Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

Project Information

1. **Proposal Title:**

   Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

2. **Proposal applicants:**

   Joshua Collins, San Francisco Estuary Institute
   Jay Davis, San Francisco Estuary Institute
   Donald Yee, San Francisco Estuary Institute
   David Krabbenhoft, USGS Wisconsin
   Mark Marvin-DiPasquale, USGS Menlo Park
   Steven Schwarzbach, USFWS

3. **Corresponding Contact Person:**

   Donald Yee
   San Francisco Estuary Institute
   7770 Pardee Lane Oakland, CA 94621
   510 559-9304
   donald@sfei.org

4. **Project Keywords:**

   Bioaccumulation
   Geochemistry
   Wetlands, Tidal

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:**

   Joint Venture

9. **Location - GIS coordinates:**

Latitude: 38.177

Longitude: -122.505

Datum:

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

The tidal wetlands along the Petaluma River

10. **Location - Ecozone:**

    2.4 Petaluma River, 2.5 San Pablo Bay

11. **Location - County:**

    Marin, Sonoma

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:**

    6

15. **Location:**

    California State Senate District Number: 3

    California Assembly District Number: 6

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?

       No

       If no, list single overhead rate and total requested funds:

Single Overhead Rate: 153

Total Requested Funds: 1037307

b) Do you have cost share partners already identified?

No

c) Do you have potential cost share partners?

No

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

No

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

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

No

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

Yes

If yes, identify project number(s), title(s) and CALFED program.

99N07	**Chronic toxicity of environmental contaminants in Sacramento splittail**	**CALFED Bay-delta Program**
00-E04	**Sonoma Creek Watershed**	**CALFED Watershed Program**
99-B06	**Association of ecological and human health impacts with Mercury in the Bay-delta**	**CALFED Bay-delta Program**
0145	**Napa River watershed stewardship**	**CALFED Bay-delta Watershed Program**

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)

21. **Comments:**

Environmental Compliance Checklist

Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

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

      No
   b) Will this project require compliance with NEPA?

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

      This research project will not significantly impact the ecosystem.

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
   Xnone

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

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

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

      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

CESA Compliance: 2081

CESA Compliance: NCCP

1601/03

CWA 401 certification

Coastal Development Permit

Reclamation Board Approval

Notification of DPC or BCDC

Other

FEDERAL PERMITS AND APPROVALS

ESA Compliance Section 7 Consultation

ESA Compliance Section 10 Permit

Rivers and Harbors Act

CWA 404

Other

PERMISSION TO ACCESS PROPERTY

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

Permission to access state land.
Agency Name:

Permission to access federal land.
Agency Name:

Permission to access private land.
Landowner Name:

6. **Comments.**

Land Use Checklist

Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

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

   No

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

   No

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

   No

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

   Research only

4. **Comments.**

Conflict of Interest Checklist

Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

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):

Joshua Collins, San Francisco Estuary Institute
Jay Davis, San Francisco Estuary Institute
Donald Yee, San Francisco Estuary Institute
David Krabbenhoft, USGS Wisconsin
Mark Marvin-DiPasquale, USGS Menlo Park
Steven Schwarzbach, USFWS

Subcontractor(s):

Are specific subcontractors identified in this proposal? No

Helped with proposal development:

Are there persons who helped with proposal development?

No

Comments:

Budget Summary

Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

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

Independent of Fund Source

Year 1												
Task No.	**Task Description**	**Direct Labor Hours**	**Salary *(per year)***	**Benefits *(per year)***	**Travel**	**Supplies & Expendables**	**Services or Consultants**	**Equipment**	**Other Direct Costs**	**Total Direct Costs**	**Indirect Costs**	**Total Cost**
1A	Project Management	60	1922	358						2280.0	3489	5769.00
1b	Subcontracting	20	641	119						760.0	1163	1923.00
1b	Subcontracting	10	231	43						274.0	419	693.00
1b	Subcontracting	30	728	136						864.0	1321	2185.00
2a	Data Management	80	1554	290						1844.0	2822	4666.00
2a	Data Management	30	646	120						766.0	1172	1938.00
2b	Data Analysis	100	4236	790						5026.0	7690	12716.00
2b	Data Analysis	30	773	144						917.0	1403	2320.00
2b	Data Analysis	60	1166	217						1383.0	2116	3499.00
3a	Field Work	80	3389	632	1000	2000	2700			9721.0	6152	15873.00
3a	Field Work	40	1030	192						1222.0	1870	3092.00
3a	Field Work	100	1943	362						2305.0	3527	5832.00
4a	USGS WI Hg/MeHg/DOC Analyses						37800			37800.0		37800.00
4b	USGS WI Field Work, Data Analysis	320			3000	3000	20800			26800.0		26800.00
4c	USGS WI Photodegradation Hg/MeHg isotopes						18000			18000.0		18000.00
5a	USGS Menlo Microbial transformation	310			6056	4542	20469			31067.0		31067.00
5a	USGS Menlo Microbial transformation	830					30628			30628.0		30628.00
6	MLML Fish sampling/homog						56900			56900.0		56900.00
7	MLML Benthos sampling/homog						32300			32300.0		32300.00
8	USFWS Bird egg sampling	750			4000	1300	68690			73990.0		73990.00
		2850	18259.00	3403.00	14056.00	10842.00	288287.00	0.00	0.00	334847.00	33144.00	367991.00

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**
1a	1a.Project Coord/Mgmt	60	2018	376						2394.0	3663	6057.00
1b	1b. Subcontracting	20	673	125						798.0	1221	2019.00
1b	1b. Subcontracting	10	243	45						288.0	440	728.00
1b	1b. Subcontracting	30	764	142						906.0	1387	2293.00
2a	2a Data Management	80	1632	304						1936.0	2963	4899.00
2a	2a Data Management	30	678	126						804.0	1231	2035.00
2b	2b. Data Analysis/Reporting	100	4658	868						5526.0	8456	13982.00
2b	2b. Data Analysis/Reporting	30	788	147						935.0	1430	2365.00
2b	2b. Data Analysis/Reporting	60	1260	235						1495.0	2287	3782.00
3a	3a. Field Sampling and Prep	80	3726	695	1000	2000	2700			10121.0	6765	16886.00
3a	3a. Field Sampling and Prep	40	1050	196						1246.0	1906	3152.00
3a	3a. Field Sampling and Prep	100	2040	380						2420.0	3703	6123.00
4a	4a. Hg/MeHg +DOC analyses 140 samples						37800			37800.0		37800.00
4b	4b. USGS WI Sample/ Consult	240			2000	3000	16700			21700.0		21700.00
4c	4c. Photodemethylation sample MeHg/Hg isotopes						18000			18000.0		18000.00
5a	5a. Microbial tranformation rates	310			6056	4542	22004			32602.0		32602.00
5a	5a. Microbial tranformation rates	830					32925			32925.0		32925.00
6	6. MLML Fish ~44 samples/yr						59750			59750.0		59750.00
7	7. MLML Benthos~44 samples/yr						33950			33950.0		33950.00

8	8. USFWS Bird egg sampling	750			4000	1300	73501			78801.0		78801.00
		2770	19530.00	3639.00	13056.00	10842.00	297330.00	0.00	0.00	344397.00	35452.00	379849.00

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**
1a	1a. Project Coord/Mgmt	90	3178	592						3770.0	5769	9539.00
1b	1b. Subcontracting	30	1059	197						1256.0	1923	3179.00
1b	1b. Subcontracting	10	255	47						302.0	462	764.00
1b	1b. Subcontracting	30	802	150						952.0	1456	2408.00
2a	2a. Data Management	80	1714	319						2033.0	3111	5144.00
2a	2a. Data Management	30	712	133						845.0	1292	2137.00
2b	2b. Data Analysis/Reporting	120	5869	1094						6963.0	10654	17617.00
2b	2b. Data Analysis/Reporting	40	1104	206						1310.0	2004	3314.00
2b	2b. Data Analysis/Reporting	80	1714	319						2033.0	3111	5144.00
3	3. Field Sampling and Prep	80	3913	729	1000	2000	2700			10342.0	7103	17445.00
3	3. Field Sampling and Prep	40	1104	206						1310.0	2004	3314.00
3	3. Field Sampling and Prep	100	2142	399						2541.0	3888	6429.00
4a	4a. Hg/MeHg +DOC analyses 140 samples						37800			37800.0		37800.00
4b	4b. Sample/ Consult	320			2000	3000	23800			28800.0		28800.00
4c	4c. Photodemethylation samples						18000			18000.0		18000.00
5	5a. Microbial tranformation rates	310			6056	4542	23655			34253.0		34253.00
5	5a. Microbial tranformation rates	830					35395			35395.0		35395.00

6	6. MLML Fish ~44 samples/yr						62800			62800.0		62800.00
7	7. MLML Benthos ~44 samples/yr						35600			35600.0		35600.00
8	8. USFWS Bird egg report	300					31458			31458.0		31458.00
		2490	23566.00	4391.00	9056.00	9542.00	271208.00	0.00	0.00	317763.00	42777.00	360540.00

Grand Total=1108380.00

Comments.

