The Relationships between Metal Speciation and Metal Biota Interactions in Harbors

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LONG TERM GOALS

My long term goal is to understand the interactions between trace metals and phytoplankton in neritic environments. This interaction is envisioned as a two-way process: Trace metals affect the growth, species composition, and biomass of phytoplankton. In response, phytoplankton adapt to their chemical environment through natural selection by genetically altering their responses to trace metals, thus accounting for many of the differences observed among phytoplankton species. These differences lead to trace metals affecting species composition. Another aspect of the interaction between chemistry and biology that we are investigating is how biology in turn affects chemistry—specifically how phytoplankton change the chemical speciation of trace metals in seawater through the production of particular organic compounds A second long term goal is to use our knowledge of trace metal-phytoplankton interactions to better evaluate the impact anthropogenic trace metal inputs to harbors and neritic waters may have on phytoplankton communities and to evaluate the validity of current water quality regulations.

OBJECTIVES

One objective is to examine the ability of a wide range of phytoplankton species to grow at high concentrations of Cu, Zn, Cd and Pb. The adaptations of different species are compared with respect to their phylogenetic histories and habitat related distributions in order to understand why some species are more resistant to trace metal toxicity than others. Also, clones of the same species from “clean” and “polluted” waters are compared to see if phytoplankton can adapt genetically to high concentrations of trace metals on a relatively short time scale. A second objective is to examine phytoplankton species composition along transects in harbors and neritic waters and compare their distributions with the gradients observed in trace metal concentrations and speciation to see if laboratory derived data accurately predict what is observed in natural waters. A third objective is to determine which organisms and to what extent these organisms alter the chemical speciation of trace metals in natural waters through the production of organic compounds that have high affinities for certain trace metals.

APPROACH

Representative phytoplankton species are being isolated into culture from San Diego Bay and San Francisco Bay and then examined for their ability to tolerate high concentrations of free Cu, Zn, Cd, and Pb. Their steady state growth rates are being measured in incubation chambers in culture media with different buffered trace metal concentrations. These data are being compared with earlier data

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collected on species isolated from coastal and oceanic waters and Cape Cod embayments. In these harbors and bays, cyanobacteria are being counted and total phytoplankton biomass is being estimated by chlorophyll concentration. These data are being compared to Jim Moffett's data on total and free ionic Cu and Zn concentrations. Various phytoplankton clonal cultures are being challenged with high concentrations of potentially toxic trace metals to determine if they excrete organic compounds that chelate and detoxify them and if they produce phytochelatins.

WORK COMPLETED

Three field trips to San Diego Bay and one to San Francisco Bay have been undertaken and numerous clonal cultures of phytoplankton have been isolated into culture and their growth rates at various free ionic Cu and Zn concentrations have been measured. Copper stressed cultures of phytoplankton have been grown and sent to Jim Moffett for analysis of chelator production and to Beth Ahner for analysis of phytochelatin content. Opportunistic experiments with John Dacey have been conducted, in which the effects of Cu, Cd, Zn, Ni, and Cr stress on dimethylsulfide production were evaluated.

RESULTS

Our previous work with coastal and oceanic phytoplankton had shown that most diatoms are killed by free ionic Cu around 10^{-10}M, dinoflagellates at around $10^{-10.5}$ M, and cyanobacteria at around 10^{-11}M, and there were no significant differences between coastal and oceanic species (Brand et al., 1986). With the species isolated from Cape Cod estuaries, San Diego Bay, and San Francisco Bay, it is being found that estuarine dinoflagellates are not significantly more resistant to Cu than coastal and oceanic species, but the estuarine diatoms are considerably more resistant than coastal diatoms. Most of the coastal and oceanic diatoms are killed around 10^{-10}M, but the estuarine species survive up to around $10^{-8.5}$ to $10^{-9.5}$M.

Most of our data show no evidence of genetic differentiation along these Cu concentration gradients in Cape Cod estuaries and San Diego Bay. This indicates that natural selection in estuarine phytoplankton generally does not lead to highly resistant populations in polluted areas, at least not on the time scale of years to decades. One exception to this is the pennate diatom Asterionella glacialis, in which populations deep inside San Diego Bay appear to be more resistant to Cu than populations at the entrance to the bay. Clones of diatom species from a bay or estuary are much more resistant to Cu than clones of the same species isolated from out on the continental shelf. These data suggest that estuarine diatoms are "preadapted" to rather high concentrations of Cu and can tolerate substantial amounts of anthropogenic Cu input, but cyanobacteria and dinoflagellates cannot.

