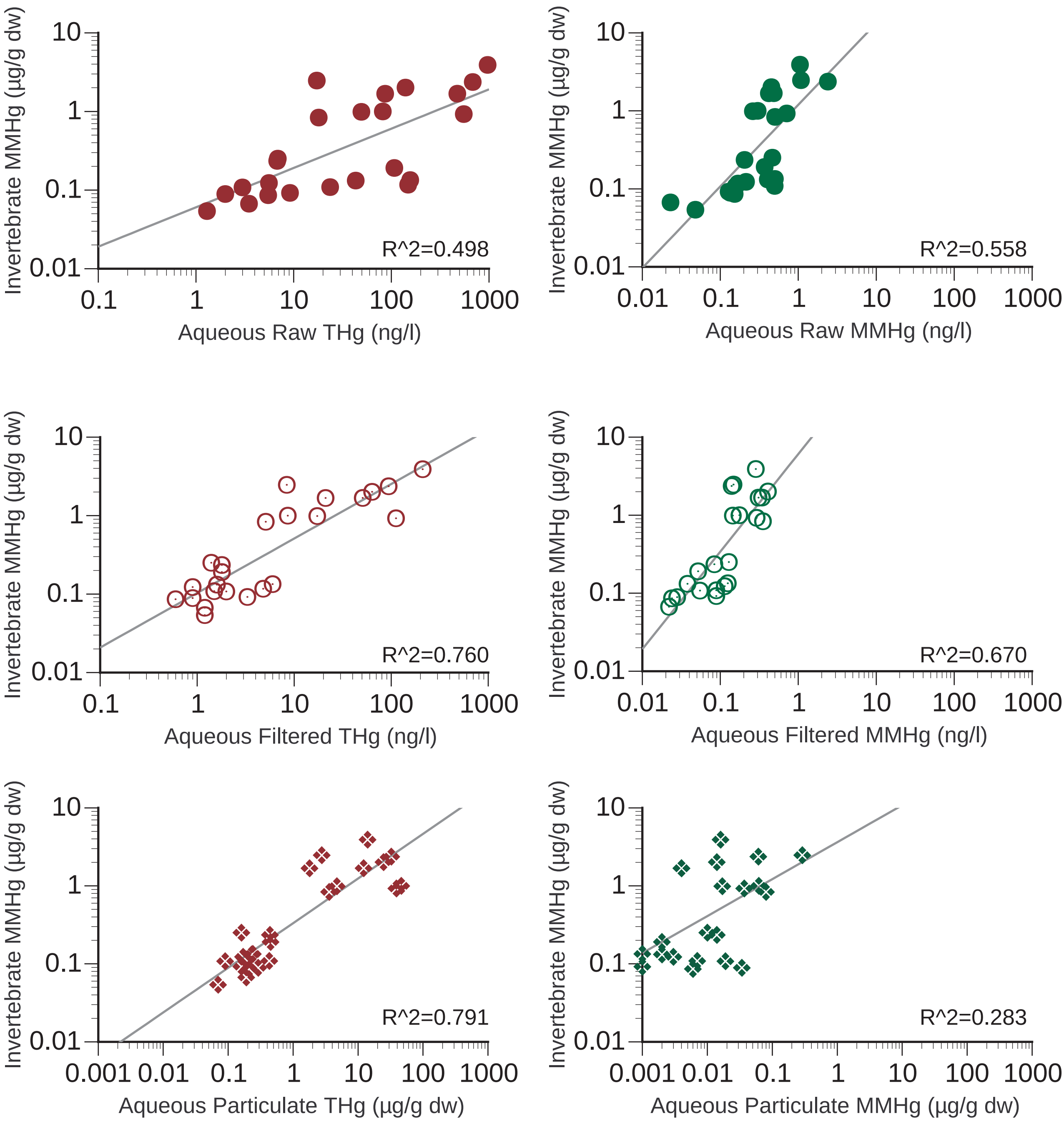


Figure 24.
Log/Log (power) regressions of composite invertebrate MMHg vs aqueous Hg fractions.
(composite invertebrate MMHg = mean site-sampling MMHg of Hydropsyche and predatory taxa)
(corresponding water data from most representative sampling(s) prior to invertebrate collection)



Appendix C

Mid-Project Meeting of the Scientific Review Committee for the CALFED Project "An Assessment of Ecological and Human Health Impact of Mercury in the Bay-Delta Watershed"

Moss Landing Marine Laboratories, Moss Landing, CA

December 4-5, 2000

Comments and Recommendations from the Scientific Review Committee

General Comments

The Scientific Review Committee (Committee) commends the CALFED Mercury Project investigators for their significant progress since the first project review in the collection of data, implementation of a QA/QC program, improvement of analytical capabilities, development of methods, and interpretation of initial results. This mercury project is a significant first step toward defining the sources, processes, and factors that control methylmercury (MeHg) exposure and associated ecological risks and health risks in the Bay-Delta watershed.

