

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 GOALS

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

OBJECTIVES

In conjunction with John Donat and David Burdige at Old Dominion University, we are studying the influence of metal speciation and metal/metal interactions on the particulate cycling and removal of pollutant metals (Zn and Cd) in the Elizabeth River and Hampton Roads Estuaries, home of the Navy's Atlantic Fleet. We are especially interested in the role of metal uptake by plankton as well as in our ability to predict removal of metals from algal uptake models. These models will be 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 conjunction with the ONR Harbor Processes grant to John Donat and David Burdige, we are conducting an integrated field study of the chemistry and biogeochemical cycling of pollutant metals in the Elizabeth River system. In July, 1999, we collected near-surface water samples along a 6-station transect from highly metal-polluted waters of the Elizabeth River to the less contaminated waters of the lower Chesapeake Bay. This transect will be sampled again during the spring of 2000. In addition to pH, salinity, and temperature, the samples were analyzed by Donat for both total and dissolved Cu, Cd, and Zn concentrations. They will also be analyzed for dissolved Mn, free ion concentrations of Cu, Cd, and Zn, and concentrations and binding strengths of chelators that complex these metals. We also measured size fractionated Chl *a* and will measure nutrients in preserved samples.

We conducted experiments in aliquots of the 6 samples to determine *in situ* rates of particulate and algal uptake of Cd and Zn and photosynthetic CO₂ fixation using ¹⁰⁹Cd, ⁶⁵Zn and ¹⁴C-bicarbonate. Sub-samples were amended with the strong chelator DTPA (diethylenetetraaminepentaacetate) and reducing solutions to help differentiate radio-labeled metals adsorbed to particles or associated with Mn and Fe oxides from those accumulated within phytoplankton cells. Parallel short-term metal uptake experiments will be conducted in filtered samples (preserved by freezing) with *Thalassiosira pseudonana*, a well-characterized estuarine diatom we have extensively studied in the laboratory.

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Following studies with field samples, laboratory experiments will be conducted *T. pseudonana* in metal ion buffer systems set at the same free ion concentrations of Cu, Zn, Cd, and Mn and the same salinity and temperature as in the field experiments. Uptake rates of Cd and Zn will be compared with those determined for *T. pseudonana* and the natural phytoplankton in the field samples. These experiments will rigorously test our ability to predict algal uptake rates in field samples from models based on laboratory measurements of algal metal uptake in metal ion buffer systems and analytical measurements of free metal ion concentrations in field samples.

WORK COMPLETED

During late July 1999 we completed the first of the two proposed field trips to the Elizabeth River and adjacent waters to study metal chemistry and biological cycling during the summer stratification period. Chlorophyll concentrations, ^{14}C -fixation, and particulate uptake of added radiotracer metals (^{65}Zn and ^{109}Cd) were measured in near-surface (1m) samples collected along a six-station transect.

RESULTS

Chl *a* and ^{14}C -fixation showed a wide range of values for the six stations sampled (Table 1). Both parameters were highly correlated ($R^2 = 0.987$) indicating that Chl *a* is a good index of photosynthetic C-fixation rate. The highest values for both parameters occurred at Station 6, located just within the mouth of the Elizabeth River. The lowest values were observed at Station 3 in Chesapeake Bay, the station least impacted by anthropogenic inputs (Sunda et al. 1990). Size fractionation showed that 80-100% of Chl *a* and fixed ^{14}C was retained on a 3 μm filter, and 60-80% was retained on an 8 μm filter. Thus, most of the phytoplankton production occurred in larger cells.

Table 1. Long-term particulate accumulation rates and rapid surface adsorption values for ^{65}Zn and ^{109}Cd in samples from lower Chesapeake Bay (St. 3 and 4), Hampton Roads (St. 5), and Elizabeth River (St. 6-8).

