



# CALFED SCIENCE FELLOWS PROGRAM



In cooperation with the  
California Sea Grant College Program

## FELLOWSHIP APPLICATION COVER PAGE

### APPLICANT TYPE



Postdoctoral Researcher



Ph.D. Graduate Student

### PROJECT NUMBER

### PROJECT TITLE

Copper-binding organic ligands in the San Francisco Bay Estuary: Evaluating current and future likelihood of copper toxicity events in a perturbed ecosystem

### FINANCIAL SUMMARY

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## Introduction

The San Francisco Bay Estuary has been heavily transformed by anthropogenic activities in and around the Bay over the last century and a half. Changes in flow and bathymetry have altered water residence times and flushing characteristics, and elevated metal contaminant inputs have generated concern for potential associated toxicity events (Nichols et al. 1986). With the California Gold Rush in 1848, people flocked to the San Francisco Bay area, and this region became rapidly developed and urbanized (Nichols et al. 1986). Historic mining activities and associated urbanization of San Francisco Bay over the last 150 years has been reflected in elevated metal loadings in dated sediment cores (Hornberger et al. 1999).

As a consequence of anthropogenic pressures on this system, pelagic fishes here have been in decline for decades. Recently, the abundances of pelagic fishes have dropped precipitously, with record lows observed between 2002 and 2005 (Sommer et al. 2007). The reasons behind this alarming decline, known as Pelagic Organism Decline (or POD), are unclear, as abundances remained unexpectedly low in the relatively wet year of 2006 (Sommer et al. 2007; Nobriga et al. 2008). This POD is particularly serious for the threatened delta smelt (*Hypomesus transpacificus*) species, which has demonstrated ambiguous responses to freshwater input flows (Bennett 2005; Sommer et al. 2007; Nobriga et al. 2008), with smaller-scale regional variability related to abiotic water quality factors (Nobriga et al. 2008). Diversions of freshwater input flows, low food supply, and toxic substances are all factors that may be affecting the success of pelagic fish in this troubled system (Bennett 2005; Sommer et al. 2007).

Copper is a ubiquitous contaminant in urban aquatic environments, and San Francisco Bay is a classic example, with copper levels that approach and sometimes exceed national water quality guidelines despite the removal of predominant point source inputs (Buck et al. 2007). This is bothersome because the toxic species of copper,  $\text{Cu}^{2+}$ , acts as a toxicant to marine microorganisms at exceedingly low concentrations, on the order of  $10^{-11}$  M (Brand et al. 1986; Sunda et al. 1987), and  $\text{Cu}^{2+}$  concentrations are not proportional to the total dissolved copper concentrations in aquatic systems. Instead, more than 99% of dissolved copper in most of San Francisco Bay has been shown to be complexed by unknown strong copper-binding organic ligands that independently control  $\text{Cu}^{2+}$  concentrations (Buck and Bruland 2005), although the extent of organic complexation of Cu in the Delta region is not known. In the absence of these ligands, current dissolved copper concentrations would be toxic to all microorganisms in the estuary and may also be sufficiently toxic to impact larger species, like fish fry and egg development (Grande 1966; Taylor and Glenn 2008), directly.

The sources, sinks and reactivity of these crucial copper-binding organic ligands remain unknown. Ambient phytoplankton are not believed to be a substantial ligand source here, as ligand concentrations have not increased significantly during bloom conditions in the Bay (Buck et al. 2007). I would suggest instead that external freshwater inputs, such as the Sacramento and San Joaquin Rivers, and the runoff from Suisun Marsh may potentially comprise substantial ligand sources to the North and Central Bay. Urban runoff and wastewater inputs, on the other hand, are expected to be smaller sources of copper-binding ligands, although their contributions of dissolved copper and  $\text{Cu}^{2+}$  may be significant (Sedlak et al. 1997). As such, I propose to determine the relative contribution of these possible ligand sources to the pool of strong copper-binding ligands in the Bay.

Water management strategies can substantially impact the supply and cycling of dissolved trace metals, with potentially magnified effects on fragile estuarine ecosystems. In the case of copper, this impact will likely be complicated by the importance of organic ligands here. It may be found, for example, that some freshwater sources to the Bay provide more dissolved copper than ligand (increasing risk of toxicity events) while others are elevated in ligand over copper (decreased risk of toxicity). In part aimed at addressing the loss of delta smelt, and at mediating the POD in general, several proposed changes in water management strategies have emerged. Some of these potential changes include increasing the input freshwater flow from the productive San Joaquin River, flooding of the Yolo Bypass in the Sacramento River basin, and restoration of historical marshlands surrounding North Bay. Because each of these freshwater sources represents an as yet uncharacterized source of organic copper-binding ligands, with potentially distinct copper-binding features, estuarine mixing behavior, and photochemical reactivity, each of these proposed shifts in water management practices may have unique results on copper cycling in the Bay that I hope to elucidate with the proposed research.

