# Development and Implementation of Bioaccumulation-Based Mercury Monitoring in Support of Restoration, Remediation, and the Regulatory Process for Cache Creek, Prospect Island and Adjacent Tracts, the Yolo Bypass, and Cosumnes River

## Project Information

1. **Proposal Title:**

   Development and Implementation of Bioaccumulation-Based Mercury Monitoring in Support of Restoration, Remediation, and the Regulatory Process for Cache Creek, Prospect Island and Adjacent Tracts, the Yolo Bypass, and Cosumnes River

2. **Proposal applicants:**

   Darell Slotton, University of California, Davis

3. **Corresponding Contact Person:**

   Ahmad Hakim-Elahi
   University of California, Davis
   Office of the Vice Chancellor for Research (OVCR) Sponsored Programs, University of California, 1 Shields Avenue, Davis, CA 95616
   530 752-2075
   vcresearch@ucdavis.edu

4. **Project Keywords:**

   **Bioindicators and Biomonitoring**
   **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: 38.250

   Longitude: -121.662

   Datum:

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

   Prospect Island, Liberty Island, Little Holland Tract (multiple sites/subhabitats in each). Cache Creek watershed (primarily Bear Creek and Harley Gulch, with some work on main stem Cache Creek at defined index locations including Rumsey). Yolo Bypass (multiple sites along N-S and E-W transects). Cosumnes River (Several sites along main stem transect above Delta region, 2-3 sites on each of the primary forks).

10. **Location - Ecozone:**

    10.1 Cache Creek, 1.1 North Delta, 11.1 Cosumnes River

11. **Location - County:**

    Amador, Colusa, El Dorado, Lake, Sacramento, Solano, Yolo

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?

    No

14. **Location - Congressional District:**

    3, 1, 11, 4

15. **Location:**

    **California State Senate District Number:** 4, 2, 5, 1

    **California Assembly District Number:** 8, 2, 1, 4

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: | 10% |
| Total State Funds: | $781,850 |
| Federal Overhead Rate: | 26% or 48.5% |
| Total Federal Funds: | $895,571 |

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?

Yes

If yes, list total non-federal funds requested:

$781,850

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):

| | | |
|---|---|---|
| **97-C05** | **Effects of Wetland Restoration on the Production of Methyl Mercury in the San Francisco Bay-Delta System** | **ERP** |
| **99-B06** | **An 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 G. Wiener** | **Univerity of Wisconsin at La Crosse** | **(608) 785-6454** | **wiener.jame@uwlax.edu** |
| **Dr. Robert P. Mason** | **Chesapeake Biological Laboratory** | **(410) 326-7387** | **mason@cbl.umces.edu** |
| **Dr. Gary A. Gill** | **Texas A & M University at Galveston** | **(409) 740-4710** | **gillg@tamug.tamu.edu** |

21. **Comments:**

    **This project will build directly upon knowledge developed in both of the previously funded UC Davis CALFED mercury projects and will be conducted in close cooperation with related projects of colleagues at this and other institutions and agencies. It will also utilize and build upon findings of additional mercury research projects conducted by the PI since 1985, eight of which have addressed issues and drainages within the Bay-Delta watershed. Though the new work will make extensive use of findings and techniques developed in the previous UC Davis projects funded by CALFED, it represents a subset of potential follow-up directions, in combination with new exploratory work. For these and additional institutional reasons, this proposal is being submitted as a new project and contract, one which focuses specifically on the development of bioaccumulation-based mercury monitoring support programs (and associated science) for certain components of the Bay-Delta watershed that are of particular concern to CALFED.**

# Environmental Compliance Checklist

## Development and Implementation of Bioaccumulation-Based Mercury Monitoring in Support of Restoration, Remediation, and the Regulatory Process for Cache Creek, Prospect Island and Adjacent Tracts, the Yolo Bypass, and Cosumnes River

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.

      Project consists entirely of research and monitoring activities in support of restoration, remediation, and regulatory actions.

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

   CEQA Lead Agency:
   NEPA Lead Agency (or co-lead:)
   NEPA Co-Lead Agency (if applicable):

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

   **CEQA**
   **-**Categorical Exemption
   **-**Negative Declaration or Mitigated Negative Declaration
   **-**EIR
   **X**none

   **NEPA**
   **-**Categorical Exclusion
   **-**Environmental Assessment/FONSI
   **-**EIS
   **X**none

   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?

      Not Applicable

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 Required, Obtained

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.<br>Agency Name: Yolo County Planning Dept. | Obtained |
| Permission to access state land.<br>Agency Name: DWR, Cal. Fish & Game | Obtained |
| Permission to access federal land.<br>Agency Name: Bureau of Reclamation | Obtained |
| Permission to access private land.<br>Landowner Name: | |

6. **Comments.**

# Land Use Checklist

## Development and Implementation of Bioaccumulation-Based Mercury Monitoring in Support of Restoration, Remediation, and the Regulatory Process for Cache Creek, Prospect Island and Adjacent Tracts, the Yolo Bypass, and Cosumnes River

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?**

   Yes

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).

   Entirely no/low impact research and monitoring activities.

4. **Comments.**

   We have the endorsement (and access authorization) from all entities in jurisdiction of the regions encompassed by this project.

# Conflict of Interest Checklist

## <u>Development and Implementation of Bioaccumulation-Based Mercury Monitoring in Support of Restoration, Remediation, and the Regulatory Process for Cache Creek, Prospect Island and Adjacent Tracts, the Yolo Bypass, and Cosumnes River</u>

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):**

Darell Slotton, University of California, Davis

**Subcontractor(s):**

Are specific subcontractors identified in this proposal? No

**Helped with proposal development:**

Are there persons who helped with proposal development?

Yes

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

**Shaun M. Ayers  University of California, Davis**

**Chris Foe  Central Valley Regional Water Quality Control Board**

**Mark Stephenson  Calif. Dept. of Fish and Game, Moss Landing Marine Laboratories**

**Charles Alpers  USGS**

**Joseph Domagalski  USGS**

**Mark Marvin DiPasquale  USGS**

**Comments:**

None

# Budget Summary

## Development and Implementation of Bioaccumulation-Based Mercury Monitoring in Support of Restoration, Remediation, and the Regulatory Process for Cache Creek, Prospect Island and Adjacent Tracts, the Yolo Bypass, and Cosumnes River

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.

State Funds

| 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 | Upper Cache Creek | 2330 | 46379 | 10945 | 960 | 2080 | 17345 | 0 | 0 | 77709.0 | 7771 | 85480.00 |
| 2 | North Delta Wetlands | 2694 | 53626 | 12656 | 1110 | 2405 | 19985 | 0 | 0 | 89782.0 | 8978 | 98760.00 |
| 3 | Yolo Bypass | 1092 | 21740 | 5131 | 450 | 975 | 2605 | 0 | 0 | 30901.0 | 3090 | 33991.00 |
| 4 | Upper Cosumnes River | 1165 | 23190 | 5473 | 480 | 1040 | 2605 | 0 | 0 | 32788.0 | 3279 | 36067.00 |
| | | 7281 | 144935.00 | 34205.00 | 3000.00 | 6500.00 | 42540.00 | 0.00 | 0.00 | 231180.00 | 23118.00 | 254298.00 |

| 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 | Upper Cache Creek | 2330 | 48695 | 11492 | 960 | 2080 | 17345 | 0 | 0 | 80572.0 | 8057 | 88629.00 |
| 2 | North Delta Wetlands | 2694 | 56304 | 13288 | 1110 | 2405 | 19985 | 0 | 0 | 93092.0 | 9309 | 102401.00 |
| 3 | Yolo Bypass | 1092 | 22826 | 5387 | 450 | 975 | 4585 | 0 | 0 | 34223.0 | 3422 | 37645.00 |
| 4 | Upper Cosumnes River | 1165 | 24348 | 5746 | 480 | 1040 | 4585 | 0 | 0 | 36199.0 | 3620 | 39819.00 |
| | | 7281 | 152173.00 | 35913.00 | 3000.00 | 6500.00 | 46500.00 | 0.00 | 0.00 | 244086.00 | 24408.00 | 268494.00 |

| 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 | Upper Cache Creek | 2330 | 51145 | 12070 | 960 | 2080 | 8987 | 0 | 0 | 75242.0 | 7524 | 82766.00 |
| 2 | North Delta Wetlands | 2694 | 59136 | 13956 | 1110 | 2405 | 10305 | 0 | 0 | 86912.0 | 8691 | 95603.00 |
| 3 | Yolo Bypass | 1092 | 23974 | 5658 | 450 | 975 | 4585 | 0 | 0 | 35642.0 | 3564 | 39206.00 |
| 4 | Upper Cosumnes River | 1165 | 25572 | 6035 | 480 | 1040 | 4585 | 0 | 0 | 37712.0 | 3771 | 41483.00 |
| | | 7281 | 159827.00 | 37719.00 | 3000.00 | 6500.00 | 28462.00 | 0.00 | 0.00 | 235508.00 | 23550.00 | 259058.00 |

**Grand Total=781850.00**

**Comments.**

# Budget Justification

## Development and Implementation of Bioaccumulation-Based Mercury Monitoring in Support of Restoration, Remediation, and the Regulatory Process for Cache Creek, Prospect Island and Adjacent Tracts, the Yolo Bypass, and Cosumnes River

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

Individual 1 (project leader) 6240 hours (3 years); Individual 2 (project manager) 6240 hours (3 years); Individual 3 (analytical/field technician) 6240 hrs (3 years); Individual 4 (field/laboratory student helper) 3120 hrs (3 years at 50% time)

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

Individual 1 (project leader): $30.31/hr; Individual 2 (project manager): $20.69/hr; Individual 3 (analytical/field technician): $17.82/hr; Individual 4 (field/laboratory student helper): $8.82/hr

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

Individuals 1, 2: 23%; Indiv. 3: 34%, Indiv. 4: 5%

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

Use of personal trucks and boats for field work (mileage): $2,200/yr. Meetings/conferences (travel/lodging/perdiem): $800/yr

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

Office Supplies: $1200/yr; Laboratory Supplies: $2500/yr; Computing Supplies: $800/yr; Field Supplies: $2000/yr

**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.

Battelle Marine Sciences Laboratories: contract analytical services for aqueous total and methyl mercury, sediment methyl mercury, and some biotic methyl mercury. Costs are on a per sample basis. Battelle analytical support is estimated at the following per Task: Task 1 (North Delta Wetlands): $35,000; Task 2 (upper Cache Creek): $35,000; Task 3 (Yolo Bypass): $15,000; Task 4 (Cosumnes River): 15,000. Frontier Geosciences Laboratories: contract analytical QA/QC oversight services (x 5% of samples) for aqueous total and methyl mercury, sediment total and methyl mercury, biotic total and methyl mercury. Costs are on a per/sample basis. Frontier Geociences QA/QC analytical support is estimated at the following per Task: Task 1 (North Delta Wetlands): $3,500; Task 2 (upper Cache Creek): $3,500; Task 3 (Yolo Bypass): $1,500; Task 4 (Cosumnes River): 1,500. Perkin Elmer Instruments (for any/all project Tasks): annual service contract for mercury analytical and associated equipment(D.G. Slotton lab): $2,500/yr.

**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.

No new equipment anticipated at this time.

**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.

Incorporated into Individuals 1 and 2 general salaries.

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

None anticipated.

**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.

Overhead includes general University of California costs associated with rent, phones, laboratory facilities, general departmental office staff, and insurance. Substantially different (reduced) rates apply to State-sourced funding vs Federally-sourced funds. We are submitting budgets with the reduced 10% University of California indirect/overhead rate applicable to State-funded projects. However, the appropriate off-campus overhead rate applicable to Federally-funded projects is 26%.

# Executive Summary

## <u>Development and Implementation of Bioaccumulation-Based Mercury Monitoring in Support of Restoration, Remediation, and the Regulatory Process for Cache Creek, Prospect Island and Adjacent Tracts, the Yolo Bypass, and Cosumnes River</u>

This proposal addresses the development and implementation of bioaccumulation-based mercury (Hg) support monitoring techniques in four regions of particular concern to CALFED: (1) the upper Cache Creek watershed, where major Hg point source remedial targets have been identified, TMDL regulation is slated to be implemented, and critical areas of uncertainty remain unresolved, (2) the North Delta Wetlands Wildlife Region, including the large CALFED-funded manipulative restoration project at Prospect Island and the relatively natural restoration controls of Liberty Island and Little Holland Tract, (3) the Yolo Bypass, which includes large new purchases intended for wildlife refuge and restoration, identified in preliminary studies as a primary Hg methylation region, for which little biological data exists, and (4) the Cosumnes River, site of extensive downstream restoration efforts, identified as the highest Hg concentration major direct tributary to the Delta, for which minimal spatial information exists on absolute and relative levels in biota. This is a research and monitoring project, in direct support of restoration, remediation, and regulatory activities. Objectives, for Cache Creek and the North Delta: identify and explain remaining areas of monitoring-related uncertainty, develop and implement bioaccumulation-based, site-specific Hg monitoring techniques that are in accordance with new EPA guidelines; for the Yolo Bypass and Cosumnes River: provide absolute and spatial information on biotic Hg, contribute to source identification, initiate monitoring of localized, biotic-based performance measures. Approaches will include sampling of water, small fishes, and invertebrates. Temporal uncertainty will be addressed with seasonal, diel, tidal, and inter-tidal sampling; spatial uncertainty with transect and sub-habitat sampling. Individual variability in bioindicator species will be tested as necessary. Hypotheses include: (a) spatial, temporal, and additional variability are confounding factors that need resolution before monitoring can be adequately performed, (b) North Delta Hg methylation, bioaccumulation, and export loading are habitat dependent, greatest in highly organic, vegetated areas, (c) small fish and invertebrate bioindicator MeHg, aqueous filtered MeHg, and raw MeHg normalized to TSS are useful performance measures, and (d) the Yolo Bypass and upper Cosumnes River contain elevated biotic Hg that varies spatially in relation to relative MeHg exposure. Expected outcomes: resolution of key areas of monitoring variability, development of new baseline data, development and implementation of bioaccumulation-based Hg performance measures in support of restoration, remediation, and regulatory programs, and new Hg-related strategies applicable to future efforts. This work is directly responsive to CALFED ERP and CVPIA priorities MR-5, SR-7, DR-2, DR-6, and BR-5.

# Proposal

## University of California, Davis

## Development and Implementation of Bioaccumulation-Based Mercury Monitoring in Support of Restoration, Remediation, and the Regulatory Process for Cache Creek, Prospect Island and Adjacent Tracts, the Yolo Bypass, and Cosumnes River

Darell Slotton, University of California, Davis

## A. Project Description: Project Goals and Scope of Work
## 1. Problem

Methyl mercury (MeHg) production, loading, and bioaccumulation have been identified as critical water quality/contaminant issues by the CALFED Bay-Delta Program (CALFED 2001). Applied research projects have been and will continue to be directed at better understanding the intricacies of these processes. At the same time, substantial land acquisition and habitat restoration projects are underway; remediation and regulatory actions are being planned. In addition to and in conjunction with the ongoing process-oriented research studies, it will be essential to develop and implement directed mercury (Hg) monitoring programs in support of restoration projects, point source remediation efforts, and the TMDL regulatory process. Biological Hg data will constitute a crucial monitoring component. Exposure of both wildlife and humans, through consumption of contaminated organisms, is the ultimate concern with regard to Hg. Additionally, biota offer integrative meaures of exposure, relative to aqueous sampling which can be highly variable. The patterns of Hg bioaccumulation in relevant prey and predator organisms can differ from methylation/demethylation processes in the bottom sediments or even apparent aqueous concentrations. The life histories of biota of concern may result in primary growth and Hg bioaccumulation during periods offset from primary Hg loading or sediment methylation cycles. Thus, it is critical to examine actual bioaccumulation of MeHg, in conjunction with aqueous testing and studies of the underlying biogeochemistry. While Hg concentrations in game fish are of great importance, they cannot typically be linked to specific time periods or fine-scale locations of exposure. In addition to the regional monitoring of game fish (Davis et al. 2000), it is crucial that performance measures of relative MeHg exposure, bioaccumulation, and loading be developed and employed that can be linked to specific exposure locations and time periods. James Wiener (2001, personal comm.) and his fellow researchers recognized the value of these types of integrating measures, developing the use of wild, age-one yellow perch as an effective indicator in milestone Hg research throughout the upper Midwest. Our project team has been researching the development and use of a variety of bioaccumulation-based, localized Hg indicator techniques for over a decade, at sites throughout the Bay-Delta watershed. Several important areas of monitoring-related uncertainty have been identified in the initial CALFED Directed Hg Action (Attachment A) and the CALFED UC Davis Delta Hg Study (Attachment B). These areas of uncertainty need to be resolved, techniques refined, baseline data collected, and appropriate monitoring conducted before, during, and after major planned actions in order to provide meaningful performance measures that are consistent with new Federal Hg bioaccumulation guidelines (US EPA 2001). Ideally, monitoring will occur at sites of important restoration, remediation, and regulatory actions, and at watershed components that are representative of future planned projects. This proposal addresses bioaccumulation-focused Hg support monitoring and scientific development at four specific regions of the Bay-Delta watershed that are of particular concern to CALFED with respect to Hg:

(1) <u>The upper Cache Creek watershed (Task 1)</u>, where significant Hg point source remedial targets have been identified and TMDL Hg regulation is slated to be implemented. This watershed has been chosen to be a model for Hg remediation and regulatory approaches in other drainages throughout the Bay-Delta watershed. Extensive work has recently been conducted throughout the Cache Creek drainage (Att. A and Slotton et al. 2001). This research has identified several areas of remaining uncertainty that will need to be resolved before meaningful

monitoring can be accomplished in support of remediation projects or the regulatory process. The major goals and objectives of Task 1 include: (a) provide the fine-scale spatial and temporal information that we now realize is needed to effectively plan, implement, and interpret future Hg remediation and TMDL monitoring of water and biota in this system, (b) demonstrate the magnitude, spatial extent, and variation in aqueous and biotic Hg contamination within the localized tributary watersheds downstream of the major remedial sites, (c) provide new episodic loading information from the primary identified point source regions, which will better define the relative contribution of these sources to the THg and MeHg budgets of downstream Cache Creek, the Yolo Bypass, and the Bay-Delta, and (d) implement, at index sites within the drainage, a Hg monitoring program that is consistent with recent EPA guidelines (US EPA 2001). Hypotheses include: (a) under most flow conditions, biotic and aqueous Hg concentrations and speciation can vary significantly in relation to sampling location and season along transects immediately downstream from major remedial targets, (b) the identified primary remedial targets supply a significant proportion of the Hg loading in the Cache Creek watershed, though much of this loading may occur episodically, and (c) upstream MeHg production near remedial targets may account for a substantial amount of the overall watershed MeHg loading.

(2) <u>The North Delta Wetlands Wildlife Region (Task 2)</u>, including the large CALFED-funded manipulative restoration project at Prospect Island (US ACE & DWR 2001) and the relatively natural restoration controls of Liberty Island and Little Holland Tract. While extensive monitoring has been provided for these restoration sites, the issue of Hg and, specifically, potentially differential Hg methylation, loading, and bioaccumulation have not been addressed. These large flooded tracts are important to monitor in their own right, in this zone of intensive wildlife and recreational use. They are also representative of two divergent restoration approaches being considered for other sites throughout the Delta. It will be valuable to monitor the Hg-related responses of these sites over time as they undergo restoration. The major goals and objectives of Task 2 are to: (a) further develop and refine MeHg monitoring techniques and tools appropriate to the region, (b) address existing areas of monitoring-related uncertainty for the North Delta system, including the assessment of spatial variability, temporal variability, and MeHg bioaccumulation factors (BAFs), (c) provide estimates of total Hg (THg) and MeHg loading off/on the tracts, (d) differentiate relative MeHg loading and bioaccumulation associated with primary habitats within the tracts, (e) provide baseline aqueous and biotic Hg information, and (f) implement a bioaccumulation-based Hg monitoring program for these flooded tracts. Hypotheses include: (a) within tracts, heavily vegetated sub-habitats with highly organic sediments will show enhanced MeHg production, localized net bioaccumulation, and export relative to sand flat, mud flat, or channel habitats with less organic sediments, and (b) elevated Hg methylation, loading, and bioaccumulation may be associated with initial flooding of previously terrestrial soils during restoration efforts.

(3) <u>The Yolo Bypass (Task 3)</u>, which includes large new purchases intended for wildlife refuge and restoration. This is an area extensively utilized by wildlife, including tremendous numbers of migratory birds as well as native fish which have been shown to benefit strongly from the seasonally flooded habitat (Sommer et al. 2001). The Bypass is also an area that has been identified in preliminary studies as a primary MeHg loading region for the Delta (Domagalski and Alpers 2001). Little or no biotic Hg or MeHg source identification data exist at this time. The primary goals and objectives of this Task are to (a) determine biotic MeHg concentrations in

wildlife prey items (together with associated warm season aqueous MeHg) across north-south and east-west spatial gradients and across primary habitat types, (b) utilize this indicator data to rank existing regions and habitat types of the Bypass with respect to net Hg bioaccumulation, (c) determine concentrations in game fish edible muscle, and (d) initiate an aqueous and biotic index monitoring program to assess bioaccumulation-based performance measures. Primary hypotheses are that (a) the Yolo Bypass provides fertile Hg methylating capability (and corresponding bioaccumulation) for inorganic Hg supplied by upstream tributaries, (b) these processes exhibit spatial variability in the Bypass, and (c) relatively elevated biotic Hg concentrations are present in portions of the Yolo Bypass.

(4) The Cosumnes River (Task 4), site of extensive restoration and research efforts (Cosumnes Research Group 2001), has been identified as the major direct tributary to the Sacramento-San Joaquin Delta which exhibits the highest concentrations of Hg in biota (Attachment C and Slotton et al. 1997a). As in the Yolo Bypass, very little spatial information exists on absolute and relative Hg levels in biota or for Hg source identification. The primary goals and objectives of Task 4 are to (a) determine biotic MeHg concentrations in wildlife prey items (together with post-runoff aqueous MeHg) along a transect of the main stem of the Cosumnes above the Delta region and on the major upstream forks of the river, (b) determine concentrations in game fish edible muscle, (c) utilize the indicator data to provide initial identification of relative watershed "hot spots" with respect to net MeHg bioaccumulation, (d) implement bioaccumulation-based Hg monitoring at index sites in the watershed, and (e) compare absolute concentrations and BAF relationships with those found in Cache Creek studies. Primary hypotheses are that (a) net MeHg bioaccumulation (and relative loading of THg and MeHg) varies significantly within the watershed, and (b) highly elevated biotic MeHg concentrations are present in portions of the Cosumnes watershed, both in wildlife prey items and in game fishes consumed by the public.

**2. Justification**.

In January 2001 the U.S. EPA set an Ambient Water Quality Criterion (AWQC) for MeHg (U.S. EPA 2001). Data from all relevant Hg studies were compiled with the intention of developing National Bioaccumulation Factors (BAFs). These BAFs were intended to be used as predictive measures of the relationship between trophic level-specific biotic MeHg and aqueous dissolved MeHg and, through "translators", between dissolved MeHg and other aqueous Hg fractions. Due to the dynamic and site specific nature of Hg methylation, flux, bioconcentration, and biomagnification, the BAFs derived by EPA ranged over two orders of magnitude and were consequently not adequately predictive. It was therefore decided to postpone setting National BAFs and, instead, the criterion was based on a MeHg tissue concentration. The tissue concentration was set at 0.30 mg MeHg/kg fish. As stated by EPA, a tissue-based criterion has many advantages, including less temporal variability and less cumbersome analysis, compared to water. However, a tissue-based criterion does not adequately support quantitative water quality assessment based on aqueous loads, such as the TMDL process. EPA encourages the development of site-specific BAFs to merge diverse regulatory needs. Based on the new EPA Ambient Water Quality Criterion, the monitoring proposed in this project will largely be fish tissue based. We are fully aware that an understanding of relative biotic trophic position is critical to the development of accurate BAFs. Stable isotope techniques, relative Hg concentrations, stomach content studies, and published literature will continue to be utilized as necessary to establish these relationships. This is being addressed for many of the target organisms in both current UC Davis CALFED projects. Also consistent with the new EPA guidelines, the subset of aqueous sampling used to characterize biotic exposure will focus on filtered MeHg. Collections of additional aqueous Hg fractions will be conducted in Cache Creek and the North Delta to assess loading and transformation processes, and to contribute to the refinement of aqueous Hg translators. A primary goal of all four Tasks of this project is to initiate the development of site-specific bioaccumulation factors that are directly applicable to the new EPA guidelines and supportive of local regulatory processes.

Task 1. Cache Creek. The Cache Creek watershed has been identified as a primary source of ongoing Hg loading to the San Francisco Bay-Delta (Foe and Croyle 1998, Domagalski 2001). Loadings from Cache Creek flow into the Yolo Bypass, through the Yolo Bypass Wildlife Area, and into the North Delta Wetlands region of the Bay-Delta. Ongoing research has found elevated levels of aqueous Hg and biotic MeHg accumulation in that portion of the Delta (Attachment B). It has also been established that major point sources of Hg are present in the Cache Creek watershed. The primary remedial targets that have been identified are (1) the Abbott/Turkey Run complex of Hg mines which drain to Harley Gulch and (2) the Sulfur Creek complex of Hg mines and geothermal springs which drain to Bear Creek (Att. A, Slotton et al. 1997, Rytuba 2000). Flows from these sites are typically highly enriched in sulfate in addition to inorganic Hg, with ample sources of organic material just downstream. These conditions have been shown to provide an optimal environment for Hg methylation (Rytuba 2000). In addition, water temperatures in these upstream tributary regions become significantly elevated over temperatures in main stem Cache Creek. Recent measurements of 8-20 ng $l^{-1}$ aqueous MeHg in Harley Gulch and Sulfur Creek are greater than concentrations downstream of many other major point source Hg discharges reported in the literature, including the New Idria Mine in California (Ganguli et al. 2000), the mercury mining belt of southwestern Alaska (Gray et al. 2000), the Oak Ridge, Tennessee nuclear weapons facility (Southworth et al. 2000), and the Idrija River in Slovenia (Hines et al. 2000). Invertebrate concentrations to over 10 µg MeHg $g^{-1}$ (dry wt) have not been uncommon in the directed and previous Cache Creek Hg bioaccumulation studies (Slotton et al. 1997, 2001). Fish in Bear Creek nine km downstream of Sulfur Creek demonstrated among the highest levels of MeHg found to date in California, with routine wet weight concentrations of 2.0-4.0 µg $g^{-1}$, and concentrations to 6.5 µg $g^{-1}$, all in piscivorous fish of only 0.6 kg size and smaller. These concentrations are multiple times greater than any state, national, or international consumption guidelines. Within the main stem of Cache Creek, the directed action study found Hg levels in large piscivorous sport fish muscle tissue to increase at least three fold between the Clear Lake outflow and the small town of Rumsey. The primary identified Hg remedial targets discharge to Cache Creek between these two points. Corresponding aqueous THg, MeHg, and the range of fluctuation also increase moving downstream along this reach. What is not well understood is the proportion of these changes that can be attributed to loading from the point source tributaries.

