Interactions Among Chemical Speciation, Algal Accumulation, and Biogeochemical Cycling of Toxic Metals in a Major US Naval Harbor (Elizabeth River, VA)

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LONG-TERM GOAL

Our long-term research goal was to determine the mechanisms and factors that regulate the uptake of pollutant metals by phytoplankton and other particles in estuaries and the effect of this uptake on the removal and biogeochemical cycling of metals.

OBJECTIVES

Our objective was to study the influence of metal speciation and metal/metal interactions on the cycling and particulate removal of pollutant metals (Zn and Cd) in the Elizabeth River/Hampton Roads Estuary, home of the US Navy Atlantic Fleet. We were especially interested in the role of metal uptake by plankton as a major mechanism in metal removal, as well as in our ability of to predict metal accumulation by field plankton from algal uptake models. These models are based on field data for free ion concentrations of controlling metals (Zn, Cd, Cu, and Mn) and laboratory data on algal uptake as functions of free ionic concentrations of these metals.

APPROACH

In collaboration with John Donat and David Burdige at Old Dominion University, we conducted an integrated field study of the chemistry and biogeochemical cycling of pollutant metals in the Elizabeth River and adjacent waters. We collected near-surface (1 m) water samples along a six-station transect from highly metal-polluted waters of the Elizabeth River to the less contaminated waters of the lower Chesapeake Bay. This transect was sampled during late July, 1999 and again during May, 2000. The samples were analyzed by Donat for total and dissolved concentrations of Cu, Cd, Zn, and Mn; free ion concentrations of Cu, Cd, and Zn; and concentrations and binding strengths of chelators that complex these metals. We (Sunda and Huntsman) measured size fractionated Chl *a*.

We (Sunda and Huntsman) made radiotracer (^{109}Cd, ^{65}Zn and ^{14}C-bicarbonate) additions to aliquots of the surface samples and then measured particulate uptake of ^{109}Cd and ^{65}Zn and photosynthetic fixation of ^{14}C as a function of time. The time-course data was analyzed to compute the fraction of ^{65}Zn and ^{109}Cd that rapidly adsorbed to particles (within the first hour) and the longer-term specific rate of radiotracer uptake by plankton. To do this, the data were fit to a first order reaction rate model:

$$-d[^{65}Zn]/dt = k[^{65}Zn] \quad or \quad -d[^{109}Cd]/dt = k[^{109}Cd]$$

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14. ABSTRACT
Our long-term research goal was to determine the mechanisms and factors that regulate the uptake of pollutant metals by phytoplankton and other particles in estuaries and the effect of this uptake on the removal and biogeochemical cycling of metals.

15. SUBJECT TERMS

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where [^{65}Zn] and [^{109}Cd] are the fractions of the radionuclides remaining in solution. Integration of the above equation gives:

$$\ln [^{65}Zn] = -k\,t + \ln [^{65}Zn]_{t=0} \quad or \quad \ln [^{109}Cd] = -k\,t + \ln [[^{109}Cd]_{t=0}$$

Linear regressions of ln [^{65}Zn] or ln [^{109}Cd] vs time for the period of 1-8 h after the addition of radiotracer generally yielded R^2 values > 0.9, indicating good fits of the data to the first order kinetics model. The slope, *k*, from these regressions gave values for the specific rate of particulate ^{65}Zn or ^{109}Cd uptake, while the intercept gave values for ln of the fraction of the radionuclide remaining in solution after rapid adsorption onto surfaces. From these values we could readily compute the fraction of added radionuclide that was rapidly adsorbed onto particles.

WORK COMPLETED

In the past year, we completed our data analysis of the radiotracer and biological studies conducted during the July, 1999 and May, 2000 field trips. We also conducted an overall synthesis of our biological and radiotracer data and the trace metal analytical data of John Donat for both sampling trips. Highlights from this overall synthesis were presented at the ONR Harbor Processes Workshop in June in Arlington and also at the Biotic Ligand Workshop held in Woods Hole in July. We are currently writing up our results for publication.

RESULTS

For both sampling trips, we observed an initial rapid particulate uptake of ^{65}Zn and ^{109}Cd, followed by a more gradual uptake that fit pseudo-first order kinetics. The initial rapid uptake, which ranged from 2 to 26% of the added ^{65}Zn and 0.4 to 2.5 % of the ^{109}Cd, probably results from adsorption of the radiotracers to particle surfaces, including plankton surfaces. The more gradual uptake was eliminated by the addition of the biological poison azide, suggesting that it represents uptake by plankton. These longer term "biological" uptake rates ranged from 1.5 to 14.5%/h for the July, 1999 sampling trip and were lower (0.5 to 3%/h) for the May, 2000 trip. These rates were on average 12-fold higher than the equivalent rates for Cd. Thus, there appears to be a more avid biological uptake and cycling for Zn.