There remains substantial concern for copper toxicity in the Delta and North Bay regions due not only to historical contamination, but also to continuing copper inputs here. For example, the ships of the 'mothball fleet' left in Suisun Bay are largely coated in copper-based antifouling paints that may pose a toxicity risk as the paint wears away in Bay waters, and National Oceanic and Atmospheric Administration (NOAA) scientists are expected to examine copper contamination from these ships sometime this summer (Mike Connor, pers. comm.). In addition, copper has been, and is still, widely used as an herbicide for weed control in the Delta and surrounding watershed. The herbicidal use of copper has unknown consequences on continued toxicity risk, with preliminary analyses from the Delta and Bay suggesting that this risk may be significant (URS report, Region 5; Mike Connor, pers. comm.), and more pronounced in the short-term (Siemering et al. 2008).

Currently, the extent of organic complexation in the Delta, as well as rivers and runoff feeding the Delta, is unknown. This is problematic for studies of copper toxicity here since the bioavailable (and, thus, potentially toxic) form of dissolved copper is the free ion  $\text{Cu}^{2+}$ , which is not simply correlated to total dissolved copper concentrations in the presence of copper-binding ligands and which will vary substantially with changes in copper-binding ligand concentrations (Buck et al. 2007). Therefore, the lack of copper speciation data from this region prevents a legitimate discussion of either ambient or resulting copper toxicity in the face of changing water management practices.

In characterizing the current sources of strong copper-binding ligands to San Francisco Bay and Delta, I hope to assess the impact of suggested water management strategies on copper cycling here. While there have been several studies on the behavior of trace metals and total dissolved organic matter across estuarine salinity gradients (Sholkovitz 1976; Sholkovitz et al. 1978; Boyle et al. 1982), the proposed work represents the first experiments to date that determine the fate of copper-binding organic ligands, which comprise <1% of the total dissolved organic matter, across these gradients. Further, the proposed work will allow the first estimates of copper-binding ligand sources and the anticipated results of changing source inputs into San Francisco Bay, where these ligands play an exceedingly important role in mediating elevated copper concentrations.

In summary, my research questions for the proposed work include:

Q1. What is the contribution of freshwater ligand sources to the Bay and adjacent coastal waters? How does this contribution compare between urban and marshland runoff, and treated and untreated runoff?

Q2. How might changes in water management practices affect ligand sources and, consequently, copper bioavailability and toxicity in the San Francisco Bay/Delta system?

### Approach

Voltammetric techniques have been used for decades to study the solution chemistry of environmentally relevant metals, providing high sensitivity with minimal sample perturbation. The competitive ligand exchange- adsorptive cathodic stripping voltammetry (CLE-ACSV) method is a powerful technique for measuring the extent of organic complexation, or speciation, of a variety of metals. The method to be used here employs salicylaldoxime (SA) as the competitive ligand (Buck and Bruland 2005). This method has been used previously in San Francisco Bay to characterize the spectrum of strong and weaker copper-binding ligands from Suisun Bay down to Dumbarton Bridge in South Bay (Buck and Bruland 2005).

From this previous work, several features of dissolved copper speciation are apparent. First, ligand concentrations did not change appreciably in South Bay between sampling periods (Jan and Mar 2003), despite a large ( $>50 \mu\text{g/L}$  chl *a*) bloom during the second sampling (see Fig. 6a, Buck and Bruland 2005). Second, ligand concentrations were highest in the North Bay sites, Suisun Bay in particular. Ligand concentrations were so high here, in fact, that they were not completely titrated (and were likely underestimated) for this station (see Fig. 6f, Buck and Bruland 2005). The measured ligand concentrations were also highest in Suisun Bay during the lower salinity ( $S=0$ ) January sampling. These observations suggest that external freshwater inputs to the North Bay may constitute a substantial ligand source.

Among these possible ligand sources here, previous work in wastewater and urban surface runoff has indicated that most, though not all, copper in these waters is strongly complexed (Sedlak et al. 1997). However, the lack of excess copper-binding ligands measured in these waters makes them more likely to be a source of inorganic, and potentially toxic, copper to the Bay than of excess copper-binding ligands.