Budget Justification

Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

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

Task 1 (under project management) Task 2a Systems Analyst 30 hrs/yr Environmental Analyst - 80 hrs/yr Task 2b Environmental Scientists 1&2&3- each 33 to40 hrs/yr Assistant Env. Scientist 40 hrs/yr Environmental Analysts 1&2 40 hrs/yr Task 3 Env. Scientist 1&2&3 25 to 30 hrs/yr Assistant Env. Scientist 40 hrs/yr Environmental Analysts 1&2 40 hrs/yr Rates of collaborating PIs provided under Services or Consultants

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

Rates for the above individuals given for the first year. Rates in subsequent years rise ~5% per year for cost of living and merit raises. Systems Analyst - $22/hr Environmental Analysts 1&2 - $20/hr Environmental Scientists 1&2&3 - $32, $37, $42/hr Asst. Env. Scientist - $26

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

Benefit rate is 19% for all individuals above. Rates for Co-PIs given under services/consulting.

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

Travel costs listed all for local travel

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

Supply costs for field sampling supplies purchase/rental, ~$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.

Task 3 - $900/yr grainsize measurements on 24 sediment samples $1800/yr analysis of ~90 tissue samples for stable isotopes Tasks 4a-c USGS Wisconsin Direct Labor Hours . Task 4b David Krabbenhoft- 160 hrs/yr (yrs 1&3) ~120 hrs/yr2 Mark Olson- 160 hrs/yr (yrs 1&3) ~120 hrs/yr2 B. Salary David Krabbenhoft $39/hr in yr 1 Mark Olson- $24/hr in year 1 Cost of living and merit increases are estimated at 7% for yr 2 & 3. C. Benefits Benefits are estimated at 30% of base salary costs and included in Service/consulting costs. D. Travel Travel costs includes travel for 2 sampling trips in year 1 for Krabbenhoft and Olson ($2000). Year 2 and 3 include travel for 1 sampling trip (~$1000/year). Additional $400 are included for Dr. Krabbenhoft to attend project principal investigator meetings and/or professional scientific meetings related to this work. E. Supplies & Expendables Primary costs are for field supplies ($2000/yr). Office and computing costs are included in USFWS overhead. F. Services or Consultants Direct labor hours and benefits and USGS overhead rate (51%) are included in this category for task 4b. Task 4a, analysis of Hg/MeHg/DOC is calculated at $270 per sample for 140 samples per year. Task 4c, analysis of Hg/MeHg isotopes at $300 per sample is calculated for 60 samples per year G. Equipment There are no permanent equipment costs for these project tasks. H. Project Management Project management for USGS tasks included in direct labor estimates for Dr. Krabbenhoft under Task 4b. I. Other Direct Costs No other direct costs are requested.

J. Indirect Costs The USGS overhead rate (51.36% of total direct costs) applied to state and federal projects includes costs associated with rent and maintenance for USGS facilities, security, phones, furniture, and general office staff (secretaries and administrators). Overhead is already contained within items in the direct cost categories for USGS Wisconsin. Task 5- USGS Menlo Park Direct Labor Hours Task 5 (MMD) This project is estimated to command a 15% annual (312 hrs) effort on the part of Dr. Marvin-DiPasquale for each funding year. It will also require an estimated 40% annual effort (832 hrs) each year, on the part of one GS-9 technician to process all samples and to assist in data analysis. B. Salary Task 5 (MMD) The current full annual salary for Dr. Marvin-DiPasquale is $69,300/yr, and is $40,200/yr for a GS-9 technician. The compensation costs for this project are calculated from these annual salaries and the percent annual effort anticipated dedicated to this project per individual, as noted above. Cost of living increases are estimated at 4% for the second and third year. C. Benefits Task 5 (MMD) All benefits are calculated at 30% of base salary costs. D. Travel Task 5 (MMD) Travel for costs are requested for Dr. Marvin-DiPasquale and two technicians, to conduct two scheduled sampling events each year ($2000/yr). This includes food, lodging (4-5 days per sampling events), and gas/maintenance of two project vehicles (Suburban and radioisotope mobile laboratory truck). Additional funds ($1,000/year in YR2) are included for Dr. Marvin-DiPasqule to attend project principal investigator meetings and at least 1 non-local professional scientific meetings related to this work. These costs include airfare, car rental, lodging and per diem. E. Supplies & Expendables . Task 5 (MMD) Primary costs are for laboratory and field supplies ($4000/yr), and include: compressed gases ($400/yr), sampling equipment (bottles, stoppers, gloves, syringes, etc $1500/yr), chemicals ($600/yr), and radioisotopes ($1500/yr). Office and computing costs will be paid for by the USGS (cost sharing). F. Services or Consultants Task 5 (MMD) There are no outside service contracts associated with this task. All salary and benefits with overhead indicated in this task. G. Equipment Task 5 (MMD) There are no permanent equipment costs exceeding $5,000. H. Project Management Task 5 (MMD) Approximately 50% of Dr. Marvin-DiPasquales time on this project will be dedicated to project management which includes: overseeing sample analysis by laboratory technicians (i.e. inspection of work in progress), validation of costs, reports preparation, giving presentations, response to project specific questions, etc The funding for this project management is included in his requested salary. I. Other Direct Costs Task 5 (MMD) No other direct costs are requested. J. Indirect Costs Tasks 1 (MMD) The USGS overhead rate (51.36% of total direct costs) applied to state and federal projects includes costs associated with rent and maintenance for the Menlo Park facility, security, phones, furniture, and general office staff (secretaries and administrators). Budget Justification- MLML (Tasks 6&7) A. Direct Labor Hours . Task 6 Estimated 3 days in field per site for crew of 3 x 22 sites/yr ~530 hrs/yr for Rusty Fairey + 2 assistants Task 7 Estimated 1 day in field per site for crew of 3 x 22 sites/yr B. Salary Rusty Fairey $31/hr, Assistant 1 $16/hr, Assistant 2 $12/hr in year 1 Cost of living and merit increases are estimated at 5% for the second and third year. C. Benefits Benefits are estimated at 25.3% of base salary costs, included in the salary. D. Travel Travel is local for sampling, ~88 days in the field, overhead included total is $23950 yr 1 E. Supplies & Expendables Field supplies + equipment + overhead total ~$11350 in year 1. Office and computing costs are included in MLML overhead. F. Services or Consultants All expenses including overhead collapsed into this category as per sample costs: Task 6 (fish sampling + homogenization) = ($1190 + $103) /sample x 44 samples/yr Task 7 (benthos sampling + homogenization) = ($631 + $103) /sample x 44 samples/yr Estimated hours given under direct labor. G. Equipment There are no permanent equipment costs over $5000 for these project tasks. H. Project Management Project management tasks included in labor described above. I. Other Direct Costs No other direct costs are requested. J. Indirect Costs The MLML overhead rate (26% of total direct costs) applied to state and federal projects includes costs associated with rent and maintenance for MLML facilities, security, phones, furniture, and general office staff (secretaries and administrators). Budget Justification- USFWS (Task 8) A. Direct Labor Hours Task 8 Staff biologists- 750 hrs/yr (yrs 1&2), ~300 hrs/yr3 B. Salary Staff biologist- $71/hr including benefits Cost of living and merit increases are estimated at 7% for the second and third year. C. Benefits Benefits are

estimated at ~30% of base salary costs, included in the salary. D. Travel Travel is local for sampling, ~70-80 days in the field yr 1&2, overhead included. E. Supplies & Expendables Primary costs are for field supplies ($1000/yr) + overhead. Office and computing costs are included in USFWS overhead. F. Services or Consultants Salary + benefits + overhead collapsed into this category. G. Equipment There are no permanent equipment costs for these project tasks. H. Project Management Project management for USFWS tasks included in direct labor described above. I. Other Direct Costs No other direct costs are requested. J. Indirect Costs The USFWS overhead rate (29% of total direct costs) applied to state and federal projects includes costs associated with rent and maintenance for USFWS facilities, security, phones, furniture, and general office staff (secretaries and administrators).

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.

There are no permanent equipment costs exceeding $5,000.

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

Listed under Task 1 on the budget sheet. Env. Scientist 1 80-120 hrs/yr (~95 average), $32/hr in year 1, +5% increase each year Accountant 10 hrs/yr, $23/hr Contract manager 30 hrs/yr, $24/hr

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

None.

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.

The SFEI overhead rate (153% of salary+benefits ONLY, none assessed on other direct costs) applied to state and federal projects includes costs associated with rent and maintenance for SFEI offices, security, phones, furniture, IT equipment and maintenance, and general office staff for tasks not directly associated with projects (payroll, etc.).