The laboratory data agree well with our observations in the Cape Cod estuaries and in San Diego Bay. In our previous work on Cape Cod, free Cu concentrations were never high enough to reduce the abundance of eukaryotic phytoplankton, and chlorophyll remained high (Moffett et al., 1997). Cyanobacteria remained high in Waquoit Bay and Great Pond, which have low total Cu concentrations (around 5 nM) and free Cu around 10^{-13}M, similar to the adjacent coastal waters. Cyanobacteria decreased by a factor of 10 in Eel Pond and Falmouth Harbor, where total Cu concentrations are around 35 to 65 nM and free Cu concentrations are around $10^{-9.5}$ ato 10^{-10}M. These results are exactly what would be predicted from the laboratory studies. We have recently obtained similar but more dramatic results in San Diego Bay. Right inside the entrance to San Diego Bay, free Cu is around $10^{-11.5}$M, but further in and throughout most of the bay, free Cu is around $10^{-9.3}$M. Chlorophyll remains high but cyanobacteria abundance drops 100-fold, as predicted by the laboratory studies. In Shelter

Island Harbor, free ionic Cu is even higher, around $10^{-8.5}$M. At this point, not only cyanobacteria but also chlorophyll declines, again as predicted. Even estuarine diatoms are dying in Shelter Island Harbor. Microscopic observations indicate that phytoplankton species diversity is also extremely low in Shelter Island Harbor compared to the rest of San Diego Bay.

Among estuarine phytoplankton, we find that dinoflagellates are more sensitive to Cu toxicity than diatoms. In the case of Zn toxicity, the reverse occurs. Diatoms are more sensitive than dinoflagellaes to Zn toxicity. The data of Jim Moffett and Ken Bruland are showing that much of the Zn in harbors is not complexed and thus potentially quite toxic. The different degrees of organic complexation for Cu and Zn, and the different sensitivities to Cu and Zn by diatoms and dinoflagellates may have important ecological implications because of their different roles in the food web and in forming harmful algal blooms.

We have found prokaryotic cyanobacteria to be much more sensitive to both Cu and Zn toxicity than eukaryotic phytoplankton. This agrees well with our observations of a large decline in cyanobacteria abundance in areas of high free Cu and Zn concentrations in Cape Cod estuaries and San Diego Bay. Although cyanobacteria are more sensitive to Cu, we have shown that they are capable of producing organic compounds that complex and detoxify the Cu (Moffett and Brand, 1996). Apparently this capacity is overwhelmed in polluted harbors and most of the Cu ends up uncomplexed and highly toxic to cyanobacteria. Although cyanobacteria excrete chelators that have very strong affinities for Cu, most eukaryotic phytoplankton do not have this capability but do produce phytochelatins. Phytoplankton species that produce dimethylsulfide have been found to produce 10 to 100 times more when under Cu stress, but apparently not under other types of trace metal stress.

Our data show that the degree of trace metal toxicity depends on the species. Concentrations of Cu and Zn typically found in “polluted” harbors appear to cause a large decline in cyanobacteria abundance, but generally not in eukaryotic phytoplankton. Because cyanobacteria are much more sensitive to Cu and Zn toxicity, their abundance may be useful as an early warning indicator of elevated concentrations of Cu or Zn.

IMPACT/APPLICATIONS

The agreement between our laboratory experiments and field observations give us confidence that we will be able to predict what impact various levels of trace metal inputs into harbors and estuaries will have on the phytoplankton community. The knowledge we have gained on the differences among phytoplankton species will also allow us to choose appropriate species for use in bioassays.

TRANSITIONS

These data should be useful to others in assessing whether or not certain concentrations of trace metals are harming the planktonic ecosystem in harbors and other embayments.

RELATED PROJECTS

This work is being done in close cooperation with Jim Moffett. Opportunistic studies have also been conducted with Beth Ahner and John Dacey.

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