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Fluxes of copper-complexing ligands from estuarine sediments

Abstract—Most studies of the organic complexation of Cu in natural waters have focused on distributions and processes in the water column, where a significant fraction of Cu-complexing ligands may be biologically produced. We present direct evidence for a flux of Cu-complexing ligands from estuarine sediments, demonstrating that sediments are a significant, yet previously unrecognized source of the ligands. Fluxes of Cu-complexing ligands from Chesapeake Bay sediments range from 300 to 1,200 nmol m⁻² d⁻¹, exceeding fluxes of total dissolved Cu by 3–40-fold, suggesting that any Cu fluxing from the sediments is likely to be organically complexed. Our results indicate that benthic fluxes may supply from 10 to 50% of the standing stock of Cu-complexing ligands in Chesapeake Bay and suggest that such fluxes may strongly influence the biogeochemistry of Cu in shallow water environments and potentially in the ocean as a whole.

An increasing number of studies in oceanic and estuarine waters have focused on the influence of speciation (i.e. the distribution of a metal among its various forms) on the biogeochemical cycling of trace metals. Dissolved trace metals in natural waters may exist as hydrated ions and in complexes with inorganic and organic ligands (Stumm and Morgan 1996). Because the various species interact differently with the geochemical and biological components of seawater, knowledge of the speciation of a trace metal is essential to understanding its biogeochemical fate and transport, as well as its toxicity and bioavailability. For example, the availability and toxicity of trace metals such as Cu to organisms have been shown to be proportional to the activities of the free ionic forms of these metals and not simply to their total concentrations (Sunda and Guillard 1976; Brand et al. 1986).

In surface oceanic and estuarine waters, dissolved Cu appears to be complexed by at least two classes of organic ligands: a very strong class (commonly termed L₁) that generally exists at concentrations ranging from 1 to 40 nM, with conditional stability constants (with respect to free Cu²⁺ ion, K') of 10¹²–10¹⁴, and weaker classes (i.e. L₂, L₃) that exist at higher concentrations (6–150 nM) but with lower values of K' (10⁸–10¹⁰) (e.g. van den Berg 1984; van den Berg et al. 1987; Coale and Bruland 1988; Moffett et al. 1990; Sunda and Huntsman 1991; Donat et al. 1994; see Donat and Bruland 1995 for detailed review). On the basis of laboratory culture experiments and field observations, certain phytoplankton species have been postulated as sources of the strongest ligand class, L₁ (Moffett et al. 1990; Moffett and Brand 1994). The specific sources of the weaker ligands are not known. In general, all classes of these ligands represent various fractions of dissolved or colloidal organic matter, including phytoplankton exudates, as well as their degradation products (Anderson et al. 1984; Seritti et al. 1986; Robinson and Brown 1991; Kerner and Geisler 1995). In addition, various sulfide and polysulfide species, particularly in

suboxic or anoxic water and sedimentary environments, may complex varying fractions of Cu and other metals (Boulegue et al. 1982; Luther and Tsamakis 1989).

The waters of estuarine and coastal sediments are commonly enriched in dissolved organic matter (DOM) relative to bottom waters (Burdige et al. 1992; Burdige and Homstead 1994; Alperin et al. 1994), and fluxes of dissolved organic carbon (DOC) from such sediments have been observed (Burdige et al. 1992; Burdige and Homstead 1994). Because ligands that complex Cu and other metals form a small but important fraction of the total DOM pool, sediment pore waters could be a source of Cu-complexing ligands to the overlying waters. The association of Cu with organic matter in pore waters has been demonstrated previously (Elderfield 1981; Boussemart et al. 1989), although the role of this association in influencing speciation and the sediment–water exchange of Cu has not been adequately addressed. By applying sensitive, low-volume analytical methods [anodic stripping voltammetry at a hanging mercury drop electrode (ASV-HMDE) for determining Cu-complexing ligands (Donat et al. 1994) and a chemiluminescence method (Sunda and Huntsman 1991) for determining total dissolved Cu], we have determined that sediments can be a significant source of Cu-complexing ligands and total dissolved Cu (TDCu) to the overlying water column. We are currently evaluating the significance of these sources and their implications for the biogeochemical cycling of dissolved Cu in sedimentary pore waters from two contrasting sites in Chesapeake Bay, a large, productive estuary on the eastern coast of the United States (Fig. 1).