Sta.	Salinity	PH	Chl <i>a</i> (nmol/l)	^{14}C Fixation Rate (% h^{-1})	Part. ^{65}Zn Uptake Rate (% h^{-1})	^{65}Zn Intercept (%)	Part. ^{109}Cd Uptake Rate (% h^{-1})	^{109}Cd Intercept (%)
3	23.1	8.14	6.19	0.29	1.54	7.6	0.24	2.34
4	24.4	8.22	10.66	0.49	3.11	15.0	0.34	1.03
5	22.1	8.13	14.04	0.57	2.19	17.3	0.20	1.06
6	20.5	8.44	52.7	3.47	14.45	28.5	0.46	2.52
7	19.8	7.88	19.1	2.45	5.51	2.2	0.45	0.40
8	19.4	7.72	20.2	2.30	3.85	2.2	0.23	0.61

In the radiolabel experiments, a much greater fraction of ^{65}Zn than ^{109}Cd was associated with particles. Size fractionation indicated a similar size distribution for particulate ^{65}Zn as was observed for fixed ^{14}C since 71 to 98% of the ^{65}Zn was retained on a 3 μm filter. At upstream stations 7 and 8, 48% and 59% of the particulate ^{65}Zn was retained on an 8 μm -pore filter. Particulate ^{109}Cd showed a similar but slightly smaller size distribution. At Stations 7 and 8, 29% and 36% was retained on an 8 μm filter. The above results are significant because they indicate that the Zn and Cd tracers are primarily associated with larger particles, which would have higher settling velocities than smaller ones would

have. The similarity in particulate size distributions for fixed ^{14}C and added ^{65}Zn and ^{109}Cd supports the idea that much of the particulate radiolabeled metals were associated with algal cells.

We subjected the ^{65}Zn and ^{109}Cd retained on the filters to a series of washes to help determine the nature of the association of the metals with particulates. These washes were 1 mM DTPA, a strong chelator that desorbs metals from surfaces; 3 mM ascorbate, a mild reductant that reductively dissolves Mn (but not Fe) oxides; and Ti-EDTA/citrate, a strong reductant-chelator mix that both dissolves Fe and Mn oxides and desorbs metals. The DTPA wash removed most of the particulate ^{65}Zn and up to half of the particulate ^{109}Cd at the lower estuarine stations 3-6 (Table 2) indicating surface adsorption is an important mechanism for particulate metal association. However, DTPA was much less effective at Sta. 8, the most upstream station, suggesting that here adsorption was less important. Ascorbate removed most of the particulate ^{65}Zn and ^{109}Cd at Station 5 in Hampton Roads. This indicates that most of the particulate radiotracer metals here are associated with Mn oxides, which are known to precipitate on algal surfaces and also to be produced by bacteria. Ti-EDTA/citrate was the most effective wash for removing the metals from particles. This wash removed 56 to 77% of the particulate ^{65}Zn and 35 to 60% of the particulate ^{109}Cd , again suggesting that adsorbed metals, including that adsorbed to Mn and Fe oxides accounts for much of particulate ^{65}Zn and ^{109}Cd .

Table 2. Percent of particulate ^{65}Zn and ^{109}Cd removed by DTPA, Ti-EDTA/citrate, and ascorbate.

Station	Hours after addition	^{65}Zn , DTPA	^{65}Zn , Ti	^{65}Zn , Ascorbate	^{109}Cd , DTPA	^{109}Cd , Ti	^{109}Cd , Ascorbate
3	6.5	53.2	66.6	9.3	35.6	59.7	11.9
4	6.7	61.4	65.8	25.1	54.3	44.8	16.9
5	3.0	74.4	-	64.9	46.9	-	60.9
6	4.1	77.9	76.9	23.0	33.5	52.0	43.8
7	6.7	-	61.9	12.1	-	35.2	28.5
8	4.9	7.7	55.7	22.6	32.46	45.5	25.7

Plots for particulate ^{65}Zn and ^{109}Cd uptake vs time showed similarly shaped curves. There was rapid particulate accumulation within the first hour, followed by a much more gradual uptake that was nearly linear over the remaining 2 to 6 hours. The rapid initial uptake was highest at Sta 3, the station with the highest percentage of adsorbed metals, as determined from the DTPA washes. It was lowest at Sta 7 and 8 where DTPA removed only a minimal fraction of the particulate radionuclides. Thus, the rapid particulate uptake appears to reflect rapid adsorption onto surfaces of cells and abiotic particles. The subsequent more gradual accumulation may reflect uptake into algae and other microplankton.