Storm loadings of THg and MeHg from the upstream primary Hg source regions are not yet well characterized. Inorganic Hg from the abandoned mine and geothermal sources may be methylated well downstream, but it is apparent that a substantial amount of methylated Hg is also incorporated into biological tissues and sediments near the upstream sources. The ultimate fate of this material is unclear. A significant fraction may conceivably be lost from the aquatic system in winged adult aquatic insects. Alternatively, much or all of this seasonally sequestered MeHg may ultimately pass to downstream regions during storm events. Additionally, annual accumulations of deposited iron oxyhydroxide precipitates and other fine grained sediments, containing highly bioavailable inorganic Hg in addition to adsorbed MeHg (Rytuba 2000), can be expected to be removed to downstream environments during storm flows. To date, we have only limited information on Hg loading during peak flow events. The potential importance of episodic transport events cannot be underestimated in these types of watersheds (Whyte and Kirchner 2000). There is a continuing need for additional storm flow water sampling from the primary remedial targets, to improve mass loading calculations and to better define the relative contribution of these upstream point sources to the THg and MeHg budgets of downstream Cache Creek, the Yolo Bypass, and the Bay-Delta. This integrated remedial region sampling will be complemented by any additional fine-scale loading data collected by the Regional Water Quality Control Board.

Preliminary findings indicate that TMDL monitoring and remediation monitoring downstream of major cleanup targets may produce significantly divergent results, as a function of sampling location on a relatively localized spatial scale. During non-storm flow periods, apparent loading of THg and MeHg may vary substantially along downstream transects due to chemical and biological scavenging and site-specific MeHg production, degradation, and cycling. The chemical scavenging of inorganic and methylated Hg onto iron oxyhydroxide particles has been put forth as an explanation for decreasing water column concentrations moving downstream from mine sites (Rytuba, 2000; Ganguli et al, 2000). Although MeHg can to some extent be formed directly in mine tailings (Rytuba, 2000), of primary concern is the formation of MeHg in downstream environments linked to the deposition of highly contaminated sediments and precipitates. The concentrations of MeHg in mining impacted streams can be dynamic and site specific, with the extent of net Hg methylation dependant on a number of environmental factors. Transect studies downstream of Hg mine sites throughout the world have found that for similar aqueous THg concentrations, MeHg concentrations and downstream distribution can vary significantly (Southworth et al. 1999, Ganguli et al. 2000, Gray et al. 2000). In the prior Cache Creek work, we have also detected a recurring seasonal pattern of variation in both aqueous and biotic Hg, with the most pronounced temporal trends in the tributary streams, particularly those draining Hg point sources. Invertebrate bioindicators were found to change their THg and MeHg body burdens in a more rapid time frame than anticipated. Directed follow-up sampling is needed to better understand the spatial and seasonal dynamics in this system, and to address additional areas of uncertainty.

<u>Task 2. North Delta Wetlands</u>. The Prospect Island restoration project is one of the most extensive manipulative restoration efforts occurring in the Delta (US ACE & DWR 2001). Liberty Island and Little Holland Tract, purchased by CALFED and U.S. Army Corp of Eng. respectively, are being allowed to return to vegetated wetland habitat along a more natural trajectory. The concern is that significant new wetland creation in the Delta will increase MeHg production, resulting in increased bioaccumulation. Wetlands have been shown to be important sites of MeHg production (Zilloux et al. 1993; Hurley et al. 1995). MeHg production in wetlands has also been implicated as a major source of MeHg to adjacent and downstream environments (e.g. St. Louis et al. 1994). During June 2001 we sampled MeHg in inflowing and outflowing tidal water from flooded tracts throughout the Delta (Att. B). MeHg concentrations were higher in water flowing off most of the tracts as compared to the same water sampled

earlier on the inflowing tide. This increase was not a TSS-related phenomenon, as suspended material was routinely lower in outflowing waters as compared to the inflow. The magnitude of the difference in inflowing vs outflowing water appears to be related to wetland successional stage. Tracts with well developed macrophyte beds (both aquatic and emergent) showed the largest differential in MeHg concentrations. Flooded tracts with deep water and/or little macrophyte growth showed no increase in MeHg concentration. The relationship to wetland stage is likely an indication of increased net methylation due to the more highly organic and anoxic sediments found in later successional wetlands. In addition, the well known phenomenon of newly flooded and re-flooded terrestrial soils producing a surge in Hg methylation may be important in new restoration projects such as Prospect Island (Bodaly et al. 1997).

Our model, based on results from our initial research (Att. B, Slotton et al. 2000, 2001) is that these large tracts receive seasonal winter loading of Hg from the Yolo Bypass and to a lesser extent the Sacramento River, and ongoing loading/redistribution from sediment resuspension; some of this Hg passes on to the wider Bay-Delta; of the Hg that deposits in these large North Delta expanses, a portion is methylated in the sediments, primarily linked to the bacterially mediated reduction of sulfur (Compeau and Bartha 1985; Gilmour et al. 1992); a portion of the sediment net MeHg production crosses the sediment:water interface or is resuspended into the water column; a portion of this aqueous MeHg is locally bioaccumulated and recycled; a portion is exported from the tracts to the wider Bay-Delta by tidal currents; relative methylation, bioaccumulation, and export loading vary with season, tract habitat, and tract location relative to primary upstream Hg loading flows.

Monitoring of these restoration sites for absolute and relative MeHg loading and bioaccumulation will be valuable. These data will provide performance measures of the different restoration approaches and locations over time and can be compared to extensive pre-project baseline data collected by our group, including from Prospect Island in 1999 prior to draw down and restoration construction. For these sites to provide the most useful information, both to track localized Hg restoration responses and to help the development of strategies applicable to other restoration projects, monitoring tools and techniques must be refined, remaining areas of uncertainty addressed, and cost-effective monitoring approaches developed and initiated.

Task 3. Yolo Bypass. The Yolo Bypass hydrologically links Cache and Putah Creeks, Knights Landing Ridge Cut, and Sacramento River flood flows with the Bay-Delta. Cache and Putah Creeks have both been shown to contain extensive Hg point sources in their upper watersheds, linked to historic Hg mining there (Slotton et al. 1997b, 1999b, Att. A). Foe and Croyle (1998) found highly significant Hg loadings from Cache Creek, relative to overall Bay-Delta loading. In the USGS portion of the recent directed Hg study, Domagalski and Alpers (2001) found aqueous MeHg to be notably elevated within the Yolo Bypass, suggesting that this is an important methylating environment for inorganic Hg derived from upstream sources. Sommer et al. (2001) found that the sporadically and seasonally flooded Bypass habitat provides an important competitive advantage for native fish species. Large numbers of migratory birds utilize the Bypass when flooded and substantial numbers of water-oriented, predatory birds and mammals are permanent residents. A 3,700 acre wildlife refuge was recently developed, including restored permanent wetland and seasonally flooded habitat. A pending purchase will increase the area of refuge in the Yolo Bypass by approximately 400%, converting farmland to mixed wetland. Our working model of the Yolo Bypass is that it receives seasonal loadings of Hg from Cache Creek and additional sources; a portion of this loading is transported directly into the North Delta and wider Bay-Delta; the Hg that deposits in the Bypass is exposed to a variety of habitats, some with a high capacity for methylation, localized bioaccumulation, and export loading of MeHg; the relative extent of these processes is both habitat and location (re source flows) dependent. Task 3 work, in conjunction with proposed USGS loading and methylation studies, will provide information in relation to the location and habitat choices for new restoration work in the Bypass. In the event that the Domagalski-led USGS project is not funded in the current round, the Task 3 studies will provide extensive biotic data and foundational MeHg source identification information.

Task 4. Cosumnes River. In a preliminary study, the Cosumnes River exhibited biotic Hg concentrations greater than all other surveyed streams in the northwestern Sierra Nevada (Att. C and Slotton et al. 1997a). Similarly, biotic concentrations in the lower (Delta) portion of the Cosumnes were found to be highly elevated relative to other Delta sites (Att. B and Slotton et al. 2000). Recent aqueous Hg load sampling conducted near the mouth of the Mokelumne River by the Regional Water Quality Control Board and Cal. Fish & Game indicated that the Cosumnes is an important aqueous Hg loading source to the overall Bay-Delta (Foe 2001). The Cosumnes is the focus of large, multi-faceted restoration and research efforts (Cosumnes Research Group 2001). An intensive Hg process-oriented study is being proposed by USGS for the Delta portion of the river. Information from upstream in the Cosumnes watershed is needed to help identify primary Hg sources, relative loading from the different tributaries, and the extent of upstream methylation and bioaccumulation. In conjunction with the linked aqueous and sediment loading work proposed by Charles Alpers at USGS, Task 4 biotic and post-runoff studies in this project will provide this information. In the event that the Alpers USGS loading project is not submitted or funded until a subsequent proposal round, the Task 4 work will provide a foundation. Our model of the Cosumnes system is that a substantial amount of elemental Hg is present within the stream bedload, with relative “hot spots” present in specific stream reaches; this bedload is transported incrementally downstream toward the Delta; some amount of in-stream methylation occurs in portions of the upper watershed, providing direct MeHg loading for localized bioaccumulation and transport downstream; loading of both inorganic elemental Hg and upstream-generated MeHg influence Hg cycling downstream in the Bay-Delta.

## 3. Approach.

General Methodology: Samples for all of the Tasks will be taken consistent with the protocols developed for the previous, directed action, multi-investigator Hg project (Puckett and van Buuren 2000). This QAPP was peer reviewed by a panel of Hg experts. Water will be characterized with centroid grabs, utilizing clean technique, appropriate preservation , and shipment to Battelle Laboratories for MeHg and/or THg analysis. Filtered water samples will primarily be obtained directly in the field using a dedicated peristaltic pump and pre-cleaned tubing and cartridge filters. A subset of aqueous Hg samples may be filtered at Battelle within 24 hours of collection. Aqueous split samples will be analyzed for TSS in our UC Davis laboratories, using standard filter-based technique. A subset of samples will be analyzed for DOC and sulfate using standard techniques. Temperature, dissolved oxygen, pH, conductivity, and redox will be field-assessed with a YSI multi-probe unit. Sediment will be taken with a variety of clean sampling devices. Aquatic insects will be collected from stream habitats with a research kick screen and from wetland habitats with a variety of nets and by passing bottom sediments through sieve buckets. Small fishes will be sampled with a backpack electroshocker and a variety of seines. Larger game fishes will be sampled by boat-mounted electroshocker and a variety of gill nets. Aqueous and biotic samples will be carefully field packaged and labeled according to protocol and placed immediately onto ice in separate, dedicated coolers. All samples will be held in suitable clean containers following accepted protocols. Biological samples will be sorted, identified, and cleaned within 24 hours, and subsequently dried and powdered, analyzed for THg and/or organic Hg at UC Davis. THg analytical work at UC Davis will follow protocols included in Puckett and van Buuren (2000) and refined over many years (modified EPA Method 245.2). Organic Hg analyses (modified from the method long practiced and tested for MeHg equivalence by the Canadian Experimental Lakes Area Mercury Research Group and others, originally modified from Uthe 1972) consists of extraction into methylene chloride and hexane after tissue homogenization in a solution of sodium bromide and copper sulfate, followed by digestion and CVAA detection as above. Extensive QA/QC and MeHg equivalence testing accompanies each analytical run. Results for both the UC Davis organic and THg techniques have been part of interlab comparison studies conducted during the CALFED directed action Hg study. Splits of a minimum of 5% of all UC Davis and Battelle Hg samples will be analyzed by a third laboratory as an additional measure of performance. A subset of biological samples will be analyzed at UC Davis for nitrogen and carbon stable isotopes.

Task 1. Cache Creek. This Task will address remaining identified areas of monitoring-related uncertainty in the Cache Creek watershed. In particular, it will better define THg and MeHg loading and potential fine scale temporal and spatial transitions in aqueous and biotic Hg along in-stream transects immediately downstream of the two primary remedial Hg targets in the Cache Creek watershed: the Abbott/Turkey Run Hg mine complex at Harley Gulch and the Sulfur Creek (Bear Creek watershed) complex of abandoned Hg mines and geothermal Hg floc sources. Seasonal variability will be addressed at a pre-existing index location on Bear Creek. Dramatic seasonal shifts in both aqueous Hg and bioaccumulation have been indicated at this and similar near-source sites. New sampling will improve our resolution of these apparent cycles, with monthly collections over an 18 month period, capturing a complete annual cycle with 1 month resolution, and inter-annual overlap of the spring/summer period of apparent peak MeHg aqueous concentrations and bioaccumulation. Aqueous collections will include raw and filtered MeHg and THg, together with ancillary parameters total suspended solids (TSS), dissolved organic carbon (DOC), sulfate, temperature, oxygen, conductivity, pH, and redox. Biological collections will include Hydropsychid caddisfly larvae (our most universal invertebrate bioindicator) and California roach fish, each collected monthly as multiple-individual composite samples, with triplicate composites taken quarterly. Invertebrate and small fish Hg has been predictive of corresponding Hg bioaccumulation in game fish in our own studies (Slotton et al. 2001) and those of many others (US EPA 2001). All invertebrate and small fish bioindicators will be analyzed for both THg and organic Hg.

We will investigate apparent fine scale spatial patterns in biotic Hg, aqueous Hg concentrations, transformations, and loading, and the relationship between aqueous and biotic concentrations (bioaccumulation factors) along the reaches of Harley Gulch and Sulfur/Bear Creeks from the Hg point source regions to the downstream confluences with Cache Creek. Transect sampling will be conducted in the spring through early summer, when the greatest spatial divergence is predicted from the initial work. Four to six sites will be studied along

Harley Gulch between the upstream Turkey Run/Abbott mine complex and the confluence with Cache Creek. The Sulfur Creek/Bear Creek transect will be investigated with six to eight study sites, extending from the Sulfur Creek source regions and upstream (control) Bear Creek to the Bear Creek confluence with Cache Creek. Transect water sampling will include raw and filtered THg and MeHg, together with ancillary parameters. Aqueous exposure conditions, relative to corresponding biotic samples, will be characterized primarily with filtered MeHg, sampled on the Sulfur/Bear transect on 2-3 dates during the six weeks preceding biotic collections. For the Harley Gulch transect sites, which are extremely remote, water (full suite) and biota sampling will be conducted simultaneously. Biotic collections will include Hydropsychid caddisfly larvae (Harley and Sulfur/Bear transects) and California roach fish (Sulfur/Bear transect; no fish are present in Harley Gulch). Biotic samples from each transect location will again consist of multi-individual composites of each species, taken in triplicate as available. Hg and ancillary analyses will be consistent with the seasonal work.

In addition to the off-peak water sampling associated with the above work, we will sample integrated storm discharges at Harley Gulch, Sulfur Creek, and Bear Creek during the winter rainy seasons of 2003, 2004, and possibly 2005. Precipitation and flow gauging stations will be monitored to determine optimal collection times. The attempt will be made to capture the primary "first flush" event of each year, together with several additional major storm events. Collections/analyses will include raw THg and MeHg, and TSS. We will additionally sample Cache Creek upstream and downstream of the Bear Creek confluence and, if possible, will sample Cache Creek upstream and downstream of the Harley Gulch confluence.

Individual variation in Hg bioaccumulation will be investigated in the primary bioindicator species, with series of individual assays as well as tests of gut contents as the potential source of anomalous results in roach. The phenomenon of potential photodegradation of aqueous MeHg (Sellers et al. 1996) will be investigated with one or more time series of aqueous collections at a clear water tributary site and the main stem Cache Creek index site at Rumsey. Following initial trials with individual water samples collected across the diel cycle, more intensive sampling will be conducted, within budgetary constraints. Annual index site monitoring of bioindicator organisms will be initiated at key, representative sites already identified throughout the wider Cache Creek drainage. Replicate composites of primary indicator species will be taken, to facilitate the inter-annual statistical comparison of these Hg performance measures. Sampling of piscivorous game fish will be conducted at Bear Creek and Cache Creek at Rumsey index sites during the fall of 2004.

Task 2. North Delta Wetlands. Initial field work will test the variability of aqueous tidal sampling. Series of water collections will be made throughout tidal cycles to determine the optimal and most representative timing of collections for the characterization of both inflowing and outflowing water. The relative importance of tidal amplitude will be explored with a series of water collections taken at the same relative point of the outflowing tide on each of several dates demonstrating a range of tidal amplitudes. When these factors are better understood, seasonal sampling of inflowing and outflowing water will be initiated. Samples will be taken every 6-7 weeks throughout an annual cycle, and then quarterly. Inflowing and outflowing water will be taken from representative levee breach sites at both Prospect Island and Liberty Island, including two sites at Liberty island representing divergent habitat types (Att. B). Raw aqueous MeHg and THg, filtered MeHg, TSS, and ancillary YSI limnological parameters will be analyzed routinely. Concentrations of MeHg and THg will be extrapolated to total tidal volumes exported from the tracts, for the calculation of loads, and to relative areal and volumetric coverage by the primary habitat types. Biota will also be utilized as integrating performance measures. Biotic sampling will focus on the most prevalent small/juvenile fish species, together with *Corbicula* clams as localized bioindicators. Localized seasonality in MeHg exposure and bioaccumulation will be investigated with quarterly collections of appropriate bioindicators from a centralized index region of each tract. Samples will consist of multi-individual composites ($n \geq 10$). Three or more composite samples of the primary bioindicator organism(s) will be taken at each tract as available each sampling, to facilitate the statistical comparison of relative net Hg bioaccumulation between tracts and times. Efforts will be made to collect same or similar species among the sites at each sampling. Additional data will be collected from other primary small fish and macroinvertebrate species during the project. All invertebrate and small fish bioindicator samples will be analyzed for THg and organic Hg. Following 18-24 months of quarterly sampling, appropriate timing for continuation bioindicator monitoring will be determined based on seasonal concentration results and relative availability of key species in appropriate sizes.

Intra-tract variation in restoration habitat outcome and associated Hg methylation, bioaccumulation, and export loading will be addressed with annual collections of inflowing and outflowing tidal water (primarily filtered MeHg) and localized bioindicator organisms from both the southern sand and mud flat regions of Liberty Island and Little Holland Tract and the northern portions where vegetated wetlands have developed. At Prospect Island, where a variety of channel, island, and open water features will be developed, we will annually sample localized biota and tidal water from representative restoration features. Results will be related to factors including macrophyte development, wetland successional stage, channel order/depth/location, and sediment organic percentage and particle size. Large fishes will be annually characterized for muscle Hg with multiple individual samples of dominant game fish species from Prospect and Liberty Islands, in conjunction with Cal. Fish and Game survey work. All collections will be coordinated with the multi-agency monitoring programs at Prospect and Liberty Islands, so as to avoid duplication in sampling effort where possible and to maximize overall data richness and usefulness. The final eight months of the three year UC Davis project will be devoted to final data integration/interpretation and report and manuscript preparation.

<u>Task 3. Yolo Bypass</u>. Sampling locations will include sites utilized by USGS in their companion loading and methylation project. Sampling will primarily be conducted at existing permanently flooded habitats during the spring/summer post-runoff period. In the event that the Bypass floods significantly during the project, sampling will additionally be conducted at representative seasonally flooded sites after potential flooding-associated methylation has had the opportunity to progress. Sampling sites will be distributed across north-south and east-west gradients, positioned so as to isolate the potential influences of Hg loads derived from the Sacramento River, Knights Landing Ridge Cut, Cache Creek, and Putah Creek. Channel/slough habitats will be compared to permanently vegetated wetlands and seasonally flooded terrestrial vegetation. A number of existing ponds, channels, and recently created wetland/refuge features are located strategically throughout the Bypass; a subset of these will be utilized as sampling locations. During the first year, a synoptic survey of biotic Hg will be conducted at a minimum of 10 sites. Based upon results of the synoptic work, a set of index sites will be chosen for biotic and aqueous sampling in years 2 and 3. Biotic sampling will focus on the most prevalent small/juvenile fish species as localized bioindicators, with numerically significant

macroinvertebrates taken as available. Some data will be collected from all primary small fish and macroinvertebrate species in the Bypass. All invertebrate and small fish bioindicator samples will be analyzed for THg and organic Hg. Samples will consist of multi-individual ($n \geq 10$) composites. Three or more composite samples of the primary bioindicator organism will be taken at each site as available, to facilitate the statistical comparison of relative net Hg bioaccumulation. Efforts will be made to collect same or similar species among the sites. Relative aqueous MeHg exposure at biotic index sites will be characterized with filtered MeHg, together with TSS and ancillary YSI parameters. Aqueous collections will be made on two dates within six weeks of the corresponding biotic collections.

In addition to providing relative measures of bioaccumulation and aqueous MeHg among the sites, the data will provide absolute Hg concentration information for a variety of wildlife prey species throughout the Yolo Bypass region. Game fish Hg will be assessed at a centralized site in the Toe Drain, with multiple individual samples from dominant species. This biotic and warm season localized aqueous work will directly complement proposed USGS research in the Bypass on aqueous Hg storm loading and subsequent sediment Hg biogeochemistry and has been designed in close consultation with that group. Three primary sampling events will be conducted during the first 28 months of the project, with repeated sampling of a subset of sites for inter-annual and seasonal variability. Sites may be added or removed, based on bioindicator availabilities and concentrations/trends encountered. Data reduction and assessment will occur throughout the project, with the final 8 months reserved for data integration, interpretation, and report and manuscript preparation.

<u>Task 4. Cosumnes River</u>. In the first year, a synoptic survey of biotic Hg will be conducted at 10 or more sites distributed throughout the watershed. Based on the results of synoptic sampling, index sites will be chosen for biotic and corresponding aqueous collections in years 2 and 3. Index sites will be distributed along a transect upstream from the Delta along the main stem of the Cosumnes, and on the primary river forks. Sites will be positioned so as to provide initial spatial data on relative localized MeHg bioaccumulation during the period of primary biotic growth. Sampling will thus be conducted in the post-runoff period of summer/fall. This work will provide an indication of relative post-runoff, in-stream MeHg exposure, MeHg available for localized bioaccumulation and possibly of significance as a direct MeHg loading source to downstream, both during warm season low flow conditions and in episodic winter flushing events. This post-runoff biotic and aqueous work has been designed to integrate fully with a proposed USGS project led by Charles Alpers which will quantify winter/spring runoff loading of Hg and further identify and characterize remediation targets. Results of our previous survey research of relative Hg bioaccumulation throughout the northwestern Sierra Nevada (Att. C) were the basis for the USGS group targeting the Bear and South Fork Yuba Rivers for extensive work on Hg loading, fine-scale source identification, and remediation. In the same way, we have jointly planned the Cosumnes River work, with our UC Davis group providing initial reconnaissance, post-runoff characterization, and ongoing biological Hg monitoring. Biotic sampling sites will be characterized for relative aqueous MeHg exposure on two dates within six weeks of biota collections. Analyses will include filtered MeHg, together with TSS and ancillary YSI parameters. Biotic sampling will focus on the most prevalent small/juvenile fish species as localized bioindicators, with numerically significant macroinvertebrates taken as available. Some data will be collected from all dominant small fish and macroinvertebrate species in the watershed. All invertebrate and small fish bioindicator samples will be analyzed

for THg and organic Hg. Samples will consist of multi-individual (n≥10) composites. Three or more composite samples of the primary bioindicator organism(s) will be taken at each site as available, to facilitate the statistical comparison of relative net Hg bioaccumulation between sites and dates. Efforts will be made to collect same or similar species among the collections.

In addition to providing relative measures of bioaccumulation and aqueous MeHg among the sites, the data will provide absolute Hg concentration information for a variety of wildlife prey species throughout the watershed. Two to three primary sampling events will be conducted during the first 28 months (2 yrs 4 mo) of the project. Sites may be added or removed, based on sample availabilities and concentrations/trends encountered. Representative game fishes will be collected at one or more index locations in the final year of field work for analysis of fillet muscle Hg; individuals of dominant game fish species will be analyzed across a range of sizes, as available. Data reduction and assessment will occur throughout the project, with the final 8 months reserved for data integration, interpretation, and report and manuscript preparation.

**4. Feasibility**.

The proposed work follows similar research studies led by the PI for many years in same or similar regions of the Bay-Delta and its watershed. The research team is fully capable of carrying out the proposed Tasks as designed, under nearly all conceivable weather conditions. Current funding and time commitments of the PI and core team will be completed before this project is scheduled to begin; virtually all of the core team's focus will be able to be devoted to this project if fully funded. Access permission has been secured or is in the process of being secured for all project components. Scientific Collecting Permits from the State of California, appropriate in scope for the planned collections, are currently held by the core team members and will continue to be renewed regularly. The only potential contingency that we foresee involves the Prospect Island component of Task 1. In the event that the base restoration project there is delayed by legal challenge, monitoring of that tract will consist of baseline work until restoration monitoring can begin.

**5. Performance Measures**.

The entire focus of this project can be described as the support science, development, and initiation of "performance measures" to be used for Hg in relation to restoration, remediation, and regulatory actions in the Bay-Delta watershed. Performance of the project itself will be evaluated in quarterly and annual progress reports, as a function of progress toward stated objectives, successful completion of Task work, and production of new strategies, techniques, data reports, and peer-reviewed journal publications that further CALFED's overall ecosystem goals and the general science of Hg biogeochemistry. Conformance with strict QA/QC guidelines, as previously set forth in prior CALFED work (Puckett and van Buuren 2000), will be a cornerstone of the program. Splits of a minimum of 5% of samples analyzed by both UC Davis and Battelle Laboratories will be additionally analyzed by a third party laboratory, to further assess overall data quality. We plan to support and participate fully in regular data sharing and scientific oversight meetings that will hopefully link all relevant mercury related projects in and out of the overall CALFED program.

**6. Data Handling and Storage**.

A system of careful data handling has been developed in previous projects of this laboratory. Appropriate field notes are collected in field/lab books containing weatherproof paper. Sample coding is assigned during initial sample processing within 24 hours of collection and entered into the books. Copies of the field/lab book pages are stored in a separate location. Sample codes include redundant identifying information, including site, date, sample type, and sub-type. Sample identification is strictly maintained throughout the processing and analytical stages through consistent protocols. Processing and analytical information is entered onto hard-copy data sheets which are filed in project-specific laboratory binders. Data, once input into computer spreadsheets by the Analyst, are QA checked by the Project Manager or the PI. Spreadsheet data are backed up regularly and stored in multiple locations. File names are coded to avoid incorrect over-writing. Participation/oversight of the Project Manager and/or PI through all stages of the field, sample processing, analytical, data entry, and data processing stages helps to ensure the correct identification of samples and data/sample associations throughout. Once QA/QC and data processing are complete, data findings and conclusions will be made widely available in the various reports, articles, web postings, presentations, and workshops noted below (A.7).

**7. Expected Products/Outcomes**.
This project will address uncertainty associated with Hg bioaccumulation-based support monitoring in the Bay-Delta watershed, explaining and/or removing some of that uncertainty. Appropriate Hg monitoring techniques and programs will be developed for four important regions. The project will also provide a set of baseline data for these critical representative regions prior to planned restoration, remediation, and regulatory activities. Findings will be shared in quarterly and annual progress reports, final reports (also to be made available over the Internet), regional and peer-reviewed journal articles (one peer-reviewed article anticipated from each of the four Tasks), and a wide variety of public presentations, workshops, data sharing and scientific oversight meetings.

