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**METAL-COMPLEXING LIGANDS AND METAL SPECIATION IN SEDIEMENT
POREWATERS: IMPLICATIONS FOR SEDIMENT/WATER EXCHANGE AND
WATER COLUMN SPECIATION**

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FINAL REPORT

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**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 were 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 were 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 consisted of both field and laboratory efforts. In FY 1997, we conducted three research cruises. In fall '96 and spring and fall '97 we sampled the sediment porewaters and water column from two estuarine sites in Chesapeake Bay, having contrasting biogeochemical and physical characteristics (Sites M and S). We also sampled the sediment porewaters and water column from a site along the mid-Atlantic shelf/slope break (WC7).

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 N₂ and sediment intervals were centrifuged at in situ temperatures. Porewater samples were filtered (0.45 μm); subsamples for total 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 (0.22 μm 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, H₂O₂, 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 ΣCO₂ were determined by standard methods.

WORK COMPLETED

We have determined TDCu concentrations, Cu-complexing ligand concentrations, and Cu complexation and speciation in the sediment porewaters of Chesapeake Bay Sites M, S, mid-Atlantic continental shelf Site WC7, and one site in the Elizabeth River. We have determined the benthic flux of TDCu and Cu ligands from Chesapeake Sites M and S, and from the Elizabeth River site. We have determined TDZn concentrations, Zn ligand concentrations, and Zn complexation and speciation in the water column of Chesapeake Bay, and in Chesapeake Bay and Elizabeth River porewaters. We conducted these studies 2-3 seasons per year.

We also conducted experiments to study the persistence and photodegradation of porewater-derived Cu-complexing ligands in the water column. 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.

To better understand the role of sediment processes in the production of metal-complexing ligands, we studied dissolved organic matter (DOM) 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 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, 1999); (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

Total Dissolved Copper (TDCu) Concentrations and Fluxes -- TDCu concentrations in the pore waters from Chesapeake Bay Sites M, S, and continental shelf Site WC7 ranged from 0.1 to 25 nM, and were usually ≤ 10 nM. These concentrations were generally similar to bottom water concentrations, and are quite low compared to other anthropogenically-impacted estuaries (e.g., Narragansett and San Francisco Bays). TDCu fluxed out of the sediments at both Sites M and S in both spring and summer. In March '95, the TDCu flux out of site M sediments ($+41 \pm 10$ nmol/m²/d) exceeded that at site S ($+7 \pm 3$ nmol/m²/d). However, in June '95, the TDCu flux at site S ($+52 \pm 25$ nmol/m²/d) exceeded that at site M ($+13 \pm 15$ nmol/m²/d). Preliminary data on TDCu fluxes for July 1998 indicate that the Elizabeth River sediment porewaters are a source of both TDCu and Cu-ligands to the overlying bottom water.

Cu Ligand Fluxes -- We measured a significant total flux (200 to 800 nmol/m²/d) of Cu-binding ligands (TL_{Cu}) out of the sediments at Sites M and S in both spring and summer, but the TL_{Cu} flux at Site M exceeded that at Site S. The TL_{Cu} was 3-60 times greater than the TDCu flux, and the ligands fluxing out were comparable in strength ($\log K' = 15$) to that of the very strong L₁ class that controls the speciation of TDCu in most marine surface waters, and previously only observed in these surface waters. Sediment fluxes of this very strong ligand in June '95 ranged from 200 to 600 nmol/m²/d, representing up to 50% of the sediment TL_{Cu} flux, and exceeded TDCu by up to 20 times. Thus,

sediments may be a significant, but previously-unrecognized, source of Cu-complexing ligands to overlying waters.

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 ($\log K' \sim 15$) comprised 3-11% of the total Cu ligand pool, whereas the weaker ligand classes L_2 ($\log K' \sim 12$) and L_3 ($\log K' \sim 8$) 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 appeared that L_3 , the weakest and least important ligand class to Cu speciation, degraded, but ~35 % persisted on appreciable timescales.

