CALFED BAY-DELTA PROGRAM

CALFED SCIENCE FELLOWS PROGRAM

In cooperation with the

California Sea Grant College Program

FELLOWSHIP APPLICATION COVER PAGE

APPLICANT TYPE [X] Postdoctoral Researcher [ ] Ph.D. Graduate Student

PROJECT NUMBER

PROJECT TITLE Mercury interactions with algae: Effects on mercury bioavailability in the San Francisco Bay Delta

FINANCIAL SUMMARY

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Will animal subjects be used? [ ] Yes [X] No

APPROVAL DATE: PROTOCOL #: PENDING:

Does this application involve any recombinant DNA technology or research? [ ] Yes [X] No

Proposed Research

I. INTRODUCTION/QUESTION/ OBJECTIVES

One of the major environmental concerns in the San Francisco Bay and Delta is mercury contamination (Thompson et al. 2000). The estuary is highly contaminated with mercury as a result of historic gold and mercury mining in its watersheds. When that mercury reaches the sediments of the estuary, it can be transformed by bacteria to methyl mercury (MeHg), which is the organic form that bioaccumulates in the food chain. MeHg bioaccumulates to concentrations of >0.4 parts per million (ppm) in San Francisco Bay fish, far exceeding the San Francisco Bay Regional Water Quality Control Board screening value of 0.2 ppm (SFEI 2000). As a result of those elevated concentrations, there are fish consumption advisories in place in the estuary (SFEI 2000). The advisories are primarily for pregnant women because mercury may affect fetal brain development and result in neuromotor, visual, and sensory impairments in developing fetuses (Mahaffey 2000). Mercury is also considered a threat to wildlife, particularly the endangered California Clapper Rail (Schwarzbach et al. 2006). Mercury decreases California Clapper Rail egg viability, and the last ~1000 breeding individuals live in the tidal marshes of the estuary (Schwarzbach et al. 2006).

To address these health and environmental concerns, research on MeHg bioaccumulation in the food chain is needed. Although research suggests that fish and birds accumulate most of their MeHg from the food chain (Boudou and Ribeyre 1997), the mechanism for mercury uptake into phytoplankton at the base of the food chain is not known. Phytoplankton concentrate MeHg by a factor of 10^5, making them the largest single step in MeHg bioaccumulation (Mason et al. 1995; Mason et al. 1996). Moreover, uptake of MeHg to phytoplankton can be modeled by understanding the chemistry of the surrounding waters. Accordingly, I plan to examine the chemical parameters that affect MeHg association with phytoplankton.

One water chemistry variable that may be particularly important for elucidating how MeHg is accumulated in phytoplankton is the amount and quality of dissolved organic matter (DOM) in the water. Organic matter enters the estuary's waters through a variety of sources, including terrestrial runoff (i.e. humic matter), wastewater treatment plant inputs, and breakdown of marine organisms. MeHg and inorganic Hg(II) may bind to the DOM through complexation to reduced sulfur groups (e.g. thiol groups) on amino acids and humic substances (Amirbahman et al. 2002; Benoit et al. 2001). Only a small portion of MeHg or Hg (II) may bind to oxygen functional groups, such as carboxylic groups on humic substances (Amirbahman et al. 2002; Reddy and Aiken 2001).

In the San Francisco Bay estuary, high MeHg concentrations have been associated with high dissolved organic carbon (DOC) (Conaway et al. 2003). That relationship between MeHg and organic matter in San Francisco Bay has been observed for a number of size fractions, including the filtered fraction (< 0.45 µm), the colloidal fraction (1 kDa - 0.45 µm), and the <1 kDa fraction (Choe and Gill 2003). A positive correlation between DOC and mercury has also been observed in a number of other systems, including lakes and rivers (Babiarz et al. 1998; Grigal 2002; Watras et al. 1998).

