Metal-Complexing Ligands And Metal Speciation In Sediment Porewaters: 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 the sediment/water exchange of metals in estuarine and coastal locations, and the importance of metal-complexing ligands fluxing from estuarine porewaters 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 porewaters; (2) concentrations and strengths of metal-complexing ligands in bottom waters and sediment porewaters; (3) the magnitude and direction of the benthic flux of metals and their ligands; and (4) the persistence of the ligands fluxing out of porewaters into overlying bottom waters and their degradation and removal processes.

APPROACH

Our approach consists of both field and laboratory efforts. In FY 1998, we conducted four research cruises. In November ‘97, we sampled the sediment porewaters and water column from two estuarine sites in Chesapeake Bay, having contrasting biogeochemical and physical characteristics. In March, April, and July ‘98, we sampled the sediment porewaters and water column from the Elizabeth River (a highly anthropogenically-impacted, major US Naval harbor). We continued our laboratory studies on porewater-derived Cu ligand persistence and degradation. We determined porewater profiles of total dissolved Zn and Zn-complexing ligand concentrations and the conditional stability constants of Zn complexes at the Chesapeake Bay sites. We determined porewater profiles of total dissolved Cu and Zn and Cu and Zn-complexing ligand concentrations and the conditional stability constants of Cu and Zn complexes at the Elizabeth River site.

Sediments were collected using a stainless steel or plexiglass box corer, and subsampled using acid-cleaned plexiglass core tubes. Sediment cores were sectioned under N_2 and sediment intervals were centrifuged at in situ temperatures. Porewater samples were filtered (0.45µm); subsamples for total

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dissolved metals were acidified (pH 2); subsamples for metal complexation and speciation analyses were kept anoxic, cold and dark until analysis. Water column samples were collected with a peristaltic pumping system through Teflon tubing attached to a weighted plastic “fish-vane”, filtered in line (0.22µm filter) during collection, and acidified to pH 2.

The persistence of porewater-derived Cu ligands was investigated by adding freshly collected sediment porewaters to a NaCl solution of the same ionic strength as the sampling site bottom water. These samples and their associated controls were incubated in acid-cleaned 2-L Teflon bottles, positioned on a shaker table on a clean-air bench. The samples exposed to light were irradiated for 12 hours/day by a 75-watt tungsten/halogen lamp. Dark samples were shielded from light with several layers of black plastic bags. All solutions were subsampled using trace metal clean techniques over a 30 to 39-day period for Cu-complexing ligands, total dissolved Cu, DOC, DO, pH, and salinity.

Cu-complexing ligand photodegradation studies were performed by adding freshly collected porewater to NaCl solutions of the same salinity as the sampling site bottom water. These samples were then irradiated by a 1.2 kW Hg-arc lamp for up to 22 hours. These solutions were sub-sampled for Cu-complexing ligands, total dissolved Cu, DOC, pH, H_2O_2, and UV/Vis-absorbance.

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, 1997 and manuscript in prep). Cu- and Zn-ligand concentrations and conditional stability constants were determined by DPASV at a hanging mercury drop electrode (Donat et al., 1994); concentrations and conditional stability constants of the strongest Cu-complexing ligand were determined by ligand competition/adsorptive cathodic stripping voltammetry (Donat et al., 1994). Porewater DOC concentrations were determined by high temperature catalytic oxidation (Burdige and Homstead, 1994); porewater Fe, Mn, sulfide, nutrients, and $\sum CO_2$ were determined by standard methods.

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 Chesapeake Bay Sites M, S, and continental shelf Site WC7, and we have determined the benthic flux of TDCu and Cu ligands from Chesapeake Sites M and S. We have 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. We also completed one experiment to study the persistence of porewater-derived Cu-complexing ligands in the water column.

In FY 98, we completed a second study of the water-column persistence of porewater-derived Cu-ligands, and we expanded this study to include an investigation into the photodegradation of Cu-ligands. These ligand persistence and photodegradation experiments were designed to help us estimate how long Cu-complexing ligands fluxing from sediment porewaters might persist in the water column, and to what extent they might influence the complexation and speciation of Cu in the water column.