Previous studies show that biogeochemical processes at the mid-Bay Sta. M are dominated by high rates of anaerobic bacterial activity and that benthic fluxes are largely controlled by diffusive transport (Burdige and Homstead 1994; Marvin 1995). Sediments at the lower Bay Sta. S are highly bioturbated, have lower overall rates of sediment carbon oxidation (as measured by ΣCO₂ production), and are dominated by mixed aerobic and anaerobic decomposition processes. The magnitude and effects of these processes vary seasonally (Burdige and Homstead 1994; Marvin 1995; also, see the DOC and ΣCO₂ fluxes in Table 1).

Sediment cores used for the porewater analyses were collected with a stainless steel box corer and subcored using acrylic core tubes (11.4-cm diam). The cores were cut into intervals of 1–3 cm using apparatus similar to that described by Shaw (1989). Pore waters were separated by centrifugation, then syringe-filtered (0.45 μm) into Teflon bottles. All implements used to collect, process, and store the samples were extensively acid-washed to prevent contamination. To prevent oxidation artifacts, all processing steps took place in N₂-filled glove bags, and samples were stored refrigerated in the dark in N₂-charged jars.

Concentrations of TDCu in pore waters at both sites during all seasons ranged from ≤0.1 to 25 nM and were usually

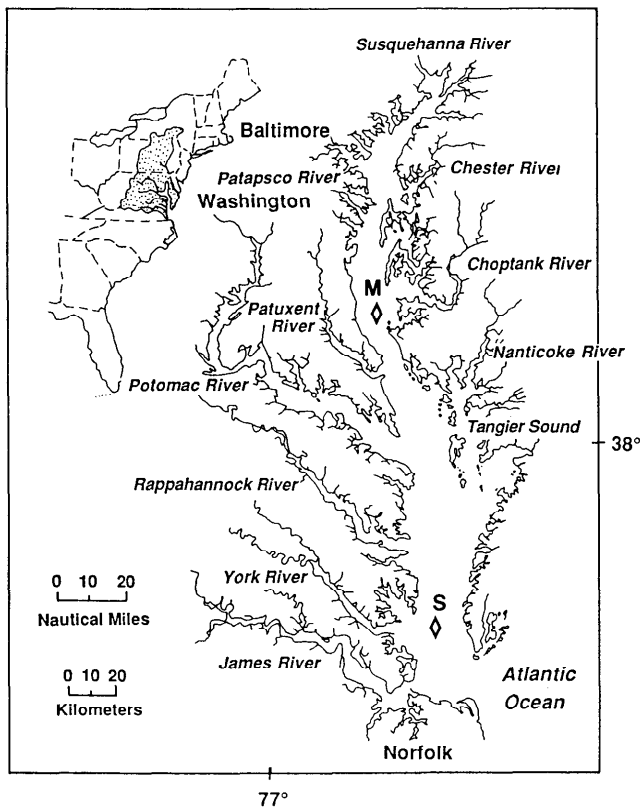


Fig. 1. Map of Chesapeake Bay, showing the locations of sampling stations M and S.

≤ 10 nM (representative data are shown in Fig. 2). This range of concentrations is relatively low in comparison to porewater and water-column TDCu concentrations from other anthropogenically affected estuaries (e.g. Narragansett Bay, south San Francisco Bay) (Donat et al. 1994; Elderfield et al. 1981; Flegal et al. 1991) but is comparable to those observed in other coastal sediment pore waters (Shaw et al. 1990; Rivera-Duarte and Flegal 1995). In Chesapeake Bay, the uppermost porewater concentrations (2–10 nM) were

typically within a factor of two of the bottom-water concentrations (4–10 nM; Donat 1994). Based solely on the gradient at the sediment–water interface, Bay sediments could be either sources or sinks of TDCu to the overlying waters.

Copper titrations using ASV-HMDE indicated that virtually all (96.9 to >99.9%) of the TDCu in pore waters and bottom waters at both sites exists in a nonlabile form, probably as organic or mixed inorganic–organic (e.g. sulfide-containing) complexes. At least two classes of Cu-complexing ligands, which we denote as weak and strong, were differentiated on the basis of the relative strengths of their Cu complexes. We estimate the conditional stability constant (with respect to ionic Cu^{2+}), K' , of the weak ligand class to be $\sim 10^7$ – 10^{10} , which is consistent with the K' of the weaker ligands (10^8 – 10^{10}) found in oceanic and estuarine waters. To date, we have obtained only a lower limit for K' for the strong ligand class (i.e. $>10^7$ – 10^{10}), which is consistent with the K' of the strong ligand class (L_1) found in seawater (10^{12} – 10^{14}) (e.g. van den Berg 1984; Coale and Bruland 1988; Moffett et al. 1990; Sunda and Huntsman 1991; Donat et al. 1994). Concentrations of the strong ligand in the pore waters ranged between 200 and 13,000 nM, whereas concentrations of the weak ligand class ranged between 100 and 6,500 nM (Fig. 2). Total concentrations of Cu-complexing ligands in the upper porewater intervals were 15 to >100 times higher than the bottom-water ligand concentrations (30–60 nM; Donat 1994), suggesting that the sediments are potentially a significant source of ligands to the overlying waters.

