

METAL-COMPLEXING LIGANDS AND METAL SPECIATION IN SEDIMENT PORE WATERS: IMPLICATIONS FOR SEDIMENT/WATER EXCHANGE AND WATER COLUMN SPECIATION

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LONG-TERM GOALS

Our long-term goals are to determine the role that complexation and speciation play in sediment/water exchange of metals in estuarine and coastal locations, and the importance of metal-complexing ligands fluxing out of estuarine pore waters to water column metal speciation on local, regional, and global scales.

OBJECTIVES

Our scientific objectives are to determine: (1) the extent of complexation and the speciation of selected trace metals in bottom waters and sediment pore waters; (2) concentrations and strengths of metal ligands in bottom waters and sediment pore waters; (3) the magnitude and direction of the benthic flux of metals and their ligands; and (4) the lifetime of the metal ligands fluxing out of pore waters into overlying bottom waters and their degradation and removal processes.

APPROACH

Our approach consists of both field and laboratory efforts. We have sampled the sediment porewaters and water column from two estuarine sites in Chesapeake Bay, having contrasting biogeochemical and physical characteristics, during fall '96 and spring and fall '97. We have also sampled the sediment porewaters and water column from a site along the mid-Atlantic shelf/slope break (WC7).

Sediments were collected using a stainless steel box corer, and subsampled using acid-cleaned plexiglass core tubes, and clean shoulder-length polyethylene gloves. All porewater samples were obtained from sediment cores sectioned under N₂ and centrifuged at *in situ* temperatures. Porewater samples were filtered (0.45µm); subsamples for total dissolved metals were acidified

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(pH 2); subsamples for metal complexation and speciation analyses were kept anoxic, cold and dark until analysis. Water column samples were collected with either a peristaltic pumping system through Teflon tubing attached to a weighted plastic “fish-vane”, or with a 30-liter GO-Flo bottle, filtered (0.22 μ m), and acidified (pH 2).

To investigate the persistence of porewater-derived Cu-complexing ligands, porewaters were added to filtered and unfiltered bottom water. Four experimental regimes were studied: porewater added to: (1) filtered and (2) unfiltered bottom water (3) exposed to light and (4) kept dark. Each regime was composed of a test solution (porewater added) and a control (no porewater added). All of these solutions were incubated in acid-cleaned 2-L Teflon bottles, positioned on a shaker table on a clean-air bench, and kept oxic. “Light” samples were exposed to light for 12 hours/day from a tungsten/halogen Capsylite PAR 38 floodlight positioned 30 cm away. All solutions were subsampled over a 30-day period for Cu speciation, total dissolved Cu, DOC, DO, pH, and salinity.

Total dissolved Cu (TDCu) concentrations were determined by chemiluminescence (Sunda and Huntsman, 1991); total dissolved Zn (TDZn) concentrations were determined by differential pulse anodic stripping voltammetry (DPASV; Donat and Henry, in prep). Cu complexation and speciation were determined by ASV (differential pulse or square wave modulation) at a rotating thin mercury film/glassy carbon disk electrode (Coale and Bruland, 1988; Donat et al., 1994), hanging mercury drop electrode (Donat et al., 1994), and by ligand (8-hydroxyquinoline) competition/adsorptive cathodic stripping voltammetry (van den Berg, 1986; Donat et al., 1994). Pore water concentrations of dissolved organic carbon were determined by high temperature catalytic oxidation (Burdige and Homstead, 1994), while pore water Fe, Mn, sulfide, nutrients, and Σ CO₂ were determined by standard methods. Dissolved carbohydrates in porewaters were determined by sulfuric acid hydrolysis and a modified MBTH method (Pakulski and Benner, 1992).

WORK COMPLETED

In the previous fiscal years' efforts, we have determined TDCu concentrations, Cu-complexing ligand concentrations, and Cu complexation and speciation in the sediment porewaters of sites M, S, and WC7, and we have determined the benthic flux of TDCu and Cu ligands from sites M and S. We also determined TDZn concentrations, Zn ligand concentrations, and Zn complexation and speciation in the water column of Chesapeake Bay. We conducted these studies 2-3 seasons per year.

During this past FY, we completed one comprehensive experiment to study the persistence of porewater-derived Cu-complexing ligands in the water column, and are in the process of completing a second (Price, Donat and Burdige, 1997; in prep.). We have obtained concentration/depth profiles for total dissolved zinc in sediment porewaters for our August '96 and June '97 cruises, and determinations of zinc complexation and speciation in porewaters are in progress.

In order to understand better the role of sediment processes in the production of metal-

complexing ligands, we have performed studies of dissolved organic matter in sediments. We recently developed a conceptual model for DOM cycling in marine sediments, based on DOC size fractionation data (Burdige and Gardner, 1997; Burdige et al., 1997), and most recently have begun determinations of dissolved carbohydrates in marine sediment porewaters (Gardner and Burdige, 1998).