In FY 98, we added another important site, the Elizabeth River, and another important trace metal, Zn, to our studies. In the Elizabeth River, we measured porewater fluxes of TDCu, TDZn, and of Cu- and

Zn complexing ligands. We also determined porewater depth profiles of TDZn and Zn-ligand concentrations, and the conditional stability constants of Zn complexes at both Chesapeake Bay sites and at the Elizabeth River site.

To better understand the role of sediment processes in the production of metal-complexing ligands, we have also continued to study dissolved organic matter cycling in marine sediments. Specifically, we developed a conceptual model for DOM cycling in marine sediments (based on DOC size fractionation data; Burdige and Gardner, 1998) and, most recently, have performed studies of dissolved carbohydrates (Gardner and Burdige, 1998) and DOM fluorescence in marine sediment pore waters (Chen and Burdige, 1998).

We have presented our results at national meetings, and have submitted or are preparing manuscripts on: (1) the biogeochemistry of Cu and Cu-complexing ligands in estuarine and continental shelf sediments (Skrabal, Donat, and Burdige, manuscript in review); (2) the flux of Cu ligands from estuarine sediments (Skrabal, Donat, and Burdige, 1997); (3) the persistence of porewater-derived, Cu-complexing ligands in the water column (Price, Donat and Burdige, 1998; and manuscript in prep.); (4) Zn complexation and speciation in the Chesapeake Bay water column (Donat and Henry, 1997 and manuscript in prep.); (5) Zn complexation and speciation in Chesapeake Bay and Elizabeth River porewaters (Byers, Donat and Burdige, 1998; and manuscript in prep.); (6) the flux of Zn ligands from estuarine sediments (Byers, Donat, and Burdige, 1998 and manuscript in prep.); (7) dissolved carbohydrates in sediment porewaters (Gardner and Burdige, 1998 and manuscript in prep.); and (8) DOM-fluorescence in sediment porewaters (Chen and Burdige, 1998 and manuscript in prep.).

RESULTS

Cu Ligand Persistence- Chesapeake Bay Site M bottom waters contained at least three classes of Cu-complexing ligands. The concentration of the strongest ligand class, L_1 (log K' ~ 15) comprised 3-11% of the total Cu ligand pool, whereas the weaker ligand classes L_2 (log K' ~12) and L_3 (log K' ~8) comprised the remaining 89-97% of the Cu ligand pool. Greater than 99.9% of total dissolved Cu (TDCu) in the bottom waters was organically complexed, and ~88% of TDCu was complexed by L_1 .

L_1 concentrations in bottom water controls were relatively constant during the 30-day incubation, indicating that bottom water L_1 does not degrade on appreciable time scales. L_1 concentrations decreased slightly in porewater-spiked bottom waters incubated in the dark, suggesting that porewater-derived L_1 may degrade to some extent in the dark (4.7 nM reduction in 30 days). However, L_1 concentrations did not decrease appreciably in porewater-spiked bottom waters incubated in light. In fact, the strong L_1 ligands not only persisted during incubation, their concentration actually increased by over a factor of two, probably due to biological production. A similar result was observed in porewater-spiked NaCl solutions incubated in light. These results indicate that porewater-derived L_1 ligands (the strongest and most important ligand class) are persistent and, once transported into the overlying water, remain on appreciable timescales.

Bottom water samples devoid of added porewater showed little or no change in L_2 concentration over the 30 day incubation period. The same persistence trend was observed in porewater-spiked bottom waters up to day 20 of the incubation. After day 20, L_2 appeared to decrease. Slight degradation of L_2

was also indicated in porewater-spiked NaCl solutions. The majority of porewater-derived L_2 ligands remained after 39 days under both light and dark conditions (87 % and 98 %, respectively).

The weakest ligand class, L_3, persisted in bottom water controls under both light and dark regimes in agreement with results obtained for L_1 and L_2. Some L_3 degradation occurred in both light (20 % in 30 days) and dark (12 % in 30 days) porewater-spiked bottom waters. More substantial L_3 degradation was observed in porewater-spiked NaCl solutions; 54 % of L_3 degraded in the light and 76 % degraded in the dark over 39 days. It appears that L_3, the weakest and least important ligand class to Cu speciation, degrades, but ~35 % persists on appreciable timescales.