The greater concentrations of the strong ligand class in pore waters relative to the weaker class contrast with previous observations in estuarine and oceanic waters, in which the strong ligand class (L_1) comprises only a small fraction of the total ligand concentration (van den Berg 1984; Moffett and Zika 1987; Sunda and Hanson 1987; Coale and Bruland 1988; Sunda and Huntsman 1991; Donat et al. 1994). The differences in concentrations of the two ligand classes might suggest that the weak ligand class in sediment pore waters may be kinetically more labile than the strong ligand class. This observation also contrasts with that suggested for Cu-complexing ligands in the water column, in that the lower

Table 1. Results of flux experiments, Chesapeake Bay sediments. All fluxes are out of the sediment.

Station	Date	Bottom water (incubation) temp. ($^{\circ}\text{C}$)	TDCu flux ($\text{nmol m}^{-2} \text{d}^{-1}$) ($n = 3$)	Total Cu-ligand flux ($\text{nmol m}^{-2} \text{d}^{-1}$) ($n = 1$)	DOC flux ($\text{mmol m}^{-2} \text{d}^{-1}$) ($n = 3$)	ΣCO_2 flux ($\text{mmol m}^{-2} \text{d}^{-1}$) ($n = 3$)
M	March 1995	6	53 ± 17	320 ± 80	0.67 ± 0.16	8.8 ± 5.8
	June 1995	22	30 ± 10	$1,200 \pm 170$	1.83 ± 0.68	16.6 ± 4.8
S	March 1995	6	11 ± 4	440 ± 160	0.20 ± 0.08	1.3 ± 2.0
	June 1995	22	85 ± 25	420 ± 95	0.63 ± 0.22	21.0 ± 5.2

These fluxes were determined by core incubation techniques described previously for determining benthic dissolved organic carbon (DOC) and ΣCO_2 fluxes (Burdige and Homstead 1994). As discussed in this reference, much of the uncertainty in these flux estimates stems from spatial variability (leading to different fluxes from cores at the same box-coring site), rather than to analytical uncertainty in the individual measurements. The DOC and ΣCO_2 fluxes reported here are similar to previously published values for these sediments at the same temperatures (Burdige and Homstead 1994).