The association between mercury and DOM may be a missing link for understanding how mercury is accumulated by phytoplankton. Previous research has demonstrated that DOM may alter processes that occur on phytoplankton surfaces (such

as uptake of metals) by binding to cell surfaces (Campbell et al. 1997). That DOM binding likely also increases the sorption of mercury to the cell surface, based on research by Gagnon and Fisher (1997) showing that fulvic coatings on particles enhanced the sorption of MeHg and Hg(II) to particle surfaces. We hypothesize that as a direct result of this three-way interaction between phytoplankton, DOM, and mercury, DOM influences mercury uptake to phytoplankton. That hypothesis is supported by results from Pickhardt and Fisher (in press) demonstrating that high concentrations of DOC increased MeHg uptake to phytoplankton.

Although Pickhardt and Fisher (in press) observed that DOC enhanced MeHg accumulation in phytoplankton, the mechanism for MeHg uptake by phytoplankton remains elusive. One possible mechanism, which is supported by these studies on the linkage between phytoplankton, DOM, and mercury, is that phytoplankton are deliberately taking up DOM and accidentally acquiring MeHg that is associated with that DOM. That explanation is consistent with previous studies showing that phytoplankton uptake of MeHg is an active process (Moye et al. 2002; Pickhardt and Fisher in press). Moreover, phytoplankton are known to uptake a variety of organic materials from the water, such as siderophores and vitamin B_{12} (Morel et al. 2004; Swift and Guillard 1978).

If phytoplankton are deliberately taking up DOM and acquiring MeHg as an accidental associate, we might expect that the quality of the DOM affects MeHg uptake to phytoplankton. For example, in areas with low carbon quality, such as the Central Delta (Stepanauskas et al. 2005), phytoplankton might take up less DOM and therefore accumulate less MeHg. Such a mechanism would explain observations that fish from the Central Delta have lower mercury concentrations than those from the rivers that empty into the Delta (Foe et al. 2003).

Furthermore, it is possible that MeHg and Hg(II) are preferentially associated with highly bioavailable fractions of the DOM (e.g. glutathione), exacerbating the MeHg accumulation for phytoplankton that are uptaking high quality DOC. This hypothesis is supported by recent research that suggests that the composition of the DOM may be more important than bulk concentration (Han et al. 2006). For example, Han et al. (2006) found that low concentrations of glutathione and phytochelatin, both ligands with biological origins, were important for complexing dissolved mercury. Knowing the fraction of the DOM with which the mercury is associated could be important for determining how mercury is accumulated in phytoplankton.

Understanding how DOM quality affects MeHg accumulation in phytoplankton is instrumental for ecosystem managers to address prospective effects of land use changes and wetland restorations. For example, current plans call for remediating 40,000 ha of agricultural land to wetlands, which is about 10% of the total Delta area (Stepanauskas et al. 2005). However, there is concern that wetland restoration could increase MeHg fluxes (Grigal 2002), creating unsuitable habitat for fish and pisciverous birds. Those increased MeHg fluxes may be associated with the high production of DOC in wetlands (Grigal 2002). Creation of freshwater wetlands from former agricultural areas may also change the quality of the DOC and result in more reactive DOC (Bossio et al. 2006). This proposal will determine how changes in DOC composition affect MeHg uptake to phytoplankton by using DOM isolates from a variety of sites, including wetlands and marshes, to study MeHg accumulation. Accordingly, this work could help determine the

suitability of constructed habitats. This outcome relates directly to CALFED's priority goal of determining how abiotic drivers, including contaminants, affect habitat quality.

To address the need for studies on DOM and mercury in the San Francisco Bay Delta, this proposal has three objectives: (1) to determine the bioavailability of MeHg and Hg(II) associated with DOM by adding radioisotopes of MeHg to phytoplankton cultured in DOM isolates from the estuary; (2) to test the association between MeHg and Hg(II), phytoplankton, and DOM quality by lagrangian sampling in San Joaquin River; and (3) to develop a model to predict the processes controlling MeHg uptake to phytoplankton, and thus to the food chain.

