Field and Laboratory Investigation of Selenium Cycling and Speciation in San Francisco Bay and the San Joaquin River-Delta Sediments

Project Information

1. **Proposal Title:**

   Field and Laboratory Investigation of Selenium Cycling and Speciation in San Francisco Bay and the San Joaquin River-Delta Sediments

2. **Proposal applicants:**

   Bruce Manning, San Francisco State University
   Matthew La Force, San Francisco State University

3. **Corresponding Contact Person:**

   Bruce Macher
   San Francisco State University Office of Research and Sponsored Programs
   1600 Holloway Ave, HHS 204 San Francisco State University San Francisco, CA 94132
   (415) 338 7091
   macher@sfsu.edu

4. **Project Keywords:**

   Environmental Education
   Heavy Metals (mercury, selenium, etc.)
   Water and Sediment Quality

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:

Longitude:

Datum:

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

The project will take place at three sites (SJR 1; 38º 130 Latitude, 121º 4930 Longitude),(Ref 2; 37º 5715 Latitude, 122º 2515 Longitude), and (SB 3; 36º 6.06 Latitude; 122º 1.58 Longitude) within the Bay

10. **Location - Ecozone:**

    1.4 Central and West Delta, 2.1 Suisun Bay & Marsh, Code 15: Landscape

11. **Location - County:**

    Contra Costa

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:**

    10

15. **Location:**

    California State Senate District Number: 7

    California Assembly District Number: 11

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:	50
Total Requested Funds:	1003467

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?

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)

Roger Fujii	**USGS Sacramento**	**916-278-3055**	**rfujii@usgs.gov**
Tetsu Tokunaga	**Lawrence Berkeley National Laboratory**	**510-486-7176**	**tktokunaga@lbl.gov**
Andrea Foster	**USGS Menlo Park**	**650-329-5437**	**afoster@usgs.gov**

Michelle Hornberger USGS Menlo Park 650-329-4467 mhornber@usgs.gov

21. **Comments:**

Environmental Compliance Checklist

Field and Laboratory Investigation of Selenium Cycling and Speciation in San Francisco Bay and the San Joaquin River-Delta Sediments

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.

      Research Only

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

Field and Laboratory Investigation of Selenium Cycling and Speciation in San Francisco Bay and the San Joaquin River-Delta Sediments

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

Field and Laboratory Investigation of Selenium Cycling and Speciation in San Francisco Bay and the San Joaquin River-Delta Sediments

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):

Bruce Manning, San Francisco State University
Matthew La Force, San Francisco State University

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

Field and Laboratory Investigation of Selenium Cycling and Speciation in San Francisco Bay and the San Joaquin River-Delta Sediments

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.

Federal 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	Field Site Location, Monitoring, and Sample Collection	2344	38839	7310	1000	2700	0	24600	400	74849.0	25124	99973.00
2	Selenium Distribution Within Bay Sediments	2336	38839	7311	0	14000	5200	0	0	65350.0	32675	98025.00
3	Protocol for Selenium Speciation in the Aqueous and Solid Phase Extracts	2336	38840	7311	0	14000	0	0	0	60151.0	30075	90226.00
7	Educational Outreach and Community Involvement	2336	38840	7311	0	0	0	0	0	46151.0	23075	69226.00
		9352	155358.00	29243.00	1000.00	30700.00	5200.00	24600.00	400.00	246501.00	110949.00	357450.00

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	Field Site Location, Monitoring, and Sample Collection	1856	32210	6134	1000	0	0	0	0	39344.0	19672	59016.00
2	Selenium Distribution Within Bay Sediments	1856	32210	6134	3000	6000	5200	0	1000	53544.0	26772	80316.00
3	Protocol for Selenium Speciation in the Aqueous and Solid Phase Extracts	1856	32210	6134	0	9800	0	0	200	48344.0	24172	72516.00
4	Selenium Speciation from Field Collected Sediment and Solution	1856	32211	6135	3000	4700	0	0	0	46046.0	23023	69069.00
7	Educational Outreach and Community Involvement	1856	32211	6135	0	0	0	0	0	38346.0	19173	57519.00
		9280	161052.00	30672.00	7000.00	20500.00	5200.00	0.00	1200.00	225624.00	112812.00	338436.00

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**
2	Selenium Distribution Within Bay Sediments	1546	27837	5362	3000	6000	5200	0	0	47399.0	23700	71099.00
3	Protocol for Selenium Speciation in the Aqueous and Solid Phase Extracts	1546	27837	5362	0	3500	0	0	0	36699.0	18350	55049.00
4	Selenium Speciation from Field Collected Sediment and Solution	1546	27837	5362	1000	4700	0	0	200	39099.0	19550	58649.00
5	Laboratory Microcosms and Lab Experiments	1546	27838	5362	3000	4600	0	0	1000	41800.0	20900	62700.00
6	Application of X-ray Absorption Spectroscopy	1546	27838	5363	0	0	0	0	0	33201.0	16601	49802.00
7	Educational Outreach and Community Involvement	1546	27838	5363	0	0	0	0	0	33201.0	16601	49802.00
		9276	167025.00	32174.00	7000.00	18800.00	5200.00	0.00	1200.00	231399.00	115702.00	347101.00

Grand Total=1042987.00

Comments.

Budget Justification

Field and Laboratory Investigation of Selenium Cycling and Speciation in San Francisco Bay and the San Joaquin River-Delta Sediments

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

PI (Manning): 16 hrs/week (40% time) during academic year PI (Manning): 40 hrs/week (100% time) during 3 Mo. summer PI (La Force): 16 hrs/week (40% time) during academic year PI (La Force): 40 hrs/week (100% time) during 3 Mo. summer Technician: 40 hrs/week (100% time) for entire year Undergrad Students (2): 400 hours per year Graduate Students (2): 1,120 hours per year

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

PI (Manning): $35.73/hr (year 1) PI (La Force): $40.97/hr (year 1) Technician: $17.11/hr (year 1) Undergrad Students (2): $12.00/hr (entire project) Graduate Students (2): $14.24/hr (entire project)

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

PI Benefits: 12% Technician Benefits: 36% Undergrad Student Benefits: 1.5% Graduate Student Benefits: 1.5%

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

Budgeted money for non-local travel to scientific meetings: year two: $6000 year three: $6000

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

The following supply costs are totals for the 3 yr. project: SSE Reagents, Supplies, Filters, Syringes: $18,000 Peeper supplies (Tubes, Parts, Construction) $17,400 Anoxic sediment sampler/storage unit: $1,700 Anoxic sampler supplies (N2, batteries, tubing) $1,000 HGAAS/Se Speciation (IC Columns, reagents) $10,100 AAS supplies (Se lamp, autosampler tubes, gases) $1,200 AA autosampler $4,000 Misc Supplies (sampling supplies, electrodes) $12,000 Digital potentiometer (dual channel) $2,100 Lab microcosm supplies $2,500

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.

ICP Time for total metal analyses (Stanford University): $65/hour x 80 hrs/year = $5,200/year (for 3 years)

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.

Three YSI Sonde 6600 Data Loggers+ Probes: $24,600

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.

Costs associated with project management have already been accounted for in the compensation for PI salaries (40% release time from academic year teaching).

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

Shipping Costs: $800 (for entire project) Publishing/Printing: $2,000 (for entire project)

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.

San Francisco State University's indirect cost rate is based on an agreement with the Federal Government. The indirect cost rate for on-campus organized research is 50%. Indirect costs (overhead rate) include costs associated with general office and laboratory requirements such as rent, utilities, phones, furniture, general office staff, etc., and are prescribed by SFSU as 50% of the modified total direct costs (i.e., total direct costs - equipment - tuition reimbursement - sub-contract costs beyond the first $25,000).

Executive Summary

Field and Laboratory Investigation of Selenium Cycling and Speciation in San Francisco Bay and the San Joaquin River-Delta Sediments

EXECUTIVE SUMMARY Contamination of the San Francisco Bay and San Joaquin River-Delta with selenium (Se) from agricultural drainage waters and local refinery activity has caused concern for the long-term ecological health of the aquatic habitat in this important region. Developing a clearer picture of the fate, transport, and bioavailability of Se will require sensitive analytical techniques capable of monitoring the temporal changes in chemical speciation of Se. This project will address the need for detailed and high-quality scientific data that reveals both the present and future impacts of Se inputs to the Bay-Delta ecosystem. Moreover, this data must be well integrated with the array of present scientific efforts underway in the Bay-Delta ecosystem. This proposal outlines a research and monitoring project which will apply advanced analytical techniques to gain new insight into the cycling of Se between the aqueous and sediment solid phases of selected Bay-Delta field sites, as well as determine the chemical speciation of Se during these transformations. Selenium that occurs in particulate matter as suspended solids will also be studied. We will take a regional approach and address CALFED restoration priorities by sampling Se contaminated sites located at the San Joaquin River-Delta, San Francisco Bay, and Suisun Bay. The overall objectives of this project involve quantitating and speciating Se in San Francisco Bay and San Joaquin River-Delta field sites, conducting laboratory experiments to investigate Se uptake and bioavailability in sediments under controlled conditions, application of advanced analytical techniques to determine the chemical speciation of aqueous and solid phase Se, and involvement of Bay Area students at the high school, undergraduate, and master’s degree levels. To achieve these objectives a work plan has been constructed for a 3-year funding period to analyze the environmental and sediment conditions that control the bioavailability of Se.

Proposal

San Francisco State University

Field and Laboratory Investigation of Selenium Cycling and Speciation in San Francisco Bay and the San Joaquin River-Delta Sediments

Bruce Manning, San Francisco State University
Matthew La Force, San Francisco State University

B. EXECUTIVE SUMMARY

Project Title: Field and Laboratory Investigation of Selenium Cycling and Speciation in San Francisco Bay and the San Joaquin River-Delta Sediments

Contamination of the San Francisco Bay and San Joaquin River-Delta with selenium (Se) from agricultural drainage waters and local refinery activity has caused concern for the long-term ecological health of the aquatic habitat in this important region (CALFED, 2001). Developing a clearer picture of the fate, transport, and bioavailability of Se will require sensitive analytical techniques capable of monitoring the temporal changes in chemical speciation of Se. There is a need for detailed and high-quality scientific data that reveals both the present and future impacts of Se inputs to the Bay-Delta ecosystem. Moreover, this data must be well integrated with the array of present scientific efforts underway in the Bay-Delta ecosystem.

Understanding the assortment of Se reactions known to occur in a wetland environment such as the San Francisco Bay and San Joaquin River-Delta will require a comprehensive chemical study using several sensitive techniques. This project will apply advanced analytical techniques to gain new insight into the cycling of Se between the aqueous and sediment solid phases of selected Bay-Delta field sites, as well as determine the chemical speciation of Se during these transformations. Selenium that occurs in particulate matter as suspended solids will also be studied due to the potential for increased Se bioavailability of this form. We will take a regional approach and address CALFED restoration priorities by sampling Se contaminated sites located at the San Joaquin River-Delta, San Francisco Bay, and Suisun Bay. Given the need for detailed chemical insight into the speciation and bioavailability of Se in the Bay-Delta sediments, the overall objectives of this project are:

(1) Quantify and speciate Se in solution, suspended particulate, pore-water, and sediment solid phases at selected San Francisco Bay and San Joaquin River-Delta field sites in order to predict future Se bioavailability;

(2) Conduct laboratory experiments to investigate Se uptake and bioavailability in sediments under controlled conditions;

(3) Apply advanced analytical techniques such as X-ray absorption spectroscopy (XAS) and HPLC-hydride generation atomic absorption spectrometry (HPLC-HGAAS) to determine the chemical speciation of aqueous and solid phase Se;

(4) Increase the awareness of community organizations, Bay Area students at the high school, undergraduate, and master's degree level to environmental issues in the San Francisco Bay region.

To achieve these objectives a work plan has been constructed for a 3-year funding period to analyze the environmental and sediment conditions that control the bioavailability of Se. The first sub-project in the work plan will be to establish field sites and characterize both the solid and aqueous phase sediment-water environment at these locations. This portion of the work will be done with close attention being paid to previous and ongoing studies by CALFED-funded projects (Van Geen and Luoma, 1999; Luoma et al., 2000 and 2001). The purpose is to link our results with progress being made in the understanding of other aspects of the Bay-Delta aquatic habitat such as Se uptake in aquatic organisms. Appropriate samples which are representative of varying Bay-Delta wetland and ecosystem environments will then be studied in more detail using XAS and laboratory experiments designed to mimic the field environment. Results from field and laboratory investigations will then be combined, interpreted, and described using available geochemical and ecosystem models used to predict Se cycling and bioavailability. The final results will be presented to the scientific, regulatory, and local community in a form conducive to aiding agency decision-making and assisting other researchers studying the Se problem in the Bay-Delta region.