The ligand persistence experiments demonstrated that porewater-derived Cu ligands persevered 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 $1.9 \times 10^{-4} \text{ s}^{-1}$. 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

($8.6 \times 10^{-8} \text{ s}^{-1}$) 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 (TDZn) and Zn-Ligand (L_m) Concentrations- TDZn concentrations in the Chesapeake Bay water column ranged from 3 to 40 nM. From 84% to $\geq 99\%$ of TDZn in the water column is organically-complexed with a single strong ligand class ($\log K'_{ZnL,Zn} = 9-10$), whose concentration ranges from 2 to 10x that of TDZn. Water column L_m concentrations were greatest in the north Bay and decreased by 10 times toward the Bay mouth. Zn^{2+} concentrations ranged from about 20 to 300pM. These Zn^{2+} concentrations lie within levels reported to be limiting and toxic to marine phytoplankton.

TDZn concentrations in Chesapeake Bay porewaters collected in November 1997 ranged from $\sim 5-60$ nM. In the mid Bay, TDZn concentrations in the upper 2cm of the porewaters (~ 10 nM) were ~ 10 x 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 ~ 20 nM at 15cm.

TDZn concentrations in Elizabeth River porewaters ranged from $\sim 1-350$ nM, with profiles similar to the Chesapeake Bay. TDZn in the Elizabeth River porewaters was highest in the upper 2cm. In March '98, TDZn in the Elizabeth River porewaters was greater than in the bottom water, but lower in the porewaters in April and July, '98.

L_m concentrations in the upper intervals of the Chesapeake Bay and Elizabeth River porewaters ranged from ~ 700 to 2000nM, with conditional stability constants of $\sim 10^7$. Porewater L_m concentrations were 100-1000x greater than bottom water concentrations. The large excess of TDZn and L_m concentrations in the porewaters suggest that porewaters may be a source of TDZn and L_m to the overlying bottom waters.

In the Elizabeth River, porewater L_m concentrations and vertical distributions were similar in March, April, and July '98. The majority (80-90%) of the TDZn in porewaters near the sediment/water interface was complexed, and there is some evidence at Site M that some of the dissolved Zn complexes may contain sulfide (as ZnS and $Zn_2S_3^{2-}$). This may suggest that Zn complexes at Site M are sulfide-containing organic complexes.

Total Dissolved Zn and Zn-Ligand Fluxes - In the Elizabeth River in April '98, a small flux of TDZn from overlying water into the sediments was observed (~ 2 mol day $^{-1}$) that could remove from 0.4 - 0.8% of standing stock of TDZn in Elizabeth River. In July '98, an opposite flux of TDZn from sediment pore waters into overlying water (~ 27 mol day $^{-1}$) was observed, that could supply from 6-11% of

standing stock in Elizabeth River

For both April and July '98, only a flux of the weaker Zn-ligand class ($\log K' \sim 7$) was observed in the Elizabeth River. In April, the Zn-ligand flux of $\sim 4.4 \text{ mol day}^{-1}$ from the porewaters into overlying water was measured; this flux could supply from 1-2% of the standing stock of the weaker Zn-ligand class in Elizabeth River. However, in July, the Zn-ligand flux into overlying water was nearly 10-times greater ($\sim 41 \text{ mol day}^{-1}$); this increased flux could supply from 8-17% of the standing stock of the weaker Zn-ligand class in Elizabeth River.

In both April and July '98, the increased flux of Zn-ligand over TDZn suggests that any Zn flux into the water column is predominantly organically complexed and not ionic Zn^{2+} .

Porewater dCHO and DOM- Dissolved carbohydrate (dCHO) concentrations in the sediment porewaters at three sites in Chesapeake Bay and continental shelf/slope sites ranged from ~ 40 to $500 \mu\text{M}$ (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: $< 3 \text{ kDa}$) 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.

Our porewater DOM studies 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 ($< 3 \text{ kDa}$) 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 (≥ 30

days), which persist long enough to escape the estuary, thus potentially influencing Cu complexation and speciation in coastal (and perhaps open ocean) waters.

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- Bruland, K.W., E.L. Rue, J.R. Donat, J.W. Moffett, and S.A. Skrabal. An intercomparison of analytical approaches to determine the chemical speciation of dissolved copper in a coastal seawater sample. Manuscript submitted to *Anal. Chim. Acta*, April 1999.
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Invited Conference Presentations:

- Burdige, D.J., S.A. Skrabal, and J.R. Donat. 1994. "The speciation of copper in pore waters and bottom waters of Chesapeake Bay and Atlantic coastal waters: Implications for sediment-water exchange." Fall AGU Meeting.
- Donat, J.R. 1994. "The speciation of dissolved copper and cadmium in the Chesapeake Bay". Fall AGU Meeting.
- Donat, J.R. 1995. "The speciation of copper and cadmium in the Chesapeake Bay". 209th National

ACS Meeting.