**8. Work Schedule**.
Work on some portions of each of the four Tasks will commence immediately upon contract implementation, including additional reconnaissance, planning of field sampling, and initial tests. Seasonal sampling on Bear Creek (Task 1) will be conducted from April 2003 through October 2004, capturing one complete annual cycle and two spring-fall methylation periods. Intensive seasonal sampling in the North Delta will commence following initial tidal sampling tests. Yolo Bypass Spring/summer synoptic sampling (Task 3) will be conducted in 2002 or 2003, depending on contract date, with index sampling in successive years Winter/spring flooded condition sampling will be done as possible if the Bypass floods. Summer/fall sampling on the Cosumnes River (Task 4) will similarly commence in either 2002 or 2003, depending on contract timing. Sampling schedules for additional subtasks will be coordinated to utilize most appropriate seasons for each, while also spreading the overall workload relatively evenly across the initial 28 months of the project. Management, sample preparation, analytical work, QA/QC, data processing, and interim data interpretation will occur throughout this period. The last eight months will be devoted to final data integration and report and manuscript preparation.

## B. Applicability to CALFED ERP and Science Program and CVPIA Priorities

**1. ERP, Science Program and CVPIA Priorities**.

This project specifically addresses many of the Hg-related Priorities linked to Strategic Goal 6 (Water and Sediment Quality), responding directly to Priorities in the Multi-Regional, Delta and East Side Tributaries, and Sacramento Regions and, indirectly, in the Bay Region. These Priorities are listed below, with excerpts of Priority text that are most applicable to the Project:

MR-5. "Stage 1 actions include assessment of mercury sources, loadings, factors affecting transformation and bioaccumulation across the watershed. Studies that would characterize these problems and where they overlap with restoration activities are needed. In particular, it is important to understand and compare mercury methylation in restored wetlands and implications for loadings to the Bay and Delta", "Data on the extent of the threat from specific sources is needed to evaluate the relative importance of different sources to support prioritization of remediation efforts".

SR-7. "Mercury evaluation and abatement work in the Cache Creek watershed is needed to support development and implementation of Total Maximum Daily Load (TMDL) for mercury; determine bioaccumulation effects in Cache Creek; source, transport, inventory, mapping and speciation of mercury", "… determine sources of high levels of bioavailable mercury", "…studies (are needed) to evaluate the efficacy of restoration and remediation approaches".

DR-2. "Restore or continue study of the values of restoring large seasonally flooded areas like the Yolo Bypass".

DR-6. "Better understand processes that determine mercury methylation in the Delta and tributaries, particularly how it is affected by restoration in different settings. Yolo Bypass, Cache Creek and the Cosumnes River are of particular interest".

BR-5. (Studies are needed on) "Mercury inputs from Yolo Bypass and their implications in Suisun Marsh and Grizzly Bay".

Project-associated ecological information will also provide partial support for Priorities MR-1, MR-6, DR-1, and DR-5, in relation to native and non-native fishes, invasive plant and animal species, land acquisitions, development of performance measures, general habitat quality, and justice issues.

**2. Relationship to Other Ecosystem Restoration Projects.**

This project will build directly upon knowledge developed in both of the previously funded UC Davis CALFED mercury projects (B.3 below). It will utilize and build upon findings of additional mercury research projects conducted by the PI since 1985, eight of which have addressed issues and drainages within the Bay-Delta watershed. The work will also continue to be conducted in close coordination with related projects of colleagues at this and other institutions and agencies. In particular: Task 1 work in the Cache Creek watershed continues to be coordinated closely with planned point source remediation, remediation studies, and TMDL regulatory actions by the Water Quality Control Board and other agencies. Task 2 work in the North Delta is fully coordinated with the large manipulative restoration efforts of DWR and the

Army Corps of Engineers at Prospect Island and the extensive non-Hg monitoring programs being implemented for that project (US ACE & DWR 2001). Similarly, that task is coordinated with the low-manipulation and no-manipulation restoration approaches of US Fish and Wildlife Service at Liberty Island and Little Holland Tract. Liberty Island is being used as a control for Prospect Island in extensive fisheries and water quality monitoring. We will work closely with these programs, sharing samples and data. For Task 3 work in the Yolo Bypass, the biotic and post-runoff aqueous spatial samplings have been designed in full coordination with USGS proposed work on THg and MeHg loading and localized methylation/demethylation. This work will also coordinate with ongoing native fisheries improvement projects and studies in the Bypass led by DWR's Ted Sommer. The Cosumnes River work of Task 4 (upstream of Delta) was developed in coordination with (a) USGS proposed Hg loading and source identification work in the upper watershed and (b) USGS proposed process-oriented Hg methylation/demethylation and bioaccumulation studies in the Delta portion of the Cosumnes and Franks Tract. The development of alternative aqueous MeHg load monitoring techniques and habitat-specific loading information at the specific project sites will be coordinated with more generalized, system-wide studies planned by the Regional Water Quality Control Board, Cal. Fish and Game, and Texas A&M University. Similarly, intensive biotic Hg information from the specific monitoring target regions will be coordinated with related data collected on a more generalized, system-wide basis by the San Francisco Estuary Institute and Cal. Fish and Game. Wildlife prey Hg data will be coordinated with wildlife exposure/uptake studies by US Fish and Wildlife Service. The Tasks developed in this proposal have been carefully chosen to address specific Bay-Delta Hg monitoring-related needs while interacting as synergistically as possible with the other primary ongoing and proposed CALFED Hg projects and the restoration, remediation, and regulatory projects associated with the monitoring targets.

## 3. Requests for Next-Phase Funding.

The previously funded UC Davis CALFED mercury projects are:

Effects of Wetland Restoration on the Production of Methyl Mercury in the San Francisco Bay-Delta System (ERP Project No. 97-C05; end date March 31, 2002).

An Assessment of Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed; UC Davis Cache Creek Components (ERP Project No. 99-B06; end date September 30, 2002).

Both of these projects are progressing well. The aspects most relevant to this proposed work are summarized in Attachments A (Cache Creek Hg Bioaccumulation and Trophic Transfer) and B (Sacramento-San Joaquin Delta Hg), respectively. Extensive final reports and associated publications for each of those projects are in process (projected publication dates 2002). In addition, a summary brief of the related "Task A" portion of the first project (direct mine site studies) can be found at the web site: http://loer.tamug.tamu.edu/calfed/reports.htm. Though the new work will make extensive use of findings and techniques developed in the previous UC Davis projects funded by CALFED, it represents a subset of potential follow-up directions, in combination with new exploratory work. For these and additional institutional reasons, this proposal is being submitted as a new project and contract.

**4. Previous Recipients of CALFED Program or CVPIA funding.**
(see above)

**5. System-Wide Ecosystem Benefits**.
The proposed work Tasks have been chosen to refine monitoring support protocols applicable to new Federal Hg bioaccumulation guidelines and to focus on some of the most urgent restoration, remediation, and regulatory challenges facing CALFED with regard to Hg. Cache Creek and the Cosumnes River have been identified as important sources of Hg loading to the entire Bay-Delta system. The Yolo Bypass connects Cache Creek and other Hg loading sources to the Delta and has been indicated in preliminary work to be an important region of Hg methylation and MeHg export loading. The North Delta Wetlands Wildlife Region includes large, funded restoration projects located immediately downstream of the Yolo Bypass and upstream of much of the rest of the Bay-Delta. This proposed work is intended to address not only the Hg-related issues at these specific sites from a bioaccumulation perspective, but to be partially or fully applicable to restoration, remediation, and regulatory projects throughout the wider Bay-Delta watershed. The project has been designed to interact as synergistically as possible with a wide variety of past, current, and proposed Hg-related and other projects. Additionally, as the research team is comprised of aquatic ecologists and fisheries and water quality experts with an understanding of general CALFED and CVPIA objectives, this Hg-focused work will also generate extensive additional information on general ecosystem/habitat quality, native fishes, desirable non-native game fishes, invasive plant and animal species, and environmental justice issues.

**6. Additional Information for Proposals Containing Land Acquisition.**
(not applicable)

**C. Qualifications** (PI and crew).

**DARELL G. SLOTTON**
Department of Environmental Science and Policy
University of California, Davis

Dr. Slotton has directed applied research projects addressing heavy metal contamination and bioaccumulation issues in California aquatic ecosystems for over 15 years, with a primary focus on mercury (Hg). He has led investigations of copper, zinc, and cadmium contamination at Iron Mountain Mine, Keswick Reservoir, and Camanche Reservoir, where sediment resuspension and metals transport, solubility, and bioavailability were investigated. Since 1985, he has run a Hg biogeochemistry monitoring and research program at Davis Creek Reservoir and a Hg analytical laboratory at UC Davis. Between 1993 and 1998, Dr. Slotton led a research program throughout the foothill gold mining region of the Sierra Nevada, primarily focusing on benthic invertebrates and fish as proxies for relative bioavailable Hg concentrations and loading. He conducted an intensive, multi-year study of Hg mass loading, bioaccumulation, and remedial options at the Mt. Diablo Mercury Mine and Marsh Creek watershed, has led numerous mercury studies throughout the California Coast Ranges, and has been associated with the Clear Lake Superfund Hg Project since its inception. Recent projects have included Hg bioassessment and source identification studies in both lower Putah Creek and its mine-impacted upper watershed. Additional projects have investigated heavy metal biogeochemistry in other regions of the West and other areas of applied limnological and wildlife research. Since 1998, a primary focus has been to manage a CALFED-funded San Francisco Bay-Delta study of Hg source detection, bioaccumulation, and methylation, and the implications for wetlands restoration projects. Since 1999, he has also been the lead PI in a directed action CALFED project in the Cache Creek watershed, determining the patterns of localized Hg bioaccumulation, primary driving aqueous chemistry, sources, and the key forms of Hg minerals that dominate Hg methylation and movement into aquatic food webs.

B.A. - Biogeography/Ecosystems Analysis, University of California, Los Angeles (1980)
M.S. - Ecology, University of California, Davis (1988)
Ph.D. **-** Applied Aquatic Ecology, University of California, Davis (1991)

<u>(Selected Publications)</u>

Slotton, D.G. and J.E. Reuter. 1995. Considerations of heavy metal bioavailability in intact and resuspended sediments of Camanche Reservoir, California, USA, with emphasis on copper, zinc, and cadmium. *Marine and Freshwater Research*, 46:257-265.

Slotton, D.G., J.E. Reuter, and C.R. Goldman. 1995. Mercury uptake patterns of biota in a seasonally anoxic northern California reservoir. *Water, Air, and Soil Pollution*, 80:841-850.

Slotton, D.G., S.M. Ayers, J.E. Reuter, and C.R. Goldman. 1997a. Gold mining impacts on food chain mercury in northwestern Sierra Nevada streams. *Technical Completion Report for the University of California Water Resources Center, Project W-816*, August 1997, 46 pp.

Slotton, D.G., S.M. Ayers, J.E. Reuter, and C.R. Goldman. 1997b. Cache Creek watershed preliminary mercury assessment, using benthic macro-invertebrates. *Final Report for the Central Valley Regional Water Quality Control Board and the National Science Foundation*, June 1997, 36 pp.

Slotton, D.G., S.M. Ayers, and J.E. Reuter. 1998. Marsh Creek watershed mercury assessment project: third year baseline data report with 3-yr review of selected data. *Report for Contra Costa County*, June 1998, 62 pp.

Slotton, D.G., S.M. Ayers, J.E. Reuter, and C.R. Goldman. 1999a. Lower Putah Creek 1997-1998 mercury biological distribution study. *Report for the Dept. of Environmental Health and Safety, University of California, Davis*, February 1999, 59 pp.

Slotton, D.G. and S.M. Ayers. 1999b. Pope Creek watershed 1998 biological mercury assessment. *Report for Public Resource Associates*, June 1999, 45 pp.

Heyvaert, A.H. , J.E. Reuter, D.G. Slotton, and C.R. Goldman. 2000. Paleolimnological reconstruction of historical atmospheric lead and mercury deposition at Lake Tahoe, California, Nevada. *Environmental Science and Technology*, 34:3588-3597.

Slotton, D.G., T.H. Suchanek, and S.M. Ayers 2000. Delta wetlands restoration and the mercury question. *Interagency Ecological Program Newsletter*, 13(4):40-50.

Slotton, D.G., S.M. Ayers, Reuter, J.E., and C.R. Goldman. 2001. Environmental monitoring for mercury in water, sediment, and biota in Davis Creek and Davis Creek Reservoir. *Report for Yolo County*. 113 pp. (similar reports from 1985-2000).

Reuter, J.E., D.G. Slotton , S.M. Ayers, R.P. Axler, and C.R. Goldman. Seasonal and long-term trends of mercury bioaccumulation in fish residing upstream and downstream from Davis Creek Reservoir, California (U.S.A.): 1985-1997. *Water, Air, and Soil Pollution* (submitted).

Slotton's core team includes:
Shaun M. Ayers, research associate and field/laboratory manager since 1993, who has played a vital role in the success of all aspects of the lab's heavy metal research program. As in prior projects, Ayers will supervise additional team members, working closely with the PI (Slotton);
Ronald D. Weyand, lead analytical technician, who has worked with Ayers and Slotton to expand and perfect analytical capabilities through both previously-funded CALFED-funded projects, with a decade of prior experience as lead analyst in commercial laboratories.
This core team is supplemented, as needed, with carefully chosen undergraduate and graduate student helpers. The group has extensive experience in successfully carrying out multiple projects simultaneously and will be available and prepared to devote virtually all of its resources to the 4 components of the proposed work, if funded. The lab contains all necessary analytical equipment for biotic and sediment Hg assays and non-Hg aqueous parameters; field capabilities include a variety of boats, vehicles, and a wide range of collecting gear; ample computing capability is present. All core team members are efficient and capable field and laboratory scientists; analytical capability and throughput are well tested; Slotton and Ayers will lead the field science, oversee the laboratory work, and take the lead in data reduction, interpretation, and synthesis. Weyand will continue as lead analyst.

The four Tasks have been designed to coordinate fully with related research, monitoring, restoration, and remediation projects associated with the four target areas and wider Bay-Delta watershed. Extensive support and coordination have been obtained from the agencies and institutions responsible for those projects. Every effort has been made to insure that this project involves no duplication of effort, but rather supplements, synergistically, the work of the related projects.

**D. Cost**
**1. Budget** (see attached Budget and Budget Justification forms).

**2. Cost-Sharing.**
Cost sharing partners to help fund this specific project have not been identified at this time. With regard to other funding and time commitments for the core group of personnel, all of their current funding and time commitments will be exhausted/completed before this proposed project is scheduled to begin. Both current CALFED projects will end in early-mid 2002. Two smaller grants (Davis Creek Reservoir biogeochemistry program; Lake Tahoe piscivorous fish introduction vs Hg and food web dynamics) have June 30, 2002 end dates. Potential work with USGS at Englebright Reservoir and the Yuba River will be completed prior to Fall 2002.

**E. Local Involvement.**
This research team has a long history of involvement and coordination with public and agency groups interested in the scientific aspects and/or study sites of our various research projects. Results and issues will continue to be discussed with groups including the Delta Tributaries Mercury Council. As described in the sections above, the proposed work was developed with

the full coordination and support of all of the jurisdictions, agencies, public groups, and related scientific teams that we are aware of, relevant to the four focus areas of the project. Site landowners and adjacent landowners are generally supportive, except in the case of the Prospect Island component of Task 2. Agricultural landowners to the east of this large planned wetlands restoration project have voiced concern over potential water table and levee stability issues. These concerns are not related to Hg monitoring development and implementation.

**F. Compliance with Standard Terms and Conditions.**

At the time of this submission, the University of California and CALFED have not finalized agreements on conflicting contractual language in several clauses. These areas that still need resolution are specified in the document supplied by UC and faxed to CALFED together with the Signature Form.

**G. Literature Cited.**

*(additional publications from this research team are listed above in Section C above)*

Alpers, C.N., and M.P. Hunerlach. 2000. Mercury Contamination from Historic Gold Mining in California: U.S. Geological Survey Fact Sheet FS-061-00, 6 pp.

Bodaly, R.A., V.L St Louis, M.J. Paterson, R.J.P. Fudge, B.D. Hall, D.M. Rosenberg, and J.W.M. Rudd. 1997. Bioaccumulation of mercury in the aquatic food chain in newly flooded areas, In: Sigel, A., Sigel, H., eds. Metal Ions in Biological Systems, New York, Marcel Decker, Inc. p. 259-287.

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**(Attachment A)**

# SUBTASK 5B: MERCURY BIOACCUMULATION AND TROPHIC TRANSFER IN THE CACHE CREEK WATERSHED
***(CALFED ERP PROJECT 99-B06)***

## Mid-Project Progress Report (Winter 2001)

**Darell G. Slotton**[a] and **Shaun M. Ayers**[a],
**Thomas H. Suchanek**[b], **Ron Weyand**[a], **Anne Liston**[a], and **Others**[b]

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## Summary of Subtask 5B Objectives

The primary objectives of this Task are as follows:

(1) Throughout the Cache Creek watershed, at sites spanning the range of existing aqueous mercury (Hg) exposure conditions, define potential relationships (if present) between aqueous Hg chemistry and Hg bioaccumulation in lower trophic level biota.

(2) Define relationships (if present) between Hg concentrations/speciation in relatively easily obtainable, site-specific, low trophic level bioindicator organisms (e.g. benthic aquatic invertebrates and small fishes) and corresponding concentrations in higher trophic levels that are of particular concern in relation to wildlife exposure and/or human health exposure.

(3) Characterize aqueous Hg chemistry that is representative of predominant Hg exposure levels to aquatic biota, both spatially and seasonally throughout the watershed. Additionally, provide seasonal aqueous total Hg (THg) and methyl Hg (MeHg) data to USGS from primary tributaries and Hg source regions, across a range of flow conditions, to supplement Hg loading calculations.

(4) Characterize watershed biotic Hg, both spatially and seasonally. Additionally, provide this data to USF&WS to address wildlife concerns (predation on small whole fish) and to OEHHA in relation to human health concerns (large fish muscle).

(5) Establish baseline, seasonal aqueous and biotic Hg data for representative portions of the watershed and downstream from potential remedial sites to (a) contribute to an estimate of the amount of load reduction needed to significantly reduce fish Hg bioaccumulation and (b) so that potential future changes in Hg loading and bioaccumulation may be readily assessed once remediation is undertaken.

## Summary of Hypotheses

- Relative biotic Hg accumulation in this region is linked to key natural and, particularly, mining-related point sources.
- Hg bioaccumulation by shorter-lived, lower trophic level organisms tracks short-term seasonal changes in aqueous Hg conditions.
- In-stream organisms bioaccumulate Hg primarily during active growing/feeding periods (spring through fall); winter storm flows and their large THg loads have little localized effect and primarily impact environments downstream of the watershed.
- Locally, there are predictable relationships between (1) Hg concentrations in successive trophic levels and (2) lower trophic level MeHg concentrations and corresponding aqueous Hg chemistry at those sites.

## Approaches / Methods

For the first year of sampling, we chose 8 primary and 4 secondary study sites for seasonal collections of water and representative biota (benthic invertebrates of several types, small/juvenile fishes, large fishes). Year 2000 sampling locations are displayed in Figure A-1. Sites were chosen based on: a range of aqueous Hg conditions (based on pre-project studies), presence of a majority of the trophic levels of interest, linkage to other project components, and logistical considerations. Water was characterized most frequently (8-11 samplings at primary stations) for both THg and MeHg in raw samples and the filtered fraction (£0.45 µm), together with TSS, allowing calculation of particle-bound THg and MeHg. Parallel collections for USGS provided auxiliary water quality parameters including pH, alkalinity, sulfate, major cations/anions, and other metals. Benthic aquatic insects and small/juvenile fishes were taken quarterly for THg (all) and MeHg (most invertebrates and a subset of the small fishes). Invertebrates and small/juvenile fish were analyzed whole body, primarily in multi-individual composite samples. Large fishes were collected during minimal flow periods in the late fall, with individual muscle MeHg characterized by THg analyses (it has been well documented that Hg in fish muscle tissue is generally entirely MeHg). Stable isotope analyses of a subset of the biological samples and gut content data from subsets of the fish will help to establish the structure of localized food webs and the relative trophic levels of sample organisms. The field sampling program is constrained to a 20 month period of January 2000-August 2001. For each aqueous and biotic Hg parameter, absolute concentrations and seasonal and spatial patterns will be determined. Potential predictive relationships between water chemistry and biotic Hg accumulation and between biotic trophic levels will be explored through statistical analysis of the data set generated. During the remainder of the field sampling and analytical effort (March-August 2001), collections will be made at a subset of the sites utilized during the first year, with directed sampling focused on process-oriented questions and specific hypothesis testing suggested by Year 1 results.

**Discussion of Progress To Date / Results / Preliminary Conclusions**

Aqueous Hg samples and biotic MeHg were analyzed by Battelle Laboratories, who conduct extensive QA/QC, overseen by Frontier Geosciences. Biotic THg was analyzed in our UC Davis laboratories. UC Davis THg analyses have undergone continual refinement and are performing at a high level, as summarized in QA/QC Table A-1.

*Water*

Water was collected from the primary index sites on 8-11 sampling dates between January 2000 and January 2001 (less frequently at secondary sites), representative of dominant hydrologic regimes during that time. An example of aqueous data over time is presented in Figure A-2. In Figure A-3, all of the annual aqueous THg and MeHg data for each of the sites are summarized in box plots showing upper and lower concentration ranges plus median values for each site and parameter. As expected, aqueous Hg occurred over a wide range of concentrations and partitioning among the locations, which were largely chosen on that basis. By aqueous "partitioning", we refer to raw vs 0.45 µm filtered THg and MeHg. Looking at the watershed as a whole, there was a general positive relationship between aqueous THg and all other aqueous Hg parameters, including MeHg. Among sites which supported piscivorous fishes, median aqueous raw THg spanned over an order of magnitude, from concentrations of <1-3 ng/L at control sites (i.e. N Fk Cache Ck, Upper Bear Ck) to approximately 50 ng/L at mid Bear Creek. Dramatically higher THg occurred during storm flows and closer to mine sites (at sampling locations such as Sulfur Ck and Harley Gulch, which did not contain fish). Corresponding median concentrations for MeHg ranged between approximately 0.08 ng/L at control sites and 0.35 ng/L at mid Bear Creek. Significantly higher concentrations were found at some of the near-mine sites. A general seasonal pattern was indicated in the main stem of Cache Ck, with reservoir release patterns influencing the effect of higher Hg tributary input. The proportional contribution of these tributary sources decreased when main stem flows were dominated by reservoir releases. Seasonal patterns were also suggested at tributary sites, with elevated THg and MeHg concentrations associated with early winter storm flows. Seasonal summer elevations were also apparent at some tributary sites, possibly attributable to dry season evaporative concentration, enhanced methylation, and/or a proportional increase in the percentage of geothermal inputs. We believe that it will be important, at a subset of the sites, to continue aqueous collections through winter 2001 and into the 2001 dry season to test these developing patterns, to improve our estimation of seasonal exposure levels, and to provide a minimal indication of inter-annual variation. Additional aqueous Hg collections, made across a range of flow conditions, are also needed to improve mass loading calculations.

*Benthic Invertebrates*

Collections of benthic invertebrates were made at primary sites in February, May, August, and November of 2000 and in February 2001, and at secondary sites in May and November 2000. All have been analyzed for THg. To date, samples have been analyzed for both THg and MeHg from February, May, and August 2000. Data for THg, MeHg, and the total:methyl ratio are presented for individual invertebrate taxa in Tables A-2a and A-2b. In Figure A-4, the general trends between sites and seasons are summarized with composite values of invertebrate MeHg, consisting of the mean MeHg of taxa including Hydropsychid caddisfly larvae and all co-occurring predatory samples. With the exception of herbivorous species, which were clearly lower, Hydropsychids and the other predatory taxa exhibited relatively consistent MeHg in individual site samplings. This was in marked contrast to our Sierra Nevada studies, where caddisfly larvae were consistently lower in Hg than predatory species such as stoneflies, which were consistently lower than top invertebrate predators such as hellgrammites. We are investigating the possibility that the Cache Creek organisms are more trophically similar than their Sierra Nevada counterparts. For the purposes of this mid-project report, the composite invertebrate MeHg measure was felt to be the best and most consistent invertebrate MeHg measure for use in inter-site, temporal, and aqueous Hg comparisons. With the expanded data set including the final year of sampling, it may be feasible to statistically investigate trends in specific taxa. In Figure A-5, seasonal trends are plotted for individual biotic taxa against aqueous MeHg, demonstrating apparently strong general correspondence.

Preliminary findings from the invertebrate Hg data to date include the following: (1) Cache watershed benthic invertebrate THg contained relatively high proportions of MeHg (77-93% in 60 diverse paired analyses, Fig. A-6), except at the most extreme, near-mine locations (17-39%, Fig. 7); (2) Invertebrate Hg may track aqueous exposure conditions on a fairly rapid time scale of weeks/months (e.g. the seasonal changes exhibited by Hydropsychid caddisfly larvae at Cache Creek below the Clear Lake outflow and exhibited by most invertebrate samples at mid Bear Creek and Sulfur Creek, Table A-2, Fig. A-5); and (3) On a watershed-wide basis at sites with highly variable Hg exposure conditions, aquatic insect MeHg, based upon analyses to date, demonstrated a general correspondence with certain aqueous Hg concentrations.

We address the issue of aqueous Hg vs bioindicator invertebrate MeHg in Figures A-8, 9. For these comparisons, we utilized the composite Hydropsychid + predatory taxa MeHg value for each site sampling, as described above. These composite invertebrate values were regressed against the most representative corresponding aqueous Hg concentrations available for each invertebrate site sampling. Aqueous concentrations were averaged from collections nearest in time to the corresponding invertebrate collection, with up to three samplings averaged for periods demonstrating significant variability.

In Figure A-8, composite invertebrate MeHg is plotted as a function of corresponding aqueous Hg concentration for raw and filtered THg and MeHg, as well as calculated particulate aqueous THg and MeHg. An appropriate statistical approach to the aqueous Hg vs invertebrate MeHg relationships was determined to be log-log treatment of the data, with corresponding power regressions. Log-log transformation expands the otherwise clustered distribution of lower-end points, while also giving less individual weight to high-end outliers in this diverse data set. The resulting power regression $R^2$ values for the aqueous Hg vs invertebrate MeHg data range from 0.28 to 0.79, with five of six comparisons demonstrating $R^2$ values between 0.50 and 0.79. This indicates that, when comparing these highly divergent Hg exposure sites throughout the watershed, a significant portion of the overall variation in the invertebrate bioindicator MeHg data may be attributable to aqueous Hg concentrations. We recognize the potential limitations of these correlations. There is a strong likelihood of co-correlations among the aqueous Hg parameters, as noted in the water discussion above. Additionally, despite the relative neutralizing effect of log-log transformation, the correlations may in part be influenced by the persisting effect of clusters of low concentration vs high concentration data.

Interestingly, the lowest $R^2$ value (0.28) was found for aqueous particulate MeHg, which we had hypothesized as potentially the best predictor of invertebrate MeHg. This may in part be due to the propagation of error near the levels of detection for raw MeHg, filtered MeHg, and TSS, all of which are used in the calculation of particulate MeHg. It is notable that the strongest correlations were found for filtered THg (0.76) and aqueous particulate THg (0.79). These strong correlations included winter storm pulse data and suggest that, in this system, seasonal THg loading may in fact be highly relevant to bioaccumulation. The watershed-wide correlations and/or those for specific index locations will be supplemented by additional sets of seasonal data (fall 2000 and winter-summer 2000-2001). For the aqueous methyl parameters, deviations about the trend lines indicate the potential importance of other ecological variables. Taken in total, when comparing these highly divergent Hg exposure sites throughout the watershed, the aqueous vs invertebrate data indicate that aqueous Hg parameters may account for a substantial amount, though not all, of the variability seen in invertebrate MeHg bioaccumulation, with the remainder due to additional factors potentially including habitat, microbiology, ancillary chemistry, and food web structure. Additionally, it is not clear that the general relationships between invertebrate MeHg and aqueous Hg parameters, on a watershed-wide basis, can be extrapolated to individual sites. In conjunction with ongoing work, we hope to obtain sufficient data to test these trends at representative individual sites.