C. PROJECT DESCRIPTION

C.1. STATEMENT OF THE PROBLEM

C.1.a Problem

The San Francisco Bay-Delta waterway is a dynamic and biologically rich ecosystem. Human impacts such as pollution from organic contaminants (Venkatesan et al., 1997; CALFED, 2001) and metals (Hornberger et al., 1997) has resulted in sediment-bound contamination. Metal contamination in the Bay includes inputs of Hg, Cu, Cd, Zn from historical mining activities in the Sierra Nevada, as well as other metals and metalloids such as Cr, Ni, Se, and V (Luoma and Phillips, 1988; Luoma et al., 1990, 1992; Nriagu, 1994). Among these toxicants, Se is of current concern due to the accumulation of this element in Bay sediments and the aquatic food chain (Luoma et al., 1992; CALFED, 2001). Selenium is potentially toxic to wildlife and historical elevated Se concentrations in the San Francisco Bay-Delta waters resulting from human activities has increased the Se burden in the ecosystem. Previous work has shown that even small increases in the Se concentration of Bay waters has resulted in food chain buildup and biomagnification in aquatic organisms (Johns et al., 1988; Cutter, 1989). Inputs of Se are primarily the result of agricultural drainage entering the watershed from the San Joaquin River and oil refinery waste disposal along the Carquinez Straits area. Despite efforts to reduce Se inputs to the Bay-Delta system by both agriculture and refining industries, a substantial Se load has been deposited and has entered the aquatic food chain.

The chemical speciation of Se determines its fate, transport, and bioavailability in the aquatic environment (Cutter, 1982; Masscheleyn et al., 1990). The environmental cycling of Se is diverse involving the gas, liquid, and solid phases (Figure 1). In addition, the cycling of Se in the aquatic environment includes both biotically- and abiotically-driven pathways that cycle Se between organic and inorganic Se species. Biological uptake and metabolism of inorganic Se generates organic Se, primarily as water soluble Se amino acids (US EPA Office of Water, 1998). Volatile Se such as dimethylselenide (DMSe) and dimethyldiselenide (DMDSe) are formed by certain aquatic primary producers such as microalgae (Frankenberger and Karlson, 1989) and can enter the atmosphere and be dispersed or oxidize and be deposited as inorganic Se. The predominant inorganic species of Se are soluble selenate (Se(VI), SeO_4^{2-}) and selenite (Se(IV), SeO_3^{2-}), insoluble elemental Se (Se(0)), and various metal and sulfur selenides (Se(-II)) (Cutter, 1982; Elrashidi et al., 1987; Masscheleyn et al., 1990).

The majority of Se entering the Bay-Delta ecosystem is from San Joaquin River waters. Dissolved Se(VI) is the principle form of Se and is the result of oxidation and leaching of irrigated seleniferous soils of the Western San Joaquin Valley. Selenate is highly soluble and mobile and is the predominant form of Se under oxidizing conditions (Elrashidi et al., 1987). Dissolved Se(VI) can become associated with sediment particles by weak adsorption on inorganic particle surfaces, coprecipitation in crystalline and non-crystalline mineral phases, complexation with insoluble organic matter, or biological uptake and formation of detritus. Microbial reduction of dissolved Se(VI) to insoluble Se(0) and Se(-II) in the estuaries, marshes, sediments of the Bay-Delta ecosystem are important reactions which contribute to the overall Se immobilization process (Cutter, 1982; Velinsky and Cutter, 1991). In contrast to Se(VI), the occurrence of dissolved selenite (Se(IV)) has been primarily from oil refinery wastes and thus represents a discrete, point-source input to the Bay which has been monitored and decreased (CALFED, 2001). Whereas Se(VI) is primarily dissolved and mobile, dissolved Se(IV), which is stable under moderately reducing conditions, undergoes adsorption reactions on inorganic and particle surfaces. Adsorption of Se(IV) on inorganic minerals has been extensively investigated using a variety of approaches including batch adsorption (Balistrieri and Chao, 1990; Neal et al., 1987), kinetic methods (Zhang and Sparks, 1990), and spectroscopic techniques including extended X-ray absorption fine structure spectroscopy (EXAFS) (Manceau and Charlet, 1994; Hayes et al., 1987) and X-ray photoelectron spectroscopy (Papelis, 1995). These studies have confirmed that the Se(IV) adsorption mechanism involves formation of a covalently linked, "specifically adsorbed" SeO_3^{2-} ion on the metal oxide surface (Manceau and Charlet, 1994; Hayes et al., 1987). The SeO_3^{2-} anionic species displays pH-dependent adsorption on metal oxide surfaces (increased adsorption at low pH) commonly found in soil and sediment (Balistrieri and Chao, 1990, 1987). Suspended particles that contain adsorbed Se(IV) can settle out of the water column and become incorporated into sedimentary deposits (Figure 1). In addition, Se(IV) that diffuses into sediment layers containing metal oxides will be adsorbed and immobilized.

Future agricultural practices involving irrigation in the San Joaquin Valley, and particularly in the Westlands Water District, will continue to contribute to the Se burden of the San Francisco Bay-Delta ecosystem. Of acute concern is the potential limitations of Bay-Delta sediments to continue to provide a sink for incoming dissolved Se. Understanding the seasonal changes in the pool of immobile and sediment-bound Se will provide a basis for evaluating the bioavailability of Se. The long-term availability of sediment-bound Se, and the ability of Bay sediments to continue to immobilize Se inputs from the water column, will be important factors in assessing the future status of the ecosystem. The need to understand and accurately predict Se bioavailability within the Bay region will require an improved knowledge of the sediment and water properties that increase the solubility and mobility Se, sediment-water processes leading to Se immobilization such as Se anion adsorption, deposition in particulate matter (particle settling), and chemical reduction to insoluble solid phases such as Se(0) and metal selenides. This project will apply an integrated field-laboratory research plan to address knowledge gaps in our understanding of the chemistry of the San Francisco Bay and San Joaquin River-Delta sediments and particularly their capacity to attenuate dissolved Se.

C.1.b. Conceptual Model

The aquatic environmental chemistry of Se is inherently complicated by the tendency of the element to exist in several oxidation states, phases, and food chain compartments. Uptake of Se by aquatic organisms such as phytoplankton results in biotransformation of dissolved inorganic Se to organic Se(-II) (Figure 1). This route of Se transformation is an important pathway leading to food chain biomagnification and increases in Se-enriched detritus in sediments. Dissimilatory microbial reduction of Se(VI) to Se(IV) enhances Se adsorption on sediment particles which lead to an enrichment in sedimentary Se. Sediment-bound Se(IV) is either redistributed to overlying waters (by surface exchange reactions or particle resuspension) or undergoes reduction in the anoxic zone of sediments to Se(0), inorganic Se(-II), or organic Se(-II). The pools of reduced, sediment-bound Se remain insoluble and immobilized until sediment conditions change to cause a release of dissolved or particulate Se back to the water column.

An assessment of the overall status of Se in the Bay-Delta ecosystem will require a detailed understanding of the concentration of Se in the sediment, as well as knowledge of the environmental factors which control recycling of sediment Se to form dissolved or suspended Se. This project will enhance the present scientific understanding of the partitioning of Se between the dissolved and solid phases in the San Francisco Bay and San Joaquin River-Delta sediment environment. The research tasks outlined in this proposal have been constructed to provide detailed information about the physical, chemical, and mineralogical properties of sediments which can be correlated with Se immobilization. Sediment-bound Se in the Bay will be measured and characterized by selective sequential extraction of sediment core samples combined with Se speciation by high performance liquid chromatography hydride generation atomic absorption spectrometry (HPLC-HGAAS). We intend to use field-based, *in-situ* data collection to provide the real-time physicochemical properties of sediment with periodic sampling of sediment-water column to study the Se immobilization process in the Bay sediments. This will allow both spatial and temporal changes which affect Se immobilization to be studied and monitored and will be coupled with sediment extractions carried out at intervals during the year.

In addition to *in-situ* field studies, this project will include detailed laboratory investigations designed to characterize the Bay sediment chemistry with regard to Se. There are several key uncertainties in the Se conceptual model in the Bay as posed in Figure 1 that can best be addressed through laboratory studies. In order to address conceptual uncertainties and enhance our current scientific understanding of Se-sediment interactions, the laboratory portion of this project will address the following key questions:

(1) *What is the Se speciation and identity of Se-bearing mineral phases in present-day sediment cores?*
(2) *What is the stability of sediment-bound Se?*
(3) *What factors control the reduction and immobilization pathways of dissolved Se(VI) and Se(IV) when introduced to Bay sediment?*
(4) *What is the Se(VI) and Se(IV) adsorption capacity of Bay sediment?*

The laboratory portion of this project will address these questions using laboratory microcosms which will mimic the Bay sediment environment. State-of-the-art speciation techniques for resolving Se oxidation states both in solution and solid phases will be used for detailed monitoring of the sediment-water system.

C.1.c. Hypothesis Being Tested

***Hypothesis 1*: Sediment-bound Se is associated with amorphous and crystalline Fe (hydr)oxides, organic matter, and as insoluble sulfide-associated Se;**

Detailed field investigations into Se speciation, mobility, and solid phase partitioning in the San Joaquin River, near refineries in San Francisco Bay, and in Suisun Bay will be conducted in order to elucidate the temporal distribution, speciation, bioavailability, and mobility of Se under changing physicochemical conditions within Bay-Delta sediment.

***Hypothesis 2:* Changes in the physicochemical sediment conditions over time can yield bioavailable forms of Se from the pool of insoluble forms such as adsorbed Se(IV), insoluble Se(0), and inorganic Se(-II);**

We intend to test this hypothesis by correlating measured redox potential, temperature, and water chemistry conditions with the concentrations of dissolved Se species and particulate Se. Both field based sampling and carefully controlled laboratory microcosm experiments will be used.

***Hypothesis 3:* A redox gradient at the sediment-water interface controls the uptake and release of soluble Se(IV) and Se(VI);**

The project will provide insight into the oxidation and reduction reaction pathways at the sediment-water interface which control Se mobilization and immobilization. Inputs to the Bay via agricultural drainage into the SJR contributes aqueous phase Se leading to deposition in sediments and/or uptake into the food chain.

***Hypothesis 4:* The Bay-Delta sediments have not yet reached their Se and adsorption capacity which is, in turn, controlled by Se(IV)/(VI) speciation and sediment mineralogy.**

This hypothesis will be tested in the laboratory using batch adsorption studies on Bay sediment collected from field sites. The overall Se adsorption capacity of sediments, and the dependence of Se adsorption on Se speciation and sediment chemistry, will be investigated by addition of low levels of Se(IV) and Se(VI) to sediment-water suspensions. This will provide information about the extent of Se surface site saturation on mineral and organic materials in Bay sediments.

C.1.d. Adaptive Management

Our adaptive management goals are to assist CALFED managers and interagency team members in the development of long-term solutions to Bay-Delta sediment and water quality problems. In order to achieve these goals we must address the Se problem at its source and identify appropriate levels of protection. For example, what solid phases are likely candidates for Se attenuation? What mechanisms are responsible for Se release to the aqueous phase? What is the toxicity and mobility of Se within the Bay-Delta? How much Se can the Bay-Delta hold? How will Se inputs from the San Joaquin River enter the food chain? This project tackles the aforementioned questions by using a multifaceted approach that starts by assessing Se bioavailability in the Bay-Delta and progresses toward understanding the specific mechanisms responsible for Se entering the food chain through precise, controlled, laboratory experiments. We must get to the heart of the matter by filling knowledge gaps pertaining to Se (and other redox active contaminants) in order to assist CALFED managers in the regulatory process. Bay-Delta management decisions are aided by scientific findings; thus, it is imperative that CALFED interagency team members and scientists have immediate access to our research findings. Consequently, we will create a real-time Web page to post results from our project and present breakthroughs in our analytical Se speciation protocols. We also hope to share our ideas and findings with other scientists (i.e., Dr. Sam Luoma et al.) working on Bay contaminant issues in order to improve our understanding of contaminant hydrodynamics--another important adaptive management goal for the San Joaquin Region (CALFED, 2001). Finally, state-of-the-art analytical techniques used in conjunction with field and laboratory studies will act as a cornerstone for future detailed investigations into contaminant toxicity and bioavailability in the Bay-Delta ecosystem.