We've presented our results at national meetings and have submitted or are preparing manuscripts on: (1) the persistence of porewater-derived, Cu-complexing ligands (Price, Donat and Burdige, 1997; 1998; in prep.); (2) the biogeochemistry of Cu and Cu-complexing ligands in estuarine and continental shelf sediments (Skrabal, Donat, and Burdige, in prep.); (3) the flux of Cu ligands from estuarine sediments (Skrabal, Donat, and Burdige, 1997; in press); (4) Zn complexation and speciation in the Chesapeake Bay water column (Donat and Henry, 1997; in prep.); (5) DOM cycling in marine sediments (Burdige and Gardner, submitted; Burdige et al., 1997); and (6) determinations of dissolved carbohydrates in sediment porewaters (Gardner and Burdige, 1998).

RESULTS

The results of our porewater Cu-ligand persistence experiments indicated that Site M bottom waters contained at least three classes of Cu-complexing ligands. The concentration of the strongest ligand class ("L₁": log K' ~ 15) comprised 7% of the total Cu ligand pool, whereas the weaker ligand classes ("L₂": log K' ~12 and "L₃": log K' ~8) comprised the remaining 93% of the Cu ligand pool. Greater than 99% of total dissolved Cu (TDCu) in the bottom waters was organically complexed, and 84% of TDCu was complexed by L₁. The concentrations of these three ligand classes were found to increase significantly when porewaters were added to the bottom waters. The concentration of the L₁ class increased over the course of this experiment. This increase in the L₁ concentration, coupled with its extremely strong conditional stability constant, resulted in its being the predominant Cu complex and in suppressing the free Cu²⁺ concentrations to levels ranging between 3×10^{-16} M to 8×10^{-13} M. These free Cu²⁺ concentrations are well below those reported to cause naupliar mortality to the copepod, *Acartia tonsa*.

The major result of this experiment was that all three Cu-complexing ligand classes persisted over a 30-day period-- that is, not only do these ligands flux out of the sediment porewaters into the overlying water column (Skrabal, Donat, and Burdige, 1997), they are not degraded in the water column on an appreciable time scale. These results represent the first direct evidence that porewater-derived Cu-complexing ligands may significantly influence Cu speciation in the water column. In addition, the persistence of these ligands may allow them to escape the estuary where they might then influence Cu complexation and speciation in coastal (and perhaps open ocean) waters.

Total dissolved zinc (TDZn) concentrations in the porewaters at sites M and S range from ~2 to 33 nM, are generally similar to bottom water concentrations, and generally decrease with depth in the sediment column. Preliminary levels of total zinc complexing ligands (TL_{Zn}) in the upper layers of the sediment column (0-3cm) range from 75 to 200 nM, are approximately 2x greater at site M compared to site S, and are as much as 15-20x greater than TL_{Zn} in the water column

(Donat and Henry, in prep.).

Dissolved carbohydrate (dCHO) concentrations in the sediment porewaters at three sites in Chesapeake Bay and continental shelf/slope sites ranged from ~40 to 500 μM (C equivalents). The dCHO percentage of porewater DOC varied greatly (7-54%) among the sites-- %dCHO was highest offshore and lowest in the organic-rich, anoxic sediments of mid-Chesapeake Bay. DOC and dCHO concentrations generally increased with porewater depth. dCHO concentrations varied inversely with both sediment-C oxidation rates and with relative concentrations of low molecular weight (LMW:<3 kDa) DOC, suggesting that high molecular weight (HMW) fractions of porewater DOC may harbor a larger %dCHO than LMW fractions. These differences in the composition of porewater DOC at the different sites may be driven partly by differences in C oxidation rates, or they may be a factor controlling these rates.

IMPACT

The speciation of metals in sediment porewaters governs both the fate of metals (by controlling the extent and speed of their cycling between sediments and the water column), and their effects on biota (by influencing bioaccumulation and toxicity). Our results indicate that pore waters contain very strong Cu ligands in very high concentrations, which should markedly influence the sediment/water exchange of Cu. These very strong ligands are fluxing out of the sediment porewaters into the overlying water column, and our recent results suggest that these ligands persist in bottom waters for significant (≥ 30 days) time periods. The persistence of these ligands may allow them to escape the estuary where they might then influence Cu complexation and speciation in coastal (and perhaps open ocean) waters.

RELATED PROJECTS

Our results compliment other ONR projects on organic diagenesis and metal cycling in sediments (Berelson, Johnson and Coale), metal speciation in sediment solid phases (Morse), physico-chemical speciation of bioactive metals in the water column (Bruland), and metal-phytoplankton interactions (Moffett and Brand, Sunda). We have active collaborations with Morse and Berelson, and we have participated in a copper-speciation methods intercomparison with Bruland and Moffett (Bruland et al., in prep.).

Work this FY has been closely allied to an project funded through ONR's Coastal Benthic Optical Properties Program (ONR award No.: N000149710005: "Colored Dissolved Organic Matter in Sediments and Seagrass Beds and Its Impact on Shallow Water Benthic Optical Properties, D.J. Burdige, PI), and a recently-completed NSF project (OCE-9302120: "Fluxes of Dissolved Organic Matter from Marine Sediment", D.J. Burdige, PI).

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