- Donat, J.R. 1997. "Determination of free Cu^{2+} and copper-organic complexes in marine and other natural waters." EPA's 20th Annual Conference on Analysis of Pollutants in the Environment.
- Donat, J.R. 1998. "Copper-complexing organic ligands in the Chesapeake Bay water column and sediment porewaters: Effects on copper speciation and implications of their sediment/water exchange". EPA's 21st Annual Conference on Analysis of Pollutants in the Environment.
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- Donat, J.R., S.A. Skrabal, and D.J. Burdige. 1995. "Copper complexation in pore waters and bottom waters of Chesapeake Bay and the Atlantic shelf/slope". 209th National ACS Meeting.
- Donat, J.R., S.A. Skrabal, and D.J. Burdige. 1996. "Effect of Speciation on sediment-Water Exchange of Metals". ONR Harbor Processes Workshop.
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Contributed Conference Presentations:

- Burdige, D.J. 1997. A conceptual model for dissolved organic matter (DOM) remineralization in marine sediments. Presented at 1997 GSA Annual Meeting.
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- Byers, D.G. and J.R. Donat. 1999. "Total dissolved zinc, zinc ligands, and conditional stability constants for zinc complexes in the sediment porewaters and bottom waters of Chesapeake Bay and the Elizabeth River, VA". Poster presentation at 1999 ASLO Aquatic Sciences Meeting.
- Donat, J.R. and C.W. Henry, III. 1997. "Concentrations, complexation, and speciation of dissolved zinc in Chesapeake Bay". Oral presentation at 213th American Chemical Society National Meeting.
- Price, D., J.R. Donat, and D.J. Burdige. 1997. "Fluxes of copper-complexing ligands from sediment to water column in Chesapeake Bay: Ligand persistence experiments." Poster presentation at the 1997 Chemical Oceanography Gordon Conference.
- Price, D., J.R. Donat, and D.J. Burdige. 1998. "Persistence of copper-complexing ligands derived from Chesapeake Bay porewaters: Implications to water column copper biogeochemistry." Oral presentation at Ocean Sciences Meeting.
- S.A. Skrabal, J.R. Donat, and D.J. Burdige. 1995. "The speciation of copper in pore waters and bottom waters of Chesapeake Bay and Atlantic coastal waters: Implications for sediment-water exchange". Poster presentation at Chemical Oceanography Gordon Conference.
- Skrabal, S.A., J.R. Donat, and D.J. Burdige. 1997. "Fluxes of strong copper-complexing ligands from estuarine sediments: A source to the water column?". Oral presentation at 213th American Chemical Society National Meeting.
- Zheng, S. and D.J. Burdige. 1997. "Dissolved organic nitrogen (DON) fluxes from coastal and continental margin sediments". Presented at 1997 ASLO Aquatic Sciences Meeting.
- Zheng, S. and D.J. Burdige. 1996. "The geochemistry of dissolved organic nitrogen in coastal sediment

pore waters". Presented at Ocean Sciences Meeting.

Invited Oral Presentations at Universities and Institutes, etc.:

- J.R. Donat: Duquesne University; 1999
 North Carolina Agricultural and Technical State University (Greensboro, NC); 1997
 University of Maryland, College Park; 1997
 Howard University (Wash., DC); 1997
 Randolph Macon College (Ashland, VA); 1997
 Old Dominion University Oceanography Dept.; 1997
 Instituto Nacional de Pesca (Montevideo, Uruguay); 1997
 Universidad Austral de Chile (Puerto Montt, Chile); 1997
 Universidad de Chile (Santiago, Chile); 1997
 Baylor University (Waco, TX); 1996
 California State University at Fullerton; 1996
 University of California, Santa Barbara; 1996
 California State Polytechnic University, San Luis Obispo; 1996
 Dalhousie University; 1996
 State University of New York, Stony Brook; 1995
 Hampden-Sydney College; 1995
 The George Washington University; 1995
- D.J. Burdige: University of Southampton (UK)
 Netherlands Institute of Ecology
 University of Utrecht (Netherlands)
 Southampton Oceanography Centre (UK)
 Texas A & M University