C.1.e. Educational Objectives

One of the primary objectives of this proposal is to engage, encourage, and educate students at the high school, undergraduate, and master's degree levels to pursue a career which includes an appreciation for the environment. The Co-PI's on this project are both assistant professors at San Francisco State University (SFSU), an institution that has the forty-fifth largest enrollment of all universities in the United States and has been certified by the US Department of Education as a minority-serving institution (MSI) with an ethnically diverse population of students (Chronicle of Higher Education, 2000). There are many elements of this project which have tremendous educational potential for students including field trips to discuss Bay-Delta environmental issues and enhance lecture topics, involvement of students in San Francisco Bay field monitoring, independent and supervised laboratory studies, and developing a practical and informed understanding of a valuable, local ecosystem.

The Geosciences Department at SFSU was recently awarded a 1.2 million dollar National Science Foundation grant (**R**eaching **O**ut to **C**ommunities and **K**ids with **S**cience in San Francisco: SF ROCKS). The grant encourages high school students to consider the geosciences as a potential career path and promotes awareness of geosciences among a broad segment of the population, including members of underrepresented groups. Dr. La Force is a Co-PI on the grant and will recruit students from the SF:ROCKS program to participate in research pertinent to this proposal, present research findings to CALFED citizen-advisors, and participate in local “town hall” meetings of community based environmental organizations (i.e., Coalition First, Literacy for Environmental Justice, Bayview-Hunter's Point Coalition on the Environment, and discussions with Ecosystem Roundtable Members). We hope to (1) increase participation in environmental careers by members of groups that have been traditionally underrepresented in geoscience disciplines by including them in our research program, (2) strengthen high school student’s quantitative scientific skills and encourage them to present their findings in a poster format for young geoscientists at a Geologic Society of America meeting, (3) inform local community based environmental organizations about environmental issues within SF Bay, and (4) assist CALFED advisors in the implementation of long-term management plan that restores ecosystem health.

In addition to the high school and community-based educational objectives are the training of college undergraduate and master's degree students in environmental science, geology, biology, and chemistry. Close proximity of the Bay-Delta ecosystem to SFSU affords us the opportunity to take undergraduate/graduate students on field excursions to enhance the educational experience. This project includes funding for two SFSU undergraduate researchers to conduct senior thesis projects and two SFSU graduate student researchers to conduct master's thesis work on the Bay-Delta system. These students will be trained in collecting field samples and monitoring of field sites, sample storage and handling, superior laboratory practices, safe handling, preparation, and storage of chemical reagents, sample preparation (weighing, centrifugation, filtering), and the intricacies of quality assurance and control during analysis of trace concentration of elements such as Se. The use of computers will be central to the project allowing students to develop their analytical and quantitative computing skills while engaging in the project's scientific objectives. Students will be required to develop research results in the form of reports and in senior/master's thesis format for submission in partial fulfillment of their degrees as well as present oral presentations summarizing their results at SFSU departmental seminars. In addition, students will be encouraged to present their findings at scientific meetings at the local, regional, and national level (e.g., CALFED annual meetings, American Chemical Society, American Geophysical Union, and Geological Society of America).

C.2. PROPOSED SCOPE OF WORK

C.2.a. Geographic Boundaries of Project

The project will be conducted at three field sites that have been carefully located to address CALFED Restoration Priorities. The sites include the inlet of the San Joaquin River-Delta, San Francisco Bay, and Suisun Bay. The results of this work are applicable to Ecozones 1 and 2. All laboratory investigations will take place at San Francisco State University.

C.2.b. Approach

OBJECTIVE 1: ***Quantify and speciate Se in solution, suspended particulate, pore-water, and sediment solid phases at selected San Francisco Bay and San Joaquin River-Delta field sites in order to predict future Se bioavailability;***

Task 1. Field Site Location, Monitoring, and Sample Collection

In order to accomplish objective (1) and test hypotheses (1 and 2) we will conduct a detailed field investigation of Se within the Bay-Delta. We have chosen three sites to ensure that future restoration efforts are not affected by degraded environmental water quality. Furthermore, we intend to collect field data to develop a spatial and time dependant conceptual model that addresses Se speciation, toxicity, and mobility within the Bay-Delta. The field component of our proposal is in direct response to CALFED's Restoration Priorities for the San Joaquin Basin which emphasizes the need to understand Se transport and mobility at the inlet to Bay-Delta from the San Joaquin River (SJR) as well CALFED's ERP highlights that exemplify a need for robust Se data in San Francisco and Suisun Bays (CALFED 2001). The sites (inlet of the Delta near the SJR, San Francisco Bay, and Suisun Bay) have elevated Se concentrations as a consequence of refineries and Se inputs via the SJR Delta (Luoma et al., 2001; CALFED, 2001) (Figure 2). Consequently, our first field site (herein referred to as SJR 1; 38º 1’30” Latitude, 121º 49’30” Longitude) will be at the inlet of the SJR (adjacent to Antioch Point) where Se inputs reach the Bay via agricultural drainage from the SJR. We have also chosen this site to remove sediment and solution for controlled laboratory microcosm studies of Se transport, speciation, and mobility via Se loading by the SJR (hypothesis 4; CALFED-ERP, Strategic Goal #6). Our second site (herein referred to as Ref 2; 37º 57’15” Latitude, 122º 25’15” Longitude) will be located below refineries and the Navy Fuel Supply Depot where anthropogenic Se inputs reach the Bay. Although Se inputs from refineries have decreased in the last decade (Luoma et al., 2001), elevated Se exists in sediment from this locale which is entering the food chain (CALFED, 2001). Finally, we will sample Suisun Bay (herein referred to as SB 3; 36º 6.06' Latitude; 122º 1.58' Longitude) where Se is of greatest concern because small impacts can have adverse effects on wildlife and there is a need for better data in this locale (CALFED, 2001). We hope to assist ongoing CALFED projects and USGS modeling efforts focused in the Region by assessing Se concentration, partitioning, and toxicity within this ecosystem.

The sites will be surveyed using a total station Topcon 312 Electronic Distance Measurer (EDM) theodolite to construct a 50 meter by 50 meter grid (10 m by 10 m grid spacing) at each site; grid points will be marked by a 2/3" PVC pipe. The theadolite and GPS units (see below) will be borrowed from the Geosciences Department at SFSU. These sites will be surveyed in the first year of the proposal and remain for the duration of the experiment. Random cores will be collected at high flow, intermediate flow following high flow, then low flow, follow current sampling protocols (Luoma et al., 2001) in order to: (1) assess the roles that organic matter, amorphous materials (i.e., ferrihydrite), crystalline materials (including acid volatile sulfides), and residual silicates have on Se abatement (hypothesis 1), (2) speciate Se in solids, particulate matter, and solution in order to understand the toxicity and bioavailability of Se within the Bay (hypotheses 2 and 3), and (3) understand how Se entering the Bay from the SJR mobilizes into the sediment and enters the food chain (hypothesis 4).

As part of the restoration priority for the San Joaquin Delta CALFED has requested proposals for "the expansion of more real-time water quality monitoring of SJR-Delta system" (CALFED, 2001). We intend to fill this niche by inserting water quality monitoring devices (YSI Sonde 6600 data loggers) at all field locations. We will utilize *in-situ* real time monitoring of Bay water in conjunction with computer chemical speciation software packages to assess Se geochemical reaction pathways. The Sonde is designed for long-term *in situ* monitoring and profiling of water quality. Data loggers will be employed to collect dissolved oxygen, open-channel flow, temperature, conductivity, nitrate-nitrogen, ammonium-nitrogen, ammonia, turbidity, chloride, salinity, and pH. Monitoring these select parameters will enable us to better understand Se geochemistry and refine our conceptual model; we intend to model this data with Visual MinteqA2 software package. Both PIs have had extensive experience utilizing this software (La Force et al., 1998; La Force et al., 2001). Water quality results will be posted monthly on a Web page such that CALFED interagencies along with other scientists and organizations (United State Geological Survey, San Francisco Bay Estuary Institute's Regional Monitoring Program, and Real Time San Joaquin River Water Quality Management Project) working on the Bay can have immediate access to this important database.

Sediments will be collected during coring expeditions of the SJR 1, Ref 2, and SB 3 at the three aforementioned hydrologic conditions. We will collect nine random cores at each site and catalogue them with a Trimble XRS-Pro global position system (GPS). Cores will be removed from each site using a 4 cm diameter PVC piston coring device (Blomquist et al., 1991; Fischer et. al., 1992). Owing to the fact the Se can change oxidations states upon aeration (Schure, 1970; Martens and Suarez, 1997); sample oxidation will be minimized upon transport to the laboratory by immediately capping the samples and placing them upright into a N_2 purged sample transporter engineered by Dr. La Force (La Force et al., 2000b). Cores collected at each site (27 total for the three sites) will be sectioned into 5-cm intervals, homogenized, and composited with three other cores yielding a total of 36 samples for solid phase analysis (see below). Composite sampling of cores into 5-cm increments will allow us to accurately assess Se partitioning, speciation, and core mineralogy through the redox boundary where we anticipate changes in Se toxicity, bioavailability, and mobility to occur; core sectioning and composite sampling will take place in a N_2 purged atmosphere glovebox at the SFSU geochemistry laboratory. Typically, the redox boundary in ponded soils of San Joaquin Valley contaminated with Se are found within the top 0-20 cm of the sediment-water interface (Martens and Suarez, 1997; Tokunaga et al., 1998). In addition, the top 20 cm is in contact with the overlying water column and is considered the most reactive and bioavailable soil fraction; therefore, we will focus our solid phase analysis on this portion of Bay sediments.

Task 2. Selenium Distribution Within Bay Sediments

A widely used technique for understanding elemental distributions in the solid phase involves the use of selective sequential extractions (SSE) [see reviews by Pickering (1981), Chao (1984), and Martin et al. (1987)]. The use of SSE's is based on the premise that chemical reagents can remove elements from specific fractions of the solid phase. In essence, the amount of any one given element extracted from a particular phase is dependant on the reagent concentration and type, extraction sequence, and solid to solution ratio, hence the term "operationally defined" (Miller et al., 1986). Nevertheless, in light of the shortcomings of selective extractions, they provide valuable information regarding general partitioning patterns and qualitative estimates of reactive Se phases within sediments. Furthermore, they provide a means to assess the reactivity of the material that is not afforded by microscopic or spectroscopic methods. Selective sequential extractions are commonly used for geochemical exploration, mineralogical analyses, and taxonomic delineation of soils (Jackson et al., 1986; Parfitt and Childs, 1988; Dahlgren, 1994; Soil Survey Staff, 1996). In this study, two separate SSE procedures will be utilized to (1) determine core make-up and Se fractionation and (2) speciate Se to address its mobility and bioavailability through the redox boundary of the sediment.

The first chemical extraction sequence will characterize Bay sediment sinks that sequester Se (and other contaminants) and evaluate Se response to varying physicochemical sediment conditions. This information will be important for understanding Se reaction pathways in the Bay and for predicting solid phase sink response to temporal changes. The extraction sequence involves using well-established procedures that utilize selectively aggressive reagents to dissolve portions of the solid phase; the procedure was designed, developed, and tested by Co-PI La Force (La Force et al., 2000). The extraction procedure utilized in this study aspires to optimize the selectivity of each extraction while preserving sample integrity. Most importantly, however, we seek to define the reactivity of Se within different extractable phases using the defined extraction sequence. Oxygenation of reduced sediment upon collection leads to redistribution and repartitioning of Se (Schure, 1970; Martens and Suarez, 1997). To circumvent this undesired phenomenon, analyses of reduced phases will be performed in a N_2 purged glovebox at SFSU. We will place 2.0 g of wet (~1.0 dry weight equivalent) sediment in an acid washed 50 mL centrifuge tube and react it with a given reagent. After each extraction step (see below), samples will be centrifuged at 8,000 rpm for 15 min and the supernatant filtered through a 0.20-μm membrane filter and acidified with concentrated trace element grade HCl prior to atomic absorption spectrophotometer (AAS) or inductively coupled optical emission spectrophotometer (ICP-OES) analysis. All supernatants will be analyzed for total Al, As, Cr, Cu, Hg, Fe, Mn, Se, and S on the ICP-OES at Stanford University's soil chemistry laboratory, and quality control will be checked every 15 samples. Both PIs have a cooperative agreement in place with this laboratory to handle aqueous and solid phase samples for this project. We will adhere to strict QA/QC protocols on all experiments by utilizing appropriate blanks as well as standard reference material (SRM 2709) to quantify any outside sources of contamination. Comparison of a total microwave digestion on separate solids with our operationally defined sums from our extraction sequence will allow us to quantify our recovery; previous results using this procedure indicate that recovery for all elements will be ~92% with a RSD <10% for each element (La Force et al., 2000).