The time-course data for the fraction of particulate radionuclide vs time was fit to a first order reaction rate model, which can be expressed as:

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

 $[^{65}\text{Zn}]$ or $[^{109}\text{Cd}]$ is the fraction of added ^{65}Zn or ^{109}Cd remaining in solution equal to 1 minus the particulate fraction. The first order rate constant k gives the specific rate of particulate Zn or Cd uptake. Integration of the above equation gives:

$$\ln [^{65}\text{Zn}] = -k_{\text{Zn}} t + \ln [^{65}\text{Zn}]_{t=0} \text{ or } \ln [^{109}\text{Cd}] = -k_{\text{Cd}} t + \ln [^{109}\text{Cd}]_{t=0}$$

Regressions of $\ln [^{65}\text{Zn}]$ vs t and $\ln [^{109}\text{Cd}]$ vs t fit the first order model for time period of 0.5 to 6 h. These regressions all show a negative y-intercept that can be used to estimate the initial rapid

adsorption of the dissolved metals. The negative slope of these regressions gives the specific rate of the slower particulate uptake. Both sets of values are given in Table 1.

The specific rates for particulate Zn formation determined from the first order rate analysis were much higher (1.5 to 14.5 % h⁻¹) than for Cd (0.2 to 0.46 % h⁻¹), as were estimates of rapidly adsorbed radionuclide (Table 1). The highest specific rates and adsorption values in all cases occurred in the high productivity, high Chl *a* Sta. 6 sample (Table 1). The percent adsorbed ⁶⁵Zn and ¹⁰⁹Cd were only loosely correlated with Chl *a* ($R^2 = 0.377$ and 0.164). Thus much of the adsorbed metal is probably not associated with algal cell surfaces, although as indicated above, some may be associated with biologically produced Mn oxides. Specific rates of particulate Zn formation were highly correlated with Chl *a* values ($R^2 = 0.964$), consistent with Zn uptake by phytoplankton being largely responsible for long-term particulate removal of Zn (Fig. 1). This hypothesis was supported the effect of the poison azide added to subsamples from Sta 4, 5, and 7. Azide had little effect on the rapid adsorption of Zn within the first hour, but strongly suppressed longer-term particulate ⁶⁵Zn uptake.