The Committee thanks the staff at the Moss Landing Marine Laboratories for their hospitality and efforts in facilitating this review.

Project-Level Comments

Conceptual model. At the initial Project review (1999), the Committee encouraged the project investigators to develop a conceptual model framing their ideas on mercury sources, cycling, and bioaccumulation in the Bay-Delta watershed. The Committee urges that the presentation and discussion of a conceptual model be a focal point of the next Project meeting. In large projects involving many investigators, the process of developing a conceptual model is useful for assembling a cohesive view of the study region and identifying important linkages between project tasks and investigators. This is especially important in a field setting as complex as the Bay-Delta watershed and in a complex investigation of mercury cycling. The Committee believes that the conceptual model of the study region and project would be greatly facilitated by application of a GIS-based land-use database for the watershed. Key geospatial themes could include land type and changes in land use, with a focus on wetland type and restoration.

Coordination and communication. In the first Project review, the Committee recommended that field work and sampling be carefully coordinated among investigators. The Committee emphasizes that Project investigators should continue to strive for improved coordination and communication – from conceptual direction, through sampling design, data analysis, sharing and interpretation of findings, and model development. The Committee would like to see more evidence of coordinated sampling (in time and space) among all groups involved with the

Project, including studies involving analyses of sediments, water, biota, and mercury processes and fluxes. The Project investigators should soon begin planning to coordinate the preparation of reports and manuscripts, and should reach agreement on the ownership and sharing of data. Advance agreement among Project investigators on these issues will greatly facilitate the integrated analysis and reporting of Project findings.

Leaping to conclusions. The Committee was asked to consider whether the Project investigators should de-emphasize work in the Bay Delta and to direct more effort toward investigations of methylmercury in major streams in the watershed. Although some of the initial data analyses have yielded interesting patterns, the Committee believes that it would be premature to leap to conclusions based on initial findings at the mid Project stage. Accordingly, the Committee believes that it would be premature to implement major changes in the overall direction of the Project. Rather, the Project investigators should strive to complete the most defensible, comprehensive possible analysis of results at the end of the Project. The Committee recommends that the project continue largely as planned, although some moderate modification is warranted. For example, the Committee believes there are compelling reasons to increase the level of emphasis on the interiors of the marshes of the Bay Delta, with less emphasis on the open water areas. Some additional, focused efforts may also be appropriate to address emerging questions, such as identification of the apparent sink(s) for methylmercury in the Bay Delta.

Collaborations with external groups. The Committee encourages Project investigators to establish collaborative partnerships with external scientists and groups knowledgeable about the biota, ecology, geochemistry, and hydrology of Bay-Delta watershed. Such interdisciplinary interactions would facilitate a more rigorous interpretation of mercury data from the Project by bringing important information and expertise into the overall effort. Most successful mercury research programs have derived as much insight from such ancillary (non-mercury) data as from the mercury analyses themselves. Specifically, the Committee recommends that the project investigators acquire access to expertise and information on ecological processes, hydrology, geochemistry, food-web structure, and production in the ecosystem under study.

Simulation modeling. In the first review, the Committee strongly recommended that the field studies be linked to efforts to model mercury sources, transport, fate, and bioaccumulation. Given that modeling has not yet been funded at mid Project, the Committee recommends that this aspect of the work be deferred until planning for the next phase of investigation is begun. The next phase of research should be process-oriented, to guide development of a simulation model useful to environmental planners and resource managers.

Quality Assurance (QA). The Committee was pleased with the successful implementation of a QA component to the project and unanimously agrees that this should remain a high-priority effort. This effort is absolutely essential for alerting project investigators to problems with sampling approaches or analytical results. For example, the sample contamination revealed by high blank levels in the glass bottles used by the USGS laboratory on the total mercury determination could have gone undetected, confounding Project results. All Project studies, regardless of the investigator or funding source, should participate actively in QA review and audit; it was not clear to the Committee that this was being done for some studies. The Committee cautions that any reliance on faulty data could impair the ability of Project investigators to (1) accurately evaluate patterns in contamination, (2) assess associated risks, (3) reliably assess responses to future restoration measures, or (4) provide decision makers with sound advice.