Executive Summary

Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

Wetland restoration projects are proposed in areas in San Pablo Bay and Petaluma River. Wetland restoration will benefit the ecosystem, but in some cases existing mercury (Hg) contamination in restoration projects areas may negatively impact wildlife and humans unless steps can be taken to minimize such risks. One concern is impacts on the endangered California clapper rail, which has been observed to accumulate potentially harmful mercury concentrations in San Francisco Bay tidal marshes. Fish also accumulate mercury, impacting other wildlife and human consumers. A special concern with Hg is its biological transformations in the environment. Specifically, methylmercury (MeHg), formed by anaerobic bacteria such as found in wetland sediments, is more toxic and bioaccumulative than elemental and ionic forms of Hg commonly produced or released by human activity. Parameters such as total Hg, salinity, sulfate, reduced sulfur, oxygen, temperature, redox, pH, and dissolved or total organic carbon have been demonstrated to influence net MeHg production. These may interact antagonistically or synergistically and can vary in an estuarine system spatially and on seasonal and daily temporal cycles. This project will examine Hg and MeHg concentrations in the sediments, water and biota of five tidal marshes along a salinity gradient up Petaluma River. Influences of seasonal and interannual variation in environmental parameters on Hg geochemistry and bioaccumulation will also be examined. Physiographic differences among marshes of different ages to be studied are also expected to impact Hg geochemistry. Relationships found previously in other estuarine ecosystems will be sought, and changes with marsh progression will be examined to project likely long-term outcomes of restoration projects. This knowledge is needed for deciding where and how to restore selected wetlands and to anticipate possible impacts of projects. For restoration projects that proceed, additional studies can then be conducted to confirm projected changes and further refine understanding of Hg transformation and bioaccumulation processes in an adaptive management process.

Proposal

San Francisco Estuary Institute

Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

Joshua Collins, San Francisco Estuary Institute
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Mark Marvin-DiPasquale, USGS Menlo Park
Steven Schwarzbach, USFWS

Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

Joshua Collins, Jay Davis, Donald Yee, San Francisco Estuary Institute*
Steven Schwarzbach, USFWS Sacramento, Mark Marvin-DiPasquale, USGS Menlo Park, David Krabbenhoft, USGS Middleton, WI.
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A. PROJECT DESCRIPTION

1. Problem Statement

Efforts to restore wetland ecosystems, including projects supported by CalFed, are being proposed or underway in various locales, among them areas in San Pablo Bay and Petaluma River. Although wetland restoration provides overall ecological benefit, in some cases restoration of mercury-contaminated areas may negatively impact wildlife and human health unless steps are taken to minimize such risks. One concern is impacts the endangered California clapper rail, which has been found to accumulate potentially harmful concentrations of mercury in San Francisco Bay tidal marshes. Fish foraging in or around wetland habitats may also accumulate mercury, impacting other wildlife and humans that consume those fish. Relatively little effort to date has been devoted to investigating these impacts in tidal wetlands, which this proposal aims to address. This study aims to improve understanding of the following:

- Spatial and temporal variation of mercury (Hg) and methylmercury (MeHg) in North San Francisco Bay tidal wetlands.
- Environmental factors influencing the net methylation of Hg in these areas.
- MeHg bioaccumulation and impacts in California clapper rails and other species at different trophic levels in these environments.

MeHg, primarily formed by bacteria in anaerobic environments like wetland sediments, is more toxic with greater potential for bioaccumulation than elemental and other inorganic forms of Hg commonly released by human activity. Previous studies have found correlations between MeHg and percentage of wetland coverage in watersheds [1-3]. Hg present in soils and vegetation is released to aquatic environments after flooding and transformed into MeHg, with resulting increases in fish tissue concentrations [4-7]. MeHg is particularly high in newly flooded wetlands, due to large quantities of organic carbon available for bacteria to generate anaerobic conditions [7].

There is a substantial and growing body of work on Hg geochemistry and bioaccumulation, but much remains to be elucidated. A number of environmental parameters such as total Hg [8, 9], salinity [10, 11], sulfate [9, 12-14], sulfide [15], temperature [16], pH [17-19], and dissolved or total organic carbon [10, 18, 20, 21] have been shown to influence Hg bioaccumulation and MeHg production or degradation. These factors may interact in antagonistic or synergistic manners and can vary in estuarine systems spatially and on seasonal and daily time scales.

This study aims to examine the environmental factors controlling Hg and MeHg distribution in sediments, water and selected biota of tidal marshes in North San Francisco Bay. Sampling will occur in two seasons for three years to evaluate influences of seasonal and interannual variations on Hg geochemistry and bioaccumulation. We expect that many relationships reported previously for other marine and freshwater

ecosystems will be similar for the local environment. Finding differences from previous work will also be instructive; by evaluating these similarities and differences, we can refine our conceptual understanding of Hg processes for the local estuarine environment.

This knowledge can be applied by CalFed in deciding where and how to proceed with tidal wetland restoration projects. For example, if net MeHg is elevated within a particular range of sulfate concentrations, restoration projects might be better pursued in areas with sulfate concentrations outside this range. Similarly, if wet-season flows deposit sediments with higher Hg than in the dry season, decisions for timing the breaching of dikes could be altered. Potential Hg methylation is only one of many factors that should be considered; timing and location of wetland restorations should also be guided by the life cycles and other requirements of particularly desired biota (e.g. species endangered or with commercial and recreational value). For restorations that proceed, additional studies can then be conducted to further refine our understanding of Hg transformation and bioaccumulation in an iterative and adaptive management process.

2. Justification

a. Conceptual model

Problems with Hg contamination arise when a number of factors occur:

- Hg is elevated above natural concentrations in the ecosystem
- Bacterial transformations convert inorganic Hg into MeHg
- Food web structure allows MeHg to bioaccumulate at harmful concentrations

This research on Hg and MeHg outside of pilot or other restoration implementation projects is necessary given the temporal and spatial scope of projects; there is great uncertainty in projecting future impacts of wetland restoration projects given large differences in physical, hydrological, biological, and chemical characteristics between older and newer marshes. Attempting course corrections by manipulating water or sediment loads after a project has significantly progressed years or decades later will be difficult if not impossible. By examining characteristics of similar wetlands at further stages of development, we can better anticipate the likely mid- and long-term progression and Hg impacts of restoration projects.

Correlations of environmental parameters to Hg in biota are found in the literature, but some of these vary in magnitude and direction (e.g. the effect of temperature on demethylation [22-24] and DOC on MeHg [8, 10, 20, 21]). Although estuarine environments often produce less MeHg than freshwater environments Hg concentrations exceeding thresholds for toxic effects are found in fail-to-hatch clapper rail eggs in this region. Furthermore, San Francisco Bay fish tissue Hg concentrations are high enough to warrant a human consumption advisory. Thus, Hg processes should be studied locally to better understand their potential role in these negative impacts.

Information on the primary influences on MeHg production and accumulation in regional food webs will be needed in decision-making processes for wetland restoration. By providing data to refine our conceptual understanding of existing local wetlands, better predictions for the outcomes of restoration projects can be made and negative impacts avoided. Evaluating correlations between Hg and MeHg in wetlands and resident biota can illuminate likely outcomes from alternative management actions. Understanding Hg transformations and trophic transfers within the local food web will allow better evaluation of restoration projects such as in choosing appropriate sampling strategies, which can then be used in choosing the next iteration of management actions.

Sampling the full range of spatial and temporal variability would be extremely resource intensive. This project as currently proposed sacrifices some spatial coverage to better examine differences for specific wetland processes. If the conceptual model hypotheses are not borne out by the data, in later years sampling could be adjusted by trading duplicate samples within a marsh for other sites or sampling in only one season but at more sites. Decisions on such adjustments would be made after each year of sampling. Similarly, if sufficient organisms of one species cannot be found at some locations some times, other organisms can be collected instead for tissue sampling. These decisions would be made as needed in the field and laboratory.

Older tidal wetlands share a common physiographic template and set of geomorphic features and processes. We hypothesize that spatial patterns in that template and seasonal variation in environmental conditions will cause differences in MeHg production and degradation within tidal marshes. Preliminary data from USFWS studies support this hypothesis; significant differences between surface sediment MeHg concentrations of first and third order channels were found. Understanding the underlying processes that give rise to these patterns will allow determination of the most highly impacted species, comparisons within tidal wetlands using a stratified sampling approach, and regional comparisons among wetlands by finding appropriate monitoring strata.

Less established marshes will not share the same physiography, but features within those wetlands will also allow a stratified sampling approach. By examining marshes of different ages within a salinity regime, differences in Hg processes arising from geomorphic dissimilarities may become apparent. The ability to make comparisons along chemical and temporal gradients will allow CalFed to select locations and methods for wetland restoration that minimize potential Hg accumulation hazards and to project likely long-term changes in site characteristics as wetland projects mature.

Our current conceptual understanding of environmental Hg processes and the information needed to test the validity of this model are presented below for the highly interrelated issues of environmental Hg distribution, biogeochemical transformation, and bioaccumulation.

1) Mercury distribution

Characterizing Hg and MeHg concentrations in tidal wetlands and linking these to other ecosystem factors such as hydrology and geochemistry of other elements are necessary to understanding possible risks to the ecosystem. Studies have found significant correlations between total Hg and MeHg concentrations in sediments [9] and water [25]. These hypotheses on Hg and MeHg in tidal wetlands will be tested:

- Hg concentrations are elevated above natural background concentrations
- Differences exist in total Hg and MeHg within and among wetlands
- Total Hg and MeHg concentrations correlate spatially and temporally

This study will examine if variations in Hg and MeHg distribution within and among marshes are significant. One key uncertainty is how total Hg concentrations in wetlands correlate with negative impact the biota. This uncertainty is reduced in this study by measuring MeHg, the Hg species that most directly impacts higher trophic level organisms. Concurrent measurements of total Hg, MeHg and other environmental parameters will reduce our uncertainty about the relationship between these factors, information needed to assess the risk posed by Hg in other wetlands and to determine if alternative management actions would be possible and effective.

