CALFED Progress Report
California Sea Grant College Program

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Project Information

ProjectNo_2C: R/SF-32 | StartDate_3a: Sept 2009 | EndDate_3b: Aug 2012
ProjectTitle_4: Copper-binding ligands in the San Francisco Bay Estuary: Evaluating current and future likelihood of copper toxicity events in a perturbed ecosystem

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Additional Research Mentors and Community Mentors

Additional Research Mentors_8:

Additional Community Mentors_9:

Project Objectives: Please type your responses, and answer the questions in a style appropriate for laymen.

ProjectObjectives_10

The objectives of this project are to determine the concentrations of organic copper-binding ligands and evaluate whether resulting bioavailable (and, therefore, potentially toxic) Cu2+ concentrations approach established toxicity levels (~10^-11 M Cu2+; Brand et al. 1986 Journal of Experimental Marine Biology and Ecology) for microorganisms in North San Francisco Bay and Delta. As copper-binding ligands render dissolved copper inert, an additional component of this work is to determine the sources of these ligands to the estuary (e.g., rivers, surrounding marshlands, and wastewater discharge) as well as potential sinks (e.g., mixing with seawater, light exposure). Dissolved copper speciation measurements will further be used to assess how much additional copper the ambient copper-binding ligands could buffer before bioavailable Cu2+ concentrations reach the likely toxicity threshold.

Summary of progress in meeting each of these goals and objectives

ProgressSummary_11

The final round of field sampling for dissolved copper speciation was conducted in April 2011. Samples were collected in collaboration with USGS aboard the R/V Polaris. Samples were collected from the same stations sampled in Year 1 (USGS stations 2, 4, 6, 8, 18), as well as the additional USGS stations 13, 21, and 24. Thus, the samples collected in April 2011 cover not only the North Bay and Delta regions sampled in Year 1, but also the transition zones between North, Central and South Bay.

All field samples from Year 1 have been analyzed for total dissolved copper, copper-binding organic ligands, and resulting bioavailable Cu2+ concentrations. Year 2 samples are currently being analyzed. A multiple analytical window approach (Buck and Bruland 2005 Marine Chemistry) has been employed to assess current bioavailable Cu2+ concentrations as well as to predict how much additional dissolved copper the system can buffer before bioavailable Cu2+ concentrations reach potentially toxic levels. For the Year 2 samples, an even wider range of analytical windows is being employed in an attempt to better characterize the potential for copper toxicity in these waters.

Mixing experiments of San Joaquin River water and Golden Gate seawater were conducted in Year 1 to assess the stability of copper-binding organic ligands across the salinity range of the estuary. Mixed samples were also analyzed for dissolved copper and copper speciation. Remaining water from Year 2 sampling will be used in photochemical experiments to assess the photolability of copper-binding ligands.

All field samples and mixing experiment samples from Year 1 were filtered through 0.4 µm (pore size) polycarbonate track-etched membrane filters prior to analysis of dissolved copper speciation. These filters were subsequently analyzed for leachable particulate copper and zinc. Leachable particulate concentrations represent the most bioavailable particulate forms of copper and zinc, defined as the concentrations leached from the filters during a 2 hour pH 2 (25%) acetic acid leach.

In collaboration with research mentor Kathy Barbeau's lab at SIO/UCSD, Year 2 samples are also being analyzed for dissolved iron speciation. Iron speciation measurements have never been reported for San Francisco Bay, and may provide additional insight into trace metal cycling in these waters.

PROJECT MODIFICATIONS: Please explain any substantial modifications in research plans, including new directions pursued. Describe major problems encountered, especially problems with experimental protocols and how they were resolved. Describe any ancillary research topics developed.

Modifications_12

The stop work order and prolonged suspension of the CALFED Fellowship during Year 1 inhibited the planning and logistics of additional sampling trips. As such, only the winter time point was sampled in the first year. With the full year reinstatement for project Year 2, a spring sampling trip was accomplished in 2011, but a summer trip was not feasible.

To compensate for fewer sampling time periods, additional parameters have been analyzed on the samples collected in Year 1 and Year 2. In collaboration with Dr. Ken Bruland at the University of California in Santa Cruz (UCSC), macronutrient samples will be analyzed from both sampling periods. Leachable particulate copper and zinc have been analyzed on 0.4 µm pore size filters from all sampling stations from November 2008. The leachable particulate metals represent the most bioavailable form of particulate metal suspended in the water column, and are defined as the concentration of metal leached from filtered suspended particles in a 2 hour pH 2 (25%) acetic acid (weak acid) leach. In collaboration with research mentor Kathy Barbeau's lab at SIO/UCSD, Year 2 samples are also being analyzed for dissolved iron speciation. Iron speciation measurements have never been reported for San Francisco Bay, and may provide additional insight into trace metal cycling in these waters.