The first extraction sequence will determine operationally defined pools of carbonates, amorphous Fe (hydr)oxide, acid volatile sulfides, crystalline Fe (hydr)oxides, and silicates and monitor there changes in response to varying hydrodynamic/temporal conditions. This information will provide needed insight into how temporal variations influence sediment reactivity within the Bay. In addition, the extraction sequence will also assess Se partitioning within these operationally defined pools. Although our primary emphasis will focus on Se we intend to collect complimentary data on other Bay contaminants (As, Cr, Cu, Hg, and Zn). It is important to note, that the effectiveness of extractions depends on the affinity and specificity of the extracting chemical for the target phase. Thus, this extraction sequence will qualitatively allow us to assess sediment reactivity and Se partitioning within the Bay. Moreover, this extraction sequence is not optimized to speciate Se; we will use a second complimentary chemical extraction sequence and X-ray absorption spectroscopy to achieve this goal (see below). The first extraction procedure starts by reacting Bay solids with 20 mL of 1 M Na-acetate/acetic acid for 5 h at pH 5 to remove the carbonate fraction of the sediment (Tessier et al., 1979; Tessier et al., 1985). Research has shown that Se has a tendency to be adsorbed by calcite (Cowan et al., 1990). Thus, qualitatively assessing the proportion of carbonates with Bay sediment as well as evaluating their role in Se sequestration will be ascertained. Next, we will remove noncrystalline materials (i.e., amorphous Fe (hydr)oxides) with 20 mL of 0.2 M ammonium oxalate (pH 3) in the dark (AOD) and shaken for 4 h (Schwertmann, 1973; Jackson et al., 1986). Selenium has a know affinity to adhere to amorphous Fe (hydr)oxides in soils (Balistrieri and Chao, 1990; Manceau and Charlet, 1994) and we anticipate this extractable pool to be a major player in Se sequestration (Fig. 1; Hypothesis 1). The potential exists for Se sorbed to Fe (hydr)oxide phases to be released into the overlying water column upon reductive dissolution of Fe by abiotic and biotic processes thereby becoming available for biological uptake (Fig. 1). We will determine the percentage of amorphous Fe (hydr)oxides within Bay sediment, assess their response to varying temporal conditions, and quantify Se affiliated with this highly reactive sink. To the remaining sediment residue, we will remove acid volatile sulfides and crystalline Fe (hydr)oxides using 1 M HCl shaken for 16 h (Morse, 1987). Velinsky and Cutter (1990), noted that sulfides can sequester Se in Coastal regions; we anticipate that Se-S species will exist within the Bay and will attempt to qualitatively asses the amount of Se associated with sulfidic material. In addition to sulfides, Se has a high affinity to sorb to more ordered crystalline Fe (hydr)oxides (Hayes et al., 1987; Balistrieri and Chao, 1987; Zhang and Sparks, 1990; Manceau and Charlet, 1994). Therefore, we intend to quantify the portions of crystalline Fe (hydr)oxides within the Bay as well and evaluate the percentages of Se associated with this reactive solid phase. The sediment remaining after the HCl extraction will be treated with sodium hypochlorite (NaOCl) at 95±5 ^{o}C three times to enhance oxidation of organic phases and subsequent removal of Se (Lavkulich and Weins, 1970; Hoffman and Fletcher, 1981; Shuman, 1983). The tendency for Se to partition with C in Bay area solids is currently being investigated (Luoma, 2001) and has been noted in other regions (Cutter and Bruland, 1984). Thus, we anticipate a large preponderance of Se to partition with organic materials within the Bay (Hypothesis 1). Finally, a total microwave digestion using nitric and hydrofluoric acid (EPA method 3052) will be utilized to remove residual minerals and silicates. We foresee this extractable pool of Se to be minimal and it should not vary temporally within the Bay.

Task 3. Protocol for Selenium Speciation in the Aqueous and Solid Phase Extracts

In addition to total Se analyses performed by ICP, speciation of Se will be performed using selective hydride generation atomic absorption spectrometry (HGAAS). Sediment pore-waters, Bay waters, particulate matter, sediment selective extracts, and laboratory microcosm experiment samples will be analyzed according to established methods for Se(IV), Se(VI), and total dissolved Se (Manning and Burau, 1995; Weres et al., 1989; Fujii, 1988; Presser and Barnes, 1984). The advantages of this technique are excellent sensitivity (detection limits below 1 part per billion Se) and selectivity for Se(IV) over Se(VI). Sub-ppb Se detection limits are achieved in HGAAS by continuously stripping hydrogen selenide (H_2Se) gas from solution which removes spectral interferences and greatly focuses Se atoms in the light path of the AA spectrometer.

All HGAAS analyses will be performed using a Varian SpectrAA FS 220 atomic absorption spectrometer equipped with a Varian VGA-77 vapor generation accessory. This instrument is a next generation fast sequential (FS) AA allowing for simultaneous, multi-element analyses similar to the multi-element capabilities of an ICP. This will allow for screening of certain Bay sediment sample extracts to be performed for a suite of metals including Cd, Cr, Cu, Hg, Ni, Pb, and Zn. Another potential advantage will be that other hydride-forming elements such as As can be determined simultaneously with Se during HGAAS. Hydride generation with the VGA-77 will be performed in a continuous, flow-through mode which mixes Se sample, 6 M HCl (Instrapure), and a 0.16 M $NaBH_4$/0.12 M NaOH solution. Hydrogen selenide produced in the reaction will be swept into an air-acetylene flame heated quartz tube in the AA spectrometer light path monitoring Se absorbance at 196.0 nm. All reagents for HGAAS analysis will be reagent grade or better (e.g., Instrapure HCl (Baker) will be used) and Se(IV) and Se(VI) standards (0, 10, 20, 30 ppb Se) will be made using reagent grade Na_2SeO_3 and Na_2SeO_4.

Step 1: Speciation of Se(IV): Determination of Se(IV) in aqueous sample solutions will be performed by direct HGAAS analysis without chemical pretreatment. Standard solutions of Se(IV) will be used to verify the selectivity of the technique to ensure that Se(VI) is not measured under the run conditions. A separate technique using high performance liquid chromatography (explained below) will be used to independently validate the Se(IV) concentration. The Se(IV) species has been shown to react with $NaBH_4$ selectively without interference from Se(VI) even under conditions where Se(VI) is well in excess of Se(IV) (Manning and Burau, 1995).

Step 2: Speciation of Se(VI): Selenium(VI) will be determined by reacting equal volumes of sample solution and concentrated HCl (5 mL) in glass digestion tubes heated in an aluminum block-type digester for 20 min. This treatment affects the reduction of Se(VI) to Se(IV) and allows total inorganic Se(IV+VI) to be analyzed by HGAAS. This allows Se(VI) to be determined by the difference between *Step 2* and *Step 1*.

Step 3: Total dissolved Se. To determine total dissolved Se, 5 mL of aqueous extract will be transferred to glass digestion tubes along with 5 mL of concentrated HCl and 0.2 mL of 2% potassium persulfate ($K_2S_2O_8$). The tube will then be vortexed and heated in the block digester at 100 °C for 30 min. This is a multi-functional reaction that first oxidizes all dissolved Se to Se(VI), then decomposes the persulfate, and finally reduces all Se(VI) back to Se(IV) in the HCl matrix. Following this treatment the extract will be analyzed by HGAAS and assumed to represent total soluble Se (Se(IV) + Se(VI) + organic Se). Organic Se is determined by the difference between *Step 2* and *Step 3*.

Advanced Speciation of Dissolved Selenium: Objective 3 of this project emphasizes the need for development of detailed Se speciation techniques and application to specific samples of Bay-Delta waters, sediments, and sediment pore-waters. In addition to direct, continuous HGAAS described above, a novel technique employing high performance liquid chromatography (HPLC) coupled with HGAAS will be used for simultaneous separation and detection of dissolved Se species in extracts and aqueous samples. Interfacing HPLC with a highly sensitive, element-specific detector such as HGAAS is the most reliable technique for trace element speciation (Van Loon et al., 1992; Ebdon et al., 1987) and has been developed and extensively applied by one of the PI's on this project for speciation of arsenic(III and V) in aqueous samples (Manning and Martens, 1997; Manning and Suarez, 2000; Manning et al., 2001).

The HPLC separation will be achieved using a Dionex DQP pump and a Dionex AS11 (4.6x250 mm) analytical anion exchange column (Dionex Corp., Sunnyvale, CA) preceded by an AS11 guard column (4.6x45 mm). The stationary phase is composed of a multi-phase substrate with a highly cross linked ethylvinylbenzene/divinylbenzene polymeric core coated with a quaternary ammonium functionalized colloid allowing both anion and reversed phase chromatography to take place. The HPLC mobile phase used will be 30 mM NaOH in 1% methanol prepared in degassed DI water and vacuum filtered through a 0.1 micron membrane. The HPLC column will be linked to a flow-through post-column (PC) reactor which converts all eluting Se species to Se(IV) using a microwave assisted coil that mixes eluent with 15 mM $KBrO_3$ and 47% HBr reagents (Gomez-Ariza et al., 2000). The PC reactor is linked directly to the VGA-77 allowing separation and detection of trace level organic and inorganic Se(IV) and Se(VI) species in sample extracts. These detailed speciation methods will be applied to pore-water samples taken from peepers at field sites and laboratory microcosm experiments.

Task 4. Selenium Speciation from Field Collected Sediment and Solution

We intend to use the aforementioned Se speciation procedures on aqueous, particulate matter, and sediment sequestered Se. For Se, problems arise with oxidation state change during an extraction sequence which can result in an erroneous conclusion regarding its speciation (Gruebel et al. 1988). However, recent Se extraction sequences have overcome artifacts associated with Se oxidation during the speciation process (Chao and Sanzolone, 1989; Fio and Fujii, 1990; Zhang and Moore, 1996; Zhang and Moore, 1997; Martens and Suarez, 1997). We will utilize the well-established procedure of Martens and Suarez (1997) to speciate Se sorbed to soil exchange sites and organic matter or precipitated as an insoluble material using the HGAAS procedure. The extraction sequence was developed to assess Se speciation and partitioning within the top 0-15 cm of contaminated wetland soils from the San Joaquin Valley (SJV). Based on the geochemical similarities between SJV wetland sediment and Bay-Delta sediments we feel this extraction sequence will be ideal for speciating Se removed from the Bay. The procedure utilizes 0.1 M (pH 7.0) K_2HPO_4-KH_2PO_4 (P-buffer), shaken for 1 h, to release soluble selenate, selenide, and ligand-exchangeable selenite. Selenium associated with this fraction of the solid phase can be readily displaced and released to the aqueous phase thereby becoming biologically available for uptake. The second step of the procedure involves Se speciation from organic matter with 0.1 M $K_2S_2O_8$ (90 ºC) for 2 h, to release selenide and selenate. Microbial consumption of organic substrates can release Se associated with this solid phase sink. Consequently, we will investigate the speciation of Se associated with organic materials in order to assess the toxicity of Se retained in this solid phase and further refine our conceptual model. The final step will utilize HNO_3 to solubilize insoluble Se remaining in the sample in order to quantify remaining insoluble Se species within Bay sediment.