Both Hg and MeHg are found naturally, so wetland restoration cannot provide habitat less contaminated with Hg than "background" conditions (prior to human influence). Background concentrations may not be achievable through local management actions, as anthropogenic atmospheric Hg has impacted environments distant from industrial activity [26]. Locally, large loads of Hg-laden fine sediments from Gold Rush mining (ca. 1850-1880) and more recent deposits (ca. 1950) from mechanized Hg mining and other industrial activities [27] have collected in the San Francisco Estuary and likely also impact regional tidal wetlands. However, recent studies in the Florida Everglades using wetland enclosures and Hg stable isotope tracers indicate that new Hg is more apt to be methylated and bioaccumulated [28], so older deposits may not be as important as current sources of inorganic Hg.

CalFed funded studies in the Delta have not yet indicated significant influence of total Hg on net MeHg concentrations [29], but interpretation may thus far be confounded by differences in sediment characteristics and water chemistry at the sampled sites. Other researchers have suggested that there is a threshold (about 5,000 ng/g dry wt.) above which additional Hg(II) does not cause any increase in MeHg production [30, 31]. However, these studies were in freshwater ecosystems, and geochemical controls and threshold values for saline tidal environments may be different. To make appropriate management decisions on wetland restoration, managers need to know if significant differences exist in total Hg of North Bay tidal wetlands, and whether these differences correspond to differences in MeHg production and accumulation.

2) Mercury transformations

Because of the importance of biological transformations in the distribution and fate of Hg in the environment, total Hg is only one of many factors that must be examined. Effects of many environmental parameters on Hg methylation have been documented in the literature but show divergent results over different ranges of these parameters. We wish to test the following hypotheses regarding Hg transformations with this study:

- Multiple biogeochemical factors mediate MeHg production and degradation among and within wetlands
- Differences among wetland features influence net MeHg production
- Geomorphology and salinity regime mediate the degree of MeHg production
- Net MeHg production varies seasonally and interannually
- MeHg degradation is important in net MeHg production

In addition to Hg and MeHg measurements, we will examine the following environmental parameters to evaluate their influences on net MeHg production: salinity, pH, sulfate, dissolved organic carbon, sediment organic carbon and sulfur, acid volatile sulfide, redox potential, temperature, and wetland geomorphology. Uncertainty arising from conflicting results in previous research for other ecosystems can be reduced by examining the influence of these factors on MeHg in the local ecosystem.

A number of parameters generally co-vary in estuarine waters. Some of these factors may affect inorganic Hg bioavailabilty and MeHg production and degradation additively or synergistically, whereas others will act antagonistically. Hg geochemistry is complex given interactions between these factors, and field studies are needed to further our understanding of Hg processes in the local environment.

Even given this likely complexity, a number of characteristics may emerge. We expect that longer inter-tidal sediment exposure periods and more "freshwater" signatures

with moderate water column sulfate [9, 12-14] concentrations will promote higher rates of net MeHg production in wetlands. Seasonal variability will likely be driven by differences in freshwater influence and effects of temperature and solar radiation on methylation and demethylation processes. Although three years of sampling provides little statistical power in evaluating interannual variability within any season, interannual information will provide at least first order estimates of uncertainty for other studies with no temporal coverage within sites. Furthermore, spatial differences in net MeHg within and among wetlands with similar degrees of marine influence will be influenced by hydrological and biological differences of morphological features. These factors are discussed in more detail below.

Sulfur: Anoxic sediments are the primary zone where inorganic Hg(II) is converted to organic MeHg by sulfate reducing bacteria (SRB) [32], although SRB can methylate Hg while operating fermentatively as well. Sulfate is one parameter that may either increase or decrease net MeHg, depending on its concentration range [15]. Increasing sulfate (SO_4^{2-}), up to approximately 1-3 mM, typically stimulates the activity of SRB in freshwater sediments [33]. A corresponding increase in SRB mediated Hg-methylation is thus often observed with increasing SO_4^{2-} [12, 34]. However, the extent of MeHg production is not only related to the activity of SRB, as they reduce SO_4^{2-} to sulfide (S^{2-}). MeHg production rates are highest under low S^{2-} (ca. 1-10 uM), while higher S^{2-} concentrations begin to inhibit the Hg-methylation process [15]. Since many factors such as O_2 mediated reoxidation of S^{2-} to SO_4^{2-} and metal-sulfide mineral formation (e.g. FeS, FeS_2, MnS, etc.) influence dissolved S^{2-} concentrations in sediments, localized physical and geochemical processes (e.g. bioturbation, microbial Fe- and Mn-reduction, plant mediated O_2 transport to the rhizosphere) dictate the zone of maximum benthic MeHg production in both time and space. The spatial and temporal coverage selected for this study will result in a range of water and sediment sulfur concentrations and speciation.

Transformation rates: Various biotic and abiotic processes also degrade MeHg. It is the competition between gross production and degradation that ultimately dictates the extent of net MeHg production [24, 35], but other than recent studies in the Florida Everglades [36], no ecosystem-level investigations to date have included simultaneous measurement of both processes. MeHg degradation in sediments may proceed by *mer*-operon mediated microbial detoxification [37, 38], microbial oxidative demethylation [39], and abiotic reductive demethylation linked to reactions with sulfide [40]. In addition, photodegradation of methylmercury can be a major sink of MeHg in some ecosystems [41, 42], and as a result water clarity or solar intensity (particularly UV light) can have a strong influence on observed MeHg levels in the water column. Understanding the relative importance of these Hg-transformations, and the environmental factors that control them, is critical to assessing the fate and transport of Hg in a given ecosystem, and in the development of cost-effective planning or remediation strategies. Measurements of biotic and abiotic methylation and demethylation rates in this study will provide an improved understanding of the role of these processes in producing observed MeHg distributions in the environment.

Geomorphology: USFWS data collected in older North SF Bay tidal marshes suggest that differences in channel order and wetland morphology result in differences in sediment MeHg concentration, production, and/or cycling [43] that conform to some of our expectations of MeHg geochemistry. Because of smaller tidal excursions and lower

flow rates associated with low-order channels, MeHg production is likely to be higher and occur nearer the surface than in higher order channels. The increased organic load found in low-order channels may also increase anaerobic bacterial activity and thus Hg methylation. Lower flow regimes in low-order channels may also disturb the sediment surface less, allowing the oxic/anoxic interface to develop nearer the surface. This may impact biota at the sediment surface, as they will reside nearer or in zones of maximum MeHg production and accumulation. Smaller channels comprise a large fraction of total surface area within wetlands, so they may also contribute a large fraction of a wetland's MeHg output to adjacent ecosystems. Another consequence of lower channel order may be increased temperature, as less cold and aerated water finds its way up the farther reaches of a marsh on each tidal cycle. Higher temperatures may increase net methylation [16, 23], even if demethylation rates also increase [24]. Physiographic differentiation in younger marshes is expected to be less distinct than in older systems, and thus net MeHg production within a less developed marsh is likely to be more uniform throughout. Site selection in this study therefore includes wetlands of different ages within a zone of similar salinity conditions to test this.

Marine influence: With increasing marine influence in an estuary, salinity, pH, and sulfate all generally increase. Salinity and sulfate influence Hg methylation non-linearly over the range of estuarine concentrations. At low and high chloride, bacterial Hg uptake and methylation is reduced relative to rates at intermediate salinity [10], and this effect is also seen on phytoplankton Hg uptake [11]. Bacterial methylation rises as sulfate increases to intermediate levels, but decreases as sulfate rises further. The ratio of MeHg to total Hg is relatively low in some estuaries [9], possibly due to higher marine sulfide concentrations. Another mechanism potentially contributing to low estuarine MeHg production is the increase in oxidative demethylation by SRB with higher sulfate concentrations in estuaries [14]. In freshwater systems, Hg methylation rates increase with decreasing pH in the epilimnion and surface sediment of lakes [19]. Others have found increased MeHg concentrations correlate well with decreased pH in lakes for fish and zooplankton, respectively [17, 18]. Increased pH with increasing marine influence might therefore be expected to decrease Hg methylation and net accumulation.

Statistical methods such as multiple regression and principal components analysis will be used to evaluate the primary influences from among the many environmental factors. For sulfate, chloride, and other parameters with non-linear effects on MeHg, transformations to models more closely approximating known chemical and biological processes (uncharged chloride species, relative methylation to demethylation rates at various sulfate levels) may be needed for proper evaluation of their influence.

3) Mercury bioaccumulation

Hg bioaccumulation will be evaluated to determine whether patterns seen in net MeHg production in sediment or water translate into patterns in food web contamination. Hypotheses of Hg bioaccumulation to be tested in this study are as follows:

- Bioaccumulated Hg correlates with trophic level of an organism
- Hg in biota correlates with MeHg concentration in water and sediment
- Hg concentrations for sessile benthic organisms therefore exhibit spatial variations similar to those of water and/or sediment

Trophic position is one of the primary factors influencing tissue Hg concentrations, with concentrations increasing with each step in the food web. Organisms from multiple

trophic levels will be sampled to assess whether spatial and temporal patterns propagate through the food web. Particular attention will be given to potential food web transfer of MeHg to clapper rails.