BENEFITS AND APPLICATIONS: Suggest the relevance of these new findings to management. Describe any accomplishment, that is significant effects your project has had on resource management or user group behavior. CALFED is looking for "management cue" (see http://science.calwater.ca.gov/pdf/soemgmtcues.pdf).

BenefitsApplic_13

Initial results indicate that dissolved copper is strongly complexed by organic ligands in all samples collected, reducing bioavailable Cu2+ concentrations to levels not likely to impose toxicity on aquatic microorganisms. Suisun Slough appears to be a much larger source of copper-binding ligands to North San Francisco Bay, on a per volume basis, than either the San Joaquin or Sacramento Rivers, all of which are elevated in Cu-binding ligands compared to North and Central Bay waters. The high concentrations of organic copper-binding ligands in Suisun Slough waters is consistent with the very high dissolved organic carbon (DOC) measured here. This water was also highest in leachable particulate Cu and Zn of the samples collected; dissolved Cu concentrations were highest at Station 8, downstream from the naval graveyard in Grizzly Bay, and second highest in Suisun Slough. Thus, Suisun Slough is a source of both labile particulate and dissolved Cu, as well as a source of copper-binding ligands. The large excesses in Cu-binding ligands present in Suisun Slough waters provide a large buffering capacity against Cu toxicity even at dissolved Cu concentrations well in excess of ambient [Cu]. All results are considered preliminary until the completion of the project in August 2012.

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PUBLICATIONS: List any publications, presentations, or posters that have resulted from this funded research. Give as many details as possible, including status of paper (e.g., in review; in press), journal name, conference location and date of presentation. Please note (as outlined in the conditions of the award) that each fellow is required to submit an abstract for an oral or poster presentation at each State of the Estuary conference and CALFED Science Conference during the duration of the fellowship.

Publications_14

Buck, K.N., B. Foli, S. Ussher, and K. Barbeau. Dissolved copper, copper speciation and leachable particulate copper in the San Francisco Bay Delta and Estuary: Evaluating current and future likelihood of copper toxicity events in a perturbed ecosystem. Poster, 6th Biennial Bay-Delta Science Conference, September 27-29 2010, Sacramento, CA.

Foli, B.A., S. Ussher and K.N. Buck. Copper and zinc distributions in Castle Harbour, Bermuda, using a chemical leach method: Comparison with contaminated San Francisco Bay, California, Delta and Estuary waters. 2010 Final report, Partnerships for Observation of the Global Ocean (POGO) program.
--Submitted to Bermuda Government, Department of the Environment, September 2010.

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COOPERATING ORGANIZATIONS: List those agencies and/or persons who provided financial, technical or other assistance to your project since inception. Describe the nature of their collaboration.

CoopOrganiz_15

-Bermuda Institute of Ocean Sciences (BIOS): Project Fellow K. Buck is an Assistant Scientist at BIOS. BIOS has provided laboratory and office space, as well as supplementary financial support in the form of salary, benefits and supplies.
-Scripps Institution of Oceanography (SIO/UCSD): Research mentor K. Barbeau is an Associate Professor at SIO/UCSD, and SIO has provided the logistical support of the financial aspects of the fellowship.
-United States Geological Survey (USGS): Community mentor R. Stewart is a Research Scientist at USGS. USGS has generously provided support for sampling on the R/V Polaris for the fellowship.
-University of California Santa Cruz (UCSC): Dr. Ken Bruland provided laboratory space for sample processing.

AWARDS: List any special awards or honors that you, or mentor or members of the research team, have received during the duration of this project.

Awards_16

K. Buck was awarded the Roger Stone Fellowship at BIOS in Year 1
K. Buck was recently asked by a consulting firm in the US to participate in the review of the newest draft US EPA water quality guideline criteria for copper in seawater.

KEYWORDS: List keywords that will be useful in indexing your project.

Keywords_17

copper, ligands, speciation, leachable particulate copper, leachable particulate zinc, iron speciation

PATENTS: List any patents associated with your project.

Patents_18

N/A

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Additions: Additional information can be added here. Please begin the text with the number of the question you are adding to.

Additions_19

N/A