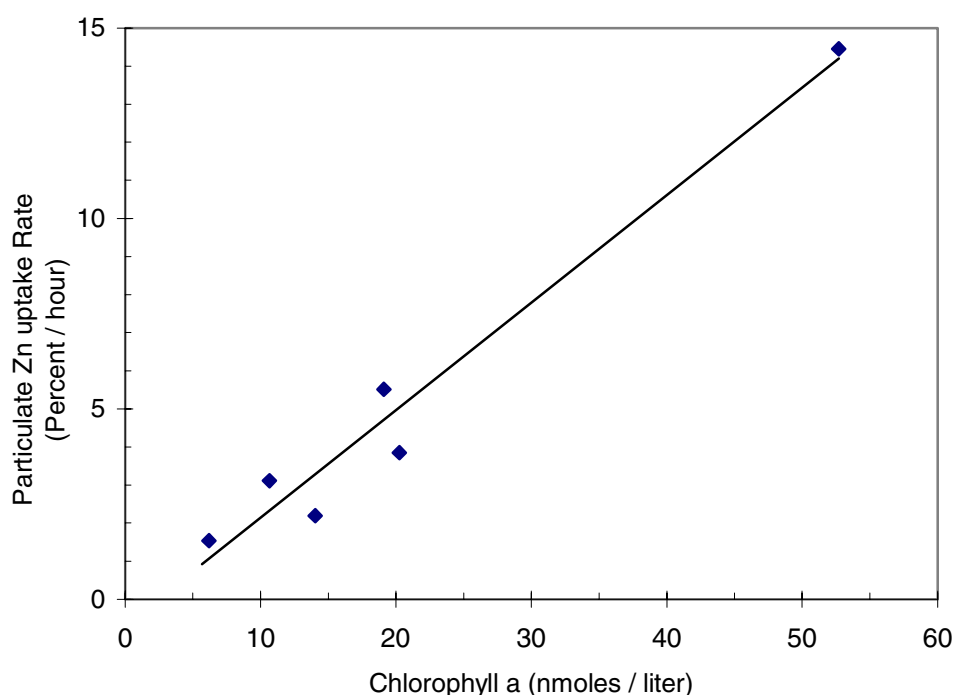


Fig1. Relationship between long-term ⁶⁵Zn uptake rates and Chl *a* in the Elizabeth River system

Our results indicate that Zn is strongly taken up by phytoplankton and other large particles in the Elizabeth R and adjacent waters, which removes it from solution and through settling, transports it to the sediments. By contrast, particulate accumulation of Cd is much lower. These results predict that both dissolved zinc and total zinc should decrease substantially with algal growth in estuarine waters. Indeed, in our transect from the upstream station 8 to the high algal biomass lower portion of the river (Sta 6), John Donat measured a 30% decrease in total zinc, and a 70% decrease in dissolved zinc (from 89 to 27 nM). As predicted from our results, he observed a much smaller decreases between these two stations for cadmium: total Cd decreased by only 11.5% and dissolved Cd by 26%. Decreases in metal concentrations at Station 5 near the mouth of the Elizabeth River showed even larger differences between Zn and Cd. At Station 5, dissolved Zn decreased to 3.7 nM, only 4% of the value at the uppermost Elizabeth River station, while the decrease in dissolved Cd was only 45%.

IMPACT

Our results indicate that the pollutant metal zinc strongly adsorbs onto large particles and is taken up by large-celled phytoplankton, which removes it from solution and transports it to the bottom. This removal process has a major impact on the concentration and cycling of zinc in eutrophic estuaries such as the Elizabeth River. The decrease in zinc concentrations should decrease zinc toxicity, while the removal to the bottom impacts zinc accumulation in harbor sediments. By contrast, cadmium shows a lower particulate accumulation, and thus, increases in the mass of phytoplankton and related particles (e.g., detritus) during algal blooms should have a lesser impact on Cd concentrations, toxicity, and transport to the sediments. This work indicates fundamental links among anthropogenic nutrient inputs, algal blooms, and the concentrations, toxicity, and fate of pollutant metals in harbor systems.

RELATED PROJECTS

This project is closely linked to ONR Harbor Processes projects conducted by John Donat and Dave Burdige at Old Dominion University and by Andrew Gordon and John Donat at the same institution. Taken together, these studies constitute an integrated, collaborative field study in the Elizabeth River examining the interrelationships among: (1) the uptake of metals by phytoplankton and other particulates responsible for metal transport to the sediments (Sunda and Huntsman, this study); (2) the concentrations and chemical speciation of toxic metals (Cu, Cd, and Zn) and controlling interactive metals (Mn and Zn) (Donat); (3) the *in situ* production of Cu-chelators by natural microbial populations in response to elevated Cu concentrations (Gordon and Donat]; and the flux of metals and chelators from the sediments back into water column (Burdige and Donat). Our study is dependent on the grant to Donat and Burdige for help in collection of water samples and for analysis of concentrations and chemical speciation of metals (Zn, Cd, Cu, and Mn) in these samples.

TRANSITIONS

Our results, in conjunction with those of Donat, Burdige, and Gordon, 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.

PUBLICATIONS

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