Past work by USFWS has found Hg concentrations in fail-to-hatch clapper rail eggs that exceed thresholds for toxic effects. Developing embryos are the most sensitive life stage for Hg toxicity. Observed Hg concentrations may be contributing to the low productivity observed for San Francisco Bay clapper rails. Because of the fidelity of individual rails to a particular marsh and even specific territories within that marsh for feeding, they may reflect the spatial variability in Hg concentrations found within and between marshes. Bird egg samples will be collected once per year, and Hg concentrations will be measured. Only fail-to-hatch eggs of California clapper rails will be collected because of their endangered status. Eggs of other marsh-nesting birds (e.g. stilts) will be sampled in areas where suitable rail eggs cannot be found.

Benthic invertebrates also do not travel between marshes, and they seldom move even within a marsh. They will therefore reflect spatial differences in MeHg among marshes and possibly among locations within marshes. The short life spans of some species may also result in observable seasonal differences in tissue Hg concentrations. Two species from each site, selected based on biomass abundance of that species, will be composited for Hg analysis. Samples will be composited at genus or higher taxonomic levels when sufficient biomass from individual species cannot be found at a site.

Tidal wetland fish species are generally more mobile than invertebrates. Fish that feed in the water column such as silversides and juvenile striped bass move easily among channels and therefore may only reflect differences among marshes and not differences within any marsh. Sampling of juvenile striped bass in 1999 found a 2-fold higher concentration of Hg in a marsh site relative to an open Bay site, suggesting that marshes may be sites of enhanced Hg accumulation. Fish such as gobies and sculpin that are territorial and feed at the sediment move less and thus may reflect the spatial variations within a marsh. Fish will be sampled once yearly from all sites. Hg will be measured in composites of two abundant species.

3. Approach

a. Site selection

Variation in environmental characteristics influencing mercury transformation rates and species concentrations will be examined by sampling five wetlands (Figure 1) during winter and summer to include high and low freshwater flow periods. Wetlands were selected to explore correlations between MeHg availability and marsh age and salinity regime. Wetlands along the Petaluma River gradient were chosen because it lacks any known local source of Hg, involves tidal marshes throughout its length, and many of these marshes have supporting scientific information. A complementary study of marsh ecology is being proposed to CalFed ERP by the Southern Sonoma Resource Conservation District. The two studies will share study plans and findings.

To examine the MeHg-marsh salinity relationship, three marshes of middle age (50-100 years) were selected along the salinity gradient of the Petaluma River: one position 8 miles upstream from San Pablo Bay, one mid-gradient 5 miles upstream, and one at the river mouth near Highway 37. Marshes of this age were chosen because they represent the physiography and community structure commonly accepted as the endpoints of restoration efforts.

To examine the MeHg-marsh age relationship, two additional marshes at the mouth of the Petaluma River of ages 10 years and about 500 years will be compared with the river mouth location of 50-100 years that is also part of the salinity gradient. These three marshes of varying age are subject to the same salinity and tidal regime. These sites will focus on marsh development to examine possible changes over time of restoration on MeHg availability. All three sites are conveniently located near each other.

b. General sampling approach

Within marshes, sediment samples will be taken from the banks of channels, where MeHg is most likely available to channel fauna, including steelhead, striped bass, and clapper rails, which are fairly abundant in some of these marshlands. Marsh sediments and water will be sampled from 2^{nd} and 4^{th} order channels where possible. For younger, less-developed marshes, samples will be taken from channel and tidal flat/vegetated plain boundary strata. This temporal and spatial sampling distribution should lead to a wide range of the key environmental parameters likely important in mediating the Hg-cycle in natural systems. Estimates of microbial and photochemical MeHg production and degradation rates will also be measured for those samples. The most abundant biota from lower taxa will be sampled from sites during both seasons. Higher trophic level biota will be sampled once annually. From this suite of measurements we will statistically assess which variables are most important in controlling spatial and temporal differences in Hg cycling for these wetlands.

c. Mercury distribution

This study will test our hypotheses that Hg and MeHg concentrations vary widely, but systematically, within and among tidal wetlands. The null hypothesis is that Hg and MeHg concentrations do not vary significantly over time and in space. To examine spatial variability at older marshes, one 2^{nd} order and one 4^{th} order channel site will be sampled in each marsh during each sampling season. Samples will be taken from surface sediments (0-2 cm) during ebb tide at edges of channels, and 8-10 subsamples composited for each site to reduce the number and expense of sample analyses for contaminants. Higher trophic level biota impacted by Hg bioaccumulation will be spatial and temporal integrators of contamination, and therefore capturing small (meter) scale variations in Hg and MeHg concentration through analyses of separate samples within a site is unnecessary. Newer marsh with little or no developed channel hierarchy will also be sampled at two strata: edges of small channels, and boundaries of tidal flat/vegetated plain. At one marsh each season, composite samples from two additional sites of a single stratum (e.g. 2^{nd} or 4^{th} order channel) will be collected.

Sediment samples will be analyzed for Hg (CVAFS, EPA 1631), MeHg (EPA Method 1630 modified [44]), TOC (loss on ignition), grain-size (wet and dry sieving), and acid volatile sulfur [45]. Temperature, pore-water redox potential, sulfide, electrical conductivity, and pH will be measured by probe in situ at the sediment surface. Pore-water sulfate and chloride will be measured in the lab via ion chromatography. Samples will be kept on ice in the field and shipped frozen to the analytical labs (USGS Wisconsin for Hg/MeHg, USGS Menlo Park for sediment ancillary measurements).

One grab sample of surface water for Hg and MeHg analysis will be collected mid-channel using clean techniques (EPA 1669) at each site. Separate grab samples will be collected at each site for suspended solids (filtered and weighed, APHA Standard Methods) and other ancillary measurements. Duplicate water grabs will also be collected

at one site per marsh. Samples for Hg/MeHg analyses will be preserved with 1% HCl. Water samples will be analyzed for MeHg, total Hg, sulfate, chloride, and DOC. Water column electrical conductivity, pH, redox potential, and optical density of the water will be measured in the field. Water and sediment sampling will be performed by SFEI staff, with Drs. Krabbenhoft's and Marvin-DiPasquale's participation on both sampling trips for the first year to provide guidance. Total Hg/MeHg and DOC in water samples will be analyzed by Dr. Krabbenhoft's lab at USGS (Wisconsin). Ancillary measurements in water samples will be made at USGS Menlo Park or subcontracted to other labs as needed subject to the collaborators' approval.

d. Mercury transformations

Microbial Hg methylation and demethylation rates will be assessed at all the described locations in winter and late summer. Potential Hg methylation rates will be measured in homogenized surface sediment (0-2 cm) using a $^{203}HgCl_2$ amendment radiotracer technique [46]. Sediment will be collected using trace-metal clean procedures, and sub-sampled in the lab anaerobically in a N_2 flushed glove bag. Short-term (≤ 6 hour) incubations will be carried out in sealed serum bottles at in-situ temperatures (± 1 ^0C). Incubations will be arrested by flash freezing. The end-product $Me^{203}Hg$ will then be organically extracted and quantified by gamma counting. Rate constants (k_{meth}) derived from these radiotracer assays will be multiplied by the in-situ pool size of "reactive" Hg(II) to estimate in situ rates of Hg-methylation. This "reactive" Hg(II) pool will be operationally defined as the amount of Hg(II) converted to gaseous Hg^0 by tin-chloride in non-acid-digested whole sediment.

Microbial MeHg degradation in 0-2 cm surface sediment will be assessed for all sites. Incubations will be conducted at the same incubation time and temperature conditions as for Hg methylation. The radiotracer [^{14}C]-MeHg amendment method will be used, with quantification of end-product gases ($^{14}CH_4$ and $^{14}CO_2$) by the CH_4-comustion/CO_2-trapping method [47]. Rate constants (k_{deg}) derived from these radiotracer assays will be multiplied by the in-situ pool size of MeHg in bulk sediment to estimate in situ rates of MeHg degradation. This approach provides a cursory measure of the MeHg reductive or oxidative degradation pathways in a particular system [48]. Such differences in pathway may have important implications on the relative production of dissolved gaseous Hg^0 or Hg(II) as potential end products of MeHg degradation, and subsequently on the residence time of Hg in the sediment.

Photochemical MeHg degradation will be measured by in situ incubation of site water spiked with MeHg synthesized from stable isotopes of mercury (e.g., $Me^{199}Hg$). Incubating sample bottles with the amended isotope spikes will be suspended at water surface following the methodology of Krabbenhoft [41]. Replicate samples will be pulled from the water column at specific time intervals to estimate photo-demethylation rates and included in the accounting for MeHg and Hg transformation rates.