The specific rates of longer term particulate Zn uptake for both sampling trips correlated closely with Chl *a* concentrations (R^2 = 0.955) and with carbon fixation rates (R^2 = 0.77), again supporting the hypothesis that these rates are due to uptake of Zn by phytoplankton. Each of these parameters had similar values during July and May at stations 3-5 in the lower Chesapeake Bay and Hampton Roads (Fig. 1). However, they all had considerably higher values during July than in May in the Elizabeth River stations (6-8) due to the presence of an intense algal bloom that centered around station 6 in the lower Elizabeth River estuary. At this station in July, the specific Zn uptake rate was 14.5%/h, suggesting that zinc was being actively cycled biologically, with a turnover time of the dissolved pool of only 7 hours. By contrast in early May, the specific rate of particulate Zn uptake was 2.4%/h at the same station, only 17% of the rate in late July. The intense biological uptake of Zn during late July relative to that in early May, coincides with two- to five-fold lower concentrations of dissolved Zn and up to 13-fold higher ratios of particulate to dissolved Zn at the Elizabeth River stations during July. Again the largest differences occurred at Station 6 where the July algal bloom was most intense. Even larger decreases were observed in free zinc ion concentrations ([Zn^{2+}]), which regulate biological uptake and toxicity of Zn. In early May, the measured zinc ion concentration at Station 6 was 89 nM,

well within the toxic range for copepods (Sunda et al. 1987), while in late July, free zinc ion concentrations were 150-fold lower (0.6 nM) and well below toxic levels.

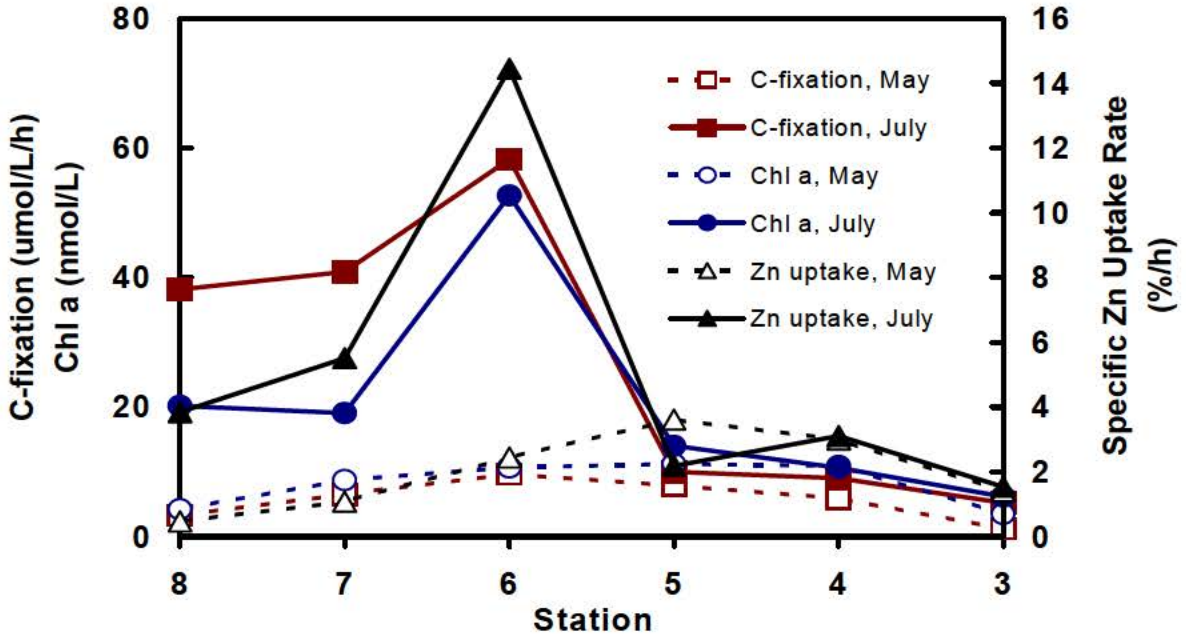

Figure 1. Specific Zn uptake rate, C-fixation rate, and Chl a in July and May at stations 8-6 in the Elizabeth River, stations 5 and 4 in Hampton Roads, and station 3 in the Chesapeake Bay. [The three parameters are similar during May and July for stations 3-5, but are considerably higher in July than in May for the Elizabeth River stations (6-8).]