Selenium speciation will occur on pore-water and particulate matter collected from SJR 1, in order to assess the toxicity of Se and define reaction pathways responsible for its release to the aqueous phase. Solid and aqueous phase analysis will be performed in unison in order to provide a detailed depiction of Se mobility upon entering the Bay from the SJR. It is important that we determine Se dynamics and concentrations in particulate matter owing to the fact that this is the primary source of Se available for biological uptake (CALFED 2001). We will use 4 membrane separated diffusion cells placed randomly at SJR 1 to assess Se speciation in particulate matter and pore-waters at low, medium, and high flow periods. Membrane separated diffusion cells (peepers) have been used extensively to monitor metal ions in solution (Carignan et al., 1985; Brandl and Hanselmann, 1991). Peepers will be created by placing 2.5-cm diameter x 8-cm length (20-mL volume) filter tubes pre-fitted with sterile 0.20-μm nylon filters (Lida Maxispin® centrifugal filter tubes) at 5-cm intervals into a slotted 70-cm height PVC supporting rod (La Force et al., 2000b). Centrifuge tubes will be filled with double-deionized water and placed in the Bay for ~3 weeks, at which point equilibrium will be reached and the samples removed and analyzed (La Force et al., 2000b). Aqueous samples will be removed from the peepers, filtered into an N_2 purged vial, acidified with concentrated trace element grade HCl, and kept on ice until metal analysis ~3 h later. A field blank of double deionized water with 2 drops of concentrated HCl will be run with the samples as a quality control. Solutions collected from each cell will be analyzed for pH, Eh(mV), total organic carbon (TOC), concentrations of Cr, Cu, Al, Fe, Mn, Se, and S via ICP; Se will be speciated with HGAAS. Total organic carbon will be performed on a Model 1010 OI analytical total organic carbon analyzer at the SFSU geochemistry laboratory, direct electrode potentials (Eh, relative to the standard hydrogen electrode) will be determined using a Corning redox combination Pt electrode with Ag/AgCl reference electrode and pH will be measured with a combination electrode in each cell after a stable reading is obtained. In addition, filters removed from the peepers will be analyzed by a HNO_3/HF total digestion to assess Se associated with particulate matter found in the overlying (20 cm) water column. We intend to input Se particulate and pore water se data along with water quality data from our data loggers into Visual MinteqA2 chemical speciation software program to determine likely solid phase Se precipitates that may remove Se from the aqueous phase.

<u>OBJECTIVE 2:</u>* *Conduct laboratory experiments to investigate Se uptake and bioavailability in sediments under controlled conditions;

Task 5. Laboratory Microcosms and Lab Experiments

Laboratory microcosm experiments will be conducted to determine the rates and mechanisms of Se transformations and the Se adsorption capacity of sediments. The laboratory investigation will help us to address the impacts of Se carried from irrigation water of the SJR to the Delta which is a Restoration Priority for CALFED (CALFED, 2001). The preliminary field work conducted in this project will eventually identify important sediment samples which are appropriate for further careful study in laboratory systems. Criteria used to choose samples to be taken for further study include clear evidence of Se enrichment in sediment above what would be considered background levels and evidence that the sampling site will continue to receive Se influxes from the water column. Sediment samples will be transported from the field to the laboratory and stored as explained above.

Approximately 50 grams (dry weight) of selected sediment materials will be placed in 4 liter glass microcosm containers containing 3 liters of Bay or Delta water and placed in an N_2 glovebag. Microcosms will be equipped with temperature-controlling water jackets, inert gas atmospheric control to enhance reducing conditions, and sealable ports for sediment/water sampling and electrode immersion (La Force et al., 1998). The temperature, pH, and redox potential will be continuously monitored using a digital potentiometer interfaced with computer for data storage and analysis. The pH will be measured with a Ag/AgCl glass combination electrode and redox potential (Eh) will be measured with a combination platinum electrode. Samples of the overlying water will be taken first at 1 hour intervals for 8 hours, followed by daily sampling. The duration of microcosm experiments will be determined based on the attainment of equilibrium or steady state conditions which are representative of field conditions. Water samples will be filtered and prepared for Se speciation. All microcosm experimental units will be triplicated to test for variability and statistical significance of results. The following treatments will be used to test hypotheses 3 and 4:

Treatment 1. Elevated dissolved Se(VI) and reducing conditions. The effects of elevated Se(VI) concentrations in the overlying water column in combination with reducing conditions will be investigated by spiking a pre-equilibrated sediment-water microcosm to produce aqueous phase concentration of ~0.5 micromolar Se (40 ppb). Though this concentration is probably higher than average Se concentrations found in the Bay waters it will be representative of concentrations found near Se sources in the Delta such as the San Joaquin River and possibly refinery wastes. For this experimental regime, pH, redox potential, and dissolved Se speciation will be monitored. At the termination of the experiment, sediment will be subjected to the aforementioned sequential extraction procedures and Se solid phase speciation achieved using XAS (as described in *Task 6. Application of Advanced Techniques for Se Speciation*).

Treatment 2. Elevated dissolved Se(IV). Dissolved Se(IV) will be investigated in a similar experimental procedure to Treatment 1. Pre-equilibrated sediment-water microcosms will be spiked to make ~0.5 micromolar Se(IV) (40 ppb Se(IV)). The overlying water will be sampled at time intervals and subject to Se speciation as described below in *Task 6*

Treatment 3. Elevated redox potential. Anoxic sediments sampled from the Bay will be subjected to moderately oxic conditions in laboratory microcosms to test the hypothesis that Se can be mobilized from Bay sediment under varying sediment physicochemical conditions. Anoxic sediment that has been collected from field sites will be gradually oxidized to determine the effective solubility of Se after sediment oxidation. During this experiment, pH, redox potential, and dissolved Se(IV) and Se(VI) will be monitored.

The use of laboratory microcosms will be primarily for verification of mechanisms of Se transformation that are deemed important in field sites. For example, the unambiguous identification of the sediment solid phases with which immobile or sediment-bound Se is associated may only be possible by tracking the transformation of added Se under a controlled environment. In addition it may not be possible to effectively monitor Se speciation in the field under carefully controlled conditions such as altered redox potential. These experiments will provide useful information regarding the capacities of Bay-Delta sediments to assimilate additional inputs of Se in the form of dissolved Se(IV) and Se(VI). In addition to the scientific objectives of laboratory microcosm work, educational opportunities will be created at the lab bench allowing direct student involvement in this portion of the project. Student researchers will be encouraged to build their own "system" for study and monitor the reactions of Se in the Bay sediment using atomic absorption spectrometry.

Task 6. Application of X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is a non-destructive technique which allows determination of the oxidation state and local atomic environment of Se in the solid phase (Tokunaga et al., 1997; Tokunaga et al., 1998). The XAS technique will be used in conjunction with, and as a compliment to, speciation of dissolved ions by HPLC-HGAAS which will provide a tremendous amount of insight into Se speciation in sediments. Both project PI's have had extensive experience planning experiments, collecting XAS spectra and analyzing data using currently available XAS data analysis software. The XAS analyses will be performed at the Stanford Synchrotron Radiation Laboratory (SSRL). Beamtime at SSRL is allotted to scientists on a peer-reviewed, short proposal basis. A beamtime proposal is being prepared and will be submitted to SSRL outlining the experimental goals of this project and the need for dedicated beam time. In addition we are also able to run XAS samples in collaboration with Dr. Scott Fendorf (Department of Geological and Environmental Sciences, Stanford University).

The chemical information gained from XAS analyses includes *in-situ* (non-destructive) determination of the predominant solid phase oxidation state of Se (Tokunaga et al., 1998; Tokunaga et al., 1996) and the nearest-neighbor atomic environment of Se atoms bound in the solid phase (Manceau, 1995; Manceau and Charlet, 1994; Hayes et al., 1987). Extended X-ray absorption fine structure spectroscopy (EXAFS) will be used for determination of the coordination number, interatomic distance, and identity of coordinating atoms in the nearest neighbor atomic environment of Se. The X-ray *K* edge region of Se (12657.8 eV) and the extended X-ray absorption region (12700-13700 eV) will be scanned at 0.3 eV increments and the intensity of emitted fluorescence energy will be measured using a solid state germanium semiconductor detector. Data analysis will be performed using EXAFSPAK (George and Pickering, 1993) and WinXAS (Ressler, 1997) software packages. The oxidation state of Se in solids will be determined using X-ray absorption near edge spectroscopy (XANES). Quantitative XANES analysis will be achieved using a linear combination of Se standard spectra of model compounds and comparing them to Bay sediment unknowns. A Levenberg-Marquardt least-squares algorithm in the WinXAS code will be used to minimize the error between the unknown and ‘reconstructed’ spectrum (Ressler, 1997) as described elsewhere (Foster et al., 1998; La Force et al., 2000a and 2000c).

A primary concern in XAS analyses is whether the concentration of Se is high enough for an acceptable signal:noise ratio. The current detection limit for synchrotron-based XAS analysis of Se is 0.025 g/kg^{-1} which is close to reported Se concentrations in Bay sediments (Tokunaga et al., 1994). To improve the detection limits of XAS for analysis of low levels of Se in Bay sediments we will use high resolution micro-XANES analysis and an environmental beamline at SSRL. Similar work has been performed previously (Tokunaga et al., 1998) to determined the fate of soluble Se(VI) in ponded, reducing sediments allowing both spatial and time resolved XANES analysis. These experiments will play a central role in this project by providing the best possible direct evidence of Se oxidation state and bonding environment in intact sediments. This information will be used to corroborate results from sequential extractions and HPLC-HGAAS speciation and will give a solid basis on which to predict the long-term stability of solid phase Se.

<u>OBJECTIVE 4</u>: Increase the awareness of community organizations, Bay Area students at the high school, undergraduate, and master's degree level to environmental issues in the San Francisco Bay region.

Task 7. Educational Outreach and Community Involvement

We will use contacts currently in place from the SF:ROCKS program to foster and support the outreach component of our proposal. We intend to actively engage high school students and community organizations in a grass roots campaign that will bring high school students into the field to collect and interpret data while actively engaging local environmental organizations by presenting the results of our findings in a series of informal discussions. Our intentions are for students to assist with field work by placing and collecting membrane separated diffusion cells (peepers) in the Bay, lend a hand in sediment coring expeditions, and collect and interpret pH data while under direct supervision of the primary PIs. We also intend to compensate high school students for their work (see undergraduate researcher/budget justification) in an attempt to promote geosciences as a potential career choice. Field sites from this project are in close proximity to SFSU; thus, both PI's intend to take students from our Environmental Chemistry, Environmental Geology, and Contaminant Hydrogeology classes on field trips to inform and educate them about local contaminant problems. This is a useful exercise that helps solidify important topics discussed in a lecture setting. We will also regularly inform CALFED advisors and ecosystem roundtable members about the results and potential management implications of our findings. Community outreach will take place by presenting our research in a manner that solicits feedback from local community based organizations.

C.2.c Monitoring and Assessment Plans

This is a research and monitoring project that involves a field/laboratory approach to address CALFED concerns pertaining to contamination within the Bay-Delta. Field monitoring will transpire using data loggers to monitor water quality data every 15 minutes for the duration of the proposal (3 years). We will update our Web page monthly to reflect changes in Bay-Delta water quality and present important findings from our research endeavors. We will also assess the spatial and temporal changes in Se toxicity and bioavailability in the aqueous and solid phase at three sites wherein Se is a major CALFED concern. The monitoring regime follows in accordance with previous research; thus, data from this experiment can be utilized by other researchers (Bay-Delta Modeling Forum, San Francisco Bay Estuary Institute's Regional Monitoring Program, and Real Time San Joaquin River Water Quality Management Project) to enhance modeling efforts and other scientific endeavors currently underway as well as improve the overall Se conceptual model of the Bay-Delta. We hope to assist CALFED managers in the decision making process that results in the formulation of long-term regulatory policies that are beneficial to all Bay-Delta users.