The limited speciation data available seems to suggest that there will be distinct differences between sources of dissolved copper and sources of dissolved copper-binding organic ligands into the Bay. Some of these sources may provide more ligand than copper, increasing the buffering capacity of the Bay for elevated copper, while others contribute more copper than ligand, thereby perhaps increasing the potential for copper toxicity. There is a fine balance currently struck for copper cycling within San Francisco Bay, where elevated dissolved copper concentrations from current and historical anthropogenic activities are mediated by the as-yet-uncharacterized sources of copper-binding organic ligands present in the Bay. Correspondingly, increases or shift in inputs to one source or another would be expected to have distinct and quantifiable effects on copper speciation, bioavailability, and toxicity here.

*Hypotheses and Anticipated Approach*

H1: Freshwater sources to Suisun Bay, including the Sacramento and San Joaquin Rivers, and surface runoff from Suisun Marsh, provide significant concentrations of strong copper-binding organic ligands to North and Central San Francisco Bay waters.

Approach: The concentrations, binding strengths, and  $\text{Cu}^{2+}$  concentrations will be determined from both North Bay waters (Suisun Bay, Carquinez Strait) and from riverine inputs to Suisun Bay (Sacramento and San Joaquin Rivers, Suisun Slough) using CLE-ACSV techniques (see Figure 1 for proposed sampling stations). Relative ligand contributions from these sources will be assessed using mixing experiments between source waters and high salinity Golden Gate waters, while the quality of these ligands will be assessed with photochemical experiments and CLE-ACSV.

H2: Comparatively, runoff from Suisun Marsh will provide higher concentrations of strong copper-binding organic ligands in excess of dissolved copper than runoff from urban runoff and wastewater discharge to the North Bay that may contribute less complexed, and potentially more toxic, copper concentrations.

Approach: The concentrations, binding strengths, and  $\text{Cu}^{2+}$  concentrations will be analyzed from treated wastewater outflow (Central Contra Costa Sanitary District, near Martinez), Sulphur Springs Creek, and Suisun Slough (Figure 1). These samples will be collected in the winter rainy season, when flow (and relative contributions) is high. Sulphur Springs Creek will provide an untreated urban runoff source, while Suisun Slough carries runoff predominantly from the surrounding marshland. The copper and ligand contributions of these treated versus untreated waters will be characterized using simple mixing experiments with Golden Gate seawater and photochemical experiments with source waters.

H3: Some changes in water management strategies, including increased river discharge and marshland extension, in North Bay will increase the concentrations of strong copper-binding organic ligands supplied to the Bay, buffering  $\text{Cu}^{2+}$  levels and reducing copper bioavailability (and, therefore, potential toxicity) in the estuary.

Approach: The results from the aforementioned mixing experiments will be used to budget ligand contributions (Figure 2) from the external freshwater sources studied, and to predict how  $\text{Cu}^{2+}$  concentrations (and copper bioavailability/ toxicity) will change in North Bay as a result of increased inputs from individual and combined sources.

In summary, the proposed work aims to characterize the potential strong copper-binding ligand sources and their relative contributions to San Francisco Bay waters by using an established CLE-ACSV technique to determine ligand concentrations in likely source waters as well as in a series of mixed source-Bay waters. This work represents a first opportunity to conduct mixing experiments for the reactivity of copper-binding organic ligands across natural salinity gradients.

## Methods

### *Sample Scheme and Collection*

I propose to sample during three distinct hydrographic periods over two years: winter 2009, summer 2010, and spring 2011. For each of these sampling periods, samples would be collected from Suisun Bay, Carquinez Strait, and the Golden Gate (Figure 1). Additional samples would be collected from wastewater outflow, urban surface runoff (Sulphur Springs Creek), and Suisun Slough during winter 2009 and from the Sacramento and San Joaquin Rivers during summer 2010 and spring 2011 (Figure 1). All samples from the freshwater sources in North Bay will be collected during ebb tides to get the most representative samples, while Golden Gate water will be collected during high tide to capture coastal seawater in the Bay.