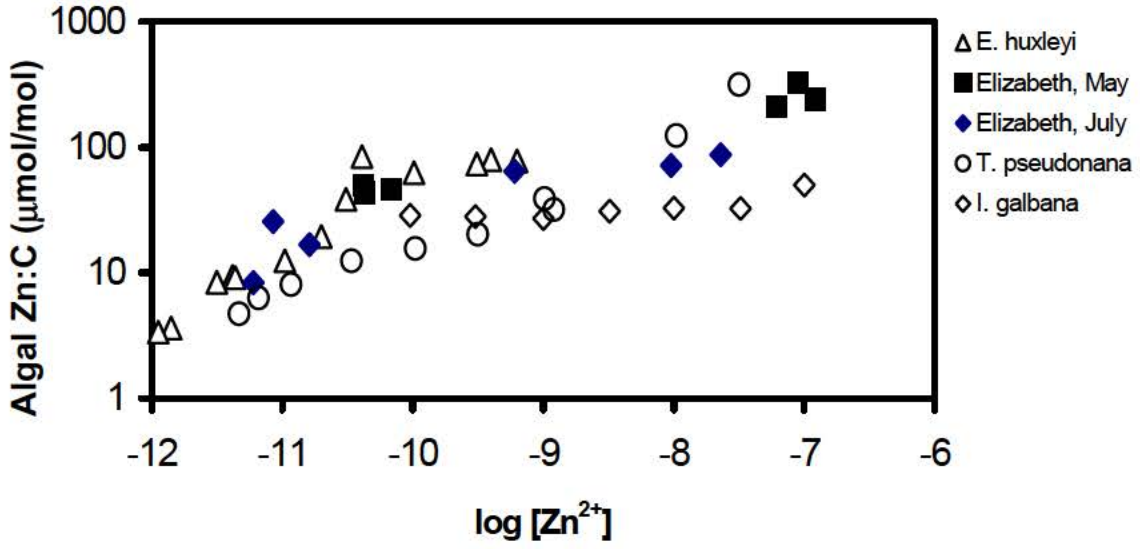

***Figure 2. Relationship between Zn:C and log [Zn^{2+}] for natural plankton in the Elizabeth River/Hampton Roads system and algal species grown in metal ion buffer systems:* Emiliania huxleyi, Thalassiosira pseudonana, *and* Isochrysis galbana.**
[Good agreement is observed for Zn:C vs [Zn^{2+}] in natural plankton and algal cultures.]

By multiplying specific rates of Zn and Cd particulate uptake by dissolved concentrations of the metals we were able to compute particulate Zn and Cd uptake rates in units of mol/L/h. These rates were then divided by the measured carbon fixation rates to yield the Zn:C and Cd:C assimilation ratios for the field plankton communities. At steady state, these ratios should equal the Zn:C and Cd:C values in the field phytoplankton. Plots of Zn:C vs the measured free zinc ion concentration fell on a single sigmoidal curve for the two sampling trips (Fig. 2). By contrast the Zn:C curves were not directly related to the dissolved Zn concentration, suggesting that free zinc ion concentration, rather than total dissolved Zn, controls algal uptake of Zn. The relationship between the field Zn:C assimilation ratios and $[Zn^{2+}]$ in the estuarine samples was similar to curves for cellular Zn:C vs log $[Zn^{2+}]$ measured in the algal cultures grown in metal ion buffer systems. The field/lab agreement again supports the hypothesis that the long-term particulate uptake of Zn in the estuarine samples results from accumulation by phytoplankton. The data plotted in Fig. 2 provides a field confirmation of our central hypothesis that the uptake of metals by phytoplankton is controlled by the free metal ion concentration.