Ecological Effects. Decisions concerning the future management and restoration of this ecosystem require an understanding of the ecological effects of methylmercury exposure in resident, at-risk wildlife. Accordingly, the efforts to quantify the exposure and biological effects of methylmercury on organisms in upper trophic levels is an important component of the Project. The studies of biological effects of methylmercury on wildlife populations are appropriately focused on reproductive effects, given the known, high neurotoxicity of methylmercury to the developing embryo. Moreover, initial results show that methylmercury levels in eggs of a number of resident bird species exceed threshold concentrations associated with adverse effects on the developing embryo. Because wading birds are an important target population, the food webs of these birds, and the potential sources of MeHg to these food webs, should be a focus of future food web studies. In short, methylmercury may be adversely affecting bird species of special concern (including endangered species). These observations should provide strong impetus for continuation of CALFED support for investigations of the biogeochemistry and ecotoxicology of mercury in the Bay-Delta ecosystem.

Setting the stage for future work. The main, stated goal of the current Project is to "understand what controls Hg cycling and bioaccumulation well enough to make recommendations on remediation." With just 1 year of funded field time remaining, the Committee believes that this goal is beyond what the Project can reasonably be expected to accomplish. Mass-balance budgets for total mercury and methylmercury and an assessment of the bioaccumulation and effects of methylmercury should be the focal points of the current project. These anticipated results will be essential for guiding subsequent efforts to define the sources, processes, and factors controlling methylmercury exposure and associated ecological risks and health risks in the Bay-Delta watershed. The Committee urges CALFED to begin planning of detailed process-oriented investigations as soon as the current project is completed.

<u>Study-Level Comments (from overhead transparencies)</u>

Estimation of Mass Balance – water column and sediment Hg/MeHg Distribution

After assessing the study at this point in time, the committee felt that a Hg and especially MeHg mass balance for the delta will be the most important scientific/data outcome of the study. With some small changes for 2001, a reliable budget should be achievable within the time frame of the project.

During 2000, a large data set was collected and underwent significant QA. The data provide the first look at Hg and MeHg distribution and transport in this ecosystem, and as such provide probably the most significant piece of the the CALFED Hg study during 2000. This work, along with Hg distrubitions in resident at-risk wildlife, provide the basis around which to focus future decisions on research and remediation directions.

Working with the substantial data set collected to date, the investigators presented a draft Hg budget that suggests a sink for MeHg within the Delta region. Construction of a draft budget and derivation of hypotheses from it substantiate the progress this group has made. The committee was asked if the sampling emphasis for 2001 should move away from the Delta as a result of these findings.

To the committee, a clear determination on whether the delta is a net site of methylation or demethylation (including open water and island sites) is the key need for the project for 2001. The committee was surprised to hear that the delta may be an area of net demethylation, because of our experiences with wetlands as net methylators. However, if it is this is a key finding that would have big implications for directions of future research. The same is true of course if the delta is a site of net methylation. The project needs to be sure that that a tight (best possible) mass balance is done this coming year (inflows, outflows, internal fluxes, mid delta sampling, etc.) to solve this issue. Because there is still substantial uncertainty in the Bay/Delta budgets, we feel it will be most valuable to do another year of similar sampling in order to produce more defensible Hg and MeHg budgets for the Bay/Delta area. After that time, future work can move into other areas with more certainty.

Water: During 2001, uncertainties in mass balances for the Delta could be reduced by sampling with increased spatial and temporal resolution, including increased sampling during high-flow periods, as well as upriver inflows (Sacramento River upstream of the Yolo Bypass), and detailed vertical sampling of the water column within the Delta. Consult with groups knowledgeable of the hydrodynamics of the Delta to chose additional sampling sites and times, and work more closely with the estuarine Hg/MeHg budget group (Gill and the Moss Landing group).

Sediments: Examine a wider range of habitats with a somewhat clearer sampling design to understand micro and macrohabitats.

Budget needs that stood out to the Committee:

Sacramento River, especially at head of Yolo Bypass and during high flow (sampling frequency should be driven by hydrology and water budgets)

At the outflow, depth-stratified sampling needed during periods of stratification.

