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The long term goal is to determine the ecological importance of specific toxic metals (copper and zinc) in harbors, through an understanding of their chemistry and biological effects at the base of marine food chains. This work provides information on potential problems with Zn and Cu, which may help to foresee problems in the future. Anthropogenic inputs of both metals are increasing; they are derived from diverse sources and are a simple function of population growth in coastal regions.

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FINAL REPORT
The Relationship Between Copper Speciation and Cyanobacterial Distribution in Harbors and other Coastal Environments

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LONG-TERM GOAL

My long term goal is to determine the ecological importance of specific toxic metals (copper and zinc) in harbors, through an understanding of their chemistry and biological effects at the base of marine food chains. The major focus is on obtaining quantitative answers to research questions in this area, to establish what concentrations of these elements are acceptable when they are derived from anthropogenic sources.

OBJECTIVES

Specific objectives were to (1) determine the relationship between the chemistry of copper and zinc, and their toxicity to organisms;(2) determine the variability of Cu and Zn chemistries in harbors, in particular their complexation by disslved organic matter; (3) combine the results in (1) and (2) to predict effects in the field, and compare them with actual data. In 1998, a specific objective was also to evaluate an in situ sampling device which holds considerable promise for monitoring and ecological assessment. Another key objective was to develop an isolation strategy for powerful Cu chelators made by marine cyanobacteria.

APPROACH

I collaborated with Larry Brand (University of Miami), who studied the toxic effects of copper and zinc on phytoplankton isolated from our primary study site, San Diego Bay. I measured the speciation of copper and zinc in the harbor, using electrochemical techniques alongside our in situ probes. I also supervised a postdoc who developed a chromatographic procedure to isolate and purify cyanobacterial Cu chelators

WORK COMPLETED

We have completed the toxicity studies, and speciation measurements are nearly complete on all San Diego Bay samples. The evaluation of the in situ probes is complete; the postdoc who performed that work is currently preparing a manuscript. Probes were also evaluated in Norfolk Harbor and Cape Cod MA, to determine their perrformance over a wide range of conditions.

Isolates of cyanobacterial Cu chelators have been purified, and, at the time of writing they are being analyzed in Nelson Frew's laboratory by electrospray mass spectrometry using an instrument purchased with DURIP funds. The stability of these chelators, particularly with respect to photodegadation, was also stusied, and a manuscript on this topic has been submitted.

RESULTS

Results show that both Cu and Zn are important in influencing phytoplankton in San Diego. In particular, the influence of Zn toxicity to diatoms may have been underestimated in previous work. Brand and I plan to combine our chemical and biological data into a paper soon. The probes show excellent agreement with electrochemical methods for estimating the inorganic (bioavailable) fraction of copper in contaminated waters, like San Diego Harbor. They tend to overestimate inorganic Cu in pristine waters. We plan to solve this problem by using a low molecular weight cutoff filter to separate the probes from the seawater in future work. However, this problem appears to be negligible in contaminated waters of interest to the navy.
We have not had time to analyze mass spectral data to get structural information on the cyanobacterial chelators.

IMPACT/APPLICATION

Our work provides the navy with a "heads up" on potential problems with Zn and Cu, which may help it to foresee problems in the future. Anthropogenic inputs of both metals are increasing; they are derived from diverse sources and are a simple function of population growth in coastal regions. Our work also provides some potential solutions; the probes may be useful as a monitoring tool to replace costly bioassays in meeting regulatory requirements and structural information about cyanobacterial chelators may reveal information about a new class of chelators useful in bioremediation.

TRANSITIONS

We have discussed specific applications of our in situ sampling devices with personnel; at Naval Base Norfolk. Specifically, we want to see if the probes could yield the same information as toxicity testing with blue mussel larvae. The latter are a good indicator of Cu toxicity, but are difficult to grow. I have also discussed this concept with officials at EPA, and feel that there is considerable receptiveness there to this type of solution.

PUBLICATIONS

Moffett, J.W. and L.E. Brand (1996). The production of strong, extracellular Cu chelators by marine cyanobacteria in response to Cu stress. *Limnol. Oceanogr.*, **41**(3), 288-293.

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Enclosure (2)