C.2.d. Data Handling and Storage

Data generated from chemical extractions will be normalized and bar graphs with error bars will be used to illustrate contaminant partitioning verse time. In addition, we will undertake a rigorous geostatistical assessment of all field collected data using WINGSLIB geostatistical software. We will use univariate and bivariate statistics coupled with standard kriging methods to decipher trends, correlations, and model spatial variability within the sites. Water quality data from our data loggers will be graphed using EcoWatch® software (which accompanies the probes) and geostatistically assessed as well. All field data will be utilized to update and refine our hypotheses and enhance our Se conceptual model. We intend to create an easy to access Web site in order to present research findings, advances in analytical methodologies, and the results from monthly water quality measurements. All data collected will be stored and backed up on standard IBM-compatible PC's and peripheral storage media such as 100 Mb Zip disks in at least three separate physical locations (separated by at least 1 mile). Data will be manipulated using standard spread sheet and scientific graphing software (EXCEL, Sigmaplot, Kaleidagraph, etc.), geochemical modeling software (Visual MinteqA2), and geostatistical software (WINGSLIB). Periodically we will encapsulate important results in the form of Powerpoint presentations which will be given at scientific meetings and local community forums and will be made available to CALFED management as an end-user product.

C.2.e. Expected Products/Outcomes

This is a research and monitoring project, and thus publication of the results in peer-reviewed scientific journals, presentations at scientific meetings (including annual CALFED meetings), and an quarterly/annual data report summarizing our results for CALFED agencies, managers, and decision-makers will be used as measures of project performance. In addition, we will create a Web site for easy transfer of data and findings to other scientists and we will encourage graduate and undergraduate students to present their research findings at scientific meetings.

C.2.f. Work Schedule

A detailed work schedule including expected analytical loads necessary to accomplish the objectives and tasks of this project is illustrated in Table 1. The tasks are designed to assess the spatial and temporal behavior of Se and are dependant on each other. The first year of the study will entail implementing a grid site, inserting data loggers at each site, and creating a Web site (Objective 1; Task 1). Additionally, we will collect 9 sediment cores which will be sectioned (5 cm intervals to a depth of 20 cm), homogenized, and composited into three cores for solid phase analysis (Objectives 1 and 3; Tasks 2 and 4). Duplicate sediment samples will be processed through the first extraction sequence (5 chemical reagents) yielding a total of ~360 samples per site for an entire year (Objective 1; Task 2) (Table 1); solid phase analysis at all three sites will continue for the first two years of the experiment. In year one, we also intend to optimize our Se speciation protocol and consistently update and refine all our analytical procedures to obtain superlative results (Objective 1 and 2; Task 3); any sampling protocol refinement will be posted on our Web site. At the end of year one we hope to (1) have our speciation protocol in working order, (2) identify solid phase sinks wherein Se resides, (3) monitor Se response to altering physicochemical sediment conditions, and (4) refine and enhance our conceptual model. During year two, we continue our solid phase sampling program but will commence speciating Se on aqueous and solid phase samples removed from SJR 1 (Objective 1 and 3; Task 4). Duplicate sediment samples for Se speciation will be exposed to three chemical reagents yielding a total of ~216 samples (Objective 1 and 3; Task 4). Furthermore, we will randomly insert 4 peepers into SJR 1 and process ~480 samples/year. Our goals are to speciate (in duplicate) Se collected at 5 cm intervals in the porewater and overlying water column (i.e., particulate matter) as well as the solid phase. At the end of our second year we hope to finalize our conceptual model of Se partitioning, bioavailability, and transport between the aqueous and solid phase. In year three, we will proceed to test our hypothesis/conceptual model via a detailed laboratory microcosm investigation consisting of various treatments (Objective 2 and 3; Task 5). We also intend to implement XAS in order to define Se toxicity and molecular level structure in the sediment columns (Objective 2 and 3; Task 6).

C.2.g. Feasibility

The feasibility of this project is assured by the local proximity of the San Francisco Bay field sites to SFSU. The majority of laboratory work proposed in this project will be accomplished on the SFSU campus and thus frequent travel to field sites, sample handling and storage, and sediment analyses will be accomplished in a minimum amount of time. One of the project PI's has specialized laboratory equipment at SFSU (HGAAS) specifically designed for Se speciation and has extensive prior experience with Se analytical chemistry (Manning, 1993; Manning and Burau, 1995). Both PI's have active collaborations with the research group of Dr. Scott Fendorf (Dept. Geol. Environ. Sci., Stanford University) including current projects applying X-ray absorption spectroscopy which are accomplished locally at SSRL. The PI's have prior experience applying X-ray absorption spectroscopy to environmental systems (soil and sediment).

Laboratory work will be carried out in the project PI's laboratories in Thornton Hall, SFSU. Both PI's are skilled laboratory scientists who will be actively engaged in the project and will train all students and technicians working on the project. A trained technician will help coordinate and oversee sample storage, handling, preparation, and analyses will work closely with the PI's to guarantee that good laboratory practices and proper QA/QC methods are adhered to. The project PI's and the technician will train undergraduate and master's level chemistry and geology students to perform extractions, sample preparation, and analytical work. In addition to adherence to proper laboratory protocols, this project will use tested methods for collecting field data including installation of pore-water samplers in the field. Sediment cores and overlying Bay water samples will be periodically removed and stored for analyses. Field work will be in wetland or shallow areas for ease of sampling. We have consulted local experts (Dr. Sam Luoma, USGS, Menlo Park, CA) about field sites which have proven useful in a prior CALFED project.

D. APPLICABILITY TO CALFED ERP GOALS

D.1. ERP GOALS AND CVPI PRIORITES

The ERP goals that will be directly addressed by this work include *Strategic Goal 6: water and sediment quality.* Results of this project will also provide valuable information pertinent to *Multi-Regional Priority 5: Ensure that restoration is not threatened by degraded environmental water quality.* All field sites have been carefully selected to address CALFED concerns and maximize restoration priority goals. Pertinent information pertaining to Se mobility and bioavailability within the Bay and it's tributaries will be generated and distributed so as to guarantee the most effective use of this information. The water and sediment quality results from this project will be effectively delivered so as to inform other researchers working on related ecosystem studies of the Bay-Delta region. Information derived from the project will be delivered as project summaries and reports, involvement in informational exchanges with CALFED and it's respective agencies, a Web site dedicated to the project, standard scientific journal articles, and presentations at meetings. Another key issue that is central to this project is the need to expand the present knowledge of the effects of inflows of San Joaquin River water to the Delta that contains inorganic Se(VI). This work will improve our understanding of the fate and cycling of inorganic Se in Bay sediments and provide a scientific basis for understanding the impacts of Se-laden agricultural drainage and irrigation waters entering the Bay-Delta ecosystem. We will couple the results of this work with current efforts to develop technologies and management strategies for minimizing wildlife exposure to Se and uptake of Se to the aquatic food chain.

D.2. RELATIONSHIP TO OTHER ECOSYSTEM RESTORATION PROJECTS

It is imperative to have multi-disciplinary researchers working together to understand Se within the Bay. Thus, we intend to take a synergistic approach to the problem by working jointly with other researchers who are actively engaged in understanding Se transport, toxicity, and bioavailability within the Bay (Luoma et al. (F-200); Luoma et al. (F-200)). Our sampling regime follows in accordance with Luoma et al., 2000; thus, data obtained from this study can be utilized in their 3-D hydrodynamic model. Our field monitoring project will compliment ongoing monitoring programs about (United State Geological Survey, San Francisco Bay Estuary Institute’s Regional Monitoring Program, and Real Time San Joaquin River Water Quality Management Project) and increase knowledge pertaining to the Bay.

Water quality data from our dataloggers will be posted monthly on our Web site. This information will be beneficial to other scientists and CALFED mangers working on the Bay.

D.3. REQUESTS FOR NEXT-PHASE FENDING

This section is not applicable to this proposal.

D.4. PREVIOUS RECIPIENTS OF CALFED FUNDING

We have not previously obtained CALFED funding.

D.5. SYSTEM-WIDE ECOSYSTEM BENEFITS

Ecosystem-wide benefits derived from this project include development of an improved conceptual model for Se cycling within Bay-Delta ecosystem, establishment of a detailed data set on the speciation and biogeochemical cycling of Se contamination originating from San Joaquin River waters, and an improved understanding of the detailed relationship between Se speciation in the overlying waters, Se speciation in pore-waters, and the distribution of solid phase Se in the sediment solids. Of critical importance is to relate bioavailable Se (defined as Se in suspended particulates plus dissolved Se(IV)) to chemical and physical properties of the sediments. Our sampling regime will simultaneously measure dissolved Se speciation in direct contact with Se contained in suspended particulates and underlying sediments. In addition, this sampling will be carried out in three locations in the Bay-Delta region allowing for extrapolation to be made to the basin-wide system. We have attempted to address in our project objectives certain key CALFED initiatives such as collection of real-time water quality monitoring data, understanding and managing Se contamination in the San Joaquin River, and providing educational outreach to the local community and students. We will provide scientific results that are well-synthesized to be used as ecosystem-wide decision-support tools by groups such as Bay Forum modelers and the Bay-Delta Ecosystem Roundtable.

E. QUALIFICATIONS

Matthew J. La Force, Assistant Professor Geosciences SFSU

Education: 00 PhD, Soil Science/Soil Chemistry, University of Idaho- Thesis Title: *Seasonal Cycling of Redox-Active Metal(loid)s within Mining-Impacted Wetlands.;* MS 96, Geology/Hydrogeology, University of Idaho; BS 94, Geology/Environmental Science (Minor: Biology), SUNY Cortland College.
Experience: 95-99 Soil Chemistry Research Assistant, University of Idaho; 00 –01 Post Doctoral Research Fellow, Stanford University; 01 Secretary/Treasurer, Western Soil Science Society of America
Research Interests: Speciation, fractionation, and transport of trace elements in contaminated wetland ecosystems. Field determination of the structure and mobility of trace elements under varying physicochemical soil conditions using chemical extractions in conjunction with advanced spectroscopic tools --X-ray absorption spectroscopy, Micro-Raman spectroscopy, and FTIR spectroscopy.
Publications: La Force, M.J., S. Fendorf, G.C. Li, G.M. Schneider, and R.F. Rosenzweig. 1998. *J. Environ. Qual*. 27:318-328; Harrington, J.M., M.J. La Force, W.C. Rember, S.E. Fendorf, and R.F. Rosenzweig. 1998. *Environ. Sci. Technol.* 32:650-656; La Force, M.J, S.E. Fendorf, G.C., Li, and R.F. Rosenzweig. 1999. *J. Environ. Qual.* 28:1195-1201; La Force, M.J., C.M. Hansel, and S.E. Fendorf. 2000. *Soil Sci. Soc. Am. J.* 64:809-811; La Force, M.J. and S.E. Fendorf. 2000. *Soil Sci. Soc. Am. J.* 64:1608-1614; La Force, M.J., G.C. Li, and S.E. Fendorf. 2000. *Environ. Sci. Technol.* 34:3937-3943; Bostick, B.C., C.M. Hansel, La Force, M.J., and S.E. Fendorf. 20001. *Environ. Sci. Technol.* In press.; La Force, M.J., C.M. Hansel, and S.E. Fendorf. 2001. *Soil Sci. Soc. Am. J.* In Press.

Bruce A . Manning, Assistant Professor Chemistry and Biochemistry SFSU

Education: Ph.D. Environmental Chemistry, 1993. University of California, Davis. Thesis Title: *Geochemical Immobilization of Selenium in Evaporation Pond Sediments*. BS Environmental Science, 1985. University of Massachusetts, Amherst**.**
Experience: 1999-present, Assistant Professor, Department of Chemistry and Biochemistry, San Francisco State University (Analytical and Environmental Chemistry); 1993-1999, Postdoctoral Research Associate, University of California, Riverside, Department of Environmental Science and USDA-ARS U.S. Salinity Laboratory; 1987-1993, Graduate Research Assistant, Department of Land, Air, and Water Resources, University of California, Davis.
Research Interests: Environmental geochemistry and surface chemistry; Separation and detection of redox sensitive elements (As(III)/As(V), Se(IV)/Se(VI), and Cr(III)/Cr(VI)) by hyphenated techniques such as HPLC coupled with AA, ICP, ICP-MS, and atomic fluorescence spectrometry. Determination of the molecular surface structures of trace elements coprecipitated and adsorbed on mineral surfaces using EXAFS and XANES spectroscopy.
Publications: Manning, B.A.; Hunt, M.; Amrhein, C. 2001. *Environ. Sci. Technol*. (Submitted). Manning, B.A.; Fendorf S.E.; Suarez, D.L. 2001. *Environ. Sci. Technol*. (*In press*). Manning, B.A.; Suarez, D.L. *Soil Sci. Soc. Am. J*. 2000. 64, 128-137. Manning, B.A.; Fendorf, S.E.; Suarez, D.L. 1999. *Proceedings of Division of Environmental Chemistry*. 39, 288-290. Manning, B.A.; Fendorf, S.E.; Goldberg, S. 1998. *Environ. Sci. Technol*, 32, 2383-2388. Manning, B.A. 1998. *In* R.A. Meyers (ed.) The Encyclopedia of Environmental Analysis and Remediation. John Wiley & Sons, New York, NY. pp. 4285-4291. Manning, B.A.; Goldberg, S. 1997. *Soil Sci*. 162, 886-895. Manning, B.A.; Goldberg, S. 1997. *Environ. Sci. Technol*, 31, 2005-2011. Manning, B.A.; Martens, D.A. 1997. *Environ. Sci. Technol*. 31, 171-177. Manning, B.A.; Goldberg, S. 1996. *Clays & Clay Miner*. 44, 609-623. Manning, B.A.; Goldberg, S. 1996. *Soil Sci. Soc. Am. J*. 60, 121-131. Manning, B.A.; Burau, R.G. 1995. *Environ. Sci. Technol*. 29, 2639-2646.