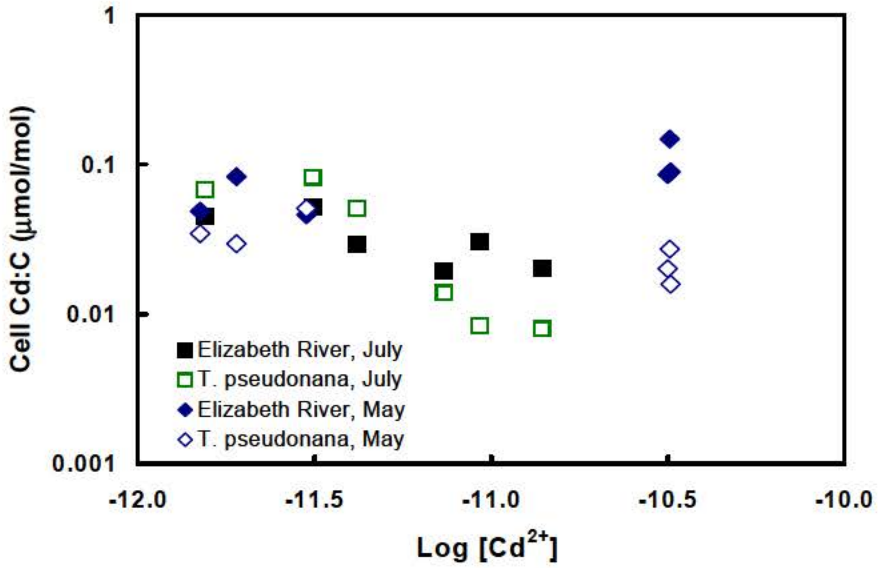

Figure 3. Relationship between Cd:C and log $[Cd^{2+}]$ in natural plankton in the Elizabeth River system and in Thalassiosira pseudonana based on Cd uptake by the Mn transport system. [Good agreement is observed between field plankton data and model results for T. pseudonana.]

Plankton Cd:C assimilation ratios for the May and July sampling trips were plotted as a function of log $[Cd^{2+}]$ (Fig. 3). As with the zinc data, a consistent relationship between plankton Cd:C and log $[Cd^{2+}]$ was observed for the two sampling trips. However, unlike the Zn:C values which increased with increasing $[Zn^{2+}]$ (Fig. 3), Cd:C values first decreased with increasing $[Cd^{2+}]$ in the free Cd ion range of 2 to 10 pM and then showed a positive slope at higher free Cd ion concentrations ($[Cd^{2+}]$) (Fig. 3). The complex behavior may be related to antagonisms between Cd and Mn, which result from the incidental uptake of the toxic metal Cd by the cells' transport system for the nutrient metal Mn (Sunda and Huntsman 1996,1998, 2000). As a result, algal uptake of Cd decreases inversely with increasing $[Mn^{2+}]$. This should be important in our field samples because, while $[Cd^{2+}]$ increases by 20-fold from station 3 to station 8, values for $[Mn^{2+}]$ increase by over 100-fold. As a result, algal Cd uptake could either increase or decrease depending on which variable (free Cd or free Mn) dominates the situation.

To test the Cd/Mn interaction theory, we computed the Cd:C ratios that would occur in the estuarine diatom *Thalassiosira pseudonana* based on models for Cd uptake by the Mn transport system in that species as functions of $[Cd^{2+}]$ and $[Mn^{2+}]$(Sunda and Huntsman 1996) and the measured values of $[Cd^{2+}]$ and $[Mn^{2+}]$ in the Elizabeth River system during the July and May sampling periods. The model values showed good agreement with the field data for particulate Cd:C assimilation ratios, suggesting that phytoplankton are largely responsible for the observed long-term particulate uptake of Cd. Furthermore, an antagonism between Cd and Mn, coupled with the large increase in $[Mn^{2+}]$ can readily explain the low particulate Cd uptake and Cd:C assimilation values in water from the Elizabeth River stations (6-8) despite the increase in Cd ion concentrations. This suppression algal uptake of Cd by Mn appears to be responsible for the low particulate uptake and removal of Cd in the Elizabeth River estuarine system.

IMPACT

Our results indicate that the pollutant metal zinc is avidly taken up by phytoplankton in harbors and other estuarine waters, which removes it from solution and transports it to the bottom. This removal has a major impact on the concentration and cycling of Zn in eutrophic estuaries (such as the Elizabeth River), which is inherently tied to annual cycle of phytoplankton productivity. As algal production and biomass increase during the Spring and early Summer, zinc is actively taken up by the emerging phytoplankton community, and is transported to the sediments by the settling of algal cells or biogenic particles, such as zooplankton fecal pellets. This process decreases the concentration dissolved zinc and free zinc ions in the water column, and thereby reduces zinc toxicity, while transport to the bottom leads to zinc accumulation in the sediments. During periods of low algal growth during the winter, bacterial regeneration of zinc from biogenic particles in bottom sediments should cycle zinc back into the overlying water, and thereby increase zinc concentrations and toxicity. Thus, our data suggest that there should be seasonal cycles for zinc in eutrophic harbors and other estuarine systems similar to those observed for major nutrients. Compared to zinc, cadmium shows a much lower uptake by phytoplankton. Consequently, algal growth should have a lesser impact on Cd concentrations, toxicity, and transport to the sediments, which may result in lower seasonal variations in cadmium concentrations. Overall our work indicates fundamental links among anthropogenic nutrient inputs, algal blooms, and the concentrations, fate, and cycling of pollutant metals in harbor systems.

RELATED PROJECTS

As pointed out above, this work is being conducted in close collaboration with the ONR Harbor Processes projects of John Donat and Dave Burdige at Old Dominion University.

TRANSITIONS

The results of this collaborative project will be used to construct more realistic conceptual and numerical models of pollutant metal cycling, fate, and biological effects in harbors and related estuarine systems.

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