II. Approach/plan of Work

To characterize DOM and look at the bioavailability of MeHg bound to DOM, I am proposing an interdisciplinary collaboration between the community mentor, Dr. Brian Bergamaschi, United States Geological Survey, and the research mentor, Dr. Nicholas S. Fisher, State University of New York at Stony Brook. Dr. Bergamaschi's research focuses on characterizing DOM and food web dynamics. Dr. Fisher's research focuses on using radiotracers to look at the bioavailability of metals to organisms, including phytoplankton. By combining these two different fields, this proposal will be able to both characterize the DOM and to examine the effects of DOM composition on uptake to phytoplankton at the base of the food chain. Specifically, we will test the following:

> Hypothesis 1: Low quality DOC limits MeHg uptake to phytoplankton in the Central Delta and thus decreases bioavailability to the food chain.
>
> Hypothesis 2: MeHg and Hg(II) concentrations are correlated with high quality DOM, not bulk DOC concentrations, and that association affects mercury concentrations and partitioning as DOM composition changes down the San Joaquin River.
>
> Hypothesis 3: The composition of the DOM and other water chemistry variables can be used to develop a biogeochemical model to predict mercury in fish hotspots in the estuary and Delta.

Sites for Hypothesis 1

To look at the bioavailability of mercury associated with phytoplankton, we will compare a variety of sites (Figure 1) in the Sacramento and San Joaquin Rivers and Delta with differing organic matter composition. Some of these sites have been previously characterized (Stepanauskas et al. 2005). Those characterizations have shown that sites in the Central Delta generally have low quality DOC of terrestrial origin and low nutritional value (Stepanauskas et al. 2005). In contrast, DOC from the Sacramento River at Hood and the San Joaquin River at Vernalis has high bioavailability to the microbial community and a higher fluorescence ratio than samples from the Delta, indicating a relatively larger contribution of phytoplankton-derived DOC (Stepanauskas et al. 2005).

Based on these previous characterizations, we will use the following sites, illustrated in Figure 1: (1) The Sacramento River at Hood; (2) The San Joaquin River at Vernalis; (3) Frank's Tract, a tidal wetland in the Central Delta; (4) Mandeville Tip, a natural freshwater marsh also in the Central Delta; (5) Prisoner's Point, a deep water channel that represents an average for Delta-exposed water; (6) Brown's Island, a brackish marsh that is the most westerly of our sampling sites, and (6) Twitchell Island Drain, a below sea level island that receives DOC from agricultural run-off. This range of sites should allow us to work with DOM before and after it has been transformed by processes in the Delta. Furthermore, isolates of DOM have already been collected from these sites and are well characterized in a wide variety of ways at considerable expense (tens of thousands of dollars), allowing us to leverage past work to begin our culture studies on the effect of DOM composition on MeHg uptake to phytoplankton.

This sampling scheme will also allow us to compare our results on bioavailability to phytoplankton with previous field observations on MeHg accumulation in clams and fish in the Delta. Some preliminary field results suggest that largemouth bass and white catfish in the Central Delta may have lower mercury concentrations than those from the Sacramento and San Joaquin Rivers (Davis et al. 2003; Foe et al. 2003). We will test the hypothesis that low quality DOC limits MeHg uptake to phytoplankton and thus explains the low concentrations of mercury in fish observed in the Central Delta. This goal addresses CALFED's priority topic area on understanding the divers that affect habitat quality.

Laboratory Experiments for Hypothesis 1

To test the effect of DOM quality on uptake to phytoplankton, three species of phytoplankton will be cultured in each of the DOM isolates described in the previous section. Those cultures will later be divided into a subculture for a control, a subculture for MeHg addition, and a subculture for Hg(II) addition. Then, a laboratory synthesis will be conducted to generate $CH_3{}^{203}HgCl$ from $^{203}Hg^{2+}$. The $CH_3{}^{203}HgCl$ and $^{203}Hg^{2+}$ will be added to the respective treatments. This will generate a high number of samples, typical of this method. Those samples will be analyzed for concentrations of $CH_3{}^{203}HgCl$ and $^{203}Hg^{2+}$ in water and phytoplankton, using established techniques (Pickhardt and Fisher in press).