Ancillary measurements in the lab for sediment will include microbial sulfate reduction rate (via ^{35}S radiotracer) [49], whole sediment acid-volatile reduced sulfur [50], organic content (loss on ignition and/or CHN analyzer), and pore-water sulfate and chloride (via ion chromatography). Measurements taken in the field will include temperature, electrical conductivity, redox potential, and pH (via probes), and sulfide (via ion specific probe). This information will us help elucidate what controls observed differences in Hg-transformations in the various benthic samples.

Hg methylation and demethylation incubations and ancillary measurements will be made by Dr. Marvin-DiPasquale's lab at USGS (Menlo Park). Photo-demethylation samples will be analyzed by Dr. Krabbenhoft's lab at USGS (Wisconsin).

e. Bioaccumulation

Spatial and temporal variations in distribution of Hg and MeHg may result in observable effects on Hg in biota. Hypothesized spatial and temporal patterns within marshes will be evaluated with non-migratory, lower trophic level species, including bivalves, amphipods, crayfish, and other benthic invertebrates. These organisms are important components of the diet for clapper rail and other marsh inhabitants. Benthic species will be evaluated as potential indicators of variation with channel order and season. Within each marsh, composite samples (with multiple individuals in each composite) will be collected at each sampling site. Variation in Hg speciation between marshes will be evaluated in benthic invertebrates, fish, and clapper rails.

Target fish species include inland silversides, staghorn sculpin, prickly sculpin, juvenile striped bass, and yellowfin goby. Inland silversides should be present in all of the marshes and have been found to be an effective indicator of Hg distribution by Slotton and coworkers [29]. The other fish species are abundant predators that reside in marshes and would be expected to accumulate relatively high Hg concentrations. Sculpin and striped bass are successfully being sampled in a separate SFEI study of two marshes in San Pablo Bay. Abundant smaller fish (e.g. silversides) will be analyzed as multi-individual composites. Striped bass are larger and less abundant and will be analyzed as individuals. Compositing strategies will be employed for other species depending on their size and abundance. Fish will be sampled twice per year in the summer using an otter trawl in the larger channels and beach seines or other devices (e.g. dip nets) in the shallower waters. Benthic invertebrate and fish samples will be collected by SFEI, frozen and sent to the lab for homogenization and analyses.

Clapper rail eggs that fail to hatch will be collected and analyzed for MeHg. We will investigate the relationship between regional variation in rail eggs and concentrations in prey and MeHg production in sediment and water. Clapper rail eggs will be collected once per year in each marsh. Stilt eggs may be sampled in areas without rails as their feeding habits are expected to be most similar. Bird eggs will be collected by Dr. Schwarzbach and USFWS personnel.

Benthic biological samples will be analyzed for MeHg, the form that is most toxic and efficiently transferred through the food web. For higher trophic levels, total Hg will be measured. Biological tissue Hg and MeHg analyses will be performed by USGS (Wisconsin). In addition, stable nitrogen and carbon isotopes will be analyzed (by UC Davis Stable Isotope Facility) as indicators of trophic position and food source. Variation in food web structure among the marshes could potentially influence Hg concentrations at higher trophic levels. Collecting the isotope data will allow us to evaluate inter- or intra-marsh variation that is caused by variation in food web structure.

f. Quality assurance

A quality assurance project plan based on that of the Regional Monitoring Program for Trace Substances will be established. Aside from duplicate samples collected in the field, labs will be required to run duplicate analyses of field and control samples to ensure adequate performance. Analyses failing data quality criteria will be reanalyzed as needed.

4. Feasibility

The collection methods and analyses described for sediment and water samples are similar to those used previously in studies of Hg and MeHg in other fresh and marine environments [9, 13, 51]. Incubation experiments for sulfate reduction, Hg methylation, and MeHg demethylation rate measurements follow methods of previously published work. Sampling sites are on public lands, and sampling is neither so extensive nor so frequent that lasting observable impacts on the sites would be expected. Eggs of endangered California clapper rails are collected only if found non-viable.

Collaborating partners on this proposed project have successfully performed similar studies for the portions of the project for which they are responsible (see qualifications), in this region and others. There are competent commercial laboratories that can perform some of the chemical analyses (e.g. Frontier Geosciences for Hg and MeHg measurements) for approximately the same cost if needed, should unanticipated demands on their time arise. However, the number of sites and sampling frequency were chosen with the availability of these collaborators and their staff in mind.

5. Performance Measures

High quality peer review is one of the best ways to ensure that the project products successfully meet objectives. Project performance can be evaluated by accomplishment of the following measures:

- Formalize agreements with collaborating partners
- Submit quarterly fiscal and programmatic reports
- Refine and approve of annual sampling plans through peer review
- Sample all matrices successfully
- Meet Chemical analyses data quality criteria
- Complete chemical analyses and QA/data reports within 5 months of sampling
- Complete peer-reviewed annual project findings and progress reports for CalFed
- Present findings at review meetings
- Produce peer-reviewed final report
- Present findings and raw data on the web
- Publish results in peer-reviewed journals

Success can be quantified by the timeliness, quantity, and quality of these products.

6. Data Handling and Storage

All data generated in the field and through laboratory analyses will be kept on a microcomputer database server at SFEI. The server is backed up weekly and copies kept offsite. Subsets of the data can be generated and exported to common formats for use by collaborators and other interested parties. SFEI will manage the data from this study using procedures developed for the Regional Monitoring Program for Trace Substances, whose data SFEI has successfully managed for the past seven years. Analytical results will be transferred to SFEI in spreadsheets or other electronic formats by the laboratory and compiled into an Oracle database, which will be maintained by SFEI. To minimize data formatting by SFEI staff, templates and guidelines explaining the structure of the database tables will be provided to the laboratories. Data will be reviewed to ensure consistency with the master database format. Results will be compiled in a cross-tabular format (e.g. site, date, variable, result) for QA review and reporting, and will be made accessible through SFEI's website.

7. Expected Products

Primary products of this research project will be reports and presentations including the following:

- Annual peer-reviewed sampling plan
- Quality assurance project plan
- Annual peer-reviewed project reports with preliminary data and interpretation
- Presentations at annual review meetings and symposia
- Peer-reviewed final report
- Peer-reviewed journal publications

Performance can be judged through successfully passing the peer-review process.

8. Work Schedule

Table 1 presents the proposed work schedule for this project. Project management is an ongoing task throughout the project, including financial tracking and other administrative tasks. More discrete project management tasks will involve an annual planning and evaluation cycle for the project, beginning with the initial project planning and coordination, and recurring each year in reviewing the data and adjusting the project plan. Given the timing of the CalFed award schedule, one option is to delay project implementation until 2003, which would allow annual reporting in the first project year to include avian egg data, and allow for a third year of egg sampling. Summer 2002 sampling could be relocated to summer 2005, and project planning and data analysis/ reporting tasks would be delayed 6 months from the timeline shown.

Wetlands sediment and water should not be sampled for Hg and MeHg separate of the biological matrices (benthos, fish, bird eggs). Although monitoring all organisms at the proposed frequency may not be necessary, monitoring none would not provide the information needed to meet CalFed ERP goals. Sampling of fish and benthos could be scaled back if the temporal variability in community structure and contaminant concentrations were found to be insignificant. Payments could be tied to annual reporting and sampling plan revision products described.

B. APPLICABILITY TO CALFED GOALS AND PRIORITES

1. Applicability To ERP, Science Program and CVPIA Priorities

This proposal addresses restoration priorities for the Bay region BR-4, and BR-5, and multi-regional priority MR-5. An information gap currently exists on the extent and impact of Hg contamination in tidal wetlands. This study will complement past and current efforts investigating Hg contamination in the Delta. We will be directly investigating Hg impacts on an endangered bird species (California clapper rail) and bioaccumulation in a sportfish (striped bass) commonly consumed by humans.

Benefits of this information extend beyond these particular species; by measuring Hg in organisms from lower trophic levels and Hg transformation processes in tidal marsh sediments and waters, we aim to better understanding of mechanisms of Hg impact on wetlands biota. This information can be used in design of monitoring strategies using similar sampling stratification schemes and to place in context factors confounding simple analyses of mercury contamination in this region and others. By including sites along a salinity gradient and through an age progression of marsh development, we aim to explore factors for evaluating sites in similar watersheds and project short and long term behavior of regional restored wetland ecosystems. By identifying factors that would

indicate a high risk for Hg contamination and bioaccumulation in wetlands, this data would allow managers to make appropriate decisions on how to manage or avoid such risks in choosing and designing restoration projects.

2. Relationship to Other Ecosystem Restoration Projects

This project would complement current and past CALFED efforts investigating mercury in the Delta and a UC Davis project on Effects of Wetlands Restoration on Methyl Hg Levels. A complementary study of marsh ecology is being proposed to CalFed ERP by the Southern Sonoma Resource Conservation District. Co-P.I.'s on this project are also working on or proposing other projects related to mercury. Dr. Collins is developing a plan for a regional wetlands monitoring program, for which data and methods from this study can be incorporated into a monitoring strategy. Dr. Davis is submitting two proposals for this round of CalFed ERP funding, investigating Hg in fish of the Delta and Central Valley. Dr. Schwarzbach is proposing investigations of Hg bioaccumulation of birds. Dr. DiPasquale is proposing work investigating Hg biogeochemistry in the Delta. These proposed studies are similarly concerned with mercury, but address different processes and have other temporal and spatial focus from this proposal. There is therefore no overlapping effort.