The ligand persistence experiments demonstrated that porewater-derived Cu ligands persevere for 30-39 days following their simulated flux into the overlying bottom water. As Chesapeake Bay water column Cu ligand concentrations do not appear to be increasing over time (Donat 1994), a degradation pathway must exist to preserve steady state concentrations. To further our understanding of the significance of porewater fluxes of Cu ligands to the overlying water column , we studied the most likely degradation pathway, photodegradation.

Cu Ligand Photodegradation- As expected, the total concentration of porewater-derived Cu-ligands (L_T) decreased when exposed to a Hg-arc light source. The experimental first order photodegradation rate was calculated to be 1.9×10^{-4} s^{-1}. We corrected this rate constant for: (a) the strength of the Hg-arc lamp compared to noon sunlight (using actinometry), (b) globally-averaged, photochemically-relevant irradiance, and (c) the attenuation of light in the water column. The corrected rate constant (8.6×10^{-8} s^{-1}) yielded a residence time of 135 days for the porewater-derived ligands in the Chesapeake Bay water column, with respect to photodegradation. Since the residence time of water in Chesapeake Bay is 9-12 months (Valle-Levinson, pers. comm.), the residence time of the porewater-derived Cu ligands, after photodegradation, suggests that although a large fraction of these porewater-derived Cu ligands may be photodegraded within the estuary, a significant export of the ligands from this source into the coastal zone may occur.

Total Dissolved Zn and Zn-Ligands- TDZn concentrations in Chesapeake Bay porewaters collected in November 1997 ranged from ~ 5- 60nM. In the mid Bay, TDZn concentrations in the upper 2cm of the porewaters (~10nM) were ~10x greater than in bottom waters, and remained at ~5 to 15nM down to 15cm. TDZn concentrations in the upper 2cm in the south Bay was ~2 to 3x greater than the bottom waters, and decreased to ~20nM at 15cm. TDZn concentrations in Elizabeth River porewaters ranged from ~1- 350nM, with profiles similar to the Chesapeake Bay. TDZn in the Elizabeth River porewaters was highest in the upper 2cm.

Zn-ligand concentrations in the upper intervals of the Chesapeake Bay and Elizabeth River porewaters ranged from ~700 to 2000nM, with conditional stability constants of ~10^7. Porewater Zn-ligand concentrations were 100-1000x greater than bottom water concentrations. The large excess of TDZn and Zn-ligand concentrations in the porewaters suggest that porewaters may be a source of TDZn and Zn-ligands to the overlying bottom waters. TDZn and Zn-ligand sediment fluxes in the Elizabeth River were analyzed using samples collected in April 1998, and samples collected in June 1998 are currently being analyzed to investigate fluxes of TDZn and Zn-ligands. Preliminary data from the April 1998 fluxes show that the sediments are indeed a source of both Zn-ligands, and very strong Cu-ligands, to the overlying water, and that the sediments in the Elizabeth River may act as a sink for TDZn.

Porewater DOM- Porewater DOM studies carried out in FY 98 have allowed us to further test and examine the porewater size reactivity model discussed above (Burdige and Gardner, 1998; also see Burdige and Zheng, 1998 and Burdige, 1998). Specifically, we have observed that the low molecular weight (< 3 kDa) porewater DOM accumulating with depth predominantly exhibits "humic"-like fluorescence, and that DOM with "protein"-like fluorescence is both produced and consumed in sediments. The molecular weight and total carbohydrate content of porewater DOM appear to be inversely related. Together these observations suggest that chemically-recognizable carbohydrates and proteins/peptides are preferentially found in the high molecular weight fraction of DOM, and that these materials may either be remineralized to inorganic nutrients or further broken down to refractory low molecular weight DOM that is no longer chemically recognizable as their biochemical precursors.

IMPACT

The speciation of metals in sediment porewaters governs both their fate (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 porewaters contain very high concentrations (up to micromolar) of very strong Cu ligands and moderately-strong Zn ligands, which should markedly influence the sediment/water exchange of these two metals. The very strong Cu ligands, and the Zn ligands, flux out of the porewaters into the overlying water column. Our most recent results indicate that the Cu-ligands persist in bottom waters for significant time periods ($\geq$ 30 days), which persist long enough to escape the estuary, thus potentially influencing 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), 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 Cu-speciation methods intercomparison with Bruland and Moffett (Bruland et al., in prep.).

The DOM fluorescence work described above was carried out with instrumentation purchased for use on another ONR project funded through the 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. Burdige PI).

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