I propose to collect the samples from the Sacramento and San Joaquin Rivers, Suisun Bay, Carquinez Strait and Golden Gate as part of the routine sampling of these waters by the San Francisco Estuary Institute (SFEI) and the U.S. Geological Survey (USGS). I have contacted Mike Connor at SFEI and Jim Cloern at USGS, both of whom have granted a possible berth on their research cruises here. The remaining stations (Suisun Slough, wastewater outflow, Sulphur Springs Creek) are more accessible by land, and I will sample these stations independently. I have attempted to contact several of the large municipal wastewater treatment plants in the North Bay regions, including the Novato Sanitary District and the Central Contra Costa Sanitary District, and will continue pursuing access to treated wastewater samples in the area.

A trace metal clean pole sampling setup will be employed in collecting 12 L of unfiltered surface samples at each sampling station, with an additional 12 L collected from the Golden Gate station. Samples will be collected into clean, conditioned polycarbonate bottles, and these samples will be used for ambient copper speciation and total copper measurements as well as for the mixing and photochemical experiments. Samples will also be collected for chlorophyll, nutrients, dissolved organic carbon (DOC), phytoplankton pigments, and microscopy; temperature, salinity and pH will be measured *in-situ*. All samples will be kept cold in the dark and processed immediately upon return to the lab. To facilitate speedy sample processing, proposed mixing experiments would be conducted, and all samples filtered, in the Bruland Lab at UCSC before transporting samples to UCSD for analyses. I have already contacted Ken Bruland at UCSC, and he has agreed to provide a laminar flow hood space for this work over the proposed sampling periods.

### *Mixing Experiments*

Mixing experiments will be conducted for each of the freshwater source samples with unfiltered seawater from Golden Gate. These experiments will be performed in the Bruland Lab at UCSC within 24 hours of sample collection from the Bay. For each experiment, freshwater and seawater samples will be mixed in six separate ratios that provide a gradient in salinity from 0 to ~35. Specifically, I will aim for salinities in the mixed samples of 1, 2, 5, 10, 15, 20, and 25. The high resolution at low salinities would better characterize mixing in North Bay, including the critical low salinity zones for salmonid species. On the other hand, the lower resolution through the full salinity range will sufficiently describe the source contributions of copper and copper-binding ligands to Central Bay and the San Francisco Bay plume. Mixed samples will be shaken every half hour for a four hour period, as described for total metal mixing experiments conducted in the Amazon River system (Boyle

et al. 1982). Samples will then be vacuum filtered through acid-cleaned 0.4  $\mu\text{m}$  polycarbonate track etched filters (PCTE) and stored frozen in clean, conditioned fluorinated polyethylene bottles for subsequent total copper and speciation analyses back at SIO.

#### *Photochemical Experiments*

Samples from each source water station (Figure 2) will be filtered through 0.4  $\mu\text{m}$  PCTE filters for use in photochemical experiments. Following filtration, samples will be stored cold in the dark for return to SIO. Photochemical experiments will be conducted in clean, conditioned quartz round bottom flasks. I propose to follow the cycling of ambient copper-binding organic ligands exposed to simulated versus natural sunlight and in the dark over a 12 hour day cycle. Samples for copper speciation would be collected every four hours, at 0, 4, 8, and 12-hour time points, and analyzed by CLE-ACSV.

#### *Dissolved Copper Speciation and Total Dissolved Copper*

I propose to measure total dissolved copper and dissolved copper speciation in field samples, as well as samples from the proposed mixing and photochemical experiments. All samples will be filtered in the Bruland Lab at UCSC and frozen for return to SIO for analyses. Frozen speciation and totals samples will be thawed and thoroughly shaken prior to analyses. A competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV) method using salicylaldoxime as the added competitive ligand (Buck and Bruland 2005) will be employed for all speciation analyses. The same methodology will additionally be applied to total dissolved copper analyses following UV-oxidation of the samples to destroy the copper-binding ligands (Buck and Bruland 2005).

#### *Ancillary and Hydrographic Data*

Samples for nutrients, DOC, phytoplankton pigments, chlorophyll *a*, and microscopy will be collected from each site. These samples will be analyzed following standard protocols. The majority of stations will be sampled from USGS or SFEI vessels with many of these measurements provided from the routine data sets. When necessary, nutrient and DOC measurements will be conducted by external analysts within the University of California system at a discounted rate. *In-situ* measurements of pH, temperature, and salinity will be done with portable meters. Salinity will additionally be measured throughout the proposed mixing experiments with a portable conductivity meter.