Increase the frequency of sampling during high flow.

Consider water residence time in the Delta in constructing budgets.

Take water samples within the Delta region.

Increase focus on Hg/MeHg dynamics on Delta islands and in the Yolo Bypass. Clarify land use and develop sampling patterns related to land use.

Eventually, sampling by habitat within the islands, including the interior of marshes (not just the canals), shallow vs deep water; channel order within the marshes where important and vegetated vs. unvegetated habitats should be accomplished. This might be a part of a future phase of this study.

Are filtration and bioaccumulation of MeHg by clams quantitatively significant to budgets?

Incorporate better estimates of analytical and field errors into uncertainty analysis. Consider approaches used for box models for other trace metals (Cutter's Se models, Gary's estuarine-dilution model).

Attempt to clarify relative importance of atmospheric deposition and mines as Hg sources.

Estimate total atmospheric load to the system using annual Hg deposition x total watershed area.

Compare atmospheric load to estimated mine loads.

Calculate watershed yield for Hg and compare results to yields from watersheds lacking mines as sources.

Future investigations (post Project) should include more detailed study of different ecosystem types, including Tuli marshes, reconstructed wetlands, and agricultural islands.

Sediment/water fluxes

This is key part of the delta of budget/bioaccumulation models and a key part of understanding Hg/MeHg cycling within various Delta habitats. Substantial information from a fairly large number of sites was collected an analyzed in 2000. The work was clearly summarized and put into the context of delta budgets. Some resolution of budgets between Gill and Foe still needs to be accomplished, but good progress has been made.

If sediment/water flux work moves into the wetlands in 2001, it might help resolve the Delta MeHg source/sink issue. Addition of diel studies to examine MeHg efflux from sediment and peats in the dark is planned for 2001, and is warranted based on studies by Gill and others in other ecosystems. Planned additional study of sediment geochemistry in cores taken near flux sites – including sulfide and sulfate in porewater profiles - will also be valuable. Examine Hg, MeHg and geochemical depth profiles of at marsh interior sites as per flux.

Delta Study (UC-Davis)

Hg/MeHg in sediments/soils: Formation of hypotheses about habitat effects on MeHg are great; but more substantiation is needed.

Food webs and indicator organisms: The rationale for choosing indicators needs to be better developed. Choices should be made based on food webs that feed important target species like wading birds and humans, rather than just abundance. To understand the delta food web data collected by this group in 2000, this group needs to know more about the delta food chain, and this could be done to some extent next year. Who is eating who? Work with Detla budget group to determine if filtration and bioaccumulation of MeHg by clams is quantitatively significant to budgets. Acquire more information on food-web structure and dynamics from other groups working in the Bay-Delta area. Are food-web organisms below *Corbicula* and silversides being examined? Clarify what is being done with stable C and N isotope analysis; it was not clear to the review committee whether entire food webs were being examined for stable isotope signatures; stable isotope data at just one trophic level provide little useful information.

There is no need to continue methylmercury determinations in whole silversides, given that all of the mercury present has been shown by initial results to be methylmercury. Future analyses of this species should be limited to total mercury

Bioaccumulation and Ecological Effects (comments pertaining to all studies)

<u>Conceptual framework</u>:

<u>The problem</u> being addressed in the Project can be defined quite simply as *methylmercury exposure*.

It follows that the <u>management challenge</u> is to reduce exposure to methylmercury. In the case of ecological restoration, the challenge is to avoid increasing exposure to methylmercury, and to reduce exposure if feasible.

The <u>scientific challenge</u> is to understand the processes and factors controlling exposure to methylmercury and their linkages to potential management actions.

<u>Interpretation of bioaccumulation data</u>:

The Project investigators should now begin taking steps needed to accomplish the most defensible, comprehensive possible analysis of final results from the Project. Knowledge of food-web structure and dynamics, biology of the studied organisms, and ecological processes are important pre-requisites for understanding and interpreting methylmercury concentrations in resident biota.

To facilitate a rigorous and defensible interpretation of project results, investigators are encouraged to (1) complete work on analysis of the diet and stable-isotope composition or organisms analyzed for mercury, (2) identify and use existing ancillary data, and (3) identify external sources of ecological expertise and follow by building collaborative partnerships, where appropriate and desirable.