In Figure A-9, bioaccumulation factors (BAFs) have been calculated for composite aquatic insect MeHg vs aqueous MeHg. As is standard for this calculation, the invertebrate MeHg concentrations have been converted to a wet weight basis, using measures of moisture percentage that we have determined for each of the primary taxa. Bioaccumulation factors quantify the proportion of bioaccumulated MeHg (µg/g = ppm) relative to the corresponding aqueous concentration (ng/L = pptr), resulting in values in the range of 10,000 to over 1,000,000. Consistent with standard presentations of this type of data, the values are displayed in log form. The mean BAF levels for each site are arranged in order of increasing absolute invertebrate MeHg. The bioaccumulation factors ranged between $10^5$ and over $10^6$ (or BAF = 5-6+), over an order of magnitude difference. This indicates that the relationship between aqueous MeHg and invertebrate MeHg is not consistent among the varied sites. However, distinct site groupings are apparent. Interestingly, the highest bioaccumulation factors (5.67-6.04) occurred at all of the near-mine, highly Hg elevated sites, including Harley Gulch, mid Bear Creek, Davis Creek both above and below Davis Creek Reservoir, and Sulfur Creek. The next highest bioaccumulation factors (5.28-5.49) occurred at the opposite end of the aqueous and invertebrate MeHg concentration spectrum, at the control sites Middle Creek, North Fork Cache Creek, and upper Bear Creek. The 4 main-stem Cache Creek sites consistently demonstrated the lowest MeHg bioaccumulation factors in the watershed (5.01-5.23). These inter-site differences could be due to actual differences in bioaccumulation efficiency, to differences in standing biomass which could lead to relative biodilution, or other factors. Of particular interest for future study is the possibility that the relative bioavailability of aqueous MeHg to the aquatic food web may be impacted by the relative presence/absence of potential MeHg aqueous ligands such as DOC. In any case, the 10 fold variation in MeHg bioaccumulation factors provides additional indication that aqueous Hg concentrations (including aqueous MeHg) cannot alone predict corresponding bioaccumulation in this system.

*Fish*

Collections of small fishes were made at primary sites in February, May, August, and November of 2000, and February 2001, and at secondary sites in May and November 2000. Identical species were not present at all of the sites. The highest Hg sites (which were tributaries near mines), contained no fish and several other sites contained only small fishes. Small fish Hg analyses were postponed awaiting compositing decisions, which have recently been made based on a series of preliminary analytical trials; analyses are proceeding at this time. The first logistically feasible opportunity to sample large fishes at main stem Cache Creek sites occurred in December 2000, during a period of halted water releases from Clear Lake and Indian Valley Reservoir. Large fish sampling was conducted throughout the watershed at that time. Analyses of muscle samples from approximately 200 individual large fish were recently completed. The resulting data are consistent with general aqueous and invertebrate spatial trends noted throughout the watershed to date. Large fish muscle Hg concentrations were generally highest at sites showing most elevated levels of aqueous and invertebrate THg and MeHg and lowest at sites demonstrating the lowest corresponding aqueous and invertebrate Hg. In Figure A-10, fresh/wet weight muscle Hg is plotted against fish size for three species of piscivorous fishes taken in December 2000 at several diverse stream sites in the watershed (four of the six sites are plotted, to avoid over-cluttering the figure). Size-normalized concentrations are compared in Figure A-11. The normalized concentrations are strictly for inter-site comparison and are based on an assumption of similar growth rates across sites (to be assessed through aging studies). The normalized fish Hg values are not representative of the highest or even the mean Hg levels at each site. A relatively small inter-comparable fish size was utilized (200 g) in order to include the range of sample sizes obtained at each of the six large fish sites.

From the piscivorous fish data, several points can be made, including: (a) strong size vs Hg correlations were found at each site ($R^2$ ranged from 0.69-0.95), (b) fish size:Hg concentration trends differed significantly between many of the sites, (c) some highly elevated fish Hg concentrations, well above any health guidelines, are present in the watershed, and (d) native Sacramento pikeminnows and smallmouth bass demonstrated similar size:Hg trends where they overlapped, indicating that pikeminnows may be useful analogs for bass at watershed sites where bass are not available.

Anomalies were also present in the large fish data, indicating again that aqueous concentrations alone cannot entirely account for corresponding bioaccumulation. In particular, the fish Hg at Upper Bear Creek, relative to the low concentrations of all measured aqueous Hg parameters there, was unusually elevated. This low gradient, clear water, high nutrient, high biological activity site appeared to be a prime mercury methylation habitat, regardless of loading. We note that this site contained the lowest median aqueous THg of all the watershed sampling sites; Hg loading here may be largely attributable to atmospheric deposition. The most obvious explanation for the relatively elevated fish Hg at this site is that they swam upstream from highly contaminated mid Bear Creek. However, we believe that the pikeminnows collected at upper Bear Creek were resident fish, as they exhibited a consistent size:Hg trend that differed from the one seen at mid Bear Creek and THg in small fish and MeHg in invertebrates also showed elevated levels at this site. We hypothesize that we may have simply missed the localized aqueous peak in Hg methylation at this secondary sampling site during Year 1, when we sampled only in spring and fall. Additionally, it is possible that photo-demethylation may have lowered our estimate of aqueous MeHg concentrations (collected during the day).

The large fish data further document a highly divergent set of Hg bioaccumulation conditions throughout the Cache Creek watershed.

We have conducted some preliminary downstream bioindicator sampling of the three tributaries in the watershed with the highest aqueous and biotic Hg concentrations, in addition to routine upstream index sampling nearer to the Hg source regions on each of these tributaries. In all three cases, dramatically lower biotic Hg was found near the downstream confluence with Cache Creek, as compared to levels nearer the upstream sources (Figure A-12). In a previous study, we found Harley Gulch aquatic insect Hg at concentrations of 5-23 $\mu g\ g^{-1}$ (ppm, dry wt) near the Turkey Run and Abbott mine sites. The mean level in our primary watershed invertebrate bioindicator, *Hydropsyche* (a ubiquitous net spinning caddisfly larva), was 9.64 $\mu g\ g^{-1}$. Several miles downstream, near the confluence with Cache Creek, *Hydropsyche* Hg was found to be 0.52 $\mu g\ g^{-1}$, 19-fold lower. A similar pattern was noted along Davis Creek, which drains a long-studied reservoir impacted by historic Hg mines. In the current study, California roach (*Hesperoleucus symmetricus*, small minnow fish) were significantly higher in Hg upstream near Davis Creek Reservoir (mean THg = 1.54 $\mu g\ g^{-1}$, dry wt; mean MeHg = 1.32 $\mu g\ g^{-1}$), relative to matching samples collected downstream near the confluence with Cache Creek (mean THg = 0.41 $\mu g\ g^{-1}$; mean MeHg = 0.31 $\mu g\ g^{-1}$). On Bear Creek, which transports the discharge from the Sulfur Creek complex of Hg mines and geothermal sources, we have found a similar, strong downstream trend, particularly in rapidly growing species with short lifespans. All of these preliminary findings indicate that regulatory monitoring and remediation monitoring downstream of major cleanup targets may produce significantly divergent results, as a function of sampling location, on a relatively localized spatial scale.

Analyses will soon be completed on the quarterly small fish samples, which are anticipated to provide a key link in the data base. Additionally, to better understand Hg bioaccumulation linkages, we have initiated the sampling of algae, periphyton/diatom “biofilm”, and sediments at selected sites. We feel that it is important, at a select subset of the sites, to continue collections through the remainder of the 20 month limited sampling window in order to test developing patterns, improve our estimation of biotic Hg levels at key sites, and provide a minimal indication of inter-annual variation. Additionally, because aqueous Hg exposure levels appear to change fairly significantly throughout the year at several of the sites, additional directed tracking of corresponding aqueous and biotic Hg should provide an improved indication of localized bioaccumulation response (or lack thereof) to altered aqueous concentrations. This information could be very useful in potential regulatory and remedial decision processes.

## Potential for Future Research / Recommended Changes in Existing Research Program

This is a work in progress. Throughout the project to date, we have made a series of alterations to the initial study design in response to concentration findings, presence/absence of various biota, and other factors. Based on results from Year 1 and input from the Scientific Review team and others, ongoing collections and analytical efforts through August 2001 will consist of directed sampling at a limited subset of the sites utilized in 2000. This ongoing work focuses on process-oriented questions and the testing of specific hypotheses suggested by first year results. Year 2 work includes:

- Intensive comparative work at 2-3 divergent sites (including mid Bear Creek and Cache Creek at Rumsey), investigating differences in habitat, aqueous and sediment Hg, ancillary chemistry, and food webs, as they may relate to ultimate differences in bioaccumulation.

- Higher frequency (monthly) sampling of water, invertebrates, and small fish at 2-3 sites which show strong seasonality, to better assess localized rates of Hg bioaccumulation and/or depuration. Overlap with above-named intensive sites. Accumulate sufficient data from mid Bear Creek and Cache Creek at Rumsey to assess site-specific correlations between aqueous and biotic Hg. Investigate seasonality, absolute bioaccumulation levels, and bioaccumulation factors in instar 1-3 *Hydropsyche* vs typical larger individuals.

- Possible transect collections for a limited subset of analyses, from one or both of the primary mine source regions downstream, to investigate the localized impact of the Hg source regions along downstream transects.

- Investigate inter-annual variability in aqueous and biotic Hg, in conjunction with the above sampling, at sites sampled in both Year 1 and Year 2.

We feel that the best use of our remaining funding and effort is to focus on these and related issues within the Cache Creek watershed, as advised by the reviewers. The Scientific Review team additionally urged that we conduct comparative studies in the Sierra Nevada gold mining region. We are addressing that suggestion with a proposal for limited, comparable work in the Cosumnes River watershed.

Following this fairly brief initial Cache Creek watershed study, recommended future work to help direct regulatory and remedial actions in this watershed (and others) includes: (a) further exploration of the relationship between specific aqueous Hg fractions and bioaccumulation; (b) further exploration of the use of various bioindicators as integrators of aqueous concentrations and as proxies for bioaccumulation in large fish; (c) investigations of the potentially critical roles of location, habitat, additional aqueous parameters, and food web structure on Hg cycling and bioaccumulation; and (d) close monitoring of any remediation work at upstream point sources of Hg by measuring the responses in downstream Hg loading and bioaccumulation, relative to the baseline data collected in this and related studies.

## Table A-1. Laboratory QA/QC summary (to date) for UC Davis Cache Creek Task 5B total mercury analyses.

| | | | | | | *Standard Reference Materials* | | |
|---|---|---|---|---|---|---|---|---|
| | Std Curve R^2 | Lab Split RPD | Field Dup. RPD | Spike Recoveries | Lab Cont. Std. Recoveries | TORT-2 Lobster | DOLT-2 Dogfish | NIST 2976 Mussel |
| Certified Level (ppm) | | | | | | 0.27±0.02 | 2.14±0.28 | 0.061±0.004 |
| Ideal Recovery | 1.000 | (0%) | (0%) | (100%) | (100%) | (100%) | (100%) | (100%) |
| Control Range (%) | (>0.975) | <25% | <25% | 75-125% | 75-125% | 75-125% | 75-125% | 75-125% |
| Tracking Method | | Control Chart | | Control Chart | Control Chart | Control Chart | Control Chart | Control Chart |
| Control Range (ppm) | | | | | | 0.20-0.34 | 1.61-2.68 | 0.05-0.08 |
| Recoveries (%) | 0.9988-0.9995 | 0.4%-7.3% | 1.6%-38.4% | 86%-102% | 104%-110% | 96%-111% | 96%-105% | 100% |
| Recoveries (ppm) | | | *(higher near MDL)* | | | 0.26-0.30 | 2.06-2.25 | 0.06-0.06 |
| (n) | n=6 | n=12 | n=16 | n=12 | n=8 | n=12 | n=12 | n=12 |
| Mean Recoveries (%) | 0.9992 | 3.3% | 6.6% | 95.7% | 106.7% | 103.4% | 99.8% | 100% |
| Mean Recoveries (ppm) | | | | | | 0.28 | 2.13 | 0.06 |

**Fig. A-1. Cache Creek Watershed: UC Davis First Year Sampling Sites**

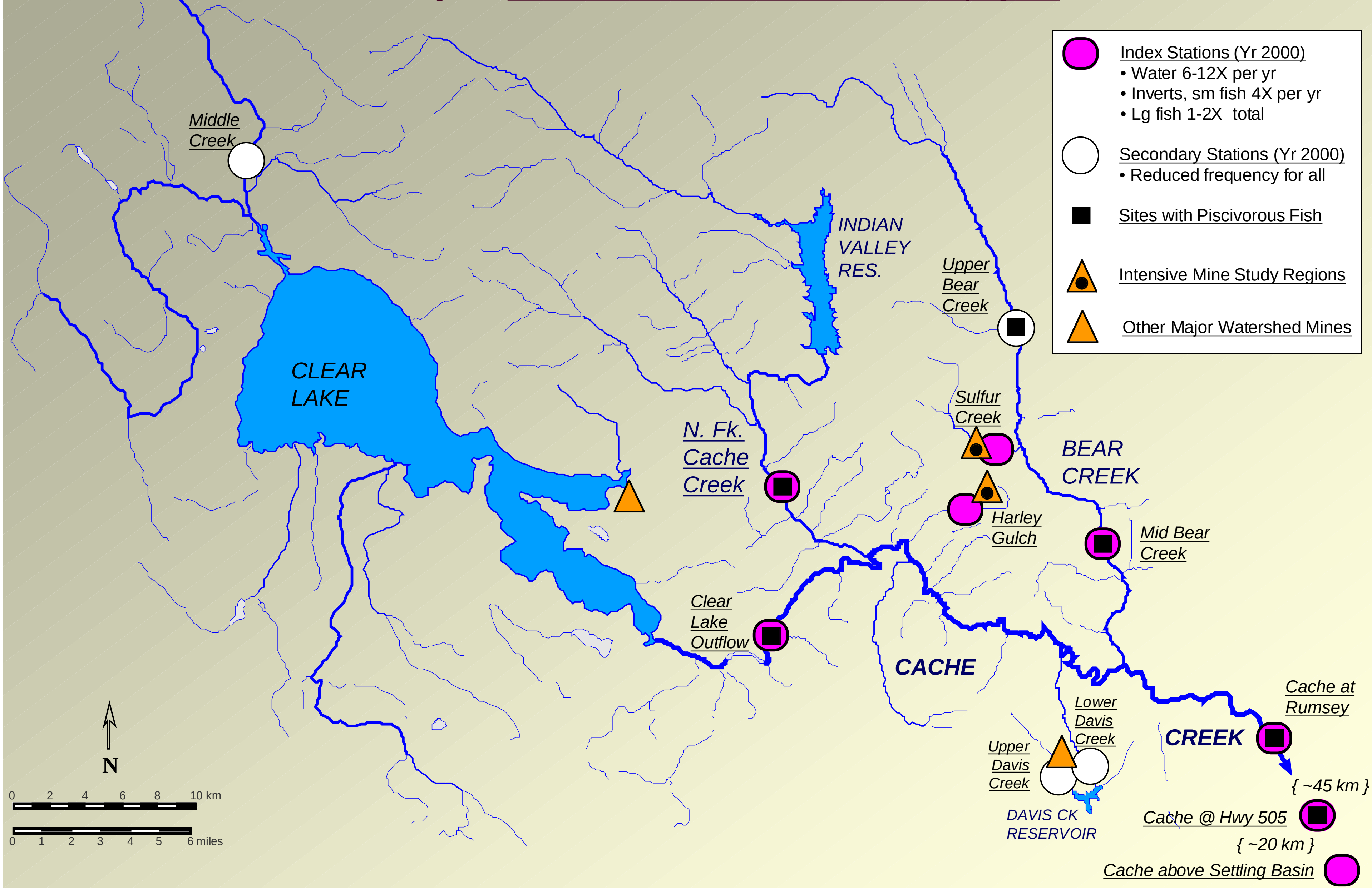
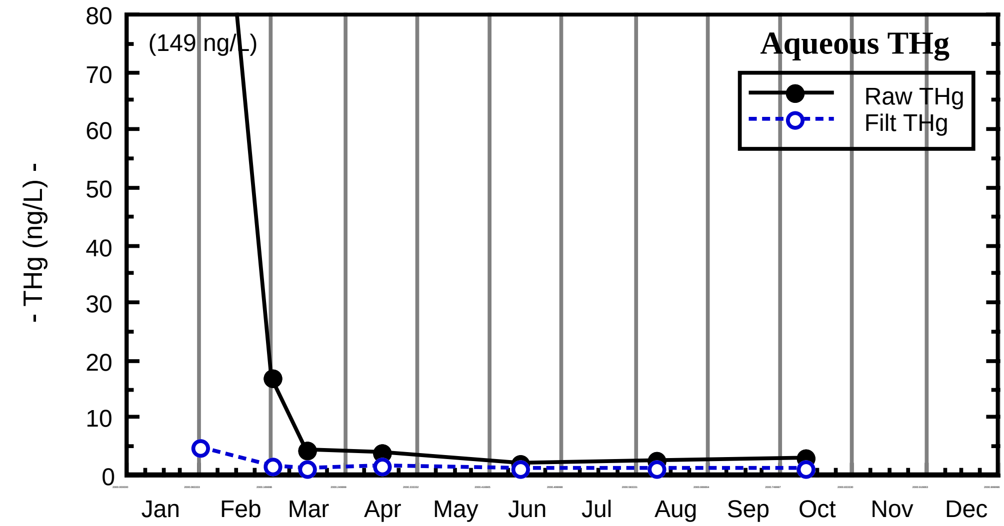


**Figure A-2. Aqueous Hg over time at a representative low-Hg/background site.**

**STATION 520 NFC (NORTH FORK CACHE CREEK)**
**YEAR 2000 WATER SAMPLES**



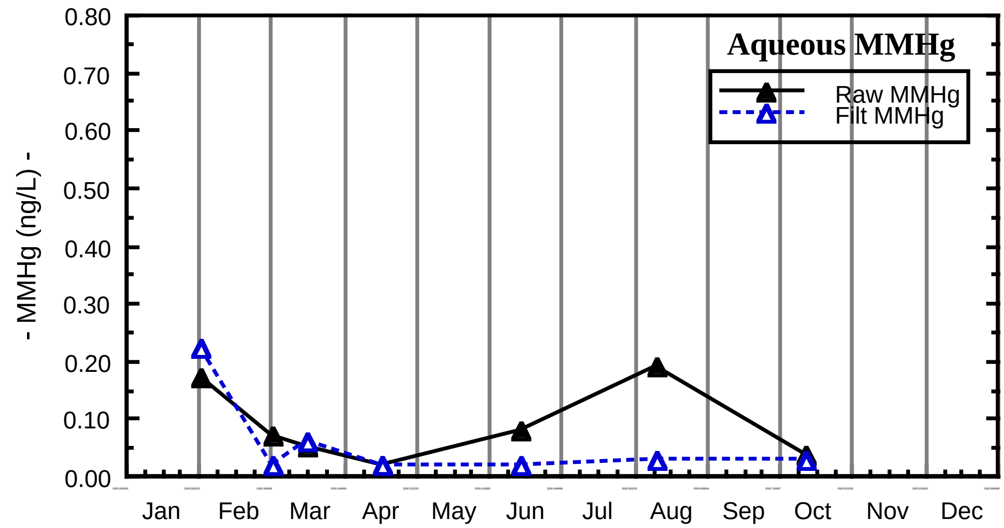



**Figure A-3.**

**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)*

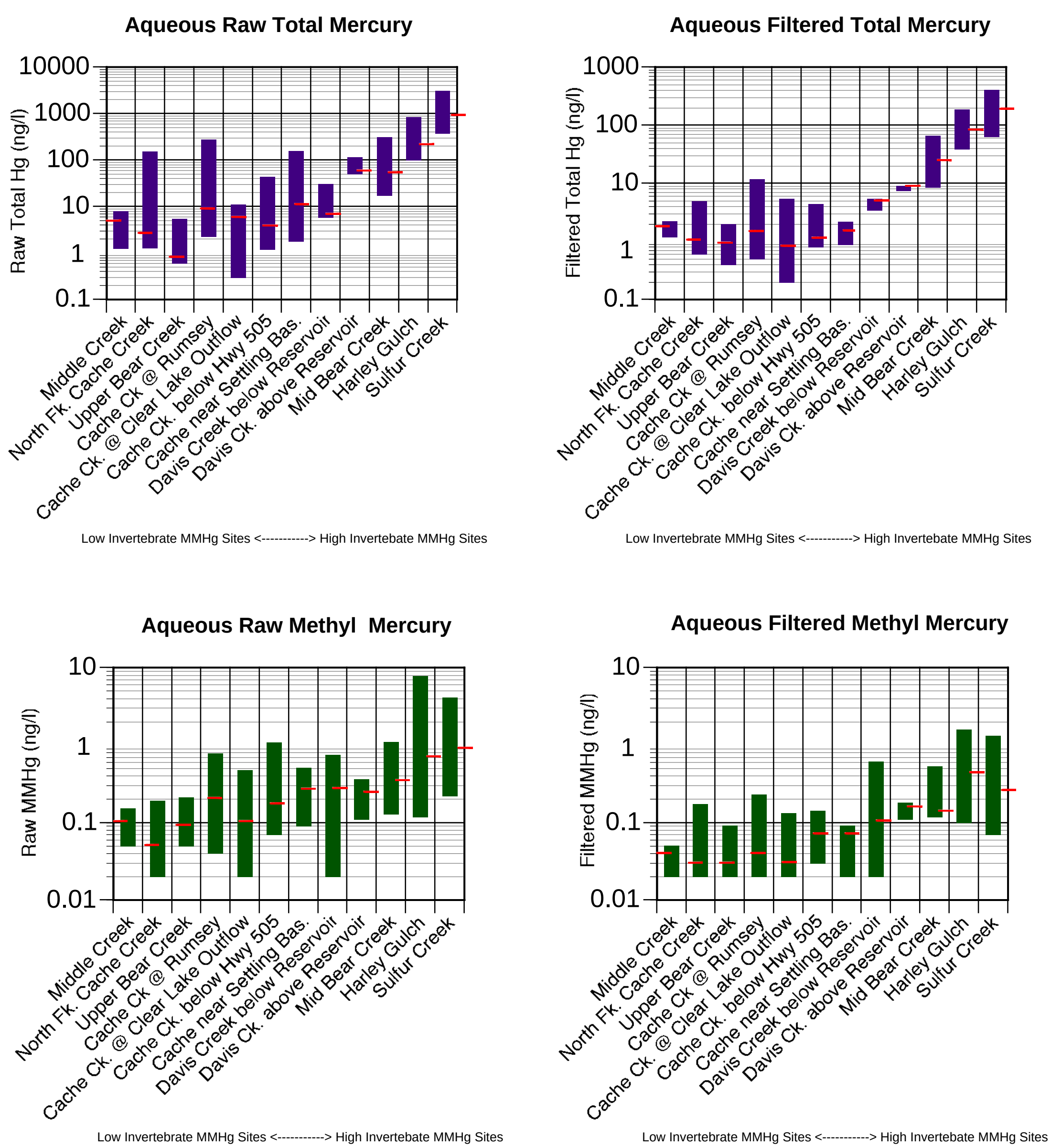
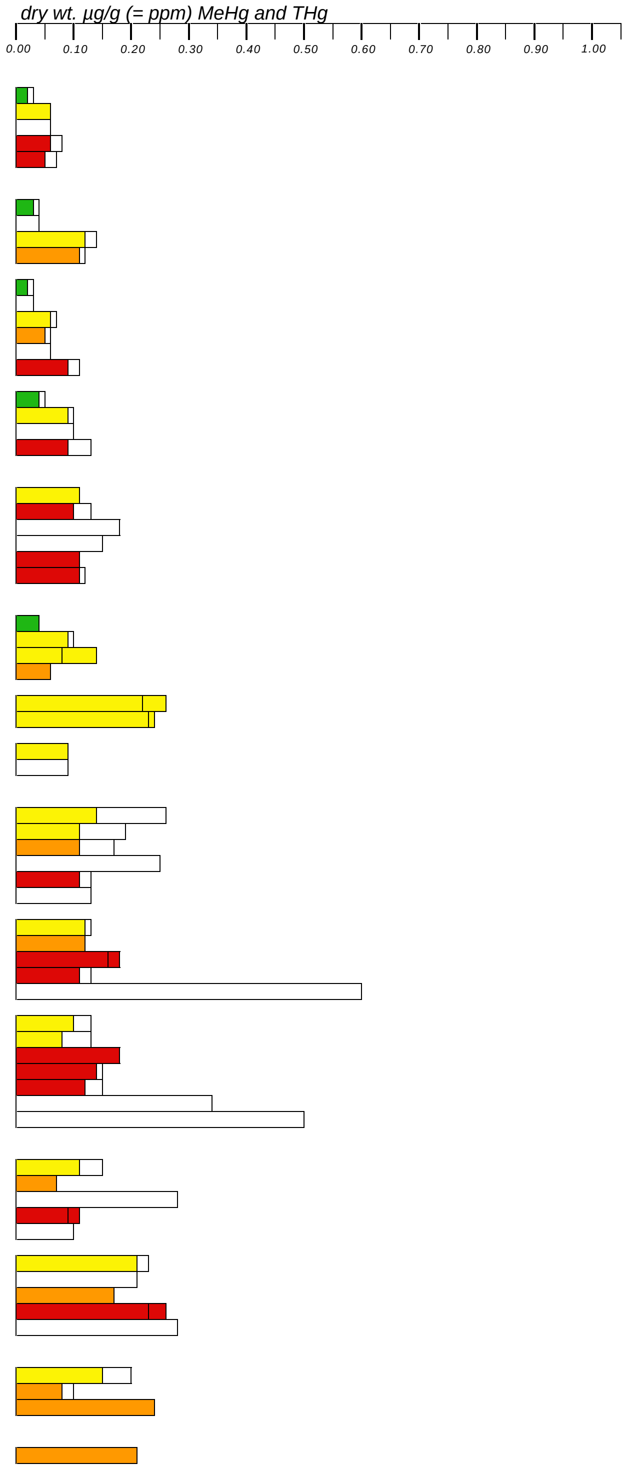