The phytoplankton species will consist of the diatom *Cyclotella meneghiniana*, the chlorophyte *Chlamydomonas reinhardtii*, and the cryptomonad *Cryptomonas ozolini*. These species were chosen because they are present in San Francisco Bay and have been used on past studies (Pickhardt and Fisher in press). Furthermore, they represent a range of cell sizes, with differing surface area to volume ratios. The surface area to volume ratio is an important consideration because as cell size increases, the proportionately reduced surface area means that metal uptake is limited by the rate of diffusion of the metal to the cell surface (Sunda and Huntsman 1998). In contrast, in smaller cells (<30 μm diameter), the rate limiting step is transport across the cell membrane (Sunda and Huntsman 1998). Accordingly, differences in the amount of uptake in different size cells might indicate which processes affect metal transport across the cell membrane. The three species of phytoplankton will be cultured in the various DOM isolates, and then radioactive mercury will be added.

To obtain radioactive MeHg, a laboratory synthesis from Hg(II) will be conducted. The Fisher laboratory regularly receives $^{203}HgCl_2$, with a specific activity of 152-325 KBq μg^{-1}, which will be used to synthesize $CH_3{}^{203}HgCl$. Following established methods (Pickhardt and Fisher in press; Rouleau and Block 1997), $^{203}HgCl_2$ will be methylated with methylcobalamin ($C_{63}H_{91}CoN_{13}O_{14}P$). The resulting $CH_3{}^{203}HgCl$ will be extracted with methylene chloride (CH_2Cl_2) (Pickhardt and Fisher in press). The CH_2Cl_2 will then be evaporated and the $CH_3{}^{203}HgCl$ will be collected in MQ and then stored in the dark in dilute Optima grade hydrochloric acid (HCl).

Next, $^{203}HgCl_2$ or $CH_3{}^{203}HgCl$ will be added to cultures of phytoplankton held in the DOM isolate from each site and concentrations of mercury in water and phytoplankton will be measured daily for a week. After addition of the spikes, final concentrations of mercury in water will range from 0.7 to 1.5 nM of $^{203}HgCl_2$ and 0.5 to 0.7 nM of $CH_3{}^{203}HgCl$. To determine how those concentrations will change, measurements of the radioactivity of mercury in water and phytoplankton (collected on filters), will be made with a LKB Pharmacia Wallac 1282 Compugamma equipped with a well-type NaI(TI) detector, following protocols previously established in the Fisher lab (Pickhardt and Fisher in press). Measurements of radioactivity will then be converted into concentrations, based on the initial concentration to radioactivity ratio. Given those concentrations, volume concentration factors (VCFs) will be calculated to assess and compare the MeHg and Hg(II) accumulation in phytoplankton cultured in different types of DOM.

Additional experiments using heat killed phytoplankton will carried out using the same protocols. The heat killed phytoplankton cells will allow us to differentiate mercury that is actively uptaken by phytoplankton versus that which is passively sorbed to the cells. Comparisons of mercury uptake to live versus dead cells have been previously used to demonstrate that the uptake of MeHg by phytoplankton is an active process (Moye et al. 2002; Pickhardt and Fisher in press).

Sampling for Hypothesis 2

To test the hypothesis that MeHg and Hg(II) concentrations are correlated with the quality of the DOM and that association affects partitioning and uptake to phytoplankton, we will conduct lagrangian sampling in San Joaquin River. By following the same water mass as it moves down river for three days, we will be able to follow the water as it receives DOM inputs from various sources, including algal production, sewage, and animal waste (Kratzer et al. 2004). Because we expect that the quality of the DOM will change as a result of these different organic matter sources, we will be able to determine which components of the DOM are correlated with MeHg and Hg(II) concentrations. Based on research in Galveston Bay, Texas (Han et al. 2006), we expect that the concentration of glutathione may be a particularly important component of the DOM for mercury binding. The aromaticity of the sample might also be an important indicator of DOC binding to metals (Mcknight et al. 1992). We will measure these parameters as described below.

