



## Copper Toxicity in the San Francisco Bay-Delta

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### BACKGROUND

San Francisco Bay has high dissolved copper concentrations – relative to nearby coastal waters – that often approach federal water quality standards put in place to protect sensitive marine life. But, how toxic is this copper?

Previous studies by other researchers have suggested that metal-binding compounds known as ligands can “grab up” more than 99.9 percent of the total available dissolved copper in seawater, rendering that copper biologically unavailable. Microorganisms that need trace amounts of copper for growth cannot readily obtain it in its ligand-bound form.

### PROJECT

Though scientists now recognize that ligand concentrations may dramatically reduce copper’s toxicity, they do not know where these ligands originate, or how they are produced. Research has shown that some microorganisms synthesize copper-binding ligands when stressed by too much dissolved copper in the water surrounding them. The breakdown of plant debris produces ligands, and treated wastewater is yet another source.

The goal of this project was to use state-of-the-art analytical techniques to map dissolved copper and copper-binding ligand concentrations at sites in the San Francisco Bay, Suisun Bay, Suisun Slough, Carquinez Strait, the Sacramento River and San Joaquin River. The Delta Science Fellow also characterized the relative contributions of the Sacramento River, San Joaquin River and Suisun Slough as ligand sources.



Antifouling boat coatings, contaminated sediments and some herbicides are among the continuous sources of dissolved copper in the San Francisco Bay-Delta. Photo: K. Buck



Christopher Brown inspects the bottom of a fouled ship in San Francisco. Copper-containing antifouling hull coatings are a source of copper contamination in marinas and bays. Photo: Smithsonian Environmental Research Center, Marine Invasions Research Lab

### FINDINGS

The main finding from this project, to date, is that dissolved copper is overwhelmingly bound by strong organic ligands in the areas sampled.

Dissolved copper concentrations were elevated in all estuarine water samples, as compared with the tidally flushed Central Bay; however, the copper-ligand complexes likely reduced the amount of bioavailable copper to levels below suspected toxicity thresholds for microorganisms.

In addition, the strong copper-ligand complexes were complemented by variable but often high concentrations of weaker ligands that buffer bioavailable dissolved copper concentrations against changes in total dissolved copper. The weak ligands (they bind to copper less strongly) soak up excess copper when copper levels are elevated.

In terms of identifying the processes that produce ligands, the water sample analyses suggest that Suisun Slough is a more important source of copper-binding ligands, on a per-volume basis, than either San Joaquin River or Sacramento River. The highest excess ligand concentrations were observed in Suisun Slough, in low-salinity reaches of the estuary and at river mouths.

# DELTA SCIENCE PROGRAM

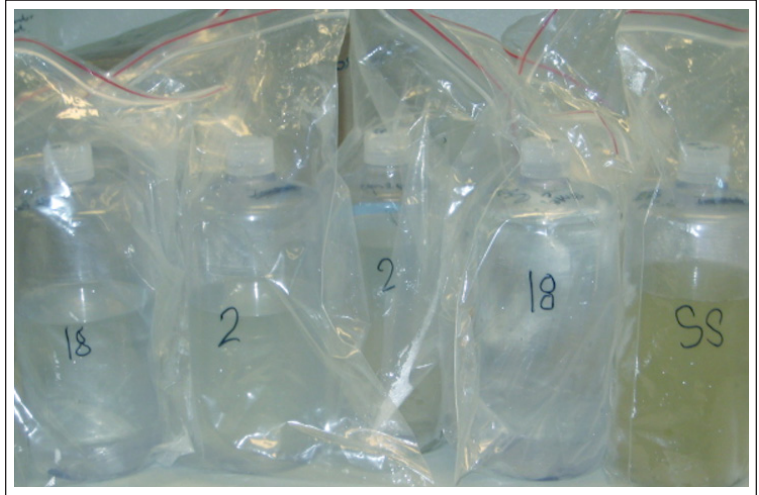
The scientists believe that the high concentration of copper-binding ligands in the samples from Suisun Slough is at least partially due to “humic” substances (natural organic debris from plants) draining from the marsh. Humic substances impart the brown color to tea and are why the water sample from Suisun Slough in the photo to the right is discolored.

## MANAGEMENT IMPLICATIONS

This project is a first step in being able to predict the effects of water diversions and land-use practices on copper toxicity in the San Francisco Bay-Delta.

Results suggest that marshlands are a significant source of protective ligands, at least at present. If this is indeed true, marsh restoration could be a tool for reducing the toxicity of copper that continues to leach from boat hulls, herbicides and legacy sediment contamination from the Gold Rush era.

Findings from this project complement ongoing research by the US Geological Survey and others to characterize copper bioaccumulation from distinct sources in bivalves and other invertebrates in the region.



Bottles of water from different sampling sites in the Bay-Delta. No. 2 was collected in the Sacramento River; No. 18, near the Golden Gate Bridge and “SS” from Suisun Slough. Photo: K. Buck



Originally a privately owned yacht, the US Geological Survey purchased the *Polaris* in 1966, retrofitting its upper salon into a laboratory. Each month, it completes several cruises on San Francisco Bay for water quality and sediment monitoring. Water samples for this Delta Science Fellowship project were collected during these cruises. Photo: R. Bundy

## PUBLICATIONS

Buck, K. N., J. R. M. Ross, A. R. Flegal, and K. W. Bruland. 2007. A review of total dissolved copper and its chemical speciation in San Francisco Bay, California. *Environmental Research* 105: 5-19.

Buck, K. N., and K. W. Bruland. 2005. Copper speciation in San Francisco Bay: A novel approach using multiple analytical windows. *Marine Chemistry* 96: 185-198.

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