Facilities

Dr. Bruce Manning's Laboratory Equipment. The laboratory facilities for performing Se analyses and speciation are located in rooms 819 and 821 Thornton Hall, on the main campus of San Francisco State University. Analyses will be performed on Varian SpectrAA FS 220 atomic absorption spectrometer equipped with a Varian VGA-77 hydride generator. We have confirmed the Se sensitivity of this instrument; a 10 ppb Se(IV) solution yields an absorbance of 0.320 AU allowing for sub-ppb analyses to be performed. The following standard laboratory equipment will be used for the project: Beckman J21 floor model temperature controlled centrifuge (for sample preparation and fractionation); Dionex ion chromatography module (for Se(IV)/(VI) separation); Orion pH meters; Mettler AE 160 microbalances (accurate to 0.0001 g); reciprocating sample shakers. In addition to the AA spectrometer an Aurora AI 3000 atomic fluorescence detector (trace detection of As, Cd, Hg, Pb, Sb, Se, and Zn) is available for the project.

Dr. Matthew La Force's Laboratory Equipment. The geochemistry laboratory at San Francisco State University is equipped with a Barnstead Nanopure Diamond water purification system, a Beckman Alegra 6 centrifuge, a Thermolyne 1400 muffle furnace, Ohaus microbalances, and a customized anaerobic flexible vinyl chamber (Coy glove bag) for sediment processing under anoxic conditions. For solid phase sampling, the lab contains an AMS core and sludge sampler and a UWSS undisturbed sediment and wet soil sampler along with a piston coring device. The laboratory is equipped with a Denver Instrument portable pH, Eh(mV), conductivity, and dissolved oxygen meter along with a Hach portable datalogging (Model 2010) spectrophotometer. In addition, the laboratory contains an OI analytical (Model 1010) total organic carbon (TOC) analyzer.

Dr. Scott Fendorf's Laboratory Equipment. The Soil chemistry laboratory at Stanford University is equipped with A Thermo Jerrel Ash IRIS Advantage/1000 Radial ICAP Spectrometer with a Solid State CID Detector, which can simultaneously analyze a sample for multiple elements.

F. COST

F.1. BUDGET JUSTIFICATION

The budget for this project has been broken down by Task in the *Budget Summary* page (submitted separately to CALFED; see appendices Table 2). In an effort to provide more detailed information on our budget which is not contained in the *Budget Summary* page we have also organized and itemized the project budget by category (Personnel, Travel, Supplies, etc.) and is included herein. The total proposed funding requested for this project is $1,042,984. We have put forth an ambitious project designed to address key CALFED priorities. In addition we intend to address these priorities by adherence to strict, current scientific protocols while maintaining strong educational and outreach components in our overall objectives.

Personnel

The PI's on the project (Dr. Bruce Manning and Dr. Matthew La Force) are requesting 40% release time from academic year teaching responsibilities at SFSU. The cost for this item is calculated from 40% of each PI's annual year salary (see dollar amounts for PI salaries itemized *Personnel* section of budget). Release time from teaching will afford the PI's the opportunity to focus efforts on field work, sample collection, data analysis, manuscript preparation, and student mentoring. Professors at SFSU are normally responsible for a "full-time" teaching load of 12 teaching units per semester which assumes little or no time conducting research during the academic year. Therefore, a 40% release time request will allow adequate time to pursue this project without removing the PI's completely from the classroom. In addition to academic year release time, the project PI's are requesting summer salary compensation for 3 months of full-time dedicated to the project. All fringe benefits are based on standard SFSU payroll benefits for full-time tenure-track faculty.

This project also seeks funding for a full-time research technician to handle Se analysis and speciation as well as assist with field monitoring, sample collection, data analysis, and laboratory experiments (total salary of $103,579 over three years, plus benefits). The need for a dedicated technician on the project is based on prior experience which has shown the importance of maintaining a skilled and well-trained individual to be responsible for daily laboratory duties including cataloging and tracking sample handling, chemical analyses, ordering supplies, basic training of students, QA/QC adherence, cleaning lab-ware, and data analysis.

One of our main objectives is to incite and stimulate student research participation within the project. Thus, we intend to fund graduate students at the master's degree level and undergraduate student researchers from the Departments of Geosciences and Chemistry & Biochemistry at SFSU to participate in the project. Both graduate and undergraduate researchers will use this project as a basis for completion of master's and senior thesis projects which are requirements for students to obtain their degrees at SFSU. In addition, we intend to pay high school researchers selected from the SF:ROCKS program to assist with field sampling and data collection; we hope this measure will stimulate students to consider the earth and environmental sciences as a viable career option (objective 1).

Travel

We have budgeted money for travel to the field sites for the duration of the experiment (~200 miles @ 0.33 cents per mile). Additionally, we have requested travel money for students and PI's to present findings of our field research (year two) and laboratory microcosms (year three) at scientific meetings (Geologic Society of America, American Chemical Society, American Geophysical Union). The cost for travel to meetings is based on both PI's traveling plus a total of four students (2 per PI research group). Additional travel to local meetings such as CAL-FED annual meetings is included in the Travel section of the budget.

Supplies and Expendables

Supplies and expendables represent only necessary materials that will be needed to conduct field monitoring, sediment extraction and analysis for total metals, speciation of aqueous and solid phase Se, and laboratory microcosm work. Large items budgeted in *Supplies & Expendables* include reagents and solution preparation materials for selective sequential extractions ($18,000 total project) and peeper supplies ($17,400 total project). We are requesting funding in year 1 for the purchase of materials necessary for the construction of the peepers ($8,000) and our subsequent years 2 and 3 funding reflects monies necessary to only maintain peepers ($4,700 per year). Construction of an anoxic sediment sampler ($1,700), will be necessary for maintaining reduced, anoxic conditions in samples removed from the field. Based on the anticipated sample load, we have included an autosampler for Se analyses by HGAAS ($4,000), chromatography expendables ($10,100), and atomic absorption supplies ($1,200) such as gases and reagents. Other lab equipment includes sample storage, gases, pipet supplies and electrodes ($12,000 total project). Laboratory equipment needed for microcosm work includes a dual channel digital potentiometer ($2,100) and other related supplies such as specialized glassware and tubing ($2,500).

Services/Consultants

Sediment cores sampled in the initial stages of the project will be subjected to extraction and the extracts analyzed for total metals (Al, As, Cr, Cu, Hg, Fe, Mn, Se, and S) by inductively coupled plasma optical emission spectrophotometer (ICP-OES) analysis. This work will be performed at Stanford University’s soil chemistry laboratory (Research Laboratory of Dr. Scott Fendorf). An hourly rate of $65/hour has been agreed upon and we estimate 80 hours of ICP time will be necessary for each year of the project ($15,600 total project).

Equipment

We have attempted to keep costs to a minimum by utilizing instrumentation already in place at SFSU. The sole item budgeted under Equipment is for purchase of three YSI Sonde 6600 data loggers with probes ($24,600 year 1 only). The data loggers will provide essential information pertaining to water quality within the Bay and will address CALFED's proposal request for more “real-time monitoring of water quality in the SJR-Delta system”. The data will be made available on a project Web site maintained by the PI's.

Other Direct Costs

Items such as shipping costs for supplies, publishing-related expenses, and printing costs are included under *Other Direct Costs*.

F.2. COST-SHARING

There will be no cost sharing for this project.

G. LOCAL INVOLVEMENT

The project involves a comprehensive plan to understand the fundamental mechanisms behind Se mobility within the Bay-Delta ecosystem and to establish a real-time monitoring and water quality forecasting system. In order to accomplish our objectives we will actively engage students from the SFROCKS program in this project as well as bring undergraduate/graduate students from SFSU on field trips to discuss Bay-Delta contaminant issues. We will present our research findings at community based environmental group meetings; informal discussions will educate members of the local community and also address their concerns about Bay-Delta water quality.

H. COMPLIANCE WITH STANDARD TERMS AND CONDITIONS

This proposal will comply with all State and Federal contract terms described in Attachments D and E within CALFED's ERP (2001) proposal solicitation package.

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Appendix: Tables and Figures

Figure 1. Conceptual model for Se cycling in the Bay sediment-water environment.

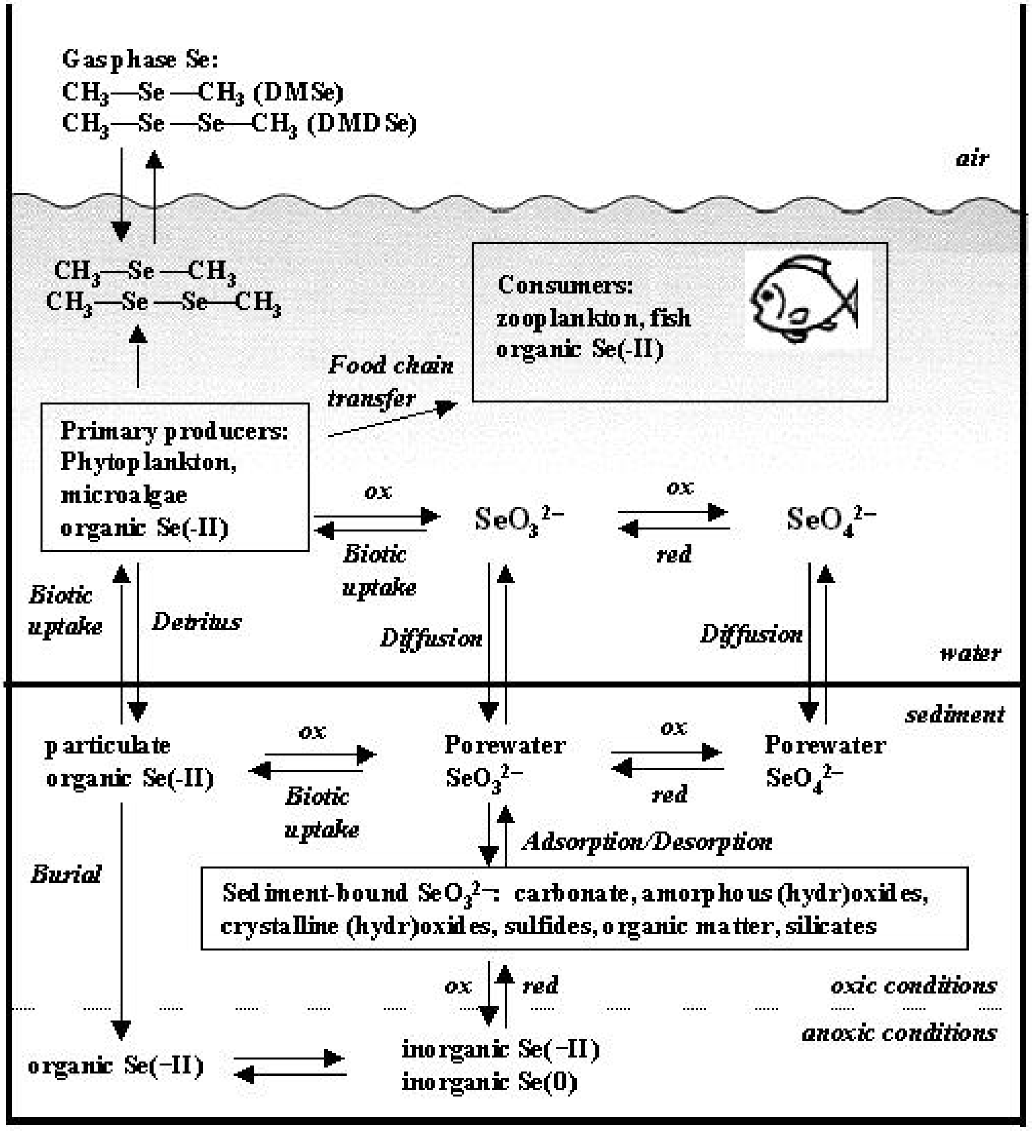

Figure 2. Location map of field sites (modified after Hornberger et al., 1997).