Analysis of Sport Fishes (human exposure pathway)

The anomaly in the mercury data for largemouth bass should be resolved (i.e., concentrations of total mercury in 4- to 7-year old fish sampled in 1999 generally exceeded that in bass sampled in 1998 by about 60%, a decidedly unusual difference). Archived samples of largemouth bass from the two years in should be re-analyzed. If the inter-year differences do not persist after re-analysis, the investigators should critically assess the implications for reliability of the larger sport fish Hg data from the 2-year period and take appropriate, corrective action.

If the inter-year differences *persist* after re-analysis of archived samples, attempt to identify causal factors that may have increased bioaccumulation of methylmercury in the 1999 fish. Potential causal factors could include net rates of methylmercury production or a shift to a higher trophic position in 1999 relative to earlier years.

Ecological Effects (at-risk wildlife)

An assessment of the ecological effects of methylmercury exposure on wildlife in upper trophic levels is an important pre-requisite to decisions concerning the future management and restoration of this ecosystem. Accordingly, examination of the exposure and biological effects of methylmercury on those organisms at greatest risk to methylmercury is an important component of this study. Moreover, the studies of biological effects of methylmercury on wildlife populations are appropriately focused on reproductive effects, given the high toxicity of methylmercury to the developing embryo.

Are feeding habits of the at-risk birds sufficiently understood (.i.e., on what and where are these birds feeding)? If not, this information should be obtained to identify pathways of methylmercury exposure.

The linkage of field studies and laboratory experiments (being done at Patuxent) is highly commended. The egg-dosing work is innovative, and eventual results from egg-dosing studies may overcome a long-standing impediment to progress in assessing reproductive effects of methylmercury exposure in avian populations.

The Committee recommends that the wildlife investigators examine the combined effects of selenium and methylmercury on avian reproduction and young in experiments incorporating environmentally relevant exposure levels.

Mercury Transport in Cache Creek

While the studies on Cache Creek are quite extensive, the SRC has a general concern that the Cache Creek results are specific to that system, and will not provide enough information to create an overall estimate of mercury loading to the entire system above the delta. The SRC recommends that additional sampling sites be added at the mouths tributaries that flow into the Sacramento River and San Joaquin rivers. The SRC assumes that these streams are gauged thus enabling estimates of mass transport.

A baseline study of a non-impacted stream system should be part of the study design as this also is critical to the development of a useful TMDL.

The presentations at Moss Landing, did not emphasize event sampling. Most of the mercury may be moving during rather short time periods of high flow, when particulate load are elevated. This event sampling, which SRC assumes is being done in conjunction with USGS, should also include sampling for TSS, so that rating curves can be developed for TSS vs. mercury transport.

Overall, the study has shown substantive localized impact of Hg mines, but impacts downstream of the mines have not been conclusively demonstrated. Assessment of changes of bioavailability of Hg as mine wastes moves downstream is being only weakly addressed, and probably won't be resolved within the present project

Bioaccumulation of Mercury in Cache Creek

The SRC was impressed by the extent of data collection on the mercury bioaccumulation by food chain organisms. The Committee is of the opinion that the benefit to be gained from another year of sampling and analyses of the aquatic macro-invertebrates would be relatively small.

Instead, the Committee recommends that comparative studies of bioaccumulation by macro-invertebrates in the mine-impacted as compared to uncontaminated streams at corresponding altitudes would be very useful. There is concern that upstream sites are not representative controls for the lower-altitude the mine-impacted sites.

It is also recommended that much could be gained by explicit comparative study with data on macro-invertebrates from streams on the eastern slopes.

Another possible direction is to compare the invertebrate concentrations to those in other systems that have been studied. Mercury concentrations do not appear to be unusually high in Cache Creek except in the area very near the mines.

The source of mercury to the biota and factors controlling its bioavailability is critical to this work. The study will provide a partial answer, but work on factors controlling rates of MeHg production should eventually be done.

The SRC was concerned that in some cases there was over interpretation of data, and caution should be taken with correlation's because of the differences in habitats, food web structures, and species

Clear Lake research: The Committee applauds the interdisciplinary work on mercury cycling and transport in Clear Lake, which includes geochemistry, hydrology and microbiology. The Clear lake study is of high quality, but the SRC is unaware of funding source for Clear lake research and questions its importance to the Cache Creek, with the exception of it being a source of mercury at the watershed level.