**Table A-2(a). Invertebrate methyl and total mercury in Feb-Aug, 2000 Cache Ck watershed samples.**
(THg in white; methyl fraction denoted with color, color coding denotes invertebrate trophic levels)
(level 1 = herbivores, 2 = drift feeders (*Hydropsyche* ), 3 = intermediate predators, 4 = top predators)
(µg/g = ppm; *dry wt. ug/g = app. 5x wet wt concentration* )

| Location | Sample Date | Type | Trophic Level | µg/g Hg in dry sample THg | µg/g Hg in dry sample MeHg | Methyl % |
|---|---|---|---|---|---|---|
| Middle Creek | 24-May-00 | Ephemerellidae | 1 | 0.03 | 0.023 | 73% |
| Middle Creek | 24-May-00 | Hydropsychidae | 2 | — | 0.047 | — |
| Middle Creek | 24-May-00 | Aeshnidae | 4 | 0.06 | | |
| Middle Creek | 24-May-00 | Naucoridae | 4 | 0.08 | 0.062 | 82% |
| Middle Creek | 24-May-00 | Corydalidae | 4 | 0.07 | 0.054 | 79% |
| North Fk. Cache Ck. | 25-Feb-00 | Pteronarcyidae | 1 | 0.04 | 0.032 | 86% |
| North Fk. Cache Ck. | 25-Feb-00 | Pteronarcyidae (FDup) | 1 | 0.04 | | |
| North Fk. Cache Ck. | 25-Feb-00 | Hydropsychidae | 2 | 0.14 | 0.118 | 82% |
| North Fk. Cache Ck. | 25-Feb-00 | Perlodidae | 3 | 0.12 | 0.115 | 94% |
| North Fk. Cache Ck. | 8-May-00 | Baetidae | 1 | 0.03 | 0.023 | 66% |
| North Fk. Cache Ck. | 8-May-00 | Pteronarcyidae | 1 | 0.03 | | |
| North Fk. Cache Ck. | 8-May-00 | Hydropsychidae | 2 | 0.07 | 0.055 | 76% |
| North Fk. Cache Ck. | 8-May-00 | Perlodidae | 3 | 0.06 | 0.053 | 88% |
| North Fk. Cache Ck. | 8-May-00 | Perlodidae (FDup) | 3 | 0.06 | | |
| North Fk. Cache Ck. | 8-May-00 | Tipulidae | 4 | 0.11 | 0.093 | 82% |
| North Fk. Cache Ck. | 7-Aug-00 | Pteronarcyidae | 1 | 0.05 | 0.043 | 80% |
| North Fk. Cache Ck. | 7-Aug-00 | Hydropsychidae | 2 | 0.10 | 0.088 | 85% |
| North Fk. Cache Ck. | 7-Aug-00 | Hydropsychidae (FDup) | 2 | 0.10 | | |
| North Fk. Cache Ck. | 7-Aug-00 | Tipulidae | 4 | 0.13 | 0.090 | 70% |
| Upper Bear Creek | 8-May-00 | Hydropsychidae | 2 | 0.11 | 0.106 | 93% |
| Upper Bear Creek | 8-May-00 | Naucoridae | 4 | 0.13 | 0.101 | 80% |
| Upper Bear Creek | 8-May-00 | Gomphidae (sp B) | 4 | 0.18 | | |
| Upper Bear Creek | 8-May-00 | Gomphidae | 4 | 0.15 | | |
| Upper Bear Creek | 8-May-00 | Libellulidae | 4 | 0.11 | 0.112 | 98% |
| Upper Bear Creek | 8-May-00 | Tipulidae | 4 | 0.12 | 0.111 | 92% |
| Cache Ck. @ Clear Lake Outflow | 24-Feb-00 | Baetidae | 1 | 0.04 | 0.038 | 89% |
| Cache Ck. @ Clear Lake Outflow | 25-Feb-00 | Hydropsychidae | 2 | 0.10 | 0.092 | 91% |
| Cache Ck. @ Clear Lake Outflow | 25-Feb-00 | Hydropsychidae (FDup) | 2 | 0.08 | 0.138 | 170% |
| Cache Ck. @ Clear Lake Outflow | 25-Feb-00 | Coenagrionidae | 3 | — | 0.059 | — |
| Cache Ck. @ Clear Lake Outflow | 24-May-00 | Hydropsychidae | 2 | 0.22 | 0.261 | 118% |
| Cache Ck. @ Clear Lake Outflow | 24-May-00 | Hydropsychidae | 2 | 0.23 | 0.241 | 105% |
| Cache Ck. @ Clear Lake Outflow | 7-Aug-00 | Hydropsychidae | 2 | 0.09 | 0.086 | 93% |
| Cache Ck. @ Clear Lake Outflow | 7-Aug-00 | Hydropsychidae (FDup) | 2 | 0.09 | | |
| Cache Ck. @ Rumsey | 17-Feb-00 | Hydropsychidae (med) | 2 | 0.26 | 0.142 | 56% |
| Cache Ck. @ Rumsey | 17-Feb-00 | Hydropsychidae (lg) | 2 | 0.19 | 0.110 | 58% |
| Cache Ck. @ Rumsey | 17-Feb-00 | Perlodidae | 3 | 0.17 | 0.171 | 99% |
| Cache Ck. @ Rumsey | 17-Feb-00 | Gomphidae | 3 | 0.25 | | |
| Cache Ck. @ Rumsey | 17-Feb-00 | Corydalidae (med) | 4 | 0.13 | 0.111 | 84% |
| Cache Ck. @ Rumsey | 17-Feb-00 | Corydalidae (lg) | 4 | 0.13 | | |
| Cache Ck. @ Rumsey | 9-May-00 | Hydropsychidae | 2 | 0.13 | 0.118 | 92% |
| Cache Ck. @ Rumsey | 9-May-00 | Perlodidae | 3 | 0.12 | 0.122 | 103% |
| Cache Ck. @ Rumsey | 9-May-00 | Corydalidae | 4 | 0.16 | 0.178 | 114% |
| Cache Ck. @ Rumsey | 9-May-00 | Corydalidae | 4 | 0.13 | 0.111 | 88% |
| Cache Ck. @ Rumsey | 9-May-00 | Nepidae | 4 | 0.60 | | |
| Cache Ck. @ Rumsey | 1-Aug-00 | Hydropsychidae | 2 | 0.13 | 0.100 | 75% |
| Cache Ck. @ Rumsey | 1-Aug-00 | Hydropsychidae (FDUP) | 2 | 0.13 | 0.084 | 64% |
| Cache Ck. @ Rumsey | 1-Aug-00 | Naucoridae | 3 | — | 0.179 | — |
| Cache Ck. @ Rumsey | 1-Aug-00 | Corydalidae (med/lg) | 4 | 0.15 | 0.137 | 94% |
| Cache Ck. @ Rumsey | 1-Aug-00 | Corydalidae (Xlg) | 4 | 0.15 | 0.116 | 76% |
| Cache Ck. @ Rumsey | 1-Aug-00 | Belastomatidae | 4 | 0.34 | | |
| Cache Ck. @ Rumsey | 1-Aug-00 | Belastomatidae | 4 | 0.50 | | |
| Cache Ck. below Hwy 505 | 22-May-00 | Hydropsychidae | 2 | 0.15 | 0.108 | 71% |
| Cache Ck. below Hwy 505 | 22-May-00 | Calopterygidae | 3 | 0.07 | 0.068 | 92% |
| Cache Ck. below Hwy 505 | 22-May-00 | Gomphidae | 4 | 0.28 | | |
| Cache Ck. below Hwy 505 | 22-May-00 | Libellulidae | 4 | 0.09 | 0.109 | 118% |
| Cache Ck. below Hwy 505 | 22-May-00 | Libellulidae | 4 | 0.10 | | |
| Cache Ck. below Hwy 505 | 1-Aug-00 | Hydropsychidae | 2 | 0.23 | 0.205 | 90% |
| Cache Ck. below Hwy 505 | 1-Aug-00 | Hydropsychidae (FDUP) | 2 | 0.21 | | |
| Cache Ck. below Hwy 505 | 1-Aug-00 | Calopterygidae | 3 | — | 0.169 | — |
| Cache Ck. below Hwy 505 | 1-Aug-00 | Naucoridae | 4 | 0.23 | 0.264 | 113% |
| Cache Ck. below Hwy 505 | 1-Aug-00 | Belastomatidae | 4 | 0.28 | | |
| Cache Ck. Btw Yolo and Settling Bas. | 22-May-00 | Hydropsychidae | 2 | 0.20 | 0.147 | 73% |
| Cache Ck. Btw Yolo and Settling Bas. | 22-May-00 | Calopterygidae | 3 | 0.10 | 0.078 | 76% |
| Cache Ck. Btw Yolo and Settling Bas. | 22-May-00 | Coenagrionidae | 3 | — | 0.235 | — |
| Cache Ck. Btw Yolo and Settling Bas. | 22-May-00 | Procambarus | | 0.17 | | |
| Cache Ck. Btw Yolo and Settling Bas. | 1-Aug-00 | Calopterygidae | 3 | — | 0.209 | — |

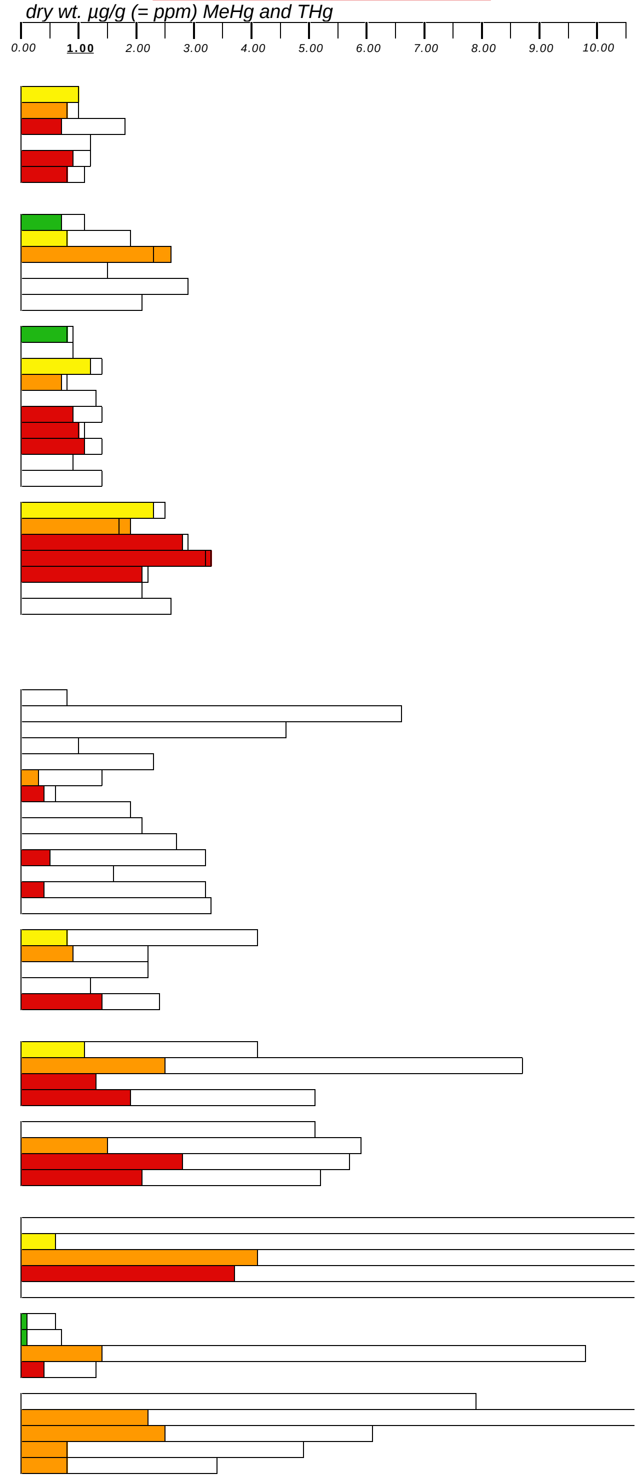


## Table A-2(b). Invertebrate methyl and total mercury in Feb-Aug, 2000 Cache Ck watershed samples

(THg in white; methyl fraction denoted with color, color coding denotes invertebrate trophic levels)
(level 1 = herbivores, 2 = drift feeders (*Hydropsyche* ), 3 = intermediate predators, 4 = top predators)
(µg/g = ppm; *dry wt. ug/g = app. 5x wet wt concentration* )

****** NOTE 10x SCALE VS TABLE 2a******

dry wt. µg/g (= ppm) MeHg and THg




| Location | Sample Date | Type | Trophic Level | µg/g Hg in dry sample THg | MeHg | Methyl % |
|---|---|---|---|---|---|---|
| Davis Ck. below Davis Ck. Res. | 17-May-00 | Hydropsychidae | 2 | — | 0.990 | — |
| Davis Ck. below Davis Ck. Res. | 17-May-00 | Coenagrionidae (sp L) | 3 | 0.95 | 0.760 | 80% |
| Davis Ck. below Davis Ck. Res. | 17-May-00 | Naucoridae | 4 | 1.84 | 0.737 | 40% |
| Davis Ck. below Davis Ck. Res. | 17-May-00 | (Mixed Dragonflies) | 4 | 1.17 | | |
| Davis Ck. below Davis Ck. Res. | 17-May-00 | Corydalidae | 4 | 1.24 | 0.871 | 70% |
| Davis Ck. below Davis Ck. Res. | 17-May-00 | Corydalidae | 4 | 1.10 | 0.823 | 75% |
| Mid Bear Creek | 14-Mar-00 | Elmidae | 1 | 1.09 | 0.704 | 65% |
| Mid Bear Creek | 14-Mar-00 | Hydropsychidae | 2 | 1.90 | 0.806 | 42% |
| Mid Bear Creek | 14-Mar-00 | Coenagrionidae | 3 | 2.34 | 2.554 | 109% |
| Mid Bear Creek | 14-Mar-00 | Gomphidae (sp B) | 4 | 1.50 | | |
| Mid Bear Creek | 14-Mar-00 | Gomphidae (med) | 4 | 2.90 | | |
| Mid Bear Creek | 14-Mar-00 | Gomphidae (lg) | 4 | 2.06 | | |
| Mid Bear Creek | 9-May-00 | Elmidae | 1 | 0.94 | 0.754 | 80% |
| Mid Bear Creek | 9-May-00 | Siphlonuridae | 1 | 0.89 | | |
| Mid Bear Creek | 9-May-00 | Hydropsychidae | 2 | 1.44 | 1.220 | 84% |
| Mid Bear Creek | 9-May-00 | Coenagrionidae | 3 | 0.83 | 0.682 | 82% |
| Mid Bear Creek | 9-May-00 | Coenagrionidae (sp S) | 3 | 1.28 | | |
| Mid Bear Creek | 9-May-00 | Naucoridae | 4 | 1.41 | 0.926 | 66% |
| Mid Bear Creek | 9-May-00 | Libellulidae | 4 | 1.13 | 0.988 | 88% |
| Mid Bear Creek | 9-May-00 | Libellulidae (FDup) | 4 | 1.41 | 1.130 | 80% |
| Mid Bear Creek | 9-May-00 | Libellulidae (sp B) | 4 | 0.94 | | |
| Mid Bear Creek | 9-May-00 | Aeshnidae | 4 | 1.43 | | |
| Mid Bear Creek | 1-Aug-00 | Hydropsychidae | 2 | 2.54 | 2.270 | 89% |
| Mid Bear Creek | 1-Aug-00 | Coenagrionidae | 3 | 1.74 | 1.880 | 108% |
| Mid Bear Creek | 1-Aug-00 | Naucoridae | 4 | 2.90 | 2.830 | 98% |
| Mid Bear Creek | 1-Aug-00 | Naucoridae (FDup) | 4 | 3.17 | 3.250 | 103% |
| Mid Bear Creek | 1-Aug-00 | Libellulidae | 4 | 2.19 | 2.130 | 97% |
| Mid Bear Creek | 1-Aug-00 | Gomphidae (sp N) | 4 | 2.09 | | |
| Mid Bear Creek | 1-Aug-00 | Belastomatidae | 4 | 2.57 | | |

***SITES IMMEDIATELY DOWNSTREAM OF HG MINES (= "NEAR-MINE SITES")***

| Location | Sample Date | Type | Trophic Level | THg | MeHg | Methyl % |
|---|---|---|---|---|---|---|
| Davis Creek above Davis Ck Res. | 17-May-00 | Elmidae | 1 | 0.80 | | |
| Davis Creek above Davis Ck Res. | 17-May-00 | Baetidae + Ephemerellidae | 1 | 6.57 | | |
| Davis Creek above Davis Ck Res. | 17-May-00 | Siphlonuridae | 1 | 4.62 | | |
| Davis Creek above Davis Ck Res. | 17-May-00 | Hydropsychidae | 2 | 0.95 | | |
| Davis Creek above Davis Ck Res. | 17-May-00 | Coenagrionidae | 3 | 2.29 | | |
| Davis Creek above Davis Ck Res. | 17-May-00 | Perlidae | 3 | 1.42 | 0.319 | 22% |
| Davis Creek above Davis Ck Res. | 17-May-00 | Naucoridae | 4 | 0.58 | 0.397 | 68% |
| Davis Creek above Davis Ck Res. | 17-May-00 | Macromiidae | 4 | 1.88 | | |
| Davis Creek above Davis Ck Res. | 17-May-00 | Aeshnidae (med) | 4 | 2.10 | | |
| Davis Creek above Davis Ck Res. | 17-May-00 | Aeshnidae (lg) | 4 | 2.71 | | |
| Davis Creek above Davis Ck Res. | 17-May-00 | Libellulidae | 4 | 3.24 | 0.530 | 16% |
| Davis Creek above Davis Ck Res. | 17-May-00 | Corydalidae | 4 | 1.62 | | |
| Davis Creek above Davis Ck Res. | 17-May-00 | Corydalidae | 4 | 3.24 | 0.380 | 12% |
| Davis Creek above Davis Ck Res. | 17-May-00 | Tipulidae | 4 | 3.32 | | |
| Davis Creek above Davis Ck Res. | 4-Aug-00 | Hydropsychidae | 2 | 4.09 | 0.769 | 19% |
| Davis Creek above Davis Ck Res. | 4-Aug-00 | Perlidae | 3 | 2.24 | 0.880 | 39% |
| Davis Creek above Davis Ck Res. | 4-Aug-00 | Macromiidae | 4 | 2.19 | | |
| Davis Creek above Davis Ck Res. | 4-Aug-00 | Aeshnidae | 4 | 1.19 | | |
| Davis Creek above Davis Ck Res. | 4-Aug-00 | Tipulidae | 4 | 2.39 | 1.350 | 57% |
| Harley Gulch | 28-Feb-00 | Hydropsychidae (med) | 2 | 4.11 | 1.060 | 26% |
| Harley Gulch | 28-Feb-00 | Coenagrionidae | 3 | 8.67 | 2.470 | 29% |
| Harley Gulch | 28-Feb-00 | Naucoridae | 4 | — | 1.260 | — |
| Harley Gulch | 28-Feb-00 | Corydalidae | 4 | 5.05 | 1.940 | 38% |
| Harley Gulch | 8-May-00 | Hydropsychidae | 2 | 5.14 | (coming) | |
| Harley Gulch | 8-May-00 | Coenagrionidae (sp S) | 3 | 5.93 | 1.460 | 25% |
| Harley Gulch | 8-May-00 | Naucoridae | 4 | 5.74 | 2.840 | 50% |
| Harley Gulch | 8-May-00 | Corydalidae | 4 | 5.17 | 2.070 | 40% |
| Sulfur Creek | 28-Feb-00 | Hydrophilidae (sm) | 2 | 25.40 | | |
| Sulfur Creek | 28-Feb-00 | Hydropsychidae | 2 | — | 0.626 | — |
| Sulfur Creek | 28-Feb-00 | Coenagrionidae | 3 | 20.48 | 4.100 | 20% |
| Sulfur Creek | 28-Feb-00 | Tipulidae (med) | 4 | 11.72 | 3.720 | 32% |
| Sulfur Creek | 28-Feb-00 | Tipulidae (lg) | 4 | 10.30 | | |
| Sulfur Creek | 8-May-00 | Ephemerellidae | 1 | 0.62 | 0.119 | 19% |
| Sulfur Creek | 8-May-00 | Ephemerellidae | 1 | 0.72 | 0.111 | 15% |
| Sulfur Creek | 8-May-00 | Coenagrionidae | 3 | 9.79 | 1.430 | 15% |
| Sulfur Creek | 8-May-00 | Naucoridae | 4 | 1.26 | 0.422 | 34% |
| Sulfur Creek | 7-Aug-00 | Hydrophilidae | | 7.88 | | |
| Sulfur Creek | 7-Aug-00 | Coenagrionidae | 3 | 10.14 | 2.230 | 22% |
| Sulfur Creek | 7-Aug-00 | Coenagrionidae | 3 | 6.11 | 2.510 | 41% |
| Sulfur Creek | 7-Aug-00 | Stratiomyidae | 3 | 4.94 | 0.829 | 17% |
| Sulfur Creek | 7-Aug-00 | Stratiomyidae | 3 | 3.35 | 0.792 | 24% |

**Figure. A-4.**

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

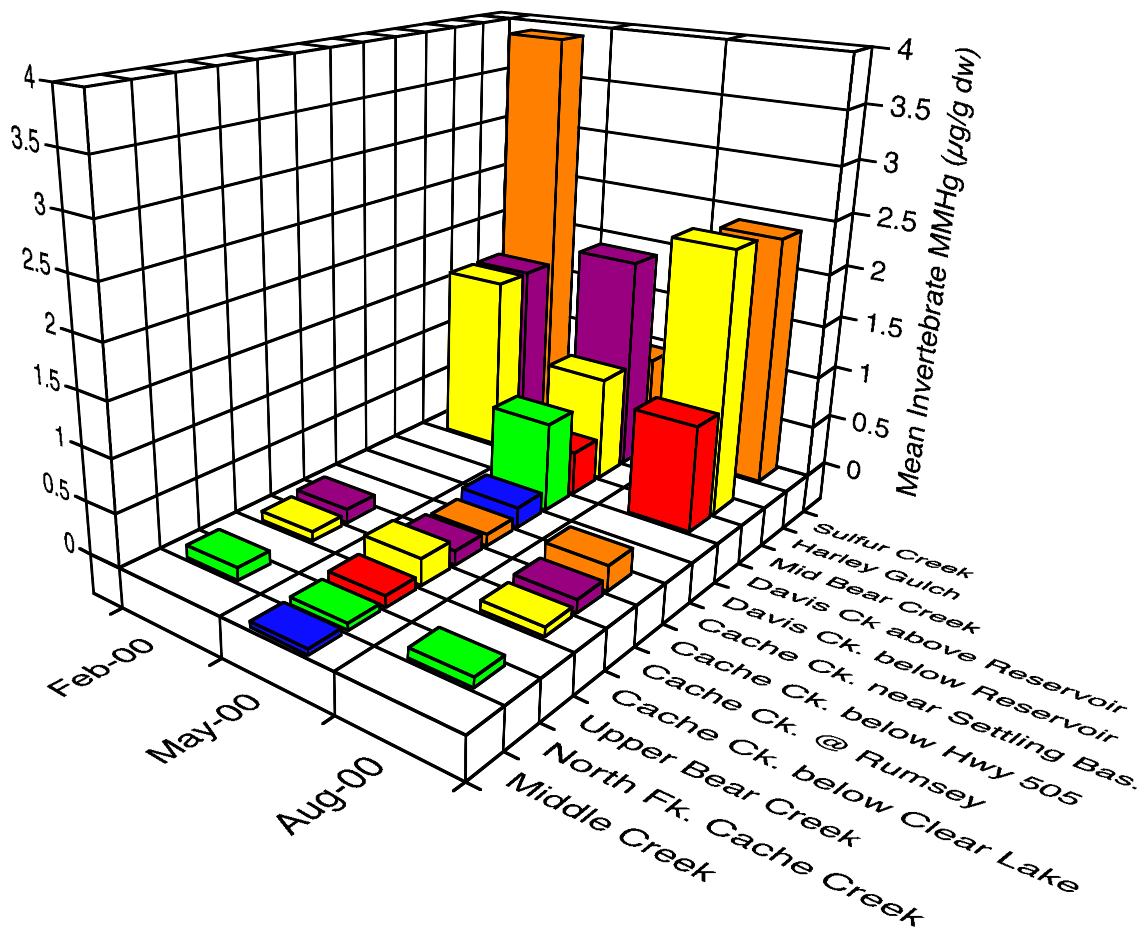
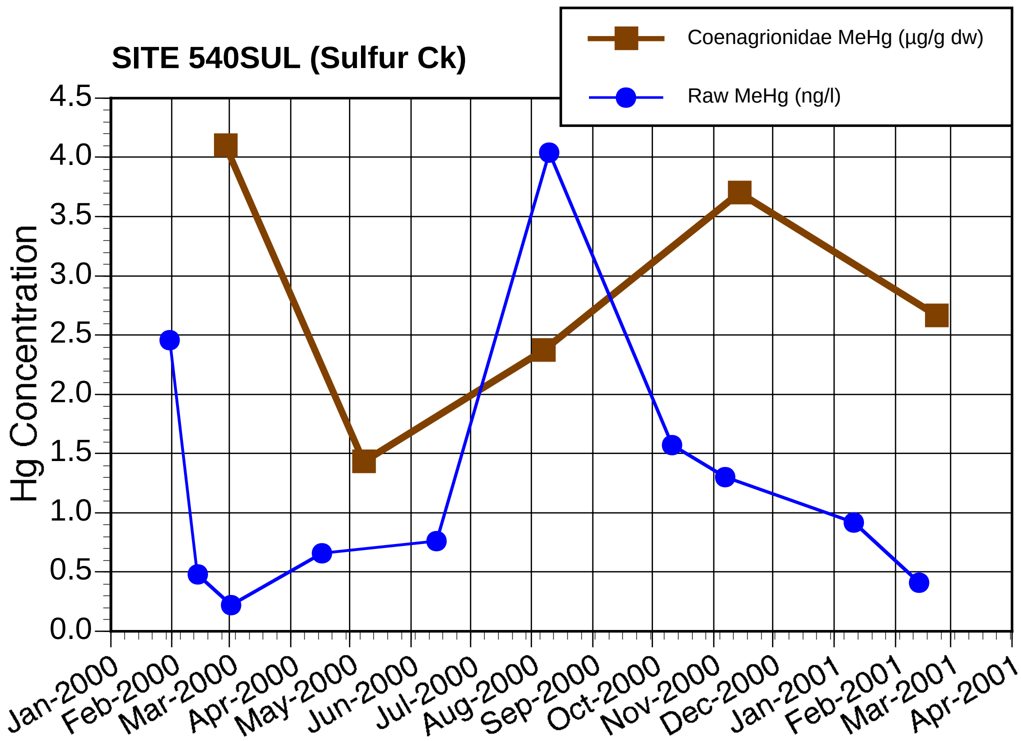
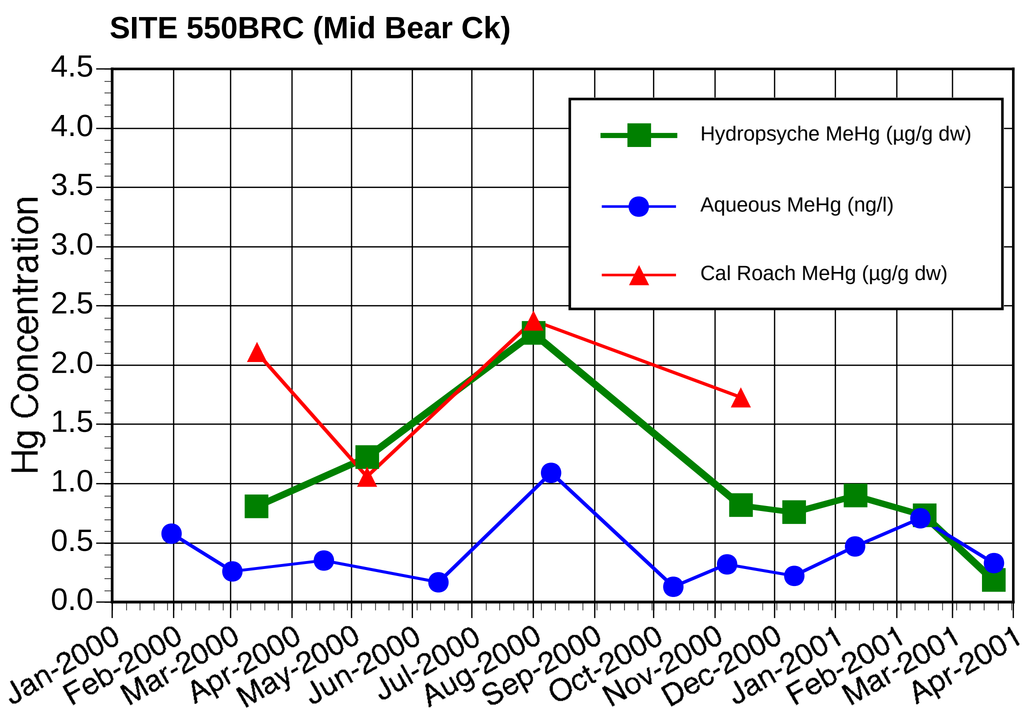