#### *Timeline*

I propose a single sampling series for the first year, which would be conducted in early November 2009 during the initial winter rains. This sampling is aimed at characterizing copper-binding ligand contributions to the Bay from surface runoff sources. These sources are likely most pronounced during this initial rainy period, when Delta discharge is still relatively low and contaminants in these waters are most concentrated after prolonged accumulation. In addition, I would use the first sampling to address any issues that arise in sampling or experimental protocols and to better tailor second year samplings and experimentation. During the second year, I propose to sample during two seasons: late summer and spring. The late summer sampling period would take place during the dry season, when Delta discharge from the rivers is low and salinity in the estuary is highest. This season presents a stark contrast to the proposed spring sampling, when discharge from the rivers is high. These samplings would be used to characterize the copper and copper-binding ligand contributions of the Sacramento and San Joaquin Rivers to the Bay.

## Anticipated Output

### *Anticipated Benefits to Participants*

The proposed research will continue my development and training as a research scientist while connecting my research to pertinent policy decisions. Further, this work would provide the opportunity for me to collaborate with agency scientists on a significant aspect of ecosystem health, where our combined efforts will substantially advance our understanding of copper toxicity and copper cycling in this estuary. My research mentor, Associate Professor Kathy Barbeau, will also benefit from these interactions, working with new collaborators and accomplishing insightful research on the cycling processes of copper. The proposed work will be published in peer-reviewed journals, and presented at international and national meetings, which will inherently benefit all participants. For my community mentors specifically, the proposed research will provide measurements of  $\text{Cu}^{2+}$  concentrations that will complement their ongoing work on copper uptake dynamics and bioaccumulation pathways in San Francisco Bay invertebrates. These measurements are especially pertinent to these studies, as  $\text{Cu}^{2+}$  is the bioavailable form of dissolved copper.

### *Anticipated Benefits to CALFED Priorities and Mission*

The proposed research will greatly further our knowledge on copper cycling in the San Francisco Bay estuary. As San Francisco Bay is heavily contaminated, and copper concentrations are correspondingly high here, the bioavailability of copper and reactivity of dominant copper-binding ligands is a crucial question in assessing the health of this ecosystem. This work would allow, for the first time, a quantitative assessment of copper toxicity under current conditions in the San Francisco Bay estuary, as well as a qualitative prediction of the effect of changing watershed management practices on copper cycling and potential toxicity events.

### *Year One*

At the completion of year one, I will have the complete evaluation of organic copper-binding ligand contributions from surface runoff sources to the North Bay, as well as the first assessment of ambient ligand photoreactivity and mixing behavior from source and Bay waters. The results from the first round of sampling and experimentation will be presented during year one at the international American Society of Limnology and Oceanography (ASLO) Ocean Sciences meeting, and at the annual CALFED or CALFED/State of the Estuary Science conference.

### *Year Two*

Year two will mark the completion of the proposed research project. From this work, potential sources of organic copper-binding ligands, from the Sacramento and San Joaquin rivers, to marshlands and urban runoff, will be characterized. Further, these ligand sources will be additionally evaluated in terms of mixing behavior and photochemical reactivity, allowing the first assessment of predicted changes in ambient ligand concentrations and copper toxicity given potential shifts in water management strategies. The proposed work will be submitted for publication in a peer-reviewed journal. This work will additionally be incorporated into the results of bioassay and uptake experiments conducted by my community mentor collaborators. The complete synthesis of our advances to understanding copper cycling, toxicity and ecosystem health here will then be presented at the CALFED/State of the Estuary Science conference.



Figure 1. Sampling sites in the San Francisco Bay Estuary. White triangles indicate proposed stations to be sampled during all three sampling periods. Blue stars depict proposed stations for freshwater end-member sources to the North Bay. Small circles indicate sites for which copper speciation data has been published.

$\text{Cu}^{2+} + \text{L}_i \rightleftharpoons \text{CuL}_i$			Resulting North Bay [Cu <sup>2+</sup> ]
Source	[L]	[Cu]	
Sacramento R.			↓
San Joaquin R.	IF [L] >> [Cu]		
Suisun Slough			
Sulphur Springs Cr.			↑
Wastewater	IF [L] << [Cu]		

Figure 2. Simplified portrayal of how proposed work will be used to deduce effects of increased inputs of potential source waters on bioavailable Cu<sup>2+</sup> concentrations, and related copper toxicity, in San Francisco Bay. If these inputs are indeed sources of copper-binding ligands ([L]), then increases in these inputs are expected to decrease Cu<sup>2+</sup> concentrations, since increasing excess ligands would disrupt the natural equilibrium and drive the formation of biologically inert CuL. The tendency to form CuL will be dependent upon the concentrations and conditional binding constants measured for the ambient ligands.

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