This sampling effort will also be an opportunity for us to relate our laboratory experiments from the first part of this study to algal uptake of mercury in the field. Portions of the San Joaquin River, such as the Stockton Deep Water Ship Channel, have low dissolved oxygen concentrations associated with organic matter from algal blooms

(Kratzer et al. 2004). Because we expect that the quality of DOM may affect uptake to phytoplankton, sampling during the blooms will allow us to determine if quality of DOM effects MeHg depletion from water.

Another important and understudied aspect of an algal bloom is its decay. Previous research has demonstrated that the decomposition of blooms may be an important period for remobilization of metals from sediments (Luengen et al. in press; Schoemann et al. 1998). During the decay of the spring phytoplankton bloom in South San Francisco Bay, concentrations of DOC and filtered MeHg increased (Luengen et al. in prep). However, the relative bioavailability of that DOC was not assessed. By measuring both the MeHg concentration and the DOM composition during decomposition events, we will be able to predict the biological fate of MeHg mobilized during those periods.

The sampling of the San Joaquin River will be conducted in conjunction with an existing USGS project on nitrate and organic carbon inputs into the San Joaquin River. This will allow us to take advantage of additional parameters measured by the USGS, including chlorophyll-a and nutrients. These parameters will also help us develop our model in hypothesis 3.

Characterization of DOM for Hypothesis 2

To evaluate the composition of the DOM collected from San Joaquin River, we will collect samples for DOC, particulate organic carbon (POC), specific ultraviolet (UV) absorbance, fluorescence, and glutathione concentration. DOC and POC measurements will provide information about the concentration of bulk organic matter, and its distribution between particulate and dissolved phases. Specific UV absorbance, measured at 254 nm, is an indicator of the percent aromaticity of the sample (Weishaar et al. 2003). Aromaticity has been correlated with the solubility and dissolution of cinnabar (HgS ore) (Waples et al. 2005), and may be an important indicator of the amount of mercury associated with DOC. Fluorescence, measured as a ratio of 450 and 500 nm under excitation at 370 nm, is an indicator of the amount of DOC of planktonic versus terrestrial origin (Mcknight et al. 2001). Finally, we will measure glutathione because it is likely an important ligand for binding mercury (Han et al. 2006).

Water samples will be collected and analyzed according to standard methods in the Bergamaschi lab. Briefly, samples for DOC concentrations will be filtered through a 0.45 micron glass fiber filter (GF/F), acidified to pH 2, and refrigerated until analysis (within two weeks). DOC concentrations will be measured on acidified samples with a Shimadzu TOC-5000A carbon analyzer according to the method of Bird et al. (2003). Samples for POC will be collected on a 0.45 micron GF/F, dried at 60 degrees C and weighed for TSS. Total inorganic sediment will be determined after combustion. Laboratory absorbance of discrete samples will be measured in a 1-square centimeter quartz cuvette using a Cary model 300 photometer (Varian, Inc, Palo Alto, CA). Samples for fluorescence will be measured with a SPEX FluoroMax-3 spectrofluorometer in a 1-square centimeter quartz cuvette using a 150-watt Xenon lamp. Excitation will range from 255 to 600 nm in equally spaced increments of 11 nm, with emission from 250 to 700 nm. All optical samples will be analyzed after equilibration to 25ºC.

Mercury Collection and Analysis for Hypothesis 2

To measure MeHg and Hg(II) associated with the DOM and during algal bloom and decomposition events in the San Joaquin River, we will collect unfiltered and filtered (0.45 μm) surface water samples. The samples with be collected with a peristaltic pump equipped with acid-cleaned Teflon tubing attached to an aluminum pole as per the methods that have been used to collect trace metal clean samples in San Francisco Bay (Flegal et al. 1991). Filtered (0.45 μm) water will be obtained by attaching an acid-cleaned polyethylene filter to the tubing of the pump. All samples will be collected into acid-cleaned PFA Teflon bottles. Samples for total mercury (Hg_T) analyses will be preserved by addition of 0.5% BrCl. Samples for MeHg analyses will be preserved by addition of either 0.4% HCl for freshwater or 0.2% H_2SO_4 for saltwater, as described by Parker and Bloom (2005).