3. Request for Next Phase Funding

This proposal is not a request for next phase funding.

4. Previous Recipients of CALFED Program or CVPIA Funding

SFEI and MLML: *ERP-99-N07 Chronic Toxicity of Environmental Contaminants in Sacramento Splittail: A Biomarker Approach* – The project is in its second year. SFEI and MLML are performing field sampling and analytical chemistry. The first year of field sampling has just been completed. *ERP-99-B06 Assessment of the Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed* – SFEI and MLML are performing fish sampling and mercury analysis. The project is in its third year. Two years of sampling and chemical analysis have been completed and a final report is in preparation.

SFEI: *XXXX CALFED Whitepaper on: Ecological Processes in Tidal Wetlands of the Sacramento-San Joaquin Estuary and Their Implications for Proposed Restoration Efforts of the Ecosystem Restoration Program.* Dr. Davis was lead author of chapter: "Mercury and Tidal Wetland Restoration." The draft report has been completed. *XXXX*

5. System-Wide Ecosystem Benefits

There is a good opportunity for synergy with the Southern Sonoma RCD study of marsh ecology being proposed. This study could inform that project on possible Hg contamination risks, and that study could provide information on food web structure, which could guide modifications of sampling design for biota in this project.

C. QUALIFICATIONS

This project is organized as a joint venture partnership. SFEI will be the lead contracting party. Project management is included as a separate task in the proposal budget. Although some tasks (e.g. sampling) are performed in concert with collaborating partners, this is included under the separate overall task for each partner individually (e.g. Microbial Transformation Rates). Should a partner be unable to perform a task, it is the responsibility of that partner to find a suitable replacement or subcontractor to perform the work.

The following investigators from SFEI are listed alphabetically:

Joshua N. Collins, Ph.D., SFEI, Environmental Scientist

Dr. Collins received his Ph.D. in Entomological Sciences at the University of California at Berkeley and has done post-doctoral studies in Geography and Ecology at the University of California at Berkeley and Davis. Dr. Collins is a landscape ecologist and regional ecological planner with special expertise in the evolution and natural maintenance of streams and wetlands. Dr. Collins has been a professional ecologist in the Public Utilities Industry and a consulting ecologist in private practice for design and review of stream and wetland restoration projects. Since Dr. Collins joined the staff of SFEI in 1993, he has been the principal author and lead scientist for the Bay Area Wetlands Monitoring Plan, the Bay Area Watersheds Science Plan, the Bay Area EcoAtlas, and the Bay Area Regional Wetlands Ecosystem Goals Project. Dr. Collins oversees the SFEI Wetlands Science Program and GIS laboratory, and co-manages the Watersheds Science Program.

Jay A. Davis, Ph.D., SFEI, Environmental Scientist

Dr. Davis has performed research on contaminant issues in the Bay-Delta for 15 years. The accumulation and effects of persistent, bioaccumulative toxicants has been an area of particular emphasis. Dr. Davis has been principal investigator on several studies of contaminant accumulation in fish, including: 1) The CALFED Mercury Project (Davis et al. 2001), a directed action evaluating many aspects of mercury contamination in the Delta region; 2) The fish contamination monitoring element of the Regional Monitoring Program (RMP) for San Francisco Bay, the sport fish monitoring program for the Bay (SFEI 1999); 3) The fish contamination monitoring element of the Sacramento River Watershed Program (Larry Walker Associates 2001); 4) The Delta fish contamination study (Davis et al. 2000); 5) Chronic Toxicity of Environmental Contaminants in Sacramento Splittail (Pogonichthys macrolepidotus): A Biomarker Approach; and 6) Coastal Intensive Site Network: San Pablo Bay where Dr. Davis is managing studies of mercury and accumulation in fish and avian eggs from San Pablo Bay and its marshes. In addition to the fish work, Dr. Davis is part of a team that manages the RMP, a $3 million/year program that monitors toxic chemicals in San Francisco Bay water, sediment, and biota. Drawing on his experience with all of these projects, Dr. Davis was lead author of the chapter "Mercury and Tidal Wetland Restoration" in the CALFED Whitepaper: "Ecological Processes in Tidal Wetlands of the Sacramento-San Joaquin Estuary and Their Implications for Proposed Restoration Efforts of the Ecosystem Restoration Program" (draft version awaiting final approval).

Donald Yee, Ph.D., SFEI, Environmental Scientist

Dr. Yee will take the lead role in project management and administrative duties, including coordination and reporting tasks.

Dr. Yee is the Quality Assurance Officer for SFEI and is part of the RMP management team. He is currently also involved in other projects investigating contaminant sources, transport, and fate in the Estuary, including a Regional Monitoring Program pilot study on atmospheric deposition of mercury (with one site on the national Mercury Deposition Network) and other contaminants. Dr. Yee received his B.S. in Chemical Engineering and his Ph.D. in Environmental Engineering from M.I.T. His dissertation research with Dr. Francois Morel focused on aqueous trace metal speciation and competitive interactions in microorganisms. Prior to joining SFEI in 1999, he has had experience in

post-doctoral research on carbon geochemistry and consulting in the private sector on environmental regulatory policy.

Collaborators:

The following researchers will be collaborating on this project as a joint venture partnership.

Steven Schwarzbach, Ph.D., U.S. Fish and Wildlife Service

Chief, Environmental Contaminants Division

Dr. Schwarzbach will lead the team sampling bird eggs for this project.

Dr. Schwarzbach serves as the chief of the Environmental Contaminants Division of the Sacramento Field Office, USFWS. He has designed and directed numerous multidisciplinary field studies of environmental contaminant impacts to fish and wildlife in California including studies in the Klamath Basin, Sacramento Valley, Tulare Basin, San Luis Refuge Complex, and intertidal marshes of San Francisco Bay. Contaminant studies in which Dr. Schwarzbach has been involved have focused on mercury, selenium, organophosphate pesticides, aquatic herbicides, organochlorines, trifluoracetic acid, acid mine drainage, ammonia, and eutrophication effects upon water quality. His personal scientific interests have most recently been particularly focused on mercury and selenium in birds of the San Joaquin Valley and San Francisco Bay. He has directed field investigations on contaminant hazards to clapper rails in the south bay in 1991 and 1992 and the north bay in 1998 and 1999 and is currently directing a Bay-wide investigation of mercury bioaccumulation in birds of San Francisco Bay for the Regional Board, and mercury bioaccumulation in birds of the delta for CalFed. Steven Schwarzbach, , is currently working on the CalFed mercury study in the Delta (tracking number 99-B06).

Mark Marvin-DiPasquale, Ph.D. U.S. Geological Survey (Menlo Park, CA)

Dr. Marvin-DiPasquale is leading the team investigating Hg microbial transformations, and his lab will be performing sediment and pore-water ancillary measurements, and analyses of the pore-water parameters in surface water.

Dr. Mark Marvin-DiPasquale completed his Ph. D. in estuarine microbial ecology in 1995 at the University of Maryland. Since that time he has been with the USGS and has focused his efforts almost exclusively on the microbial cycling of mercury in various ecosystems throughout the U.S. Mark was a co-principle investigator on the Aquatic Cycling of Mercury in the Everglades (ACME) Project, one of the largest mercury research efforts ever conducted. He conceptualized, coordinated, and conducted a major EPA sponsored study of the microbial cycling of mercury in sediments of the Carson River System (Nevada), which included the simultaneous assessment of mercury-methylation and methylmercury degradation along a 100 km stretch of the Carson River and associated wetlands. He has collaborated with junior scientists from UC Santa Cruz in an investigation of mercury cycling associated with the New Idria Mercury mine (California), an effort that represented the first time microbial methylmercury degradation processes had been examined in such a mining area. He has collaborated with USGS colleagues in an assessment of microbial mercury cycling in historically mercury impacted gold/silver mining areas in the Sierra Nevada and San Francisco Bay. Mark has been the lead author on 4 peer reviewed journal papers or book chapters, and has been a co-author on a number of others and has served as a colleague reviewer on over a dozen peer reviewed published articles.

David Krabbenhoft, Ph.D. U.S. Geological Survey (Wisconsin)

Dr. Krabbenhoft is leading the team measuring Hg and MeHg in sediment, water, and biota samples, photo-demethylation rate experiments, and water DOC measurements. Dr. David Krabbenhoft is a senior research scientist with the U.S. Geological Survey. He has general research interests in geochemistry and hydrogeology of aquatic ecosystems. Dave began working on environmental mercury cycling, transformations, and fluxes in aquatic ecosystems after completing his Ph.D. 1988, and the topic has consumed him since. For the past 4 years he has served as the project leader for the USGS National Mercury Project. This project is responsible for the execution of studies that will lead to a better understanding of mercury contamination of aquatic ecosystems at the national scale. In 1995 Dave established the USGS Mercury Research Laboratory in Wisconsin. This laboratory is a state of the art, analytical facility strictly dedicated to the analysis of mercury, with low-level speciation. Recently, they acquired a Quadra-pole, ICP-MS dedicated for the analysis of mercury isotopes that are used at several research sites to further our understanding of the important pathways and controlling processes of mercury in the environment.