**Figure A-5.**
**Comparison of aqueous MeHg concentration vs. MeHg concentration in biota over time at selected high Hg sites.**
*(Note aqueous conc. in ng/l and biota conc. in µg/g, dry wt)*



**Figs. A-6, 7. Invertebrate methyl Hg % of total Hg in Cache Ck watershed samples.**
(mean MeHg % ± 95% confidence intervals)

**Fig. A-6. Invertebrate Methyl Hg % of total Hg from all sites other than directly below major mines (Jan-Aug, 2000).**

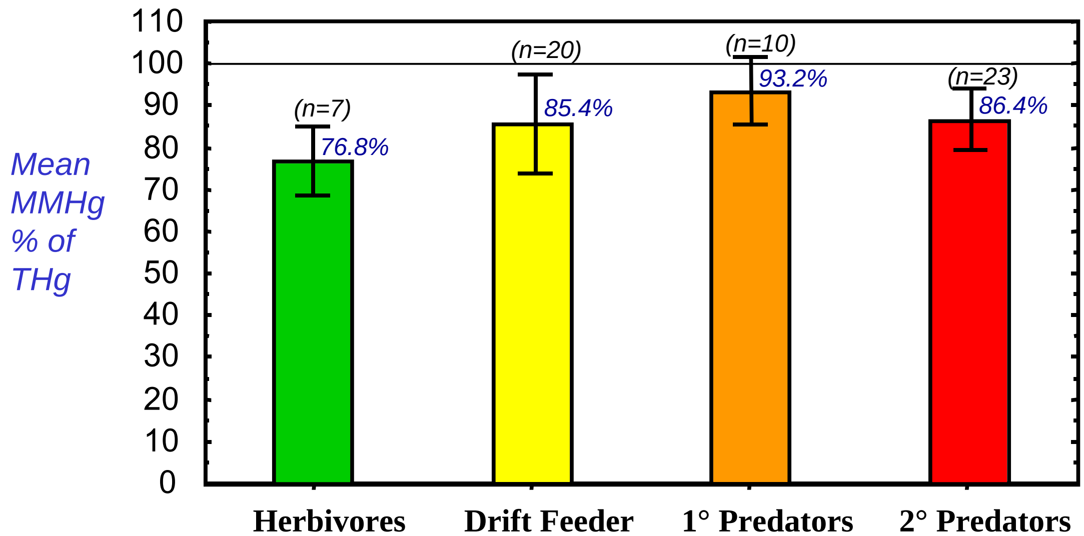



**Fig. A-7. Invertebrate Methyl Hg % of total Hg directly below major mines (Jan-Aug, 2000).**

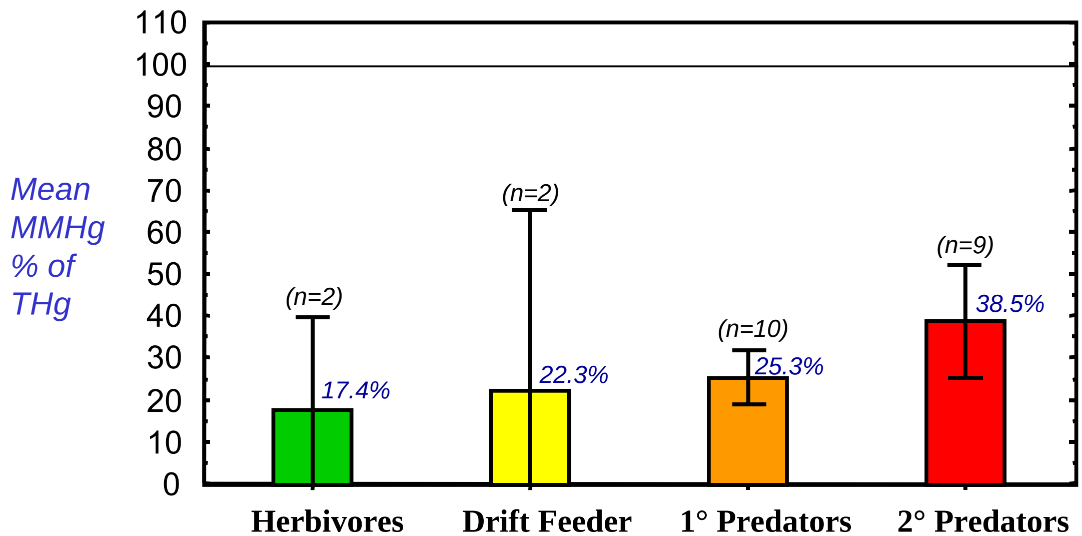


**Figure. A-8.**

**Log/Log (power) regressions of composite invertebrate MeHg vs aqueous Hg fractions**

*(composite invertebrate MeHg = mean site-sampling MeHg of Hydropsyche and predatory taxa)*

*(corresponding water data from most representative sampling(s) prior to invertebrate collections)*

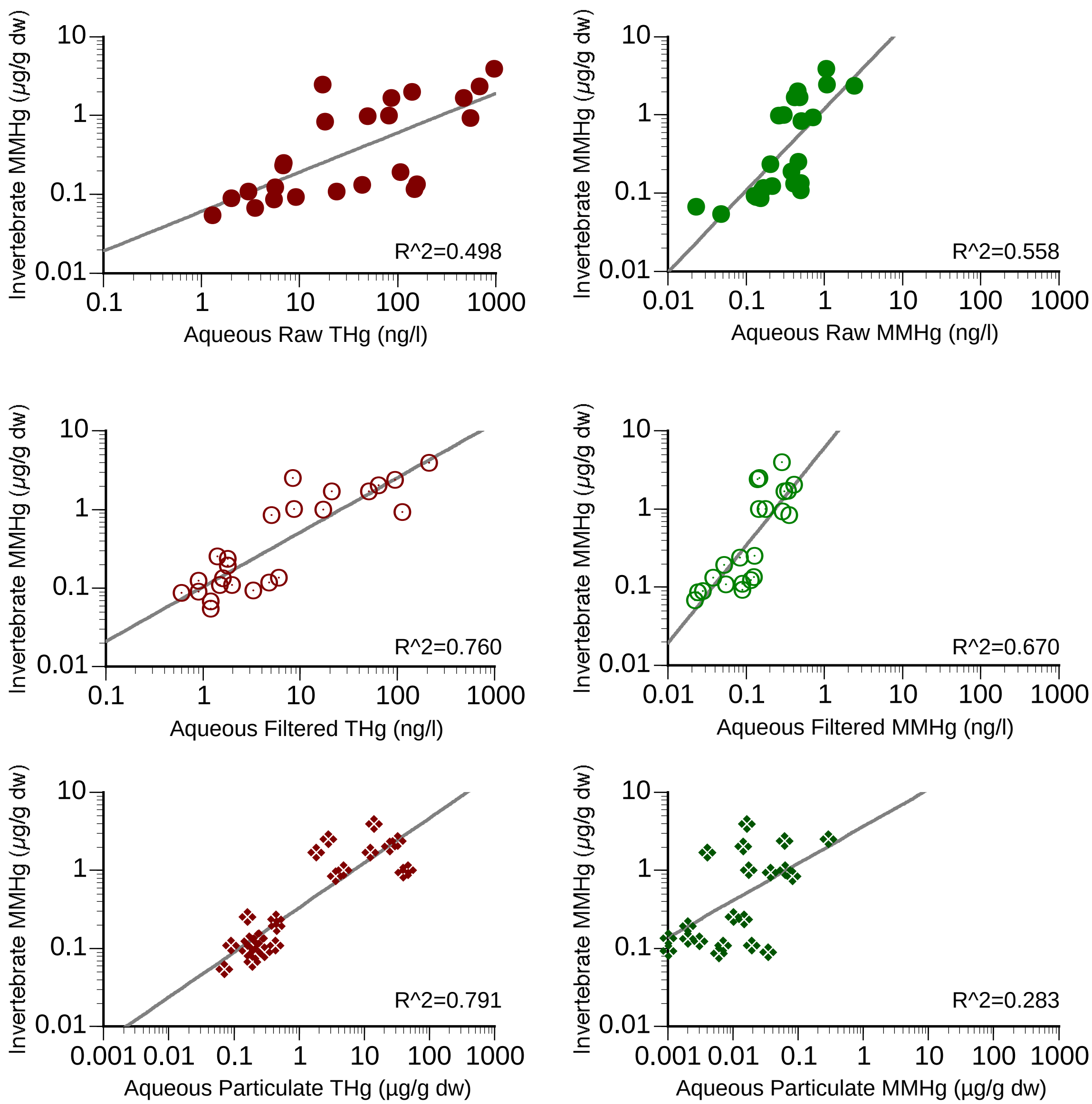
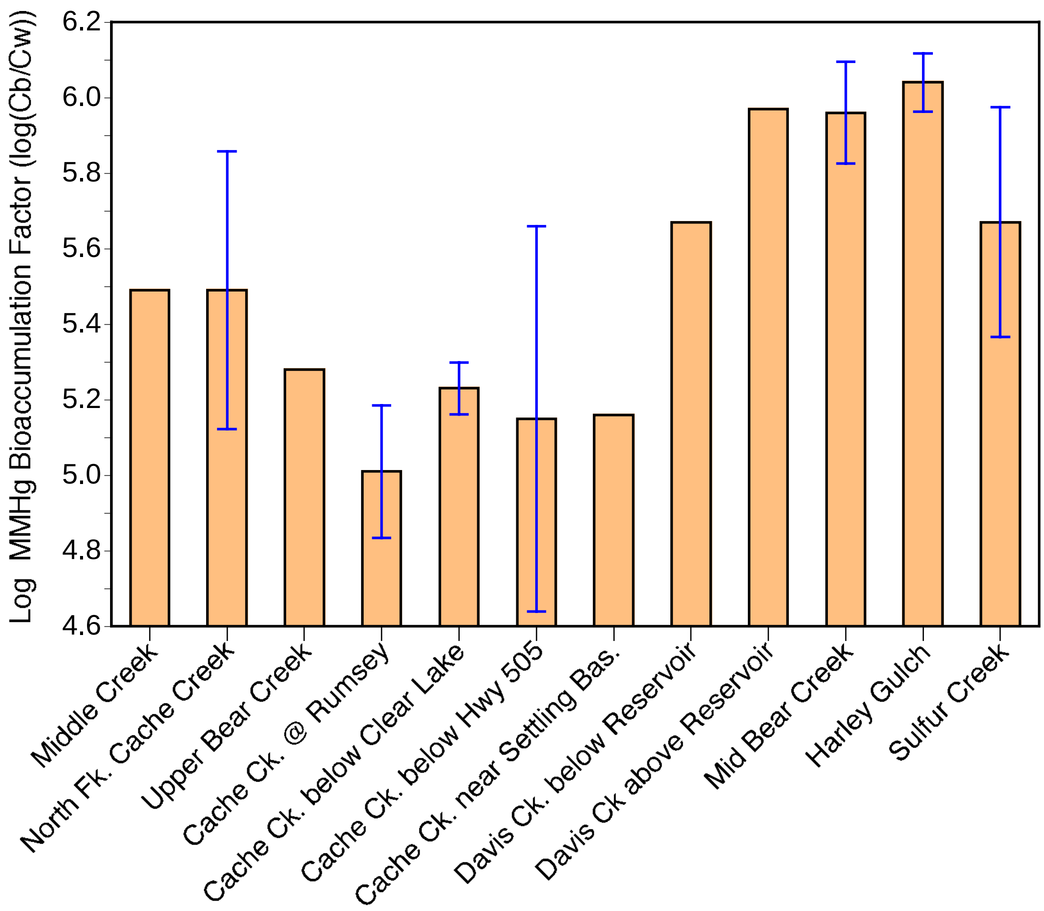


**Figure A-9.**

**Methyl mercury bioaccumulation factors (BAF) for aquatic invertebrates in the Cache Ck. watershed.**

*BAF calculated using mean invertebrate MeHg concentration (wet weight) and mean aqueous MeHg concentration for the hydrologic period prior to collection. Bars represent standard deviation of mean.*




Low Invertebrate MMHg Sites <-------------------> High Invertebate MMHg Sites

**Fig. A-10. Cache Creek Watershed: Adult Piscivorous Fish Mercury vs Size for Different Sites.**

**(Collections made in December 2000)**

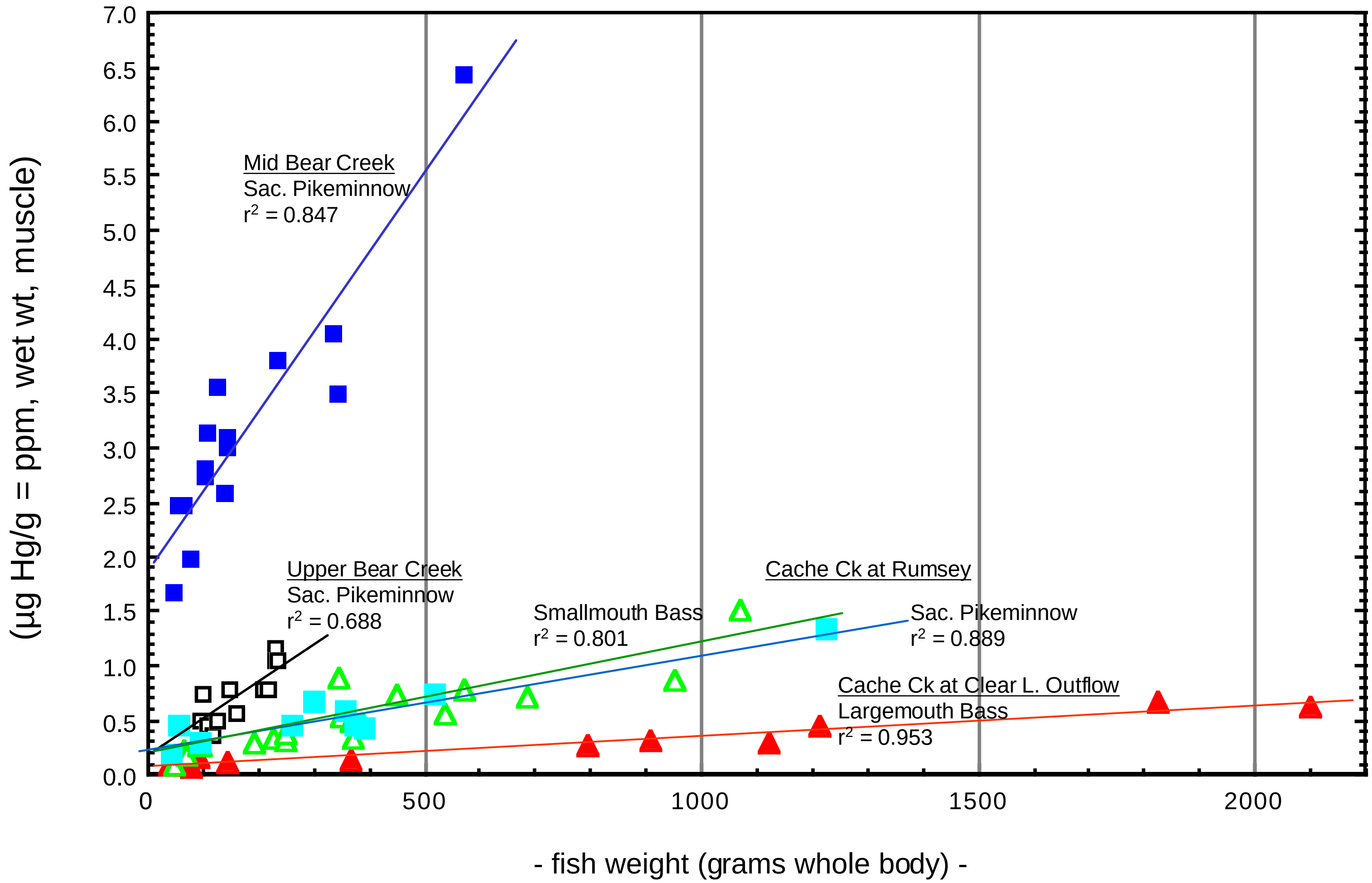


**Figure A-11.**
**Normalized muscle mercury (from size:Hg regressions) in piscivorous fish species taken throughout the Cache Creek watershed.**

*(200 gram normalization; = intersection of 200 g line with size:Hg regressions)*

*(fish collected December 2000)*

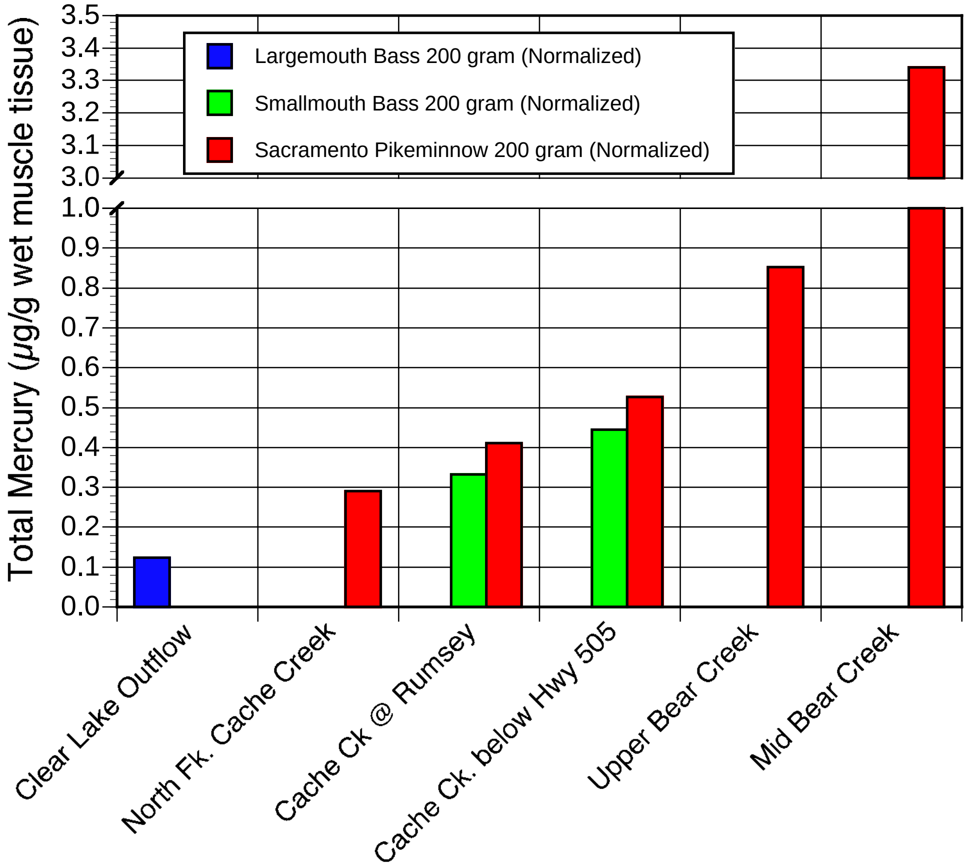
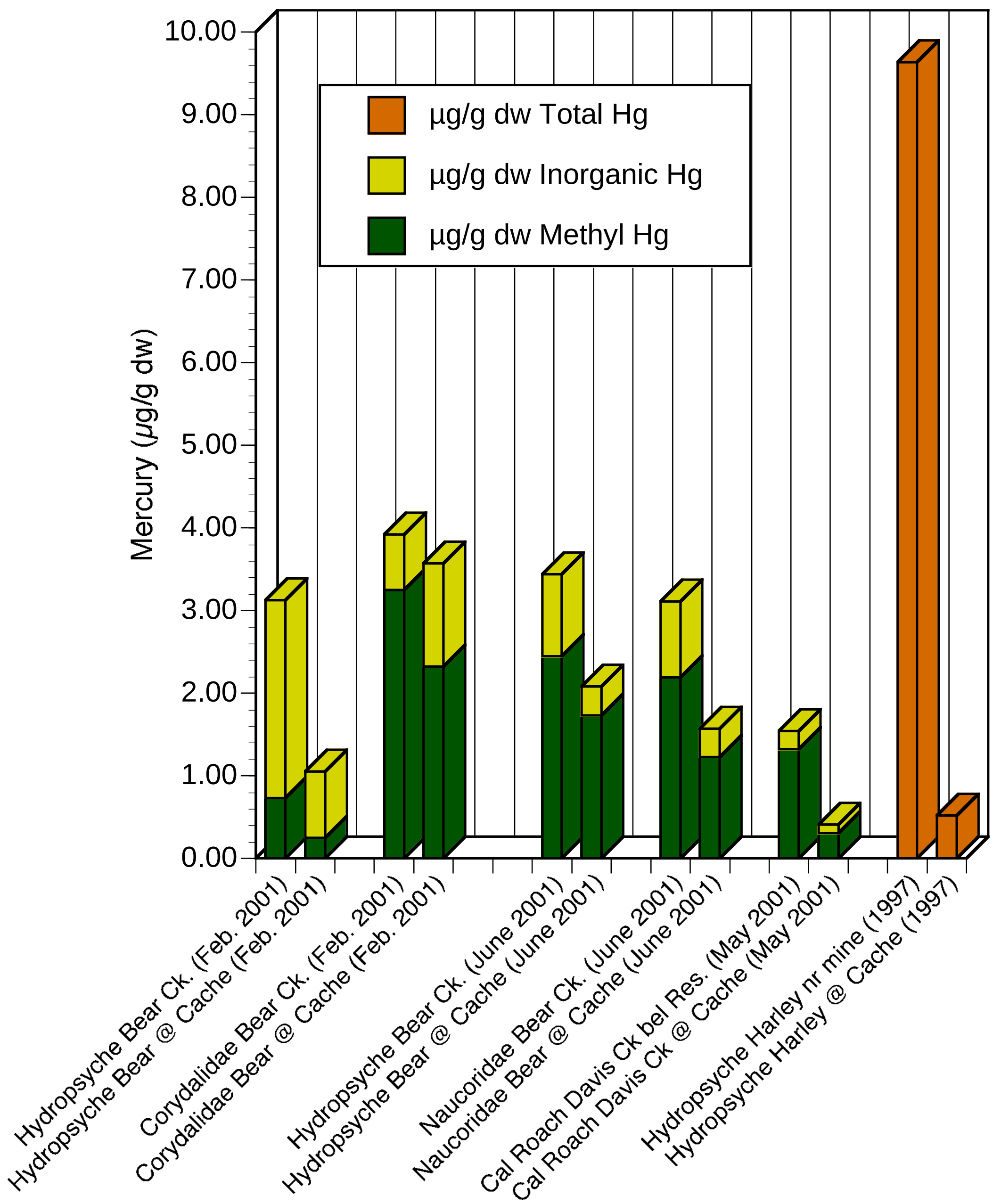


**Fig. A-12**
Mercury concentration in composite biological samples from mine/geothermal impacted streams. Each sample is paired with an identical sample collected on the same date approximately 5-10 miles downstream. Note decrease in Hg across multiple species, dates, and locations.



**(Attachment B)**

# EFFECTS OF WETLAND RESTORATION ON THE PRODUCTION OF METHYL MERCURY IN THE SAN FRANCISCO BAY-DELTA SYSTEM

*(CALFED Contract No. 97-C05)*

**THIRD YEAR PROGRESS BRIEF**
**August 18, 2001**

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## Summary of Task Objectives

Determine the potential relationship between wetlands restoration projects and methyl mercury (MeHg) production in the Sacramento-San Joaquin Delta. Utilize existing wetland tracts of varying ages (caused by breached levees) to identify the potential time sequence of MeHg production enhancement in this system. Determine the spatial patterns of net MeHg bioaccumulation throughout the Delta. Identify potential trends and possible driving variables.

## Summary of Hypotheses

- Organic rich, vegetated wetland habitats in the Delta provide ideal environments for mercury (Hg) methylating microbes.
- These marsh environments produce MeHg at enhanced rates relative to other existing Delta aquatic habitats; a "new flooding" surge of methylation may also exist.
- Implementation of large Delta wetlands restoration projects might significantly increase the production and bioaccumulation of MeHg in the Delta, both locally and throughout.
- Historic deposition of Hg within the Delta is sufficient to maintain elevated concentrations of biotic MeHg.

## Approaches/Methods

Field and laboratory approaches were developed to test net sediment mercury methylation and biotic mercury accumulation in the Sacramento-San Joaquin Delta. Relative sediment Hg methylation was first addressed by measuring direct efflux of MeHg from cores containing a variety of natural Delta sediments, but this was found to be problematic analytically. A second approach utilized a Hg-spiked slurry methylation potential technique. MeHg and total Hg (THg), and ratios of the two fractions, were assessed for various Delta sediments and, particularly, existing flooded tract and adjacent channel or mudflat control pairs. Localized net Hg bioaccumulation was investigated throughout the Delta. A variety of relatively sessile aquatic macrofauna were surveyed across the system and assessed for Hg concentrations. Some species were ubiquitous enough to be used as bioindicator tools to compare Hg concentrations between sites or regions. Localized sediment MeHg production potential and biotic accumulation results were evaluated against potential driving variables.

## Discussion of Progress To Date / Results / Preliminary Conclusions

MeHg was analyzed by Battelle Marine Sciences Laboratory, Sequim, Washington. THg was analyzed in our UC Davis laboratories; QA/QC information is presented in Table B-1.

Sediment MeHg concentrations (Figure B-1) and MeHg:THg ratios (Figure B-2) were significantly greater in highly vegetated marsh habitats as compared to adjacent Delta channel and mudflat environments. Methylation potential experiments showed that flooded wetland sediments exhibited 2-30 times greater potential to produce MeHg than aquatic sediments of adjacent channels and flats (Figure B-3).

However, biological findings to date (Figures B-4 through B-8) indicate no discernible localized increase in net MeHg bioaccumulation in flooded wetland tracts vs adjacent aquatic habitats within Delta sub-regions. Some of the most well developed, highly vegetated wetland tracts exhibited *reduced* levels of localized net Hg bioaccumulation. These results suggest that wetland restoration projects may result in localized Hg bioaccumulation at levels similar to, but not necessarily greater than, levels within their surrounding Delta sub-region.