Water samples for MeHg analyses will be analyzed by distillation, aqueous phase ethylation, volatile organic trapping, and analyses by cold vapor atomic fluorescence spectrophotometry (CVAFS) (Bloom 1989; Horvat et al. 1993). Water samples for Hg_T will be analyzed using CVAFS following tin chloride reduction and two-stage gold amalgamation trapping (Bloom and Fitzgerald 1988; Gill and Fitzgerald 1987).

To ensure accurate results, certified reference materials (CRMs) for Hg_T in water (ORMS-3) will be analyzed. Although there is no CRM for MeHg in water, we will digest and dilute DORM-2, a dogfish CRM, to check accuracy, as per the methods routinely used by Nicolas Bloom (CEO, Studio Geochimica). We will also check for acceptable MeHg recovery after distillation by using matrix spikes and matrix spike duplicates.

Model for Hypothesis 3

To predict MeHg and Hg(II) bioavailability to phytoplankton, will use the water chemistry parameters collected during the lagrangian sampling of the San Joaquin River and the results from our studies on uptake of MeHg and Hg(II) to develop a biogeochemical model. The effort will build on statistical models that I have developed to assess which factors govern trace metal concentrations in South San Francisco Bay (Luengen et al. in press). We plan to use the statistical package Systat to conduct our analyses. Those analyses will include the development of general linear models to determine which components of the DOM are important for predicting mercury concentrations.

The biogeochemical model will also include a spatial component, developed from our results in the first section looking at DOM quality and mercury accumulation at different sites in the Delta. Development of a spatial model to characterize anticipated stressors is one of the key components listed for Priority Topic 4: Habitat Availability and Response to Change. Thus, this component of the research will directly address CALFED's needs.

We will compare our model results with data collected on MeHg and Hg(II) concentrations in water and fish from the Sacramento and San Joaquin Rivers and Delta. The comparison will include a spatial component, based on the hypothesis from Foe et al. (2003) and Davis et al. (2003) that organisms in the Central Delta have relatively low mercury concentrations. Those researchers based their hypothesis on measurements of mercury concentrations in largemouth bass, white catfish, inland silversides, bluegill

sunfish, signal crayfish, threadfin shad, gambusia (mosquito fish), and clams (*Corbicula* sp.). We will also compare our data on water concentrations of Hg_T and MeHg to those measured by Domagalski (1998; 2001) for the Sacramento River basin. Additional measurements of MeHg and Hg(II) in the rivers are available in Choe and Gill (2003), Choe et al. (2003), and Conaway et al. (2003). The overall goal is to use our results on DOM quality and DOM interaction with phytoplankton and existing data on mercury concentrations to explain patterns and predict mercury bioavailability at other sites in the estuary.

Timeline

During the first year of this study, I will conduct the laboratory studies on MeHg and Hg(II) uptake to phytoplankton cultured in isolates with differing DOM composition. I expect to complete those studies in nine months, and then write-up the results for publication in a peer reviewed journal by the end of the first year. I also plan to present those results at the State of the Estuary Conference in October 2008.

The second year of this study will focus on the lagrangian sampling in the San Joaquin River. That sampling will be conducted at least twice that year, to capture seasonal variability in DOM composition. I anticipate that work will result in at least two publications- one on DOM composition and the other on association with MeHg and Hg(II). One of those publications will be completed by the end of the second year. In March 2008, I also plan to present results from the first study at the Society for Limnology and Oceanography (ASLO) Ocean Sciences meeting. That fall, I will present preliminary results from the San Joaquin River Study at the State of the Estuary conference.

During the third year, I will finish the second publication from the San Joaquin sampling. I will also use the previous results to develop the biogeochemical model for the third component of this proposal. By the end of the third year, I will complete the paper on the biogeochemical model. I also plan to attend the Ninth International Conference on Mercury as a Global Pollutant in Guiyang, China in June 2009. That will be an opportunity for me to present a synthesis of my research and interface with other mercury researchers. The final summary of my work will be presented at the State of the Estuary Conference in October 2009.