Source Bioavailability for Methylation

The UC Davis group has a "methylation potential" assay under development with the objective of examining the relative rate of MeHg production from the various Hg source materials in the upper creeks. A common sediment from the Bay/Delta area, with known high methylation potential, would be mixed with mine source materials, incubated, and the net production of MeHg measured. The method being developed appears to be an empirical one in which the outcome (MeHg production) is measured, but the underlying biogeochemistry is not examined. Over the last decade, the biogeochemical controls on methylation have proved to be complex. Mercury methylation is a function of both microbial activity and Hg bioavailability for methylation. In the Sacramento River system both the chemical form of Hg and microbial communities change as the source material moves downstream.

Although it would be impossible to examine all of the mechanisms that influence methylation in the context of this study, the committee felt that that the method being developed will not achieve the objective of understanding the bioavailability of source materials for methylation. It is unlikely that native sources materials would move downstream without geochemical processing. So, knowing the rate of MeHg production of a source material in a downstream sediment doesn't provide much information on how that source material might be methylated in the real world.

Nevetheless, a process-level understanding of the bioavailability of various Hg minerals to methylating bacteria would be a valuable contribution to understanding how Hg is methylated, and valuable in the context of the CALFED study objectives. However, such research would require detailed chemical determinations of the form and speciation of Hg during the assays, as well as understanding and control of microbial activity in the assays. As presented in Monterey, the method being developed by the CALFED group does neither. As presented to us, the committee felt that the assay being developed will provide neither new information on underlying processes, nor system-level information on MeHg production.

The committee feels that the methylation assays under developent should be rethought in the context of a conceptual model for MeHg production in this ecosystem. Is the goal to specifically test the bioavailability of certain forms of Hg (e.g. cinnabar or other mine materials) to methylating bacteria? Then the assay should include measures of dissolved and solid phase Hg, measures of anciallary chemistry needed to develop models of dissolved Hg speciation, etc. If the goal is to examine MeHg production from source materials as they move through the ecosystem, then methylation studies should be tightly linked to work on sediment and soil goechemistry. Proposed studies in collaboration with Nicolas Bloom may be moving in this direction, but the Davis group does not seem to have collaborated with Frontier in any significant way to date. Is the goal to understand how microbial community structure affects methylation potential? One of the strengths of this team is Nelson's prior work in this area. The committee was disappointed to see presentation of work from many years ago without any new effort. The committee encourages efforts in this area as part of the current project.

This is a very difficult research topic, which requires cutting edge investigative approaches. The SRC was not provided with a written summary of progress for this study, and based on the verbal presentation the Committee concerned that this research is not making significant progress.

Solid-Phase Speciation (Frontier GeoSciences)

This work is improving our understanding of how Hg source materials are processed as mercury in contaminated areas moves downstream from mines. This is valuable basic information that has not sytematically for any ecosystem other than marine sediments before, and the committee applauds this contribution to our basic understanding of Hg geochemistry. The work is also a key part of what is needed to get from Hg sources to MeHg exposure in this Sacramento River/Delta system.

The Committee recommends that this study be expanded to inlcude solid-phase mercury speciation much further downstream, and perhaps into the delta and estuary. A whole-ecosystem scale approach using these methodologies could be very instructive for the planning of future mechanistic research on the biogeochemistry of mercury in the river/delta/ bay ecosystem.

The next steps are understanding how these materials dissolve or partition back into interstitial waters as they move downstream, and how much these materials are available to methylating bacteria. In 2001, this effort should be linked to microbial studies examining bioavailability. However, these studies will need to include a much more detailed examination of Hg partitioning and speciation in the assays that what has been proposed.

Mine Site Assessment

Mine site assessment is important for remediation and for mercury loadings. This study appears to be designed to map Hg concentrations in soils and tailings. This effort will not assess Hg fluxes from mine sites. Such information would be useful in setting priorities for remediation and would require estimates of erosion, groundwater movement, and associated mercury concentrations. The presentation revealed little evidence of progress since the first review, and no clear indication on how data will be used to design remediation strategies. The Committee recommends that this effort move quickly beyond the descriptive stage, and that this effort be more closely linked with groups studying Hg concentrations and speciation downstream. As planning for remediation begins, CALFED should explore potential approaches for critically assessing the effectiveness of remediation with before and after studies in impacted areas that are down gradient from remediated mine sites.