On a larger spatial scale, though, significant differences in bioaccumulation were identified across the Delta (Figures B-6 through B-8). Delta locales with elevated biotic mercury concentrations included areas fed by inflows from the Cosumnes River, Yolo Bypass and, to a lesser extent, Sacramento River. The Central and South Delta were markedly lower, despite high signals in some southern tributaries to the San Joaquin River and the presence of numerous flooded tracts in the Central Delta. An additional zone of elevated Hg bioaccumulation was identified in the West Delta between the Sacramento-San Joaquin confluence and Carquinez Strait, potentially resulting from historic mining depositional patterns and/or coincidence with the estuarine entrapment zone. Potential mechanisms for this apparent West Delta elevation in Hg bioaccumulation include elevated sulfate and organic material, supporting methylating microbes, and chemistry of the neutral form of inorganic Hg potentially being more readily transported across microbial membranes. Apart from the West Delta zone of elevated Hg bioaccumulation, the primary regions of elevated biotic Hg that were identified in this work can all be characterized as being dominated by ongoing new inflows of Hg from upstream San Francisco Bay-Delta tributaries. Inputs of both elemental mercury from historic gold mining in the Sierra Nevada and abandoned mercury mine cinnabar in the Coast Range appear to be of importance. This suggests that upstream remediation efforts on either side of the watershed may be more meaningful than previously anticipated.

Inland silversides fish (*Menidia*) and Asiatic clams (*Corbicula*) within specific size classes (Figure B-4) were found to be the most ubiquitous and consistent measures of relative localized Hg bioaccumulation available throughout the system. Inorganic Hg and MeHg:THg ratios were highly variable in the bivalves (Figures B-5, B-6), though MeHg was fairly consistent (Figure B-6). Hg in silversides whole fish composites was found to consist entirely of MeHg (103% ± 17% of THg in 64 paired analyses; Figure B-7). In Figure B-8, silversides THg is plotted alone; QA/QC for THg was far tighter than that for MeHg. We believe that Figures B-8 (silversides THg) and B-6 (*Corbicula* MeHg) represent the best Delta-wide measures to date of fine-scale spatial variability in apparent MeHg exposure and bioaccumulation.

*Summer 2001 Update:* In June 2001, we directly tested a wide cross section of flooded Delta tracts for potential net export of aqueous MeHg. This was accomplished with a series of tidal water collections, in which we sampled inflowing and subsequent outflowing tidal Delta waters during high amplitude tidal cycles. Samples representing initial/inflowing water were taken toward the end of inflowing (rising tide) cycles at prominent breaches of the targeted flooded tracts. Corresponding samples representing export from the flooded tracts were taken at the same locations toward the end of the subsequent outflowing (lowering tide) cycle. Standard clean sampling protocols were used for all collections. Because of recurring detection problems with filtered aqueous MeHg in the Delta (reported by other CALFED researchers), we tested an alternate approach, utilizing raw aqueous MeHg (preserved/fixed same day with ultra-clean hydrochloric acid) in conjunction with corresponding samples of total suspended solids (TSS). The results (Figures B-9 and B-10) were both illuminating and promising as an ongoing sampling technique.

In Figure B-9, absolute concentrations of raw aqueous MeHg are plotted for inflowing vs outflowing tidal water at eight important flooded Delta tracts and two integrating channel regions. At two large North Delta tracts with distinctly different habitats at either end (Liberty Island and Little Holland Tract), inflowing and outflowing water samples were taken from both the sand flat southern ends and the developed tule marshes at the northern ends. In nearly all sample pairs, taken throughout the Delta, outflowing aqueous MeHg was elevated over inflowing water. Taken alone, this data could suggest that the flooded Delta tracts may function as relative MeHg sources for their surrounding regions (and the Bay-Delta as a whole). In paired samplings from the North Delta export-integrating site at Lower Cache Slough, though reduced in absolute concentration, the MeHg level in outflowing water was double that of the inflowing tide. However, these apparent elevations in export water could be partially or largely a function of tidal flushing and associated sediment resuspension.

In Figure B-10, the raw aqueous MeHg data have been normalized to corresponding suspended particulate concentrations. The data are plotted as ng aqueous MeHg per gram TSS. While strong relationships have been shown between TSS and total Hg in the Bay-Delta, the association between MeHg and particulates has not been clearly established for this system. By normalizing to TSS, we are not implying that all of the aqueous MeHg is associated with the corresponding particulates; we are simply factoring out the particulate load as the explanation for the variation in aqueous MeHg. Plotted in this way (Figure B-10), the elevated MeHg in outflowing water at Lower Cache Slough in Figure B-9 appears to be entirely a function of increased suspended solids in the outflowing water. The large sand flat expanses of Liberty

Island and Little Holland Tract (and Mildred Island) demonstrated a net *decrease* in outflowing aqueous MeHg concentration when normalized to suspended solids. However, in virtually all of the tested flooded tract sites characterized by dense aquatic plant growth and organic-rich sediments, TSS-normalized aqueous MeHg was elevated in outflowing vs inflowing tidal water. This indicates that organic-rich wetland habitats may indeed be local and regional sources of aqueous MeHg. The most notable relative MeHg export occurred in the highly developed tule marsh habitat of representative site Mandeville Tip Island and the dense macrophyte beds of representative Little Franks Tract. The marshy northern ends of the North Delta tracts were also net export regions while the predominant sandflat habitats there were not.

These results contrast with the biotic data: within each Delta region, Hg bioaccumulation was typically similar in marsh, sand/mud flat, and channel/slough habitats. One possibility is that regional Hg bioavailability may be largely a function of methylation in flooded marsh zones, with this MeHg being subsequently distributed throughout adjacent aquatic habitats as a result of vigorous tidal mixing. However, the fact that the Central Delta, with a demonstrated high Hg methylating potential and the ability to export aqueous MeHg, was the lowest fish Hg bioaccumulation region of all indicates that several potentially competing processes may be involved in the dynamics of Hg bioaccumulation associated with flooded tracts. In particular, the potential role of aqueous MeHg ligands (DOC), as they effect actual bioaccumulation of aqueous MeHg, may be a fruitful area of new research. It may be that the vegetated wetland habitats are exporting aqueous MeHg that is not immediately available for local bioaccumulation.

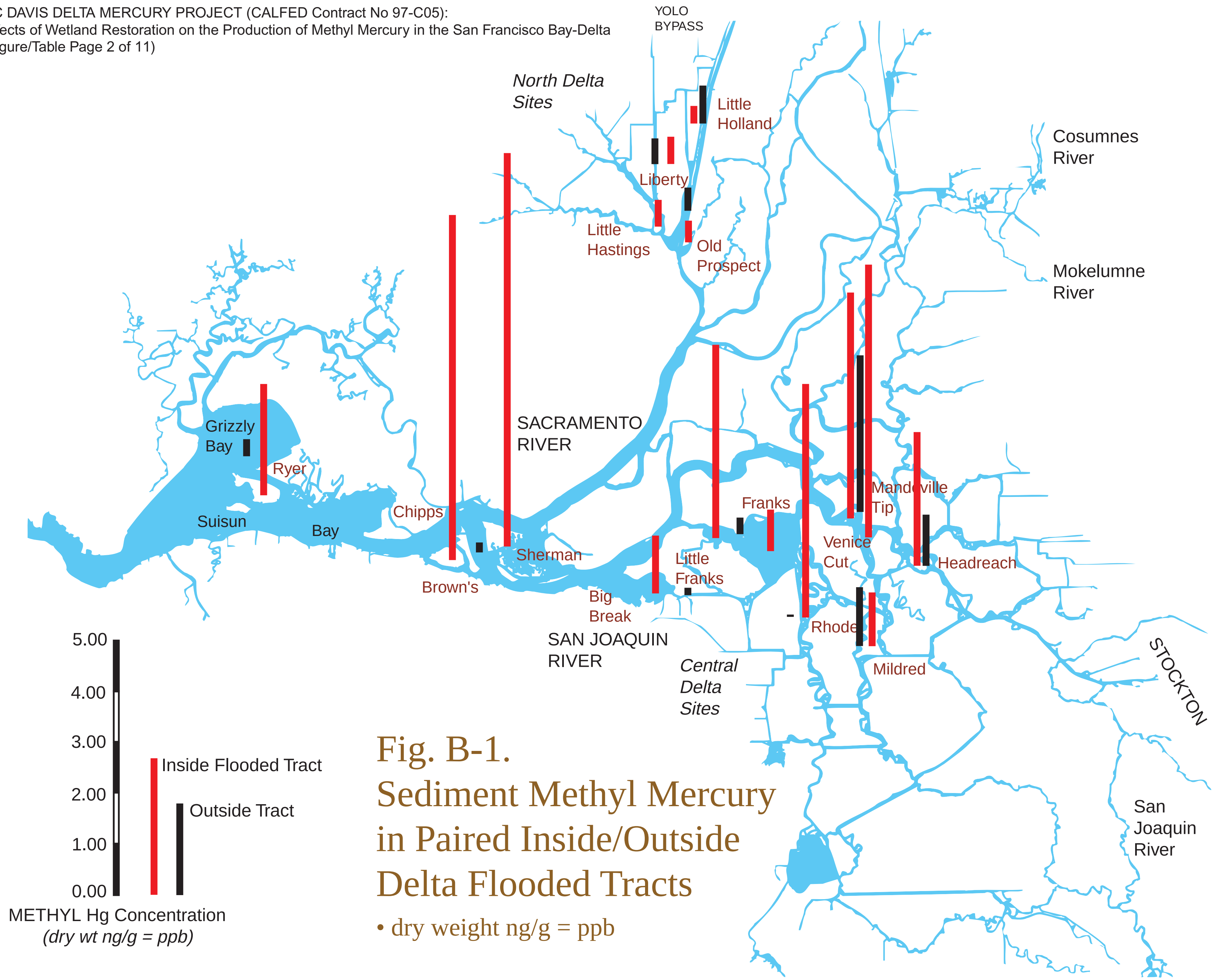
In other developments, significant progress has been made in the analysis and interpretation of nitrogen and carbon stable isotopes in biological samples taken throughout the Delta. These data indicate some notable regional trends in carbon loading at the base of the food chain, which transfer trophically within regions. The analysis of nitrogen isotopic data continues in relation to the potential variation in relative trophic level of similar Hg bioindicator organisms from different locations. Stable isotope results (as well as all other project components) will be discussed fully in the final project report.

## Potential for Future Research / Recommended Changes in Existing Research Program

The localized indicators developed in this work, particularly the inland silversides, *Corbicula* clams, and aqueous MeHg normalized to TSS constitute useful new monitoring tools that should be utilized into the future as new restoration projects and water diversion modifications are instituted. Further study is warranted on the potential role that wetland methylation may have on MeHg loading, both locally and for the Bay-Delta as a whole. Conversely, further study is warranted on the mechanisms resulting in apparent MeHg scavenging in organic-rich, MeHg exporting sites, which would otherwise be expected to demonstrate elevated localized MeHg bioaccumulation.

**Table B-1. Laboratory QA/QC summary (to date) for UC Davis Delta Project total mercury analyses.**

| | | | | | | *Standard Reference Materials* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Std Curve R^2 | Lab Split RPD | Field Dup. RPD | Spike Recoveries | Lab Cont. Std. Recoveries | BCR Cod | TORT-2 Lobster | DOLT-2 Dogfish | NIST 2976 Mussel |
| Certified Level (ppm) | | | | | | 0.56±0.02 | 0.27±0.02 | 2.14±0.28 | 0.061±0.004 |
| Ideal Recovery | 1.000 | (00%) | (0%) | (100%) | (100%) | (100%) | (100%) | (100%) | (100%) |
| Control Range (%) | (>0.975) | <25% | <25% | 75-125% | 75-125% | 75-125% | 75-125% | 75-125% | 75-125% |
| Tracking Method | | Control Chart | | Control Chart | Control Chart | | Control Chart | Control Chart | Control Chart |
| Control Range (ppm) | | | | | | 0.42-0.70 | 0.20-0.34 | 1.61-2.68 | 0.05-0.08 |
| Recoveries (%) | 0.9970-0.9999 | 0.0%-15.0% | 0.2%-95.4% | 88%-105% | 95%-112% | 89%-94% | 88%-111% | 93%-108% | 85%-126% |
| Recoveries (ppm) | | | *(higher near MDL)* | | | 0.50-0.53 | 0.24-0.30 | 2.00-2.31 | 0.05-0.08 |
| (n) | n=40 | n=224 | n=98 | n=220 | n=115 | n=12 | n=112 | n=106 | n=60 |
| Mean Recoveries (%) | 0.9995 | 2.90% | 13.58% | 96.4% | 101.3% | 91.7% | 101.7% | 97.9% | 96.7% |
| Mean Recoveries (ppm) | | | | | | 0.51 | 0.27 | 2.10 | 0.06 |




# Fig. B-1.
# Sediment Methyl Mercury in Paired Inside/Outside Delta Flooded Tracts

• dry weight ng/g = ppb

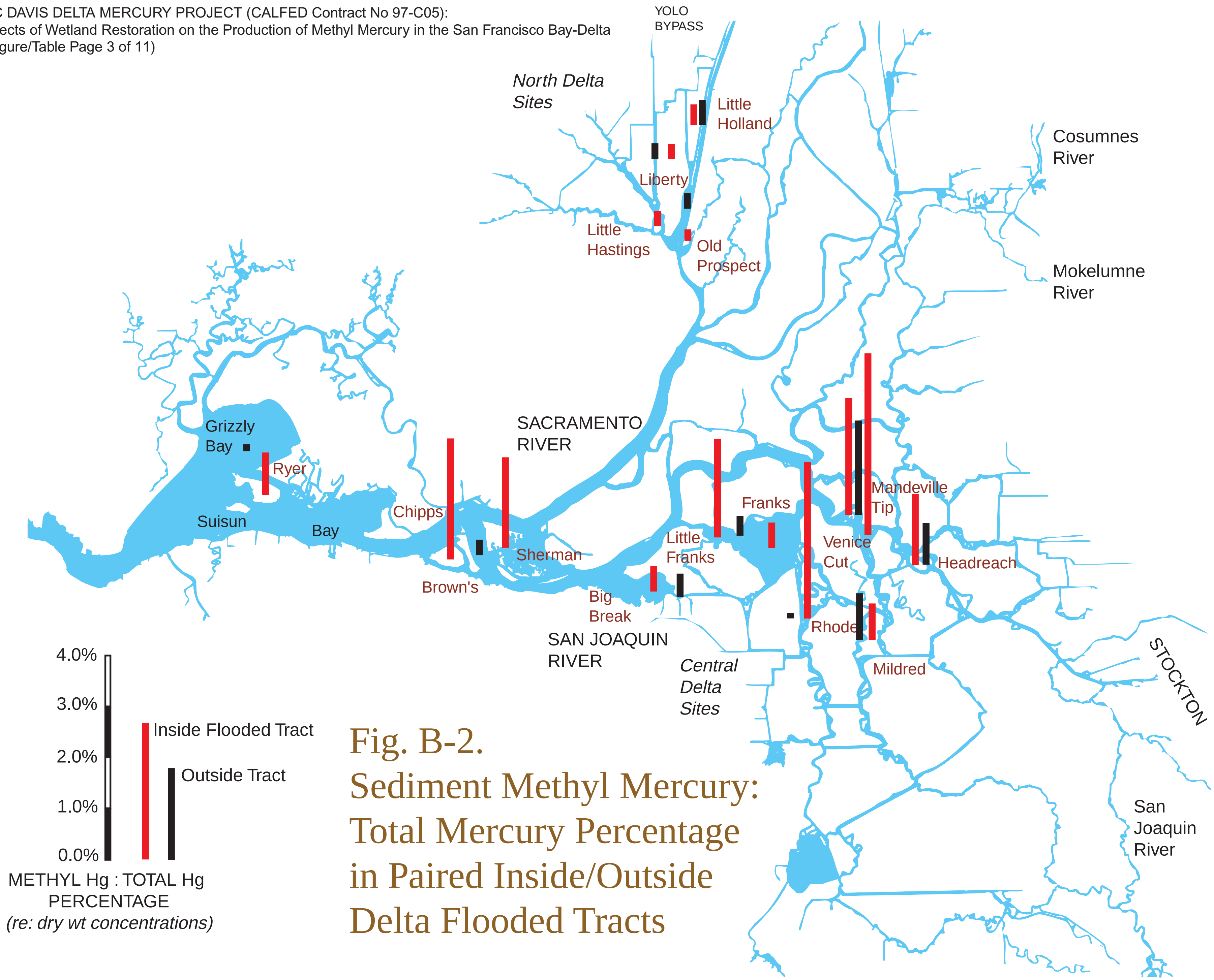



Fig. B-2.
Sediment Methyl Mercury: Total Mercury Percentage in Paired Inside/Outside Delta Flooded Tracts

**Fig. B-3.**
**Relative mercury methylation potential of representative Delta marsh habitats vs adjacent aquatic habitat.**
*(Mean maximum methyl mercury concentrations in inorganic mercury addition experiments to 1.00 µg Hg $g^{-1}$; methyl mercury concentrations in dry wt ng Hg $g^{-1}$ = ppb).*

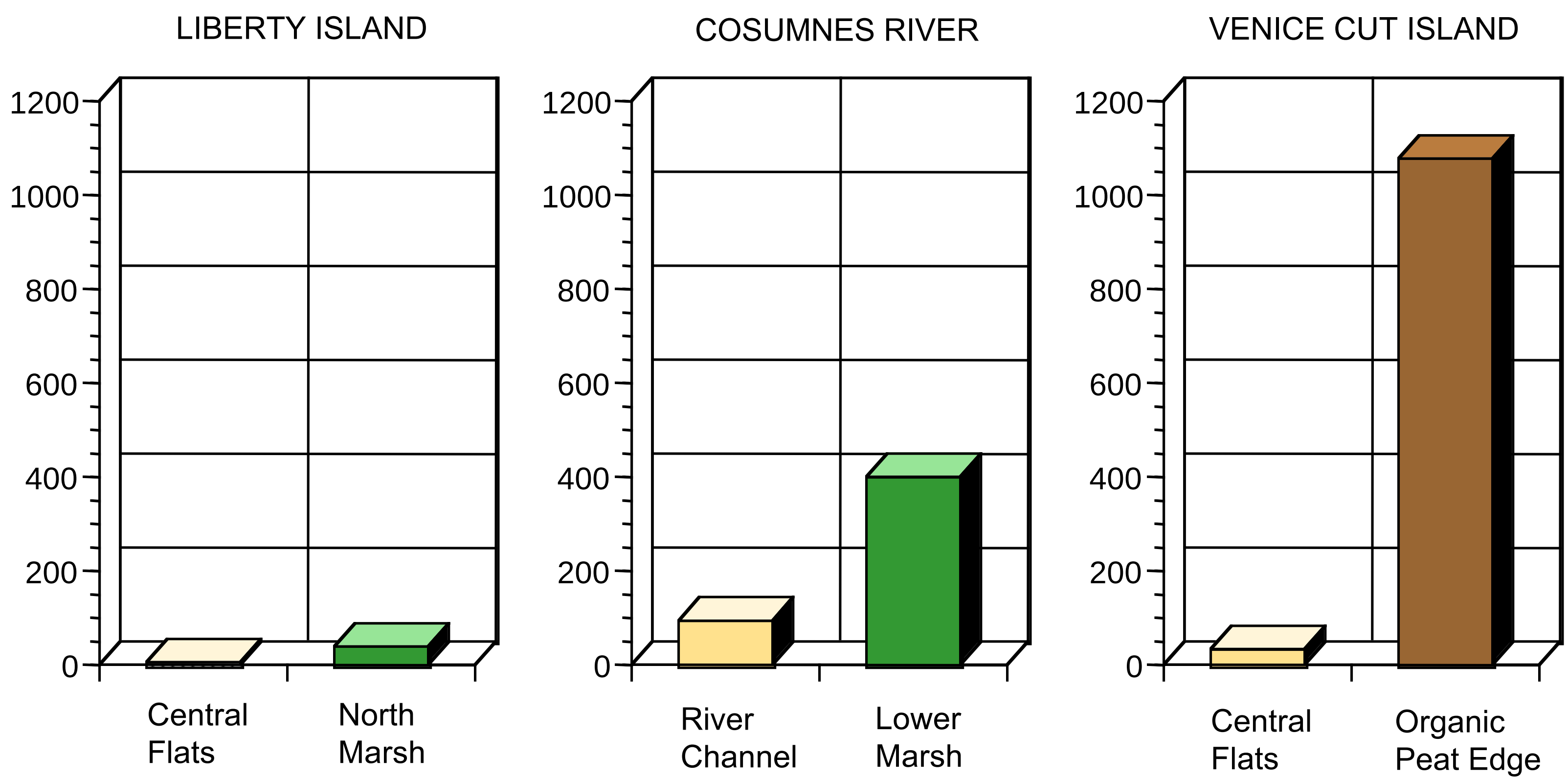
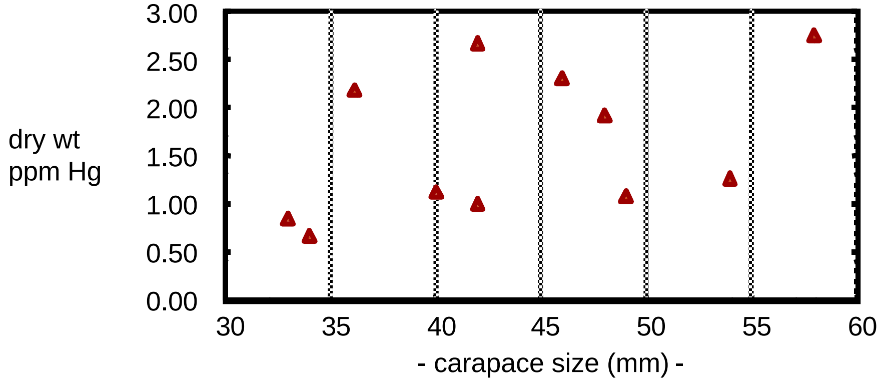
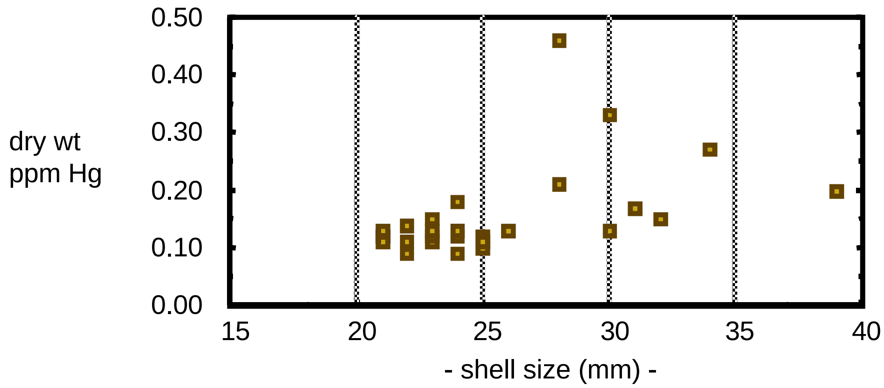


**Fig. B-4.**
**Examples of individual variability in mercury content among potential bioindicators.**
*(individual dry wt µg/g Hg = ppm, plotted as a function of organism size/age)*
*(dry wt concentrations = app. 5x wet wt concentrations)*

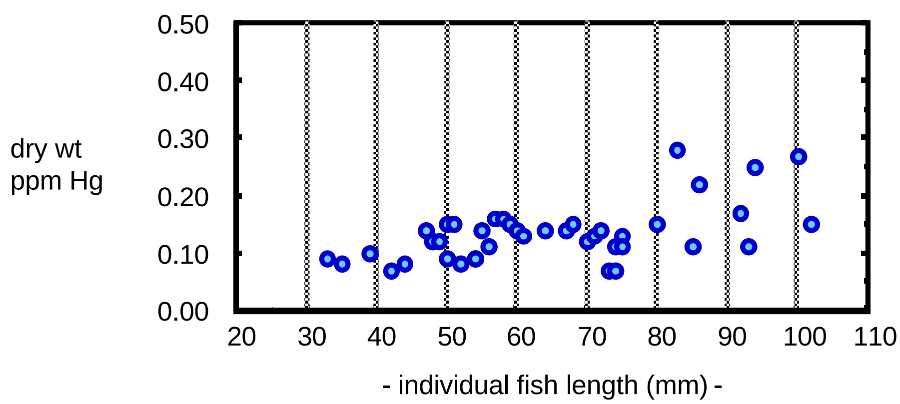
**Crayfish (*Pacifasticus*) Individual Mercury Variability**
(Sacramento R. at Isleton 12/9/99; tail muscle; gut removed)

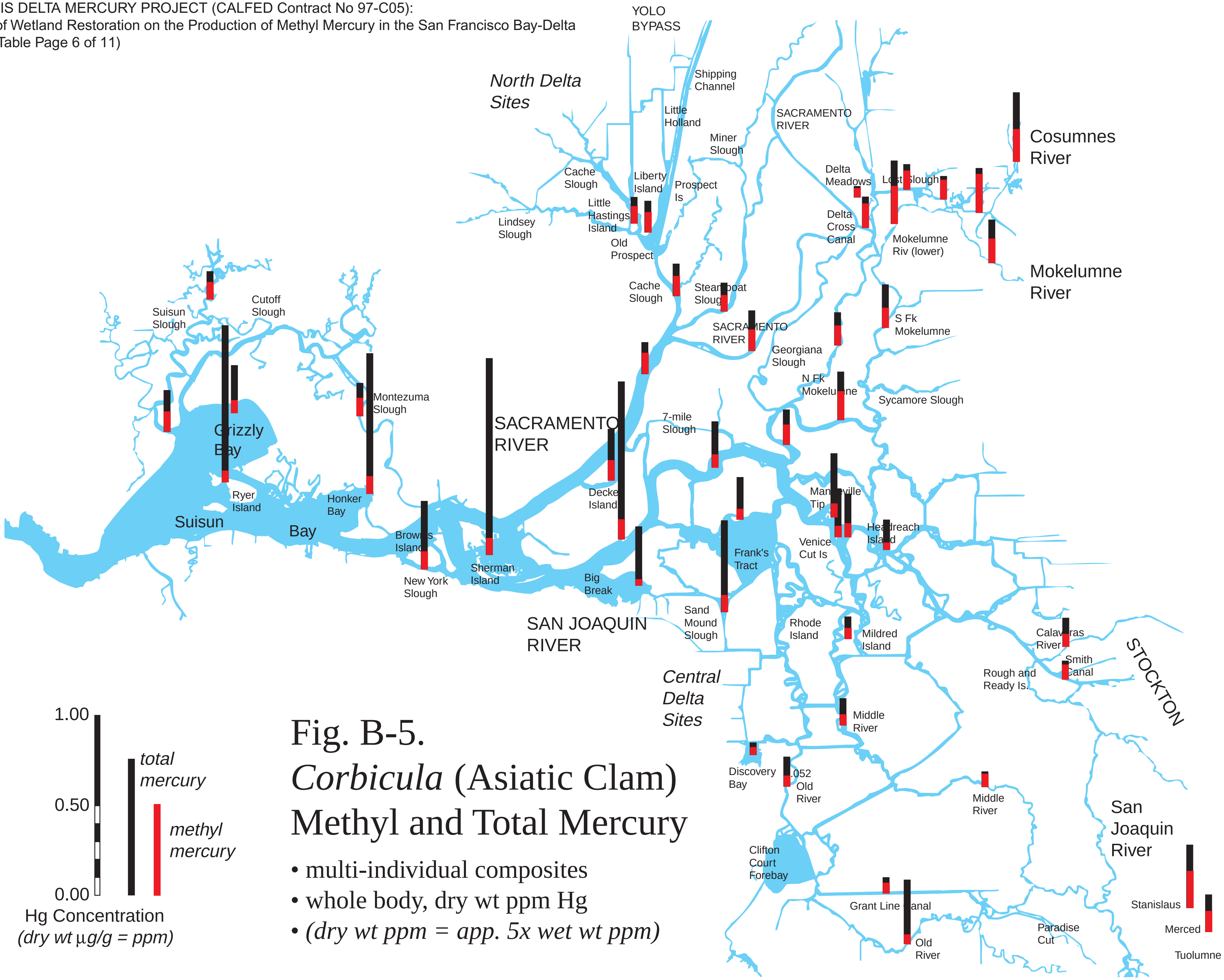



**Corbicula (Asiatic Clam) Individual Mercury Variability**
(Cosumnes N Slough 10/26/99); whole body Hg; clams purged 4 days)