III. OUTPUT/ANTICIPATED PRODUCTS AND OR BENEFIT

Anticipated Outcomes

This research will result in 4 published papers. They will be (1) Effects of DOM composition on MeHg and Hg(II) uptake to phytoplankton; (2) DOM composition in the San Joaquin River; (3) Association between MeHg, Hg_T, DOM, and algal blooms during continuous sampling of the San Joaquin River; and (4) A biogeochemical model for predicting MeHg availability to phytoplankton in the San Francisco Bay and Delta. The expectations for when these will be completed and the anticipated per year outcomes are given in the previous "timeline" section.

Benefits to the Scientific Community, Calfed, and Regional Water Quality Control Board

One of the most important outcomes of this research will be an increased understanding of factors controlling MeHg uptake to phytoplankton. That outcome is important scientifically, since phytoplankton have been observed to actively accumulate MeHg, but the mechanism is not known (Moye et al. 2002; Pickhardt and Fisher in press). Because phytoplankton are at the base of the food chain and transfer of MeHg from water to phytoplankton is the largest single step in mercury bioaccumulation (Mason et al. 1995; Mason et al. 1996), elucidating that mechanism will help predict what conditions will cause high MeHg concentrations in fish.

Knowing how mercury enters the food chain is also important for CALFED's mission. CALFED's Preferred Programs, which shape the agency's direction over the next 30 years, include a Water Quality Program, which includes components on reducing the impacts of trace metals and reducing mercury concentrations (CALFED Bay-Delta Program 2000). To reduce the impacts of mercury pollution, CALFED will benefit from knowing what factors make that mercury bioavailable. Furthermore, research on how MeHg and Hg(II) are associated with DOM will help elucidate how mercury is transported in the estuary, and will help address CALFED's Priority 1 on factors to consider when allocating environmental water.

A second CALFED Preferred Program is Ecosystem Restoration. A component of ecosystem restoration that is emphasized by Priority Topic 4 is assessing the effects of future activities on Delta Habitat. Future plans for the estuary include restoration of wetlands. Wetlands are known sites of MeHg production (Grigal 2002) and reactive DOC production (Bossio et al. 2006). This research will benefit regulators by determining how the combination of those two factors could affect MeHg to phytoplankton.

This research will also help the San Francisco Bay Regional Water Quality Control Board. One of the main challenges faced by that agency in trying to implement the mercury Total Maximum Daily Load (TMDL) is that it is difficult to reduce mercury loads because there is a lot of mercury already in the system from legacy mining sources (personal communication, Richard Looker, Water Resource Control Engineer at the San Francisco Bay Regional Water Quality Control Board). Therefore, the water board needs information on how mercury is taken up the food web to develop effective management strategies.

Benefits to Fellow, Research Mentor, and Community Mentor

The fellow, research mentor, and community mentor will benefit from the exchange of methods and expertise that will occur during this interdisciplinary project. As the fellow, I will contribute my expertise on measuring trace metals, including mercury, and developing statistical models to describe metal concentrations. The research mentor, Dr. Nicholas Fisher, will provide his laboratory and techniques for radiotracer methods. The community mentor, Dr. Brian Bergamaschi, will serve as our DOM expert and provide the DOM isolates. Together, we will be able to complete a project that none of us could tackle on our own.

The research will also be complimentary to our previous projects. For example, Dr. Fisher has previously looked at MeHg and Hg(II) bioavailability to phytoplankton cultured in water from Franks Tract and the Cosumnes River (Pickhardt and Fisher in

press). Unfortunately, that work was only able to look at concentrations, not composition of DOM. Similarly, Dr. Bergamaschi has an on-going interest in the nutritional value of DOM to the food web and this work will complement those studies. Finally, as the fellow, this research will enable me to build upon my past studies of metal cycling during a phytoplankton bloom (Luengen in prep.; Luengen et al. in press). Furthermore, I will learn new techniques that will build upon my interdisciplinary background.