D. COST

The budget is provided via the web form. There are no plans for cost sharing.

E. LOCAL INVOLVEMENT

This research project will have minimal physical impacts on the system.

F. COMPLIANCE WITH STANDARD TERMS AND CONDITIONS

The applicants will comply with all state and federal standard terms, with exception of USFWS, which objects to the following:

The Fish and Wildlife Service (Service) cannot agree to a standard clause requested for State funded projects. Attachment D, Terms and Conditions for State Proposition 204 Funds, Section 3, states "Performance Retention: Disbursements shall be made on the basis of costs incurred to date, less ten percent of the total invoice amount. Disbursement of the ten percent retention shall be made either: (1) upon the Grantee's satisfactory completion of a discrete project task (ten percent retention for task will be reimbursed); or (2) upon completion of the project and Grantee's compliance with project closure requirements specified by CALFED (ten percent retention for entire project will be disbursed)".

The Services's authorization to enter into agreements with non Federal entities was changed in FY 2000. Our FY2000 Appropriations bill authorizes the Service to enter into contracts with State agencies when advance payment to the Service is not possible. In accordance with the requirements imposed by Congress in the FY2000 Appropriations bill and report language, the Services Director must approve a project when advance payment is not possible and certify that payments will be made in full by the State within 90 days after the Service issues an invoice.

Specifically, the 10% retention clause cannot allow timely payments for the following reasons:

In our Federal Financial System (FFS) accounting program, a periodic invoice (either quarterly or monthly depending on the terms of the contract) is automatically issued from our finance center based on actual expenditures of the Service on a project. Invoices include a payment due date on the invoice and when payment is not received in full by that due date, the system automatically shows the unpaid balance as delinquent.

Depending on how delinquent the payment is, interest, penalty and administrative charges may also accrue. With 10% retention withheld on each invoice, the 10% retention amount then causes applicable invoice record in FFS to be partly delinquent and remain delinquent until the project or individual tasks identified in the contract are completed and the retention is released.

The Service's Finance Center must report to the Department of Treasury if the Service is owed funds by any entity. Therefore, when accounts remain delinquent due to the 10% retention of payments owed the Service, that delinquency continues to be reported to Treasury. The Service has previously entered into agreements with the State of California that do not contain the 10% retention clause. We have asked the States Deputy Attorney General to provide clarifying guidance to the Department of Water Resources that is general in scope, which can also be applied to contracts related to the CALFED program.

Our offices will continue to work with the State closely on State funded projects. If the State is not satisfied with the work performed by the Service, the State project manager should contact the Service's project manager to correct the performance problem. If needed, upon notification interim billings can be canceled until the State is satisfied with the Services performance.

We can comply with all other State and Federal standard clauses.

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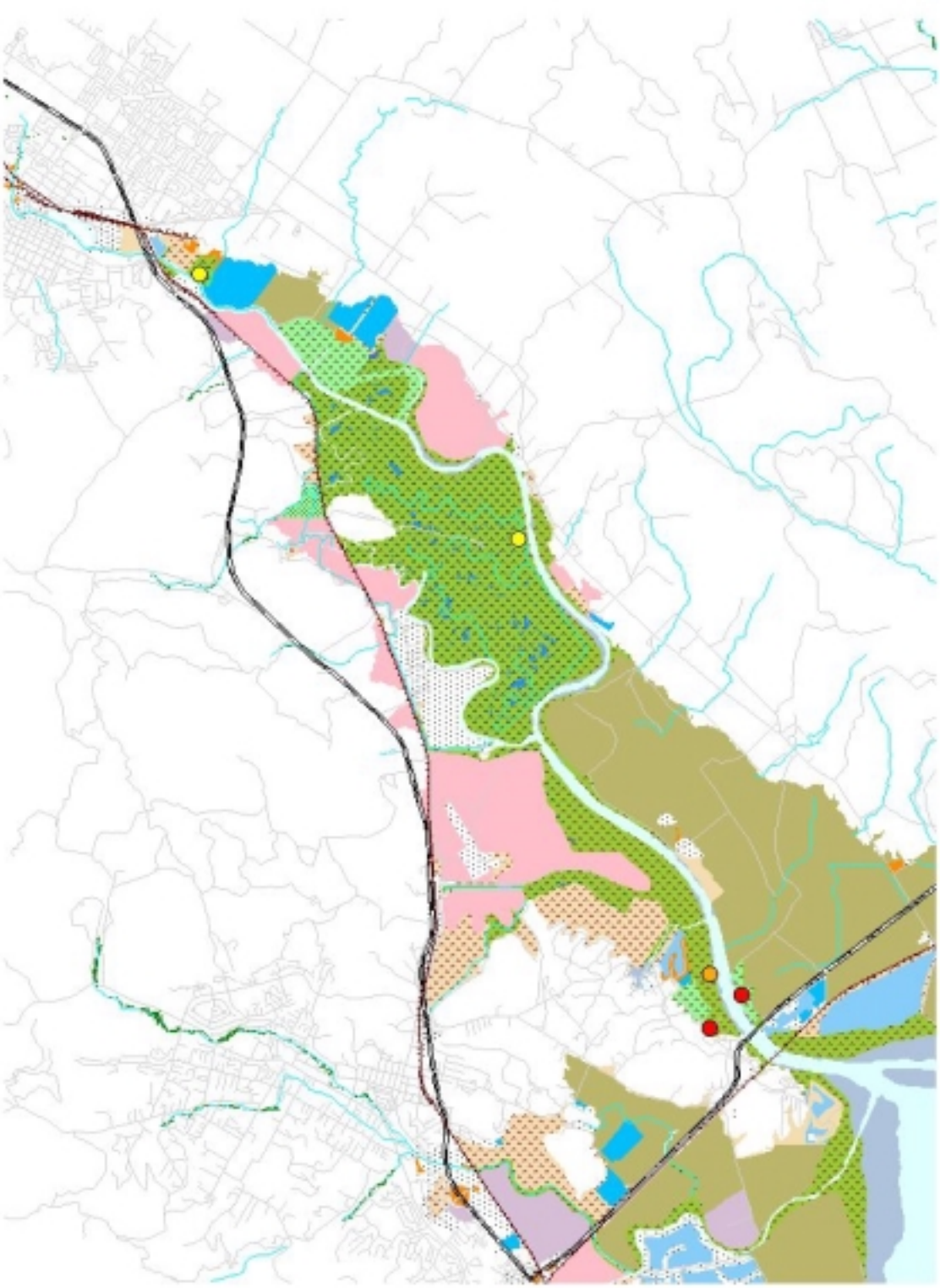

Figure 1 Petaluma River Tidal Wetland Study Locations –Three marshes (2 red, 1 orange point) at the mouth of the Petaluma River near Highway 37 cover a range of marsh ages of 10, 50-100, and 500+ years. The two yellow points up the river and the orange point at the mouth cover a range of salinity for tidal wetlands 50-100 years old.

Table 1 PROJECT TIMELINE

	1. Project Management and Planning	2. Data Analysis and Reporting	3. Field Sampling	4. Hg and MeHg Chemical Analysis	5. Microbial Transformation Rates	6. Fish sampling and Analysis	7. Benthos sampling and Analysis	8. Egg Sampling and Analysis
2002 May	Coordination QA, Other Planning		Field Prep	Field Prep	Field Prep	Field Prep	Field Prep	
Jun			Sampling	Sampling	Sampling	Sampling	Sampling	
Jul				Analysis	Analysis	Analysis	Analysis	
Aug								
Sep								
Oct								
Nov								
Dec			Field Prep	Field Prep	Field Prep	Field Prep	Field Prep	
2003 Jan			Sampling	Sampling	Sampling	Sampling	Sampling	
Feb				Analysis	Analysis	Analysis	Analysis	
Mar								Field Prep
Apr								Sampling
May	Evaluation/ Adjustment	Annual report						
Jun			Field Prep	Field Prep	Field Prep	Field Prep	Field Prep	Analysis
Jul			Sampling	Sampling	Sampling	Sampling	Sampling	
Aug				Analysis	Analysis	Analysis	Analysis	
Sep								
Oct								
Nov								
Dec			Field Prep	Field Prep	Field Prep	Field Prep	Field Prep	
2004 Jan			Sampling	Sampling	Sampling	Sampling	Sampling	
Feb				Analysis	Analysis	Analysis	Analysis	
Mar								Field Prep
Apr								Sampling
May	Evaluation/ Adjustment	Annual report						
Jun			Field Prep	Field Prep	Field Prep	Field Prep	Field Prep	Analysis
Jul			Sampling	Sampling	Sampling	Sampling	Sampling	
Aug				Analysis	Analysis	Analysis	Analysis	
Sep								
Oct								
Nov								
Dec			Field Prep	Field Prep	Field Prep	Field Prep	Field Prep	
2005 Jan			Sampling	Sampling	Sampling	Sampling	Sampling	
Feb				Analysis	Analysis	Analysis	Analysis	
Mar								
Apr		Final Report						
May								
Jun								
Jul								
Aug								
Sep								
Oct	Project End							
Nov								