**Inland Silversides (Small Fish) Individual Mercury Variability**
(Mildred Island 11/9/99; whole body Hg; dry weight)






# Fig. B-5.
# *Corbicula* (Asiatic Clam) Methyl and Total Mercury

- multi-individual composites
- whole body, dry wt ppm Hg
- *(dry wt ppm = app. 5x wet wt ppm)*

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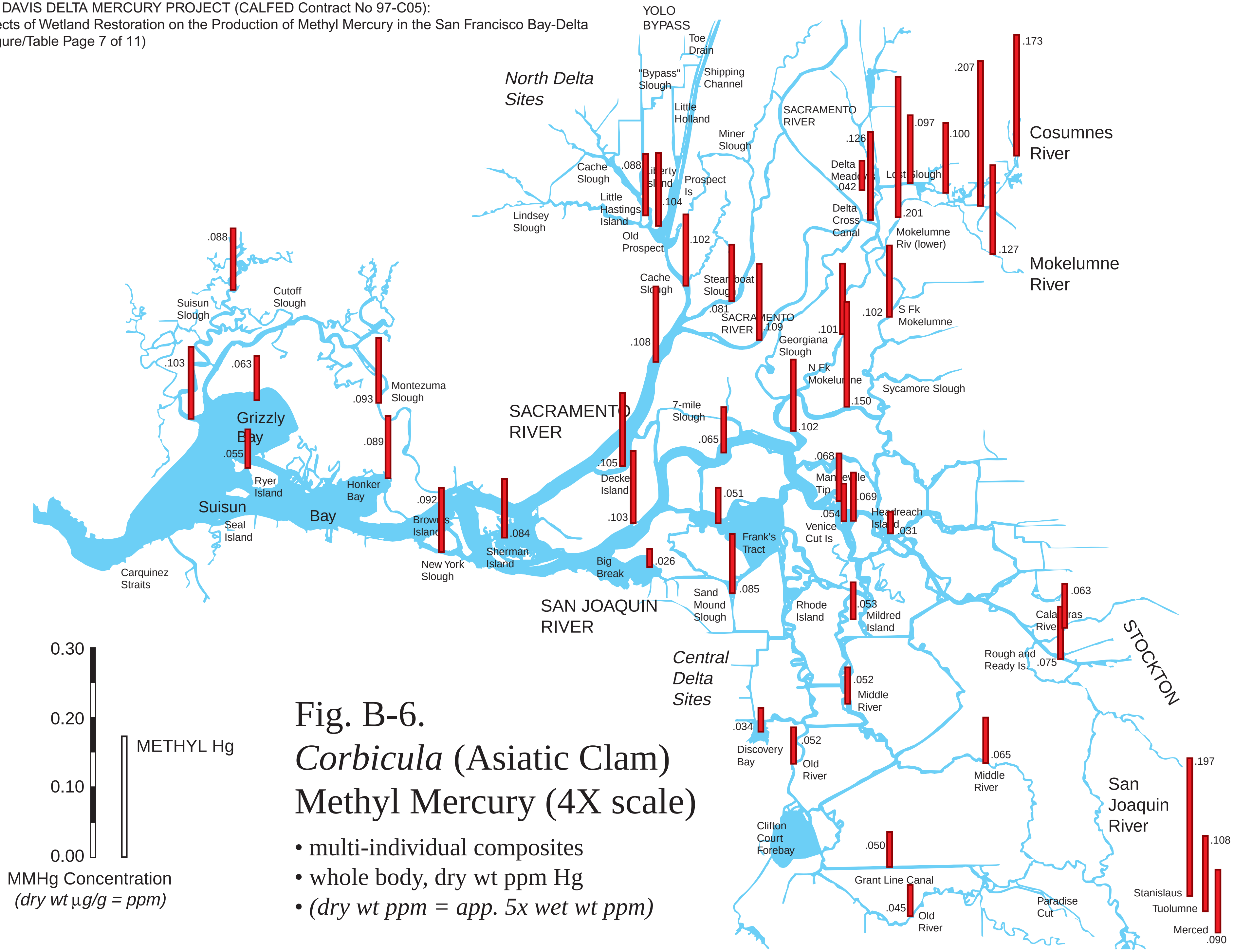
Effects of Wetland Restoration on the Production of Methyl Mercury in the San Francisco Bay-Delta
(Figure/Table Page 7 of 11)

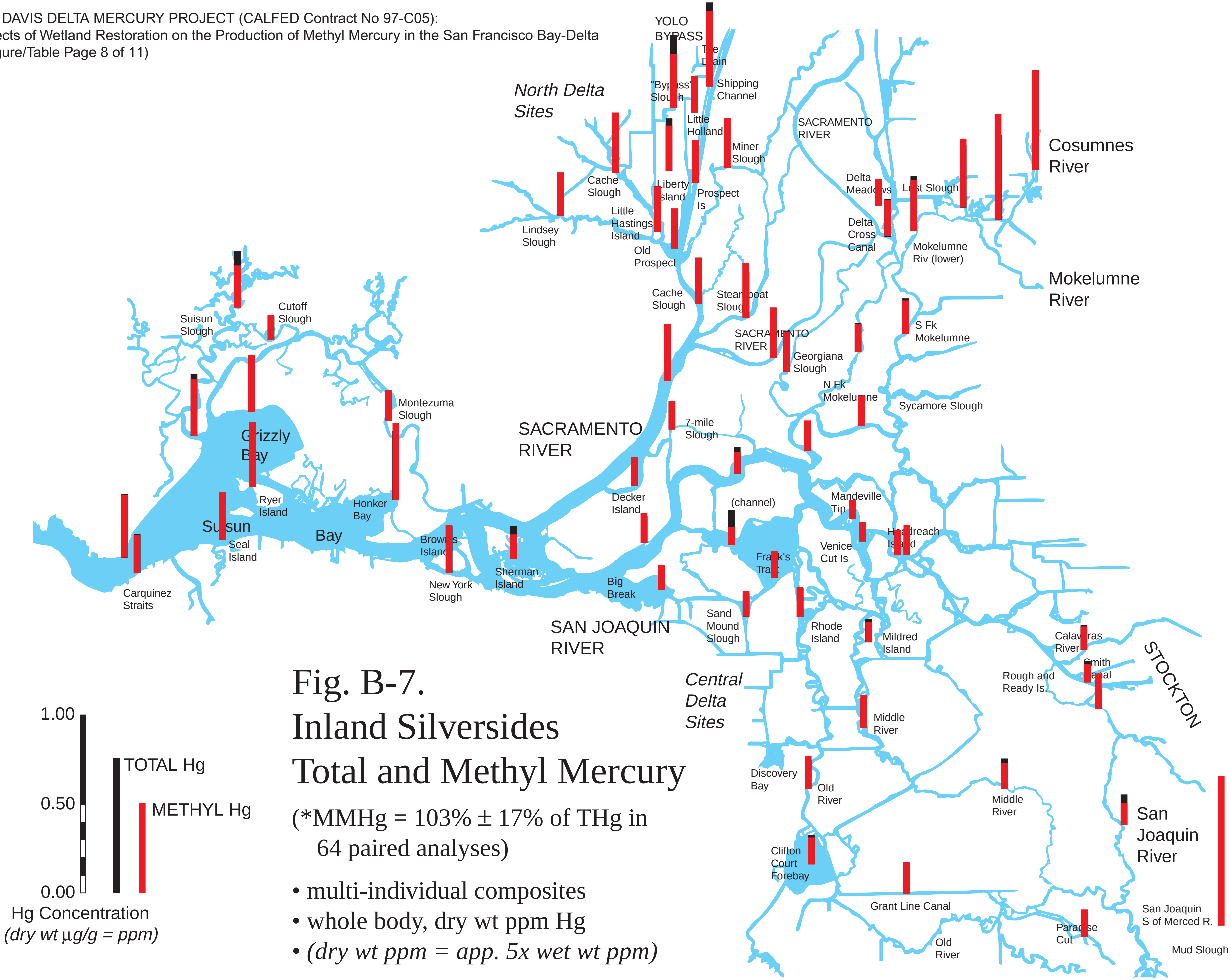



# Fig. B-6.

## *Corbicula* (Asiatic Clam) Methyl Mercury (4X scale)

- multi-individual composites
- whole body, dry wt ppm Hg
- *(dry wt ppm = app. 5x wet wt ppm)*

UC DAVIS DELTA MERCURY PROJECT (CALFED Contract No 97-C05):
Effects of Wetland Restoration on the Production of Methyl Mercury in the San Francisco Bay-Delta
(Figure/Table Page 8 of 11)




# Fig. B-7.
# Inland Silversides
# Total and Methyl Mercury

(*MMHg = 103% ± 17% of THg in 64 paired analyses)

- multi-individual composites
- whole body, dry wt ppm Hg
- *(dry wt ppm = app. 5x wet wt ppm)*

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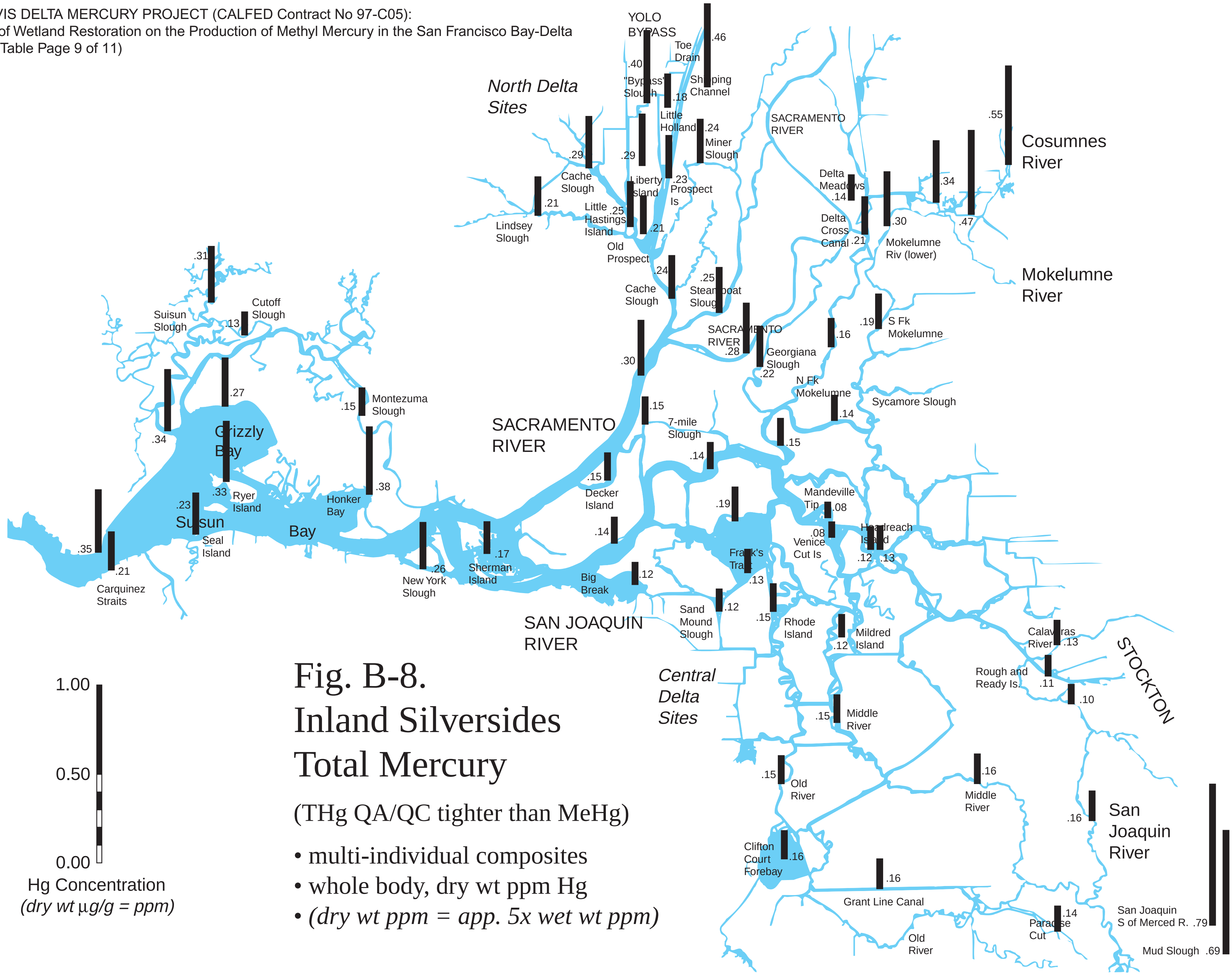
Effects of Wetland Restoration on the Production of Methyl Mercury in the San Francisco Bay-Delta

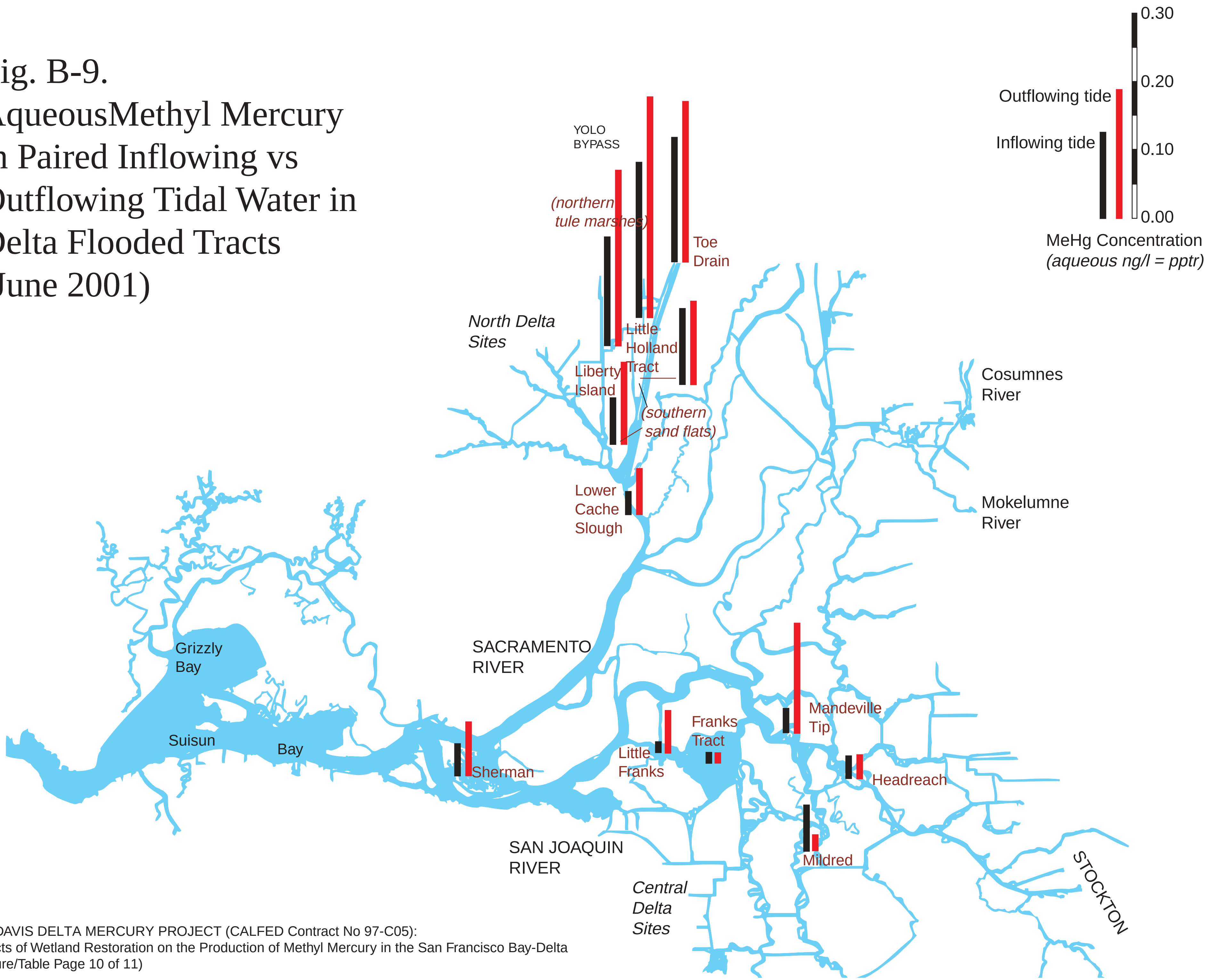




# Fig. B-8.
# Inland Silversides
# Total Mercury

(THg QA/QC tighter than MeHg)

- multi-individual composites
- whole body, dry wt ppm Hg
- *(dry wt ppm = app. 5x wet wt ppm)*

# Fig. B-9. AqueousMethyl Mercury in Paired Inflowing vs Outflowing Tidal Water in Delta Flooded Tracts (June 2001)

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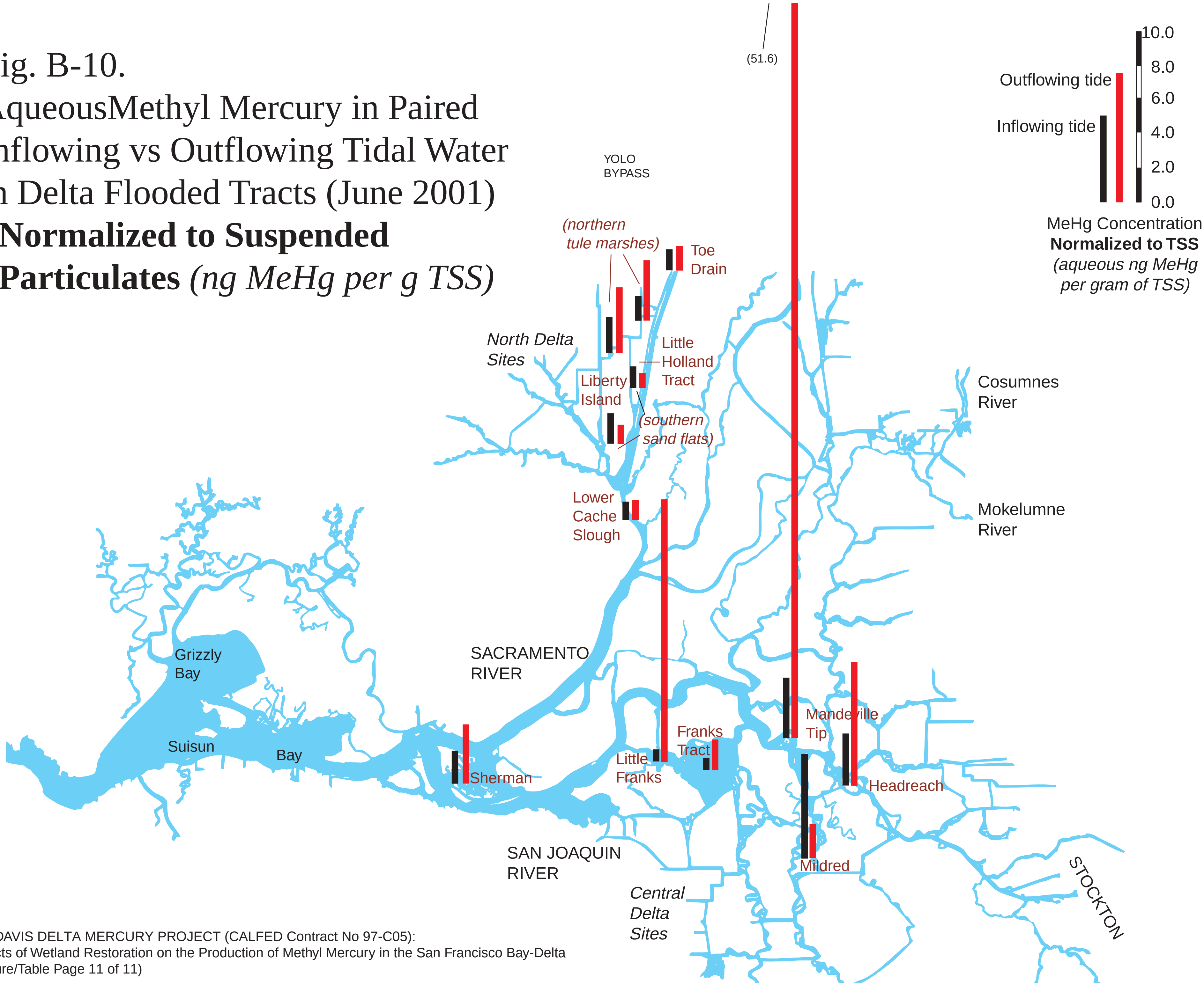
# Fig. B-10.
# AqueousMethyl Mercury in Paired Inflowing vs Outflowing Tidal Water in Delta Flooded Tracts (June 2001)
# *Normalized to Suspended Particulates *(ng MeHg per g TSS)*

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(Attachment C)

# GOLD MINING IMPACTS ON FOOD CHAIN MERCURY IN NORTHWESTERN SIERRA NEVADA STREAMS

**Darell G. Slotton, Shaun M. Ayers, John E. Reuter, and Charles R. Goldman**

*(1993-1996 UC Davis Research Project; Slotton et al. 1997a)*

## ABSTRACT / EXECUTIVE SUMMARY

In this research, we investigated mercury (Hg) levels in aquatic invertebrates and trout within the historic gold mining region of the northwestern Sierra Nevada, in order to determine the localized biological impacts of mining-derived Hg. These organisms were used as indicators of specifically the bioavailable fraction of Hg, that portion which can enter, transfer through, and be concentrated by the food web. The biota samples were used to determine relative "hot spots" of Hg contamination and to rank the various streams and rivers as to relative bioavailable Hg levels. Trout Hg was investigated also from a health perspective, for comparison with existing Hg guidelines.

Fifty-seven sites were sampled throughout the region during the three years of this study. A clear signature of mining-derived Hg was found, with notably elevated levels in the aquatic food webs of the South and Middle forks of the Yuba River, the mid-section of the Middle Fork of the Feather River, Deer Creek, the North Fork of the Cosumnes River, and tributaries throughout the Bear River drainage. Hg was low throughout most of the American and Feather River watersheds and in many tributaries away from the most intensively mined stretches of rivers. Elevated Hg regions did not demonstrate a point source signature. Where biotic accumulations of Hg were elevated, this elevation was generally distributed across many miles of stream or river. The elevated bioavailable Hg regions could thus be localized to specific tributaries or series of river miles, but not to highly localized "hot spot" point sources. This is consistent with the historic widespread use of Hg throughout the gold mining region and its subsequent redistribution downstream.

Mercury concentrations in trout, while variable, were found to be uniformly below existing health standards, indicating the lack of a direct health hazard within the region itself. Foothill reservoirs were found to operate as interceptors of bioavailable Hg, in addition to trapping much of the sediment-associated inorganic load. Significantly lower bioaccumulated levels were found throughout the food web below several reservoirs, as compared to upstream. Concentrations of Hg in aquatic indicator organisms increased in a predictable pattern with increasing trophic feeding level. Aquatic invertebrate samples can be used to determine relative Hg presence and bioavailability, to predict Hg levels in co-occurring trout, and to integrate localized bioavailable Hg conditions across various temporal scales, relative to the ages of the respective organisms.

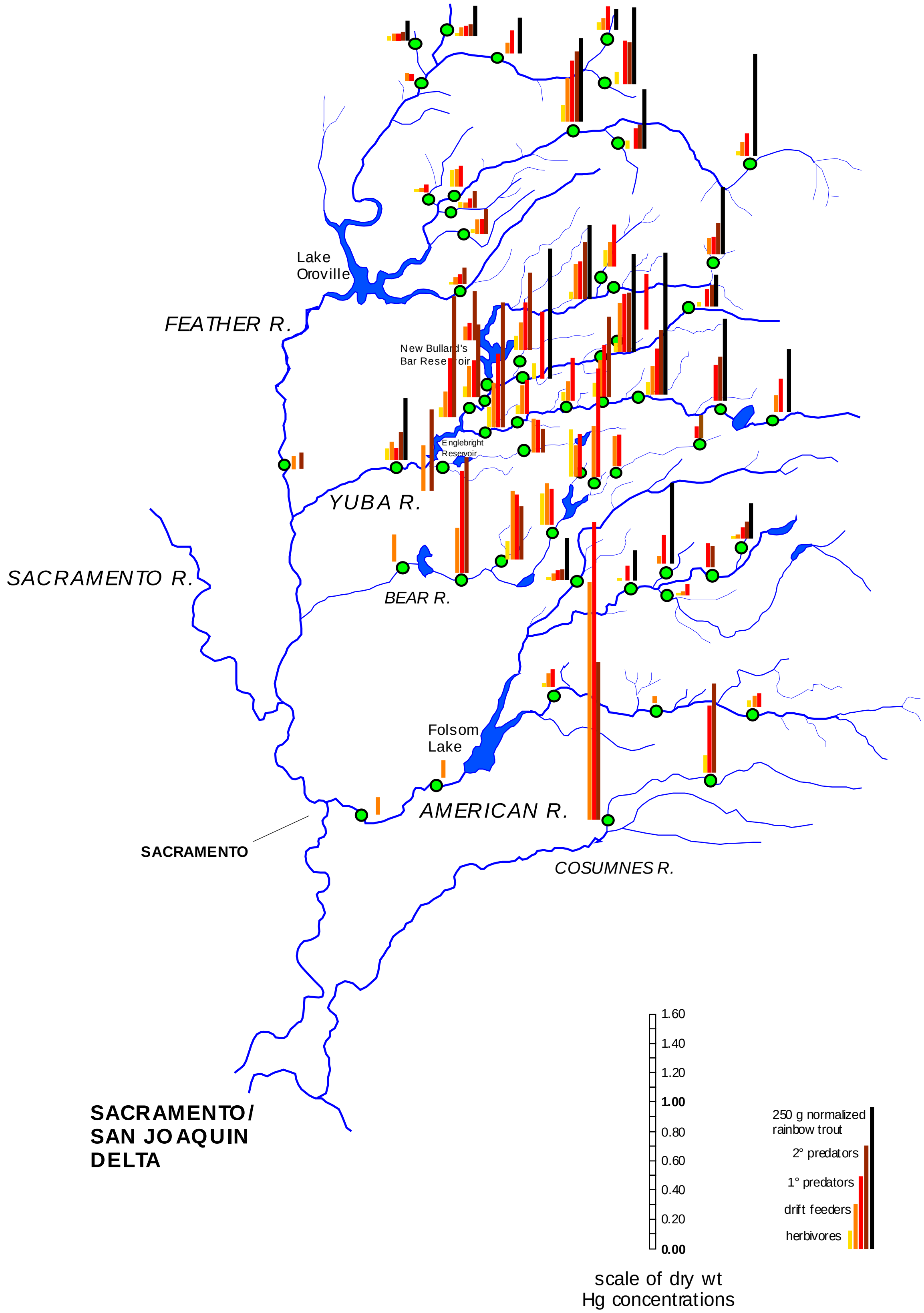


**Fig. C-1. Northwest Sierra Nevada Invertebrate and Trout Bioindicator Mercury Data**
*(adapted from Slotton et al. 1997a)*