Appendix D

Proposal Title Page and Executive Summary

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

A proposal submitted to:

Calfed Bay-Delta Ecosystem Restoration Program
2002 Proposal Solicitation

by

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Proposal Submission Date:

October 4, 2001

Executive Summary

The San Francisco Bay-Delta and its tributaries have significant mercury (Hg) contamination and associated fish advisory problems, stemming in part from the historical mining of Hg in the coast range and historical use of Hg in gold mining operations in the Sierras. This current proposal seeks to advance our understanding of the environmental behavior of Hg and monomethyl mercury, MMHg, (it's most toxic and bioaccumulated form) through a series of interrelated research investigations in the Bay-Delta and its tributaries. The **primary goal** of this proposal is to develop an understanding of the transport, cycling, and fate of mercury (Hg) and monomethyl mercury (MMHg) in the San Francisco Delta and tributary watersheds on both a temporal and spatial basis using a biogeochemical mass-balance framework as an integrating tool to assess sources, sinks and biogeochemical processes. This information will be highly beneficial to addressing Hg contamination and remediation issues in conjunction with CALFED Ecosystem Restoration efforts.

This current proposal represents a continued **scientific research effort** to understand environmental Hg issues that was initiated with our currently on-going Calfed Mercury Research Project. This currently proposed research program seeks to expand upon our current findings by: (1) Filling in data gaps in our current conceptual understanding of Hg and MMHg sources, sinks, and cycling in the Bay-Delta and its watershed; (2) Verifying and quantifying seasonal variations of MMHg in sediments and in the water column with respect to habitat type; (3) Accurately characterizing the spatial distribution of total Hg and MMHg in the Delta; and (4) Providing a foundation and framework for long term monitoring of Hg contamination issues in the Delta.

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

We propose a series of interrelated tasks to address the goals and objectives described above including: (1) Determine mass loading estimates for Hg and MMHg into, and freshwater export from, the Delta. This is a continuation of the characterization begun in our currently funded project to address bias concerns related to temporal variability (the study period to date was during low flow conditions); (2) Characterize tributary and regional input sources of MMHg and Hg for several regional segments of the Sacramento and San Joaquin Rivers to determine if loading is focused in specific river segments; (3) Conduct sub-watershed studies of tributaries or source regions of MMHg and Hg within a watershed; (4) Conduct Atmospheric Mercury Deposition Studies to assess the relative importance of this Hg source; (5) Continued monitoring and characterization of the Delta (with a new focus on wetlands) is proposed using benthic flux chamber studies to characterize and quantify the flow of Hg and MMHg form sediments to the

Delta. Of special significance in this current proposal is the new effort to begin process-oriented studies in conjunction with the characterization studies. Proposed process-oriented studies include: (6) Monomethyl mercury photo demethylation studies are proposed to assess the significance of this loss term, particularly with respect to assessing whether this mechanism is responsible for the loss of MMHg that has been observed between the Sacramento river and export pumps; (7) Delta transect and cross channel studies are proposed to verify and quantify the MMHg loss in the Delta and to help elucidate this phenomena. This effort will be integrated with a numerical model of hydrodynamic transport, dilution and advection and shall form the basis from which the predicted mercury inputs from the tributaries and subsequent tidally diluted concentrations in the Delta shall be compared to field measurements. Discrepancies between the predicted and measured values will inform studies of sources and sinks within the Delta region which in turn will be used to refine the numerical model; (8) Wetland mass loading and sediment biogeochemistry studies are proposed to investigate the importance of wetlands as sites of MMHg production. This effort has particular significance to wetland remediation and construction efforts; (9) We propose to Conduct Air-Water Exchange Studies of Dissolved Gaseous Mercury to assess the relative importance of this loss term relative to other sources and sinks. This sink has never been evaluated for the Delta and its importance is currently not know; (10) Finally, we propose to use GIS as an integration, assessment, and presentation tool, for all the interrelated efforts, both with the currently funded work and this current proposal. The **study area** for this project encompasses the entire Delta, its tributaries and watershed, focusing in particular on wetland study sites for biogeochemical investigations.

The studies described above will directly address several **CALFED priorities** where mercury contamination is an issue, including Goal 6 (Sediment and Water Quality) of the Ecosystem Restoration Program Draft Stage 1 Implementation Plan; MR-5, (ensure that restoration is not threatened by degraded environmental water quality). SR-7 (develop conceptual models to support restoration efforts); DR-6 (restore shallow water habitats); DR-7 (optimize the use of Delta Cross Channel); and BR-5 (restore shallow water, local stream and riparian habitats).