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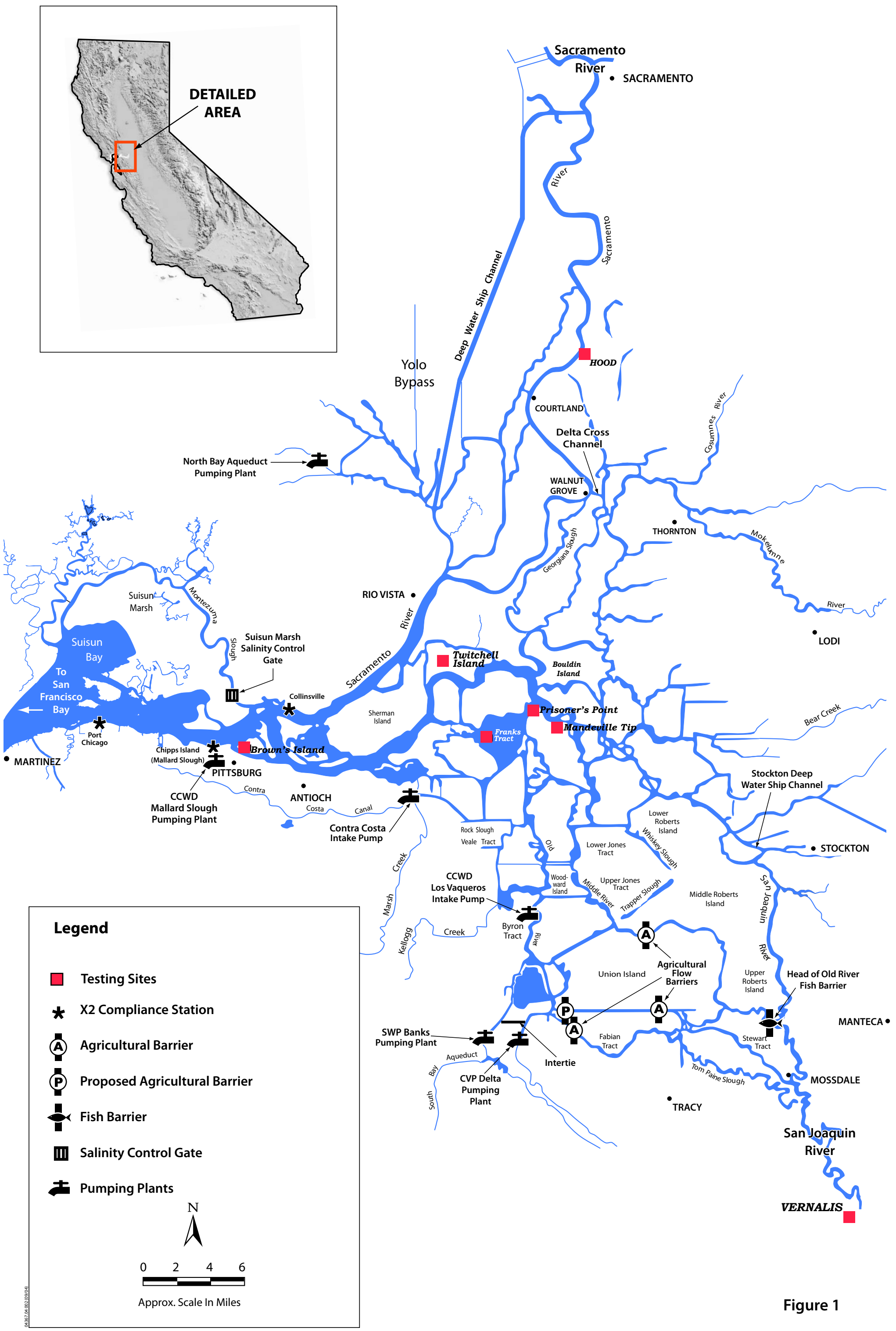
Figure 1. Proposed sites for testing the hypothesis that DOM quality affects MeHg uptake to phytoplankton.
Map courtesy of CALFED Science Fellow Program (http://www-csgc.ucsd.edu/EDUCATION/CALFED/CALFEDpdf/AppxB_BayDeltaSystMap1_A.pdf