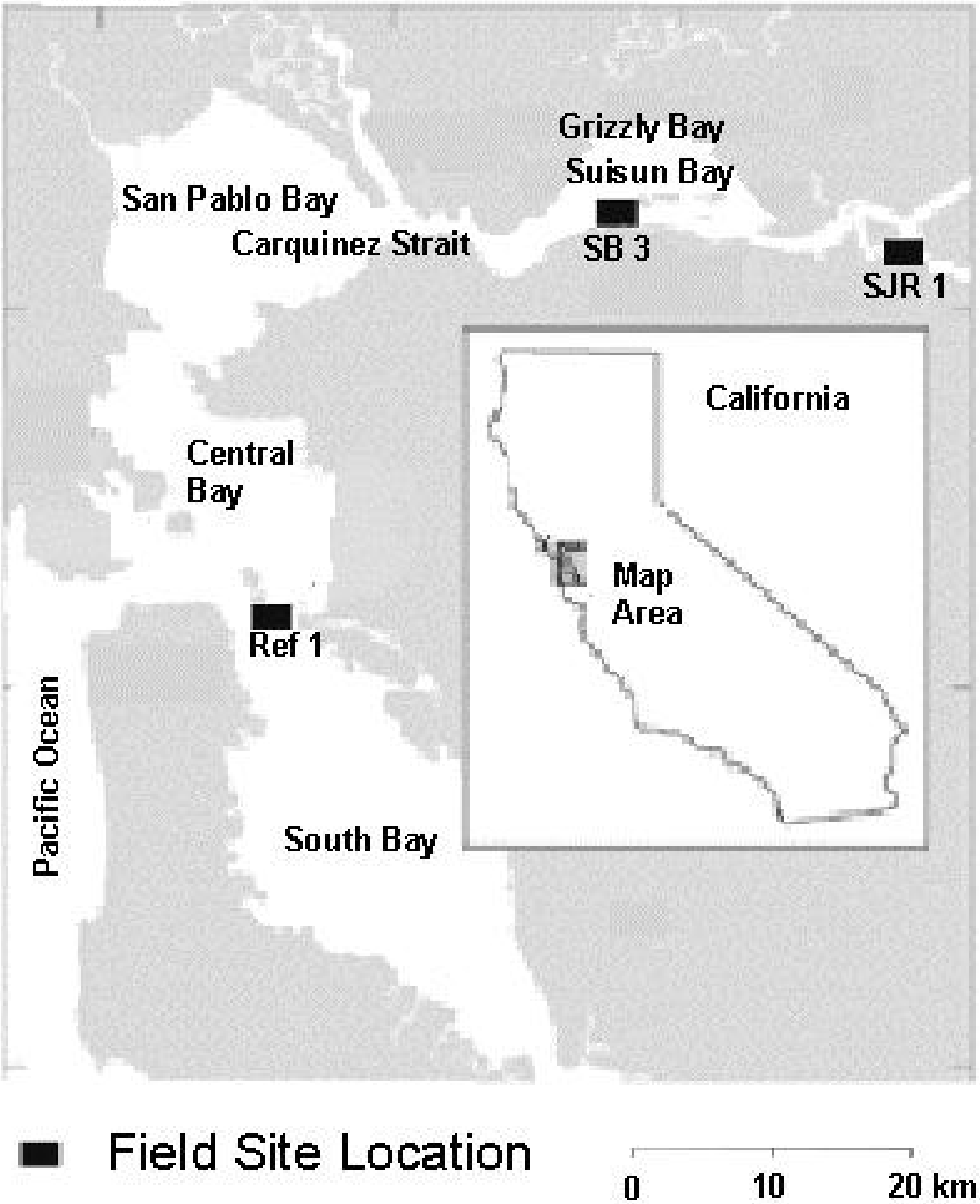

Table 1. Work schedule for field and laboratory experiments

OBJ. 1 **Task 1. Field Site Location, Monitoring, and Sample Collection** -*Setting up grids and web site (1st year); Monitoring the sites (3 years)*

OBJ. 1 **Task 2. Se Distribution Within Bay Sediments** -*Process sediment cores collected 3 times yearly (3 years)*

Field Site	**Analysis**	**Composite Cores**	**Sed. (0-20 cm)**	**Total Samples**	**Extracts**	**Reps**	**Samples per time pt**	**Time/yr**	**Analyses per year**
site 1 SJR1	Cores (total elements by ICP)	3	4	12	5	2	120	3	360
site 2 REF2	Cores (total elements by ICP)	3	4	12	5	2	120	3	360
site 3 SB3	Cores (total elements by ICP)	3	4	12	5	2	120	3	360
								Total	**1080**

OBJ. 1, 2 **Task 3. Protocol for Selenium Speciation in the Aqueous and Solid Phase** *(3 years)*

OBJ. 1, 3 **Task 4. Selenium Speciation from Field Collected Sediment**- *Speciate Se extracted from sediment cores collected 3 times yearly (year 2)*

Field Site	**Analysis**	**Composite Cores**	**Sed. (0-20 cm)**	**Total Samples**	**Extracts**	**Reps**	**Samples per time pt**	**Time/yr**	**Analyses per year**
site 1 SJR1	Cores (total Se (SSE; AA), speciation HGAAS)	3	4	12	3	2	72	3	216
								Total	**216**

OBJ. 1, 3 **Task 4. Selenium Speciation from Field Collected Solution**. -*Speciate Se extracted from peepers collected 3 times yearly (year 2)*

Field Site	**Analysis**	**Soln. Samples**	**Sed. & H_20 (+20 to -20 cm)**	**Samples**	**Extracts**	**Reps**	**Samples per time pt**	**Time/yr**	**Analyses Per year**
site 1 (SJR)	4 Peepers (total elements by ICP)	4	8	32	1	2	64	3	192
	4 Peepers (speciation HGAAS) soln	4	8	32	1	2	64	3	192
			Overlying water column +20cm						
	4 Peepers (speciation HGAAS) particulate matter (Se(T))	4	4	16	1	2	32	3	96
								Total	**480**

OBJ. 2, 3 **Task 5. Laboratory Microcosms and Lab Experiments**-*Speciate Se from microcosms (year 3)*

Field Materials	**Analysis**	**Microcosm**	**Total Samples**	**Extracts**	**Total Extracts**	**Analyses Per year**
site 1 (SJR)	Solution (speciation HGAAS)	3	20	1	20	20
	Cores (speciation HGAAS)	3	20	3	60	60
					Total	**80**

OBJ. 2, 3 **Task 6. Application of X-ray Absorption Spectroscopy** *Conduct XAS work on random samples from microcosm experiments (year 3)*

OBJ. 4 **Task 7. Educational Outreach and Community Involvement** *(3 years)*

Table 2. Budget Summary

		Total Requested Yr 01	Total Requested Yr 02	Total Requested Yr 03	Total Project Cost
PERSONNEL					
Principal Investigator, Bruce Manning					
$51,456	Academic Year Salary				
$4,288	Per Month				
$5,717	Per Summer Month				
40%	Reimbursed Release Time	$20,582	$21,612	$22,692	$64,886
28%	Fringe Benefits	$5,763	$6,051	$6,354	$18,168
3	Summer Months	$17,152	$18,010	$18,910	$54,072
12%	Fringe Benefits	$2,058	$2,161	$2,269	$6,489
Principal Investigator, Matt La Force					
$59,004	Academic Year Salary				
$4,917	Per Month				
$6,556	Per Summer Month				
40%	Reimbursed Release Time	$23,602	$24,782	$26,021	$74,404
28%	Fringe Benefits	$6,608	$6,939	$7,286	$20,833
3	Summer Months	$19,668	$20,651	$21,684	$62,003
12%	Fringe Benefits	$2,360	$2,478	$2,602	$7,440
Research Technician, TBN					
$32,856	Calendar Year Salary				
$2,738	Per Month	$32,856	$34,499	$36,224	$103,579
36%	Fringe Benefits	$11,828	$12,420	$13,041	$37,288
Undergraduate Student Assistants (2)					
$12	Hourly				
800	(40 hrs/week x 10 weeks x 2)	$9,600	$9,600	$9,600	$28,800
2%	Fringe Benefits	$144	$144	$144	$432
Graduate Student Assistants (2)					
$14.24	Hourly				
$1,280	(20 hrs/week x 32 weeks x 2)	$18,227	$18,227	$18,227	$54,682
$960	(40 hrs/week x 12 weeks x 2)	$13,670	$13,670	$13,670	$41,011
2%	Fringe Benefits	$478	$478	$478	$1,435
Total Salaries		**$155,358**	**$161,051**	**$167,028**	**$483,436**
Fringe Benefits		**$29,241**	**$30,671**	**$32,174**	**$92,086**
TOTAL SALARIES AND BENEFITS		**$184,598**	**$191,722**	**$199,202**	**$575,522**
TRAVEL					
Travel to Field Sites		$1,000	$1,000	$1,000	$3,000
Travel to GSA and CALFED Meetings			$6,000	$6,000	$12,000
Travel Subtotal		**$1,000**	**$7,000**	**$7,000**	**$15,000**

Table 2. Budget Summary Continued.	**Total Requested Yr 01**	**Total Requested Yr 02**	**Total Requested Yr 03**	**Total Project Cost**
SUPPLIES & EXPENDABLES				
SSE Analysis --Reagents, Supplies, Filters, Syringes	$6,000	$6,000	$6,000	$18,000
Peeper Supplies (Tubes, Parts, Construction)	$8,000	$4,700	$4,700	$17,400
Anoxic sediment sampler/storage unit	$1,700			$1,700
Anoxic sampler supplies (N2 regulators, battery pack, tubing, N2 gas)	$1,000			$1,000
Hydride generation/Se Speciation (IC Columns, tubing, reagents)	$4,300	$4,300	$1,500	$10,100
Atomic absorption supplies (Se lamp, autosampler tubes, gases)	$700	$500		$1,200
AA autosampler	$4,000			$4,000
Misc Supplies (sample storage, gases, pipet supplies, pH and redox electrodes)	$5,000	$5,000	$2,000	$12,000
Benchtop digital potentiometer (dual channel, for microcosms)			$2,100	$2,100
Lab microcosm supplies			$2,500	$2,500
Supplies & Expendables Subtotal	**$30,700**	**$20,500**	**$18,800**	**$70,000**
SERVICES/CONSULTANTS				
ICP Time Stanford $65/hour X 85hrs/yr	$5,200	$5,200	$5,200	$15,600
Services/Consultants Subtotal	**$5,200**	**$5,200**	**$5,200**	**$15,600**
EQUIPMENT				
3 YSI Sonde 6600 Data Loggers+ Probes	$24,600			$24,600
Equipment Subtotal	**$24,600**	**$0**	**$0**	**$24,600**
OTHER DIRECT COSTS				
Shipping Costs	$400	$200	$200	$800
Publishing/Printing		$1,000	$1,000	$2,000
Publication Costs/Documentation/Dissemination	$0	$0	$0	$0
Consultant Services	$0	$0	$0	$0
Computer Services	$0	$0	$0	$0
Sub awards	$0	$0	$0	$0
Other	$0	$0	$0	$0
Other Direct Costs Subtotal	**$400**	**$1,200**	**$1,200**	**$2,800**
TOTAL DIRECT COSTS	**$246,498**	**$225,622**	**$231,402**	**$703,522**
INDIRECT COSTS	**$110,949**	**$112,811**	**$115,701**	**$339,461**
TOTAL DIRECT AND INDIRECT COSTS	**$357,447**	**$338,433**	**$347,103**	**$1,042,984**