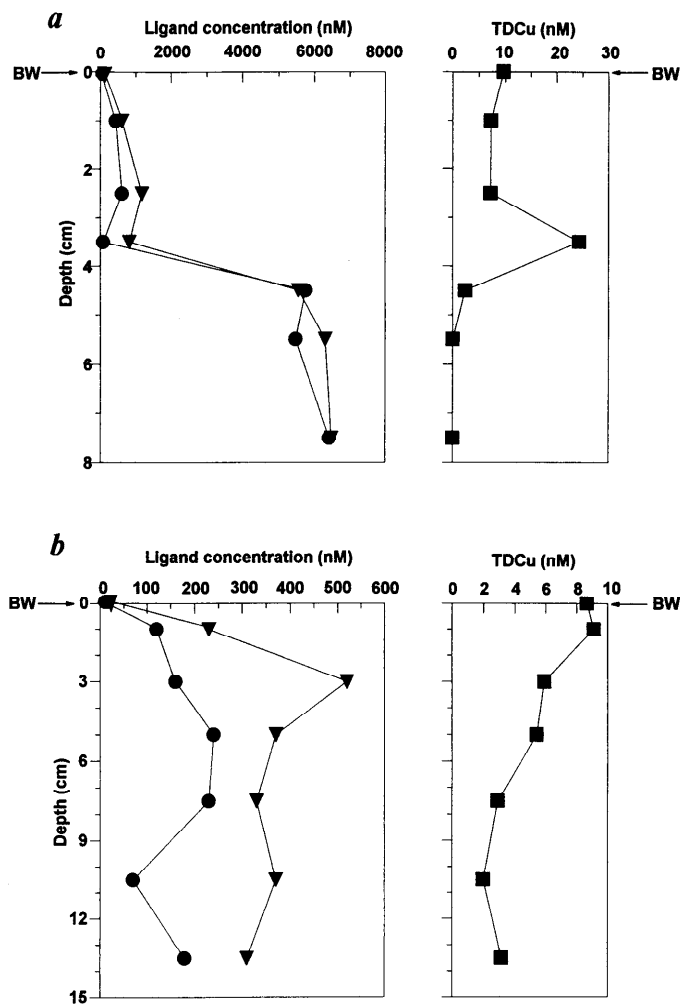


Fig. 2. Porewater distribution of weak Cu-complexing ligands (●), strong Cu-complexing ligands (▼), and TDCu (■) at Sta. M (a) and Sta. S (b) in Chesapeake Bay, April 1994. Bottom-water ligand and TDCu concentrations are denoted by BW.

concentrations of the stronger ligands and their appearance only in surface waters suggests greater kinetic lability (e.g. Donat et al. 1986; Coale and Bruland 1988, 1990; Moffett et al. 1990). However, the exact sources and lability of these ligands, in either the water column or in sediment pore waters, are not presently well defined.

Direct measurements of fluxes of TDCu and total Cu-complexing ligands were obtained using incubated cores collected in March and June 1995, using the approach described in Burdige and Homstead (1994) but modified for trace metal analysis (using 14-cm diam, acid-washed acrylic cores, rather than glass cores). Sample aliquots were withdrawn from water overlying the sediment cores and analyzed for total ligand concentration (which includes the sum of the weak and strong fractions as described above), TDCu, DOC, and ΣCO_2 . The withdrawn water volumes were replaced by equal volumes of bottom water collected at the same time as the sediment cores. Fluxes were determined by linear least-squares fitting of the data points, taking into account any changes with time in Cu-complexing ligand concentra-

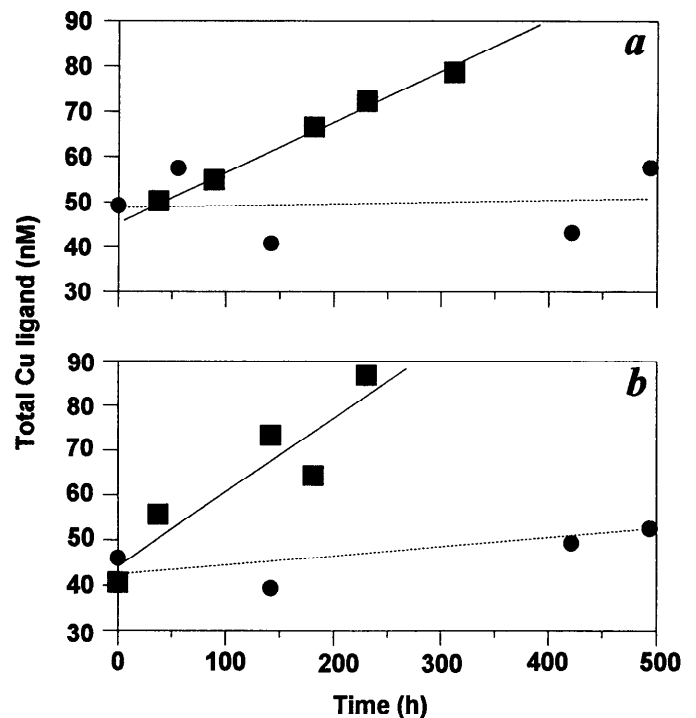


Fig. 3. Concentration of total Cu-complexing ligands (■) vs. time in core incubations of sediments from Sta. M (a) and Sta. S (b), Chesapeake Bay, March 1995. Regression lines are shown for the water overlying the core (—) and for the recharge water (denoted by ● and ---).

tions in the recharge bottom water used to replace that removed from the water overlying the core. The corrected time rates of change in Cu-complexing ligands were converted into benthic fluxes, accounting for both the volume of water overlying the cores and the surface area of the core tubes. Further details of the flux calculations are described in Burdige and Homstead (1994) but modified for trace metal analysis. The excellent agreement between the DOC and ΣCO_2 flux results of this study and those of Burdige and Homstead (1994) support the validity of this approach for measuring benthic fluxes.

The March results indicate a small flux of TDCu from sediments at Sta. M into the overlying waters and a negligible benthic TDCu flux from sediments at Sta. S (Table 1). Results from June 1995 show a relatively low benthic flux of TDCu from sediments at Sta. M and a relatively high flux from Sta. S sediments (Table 1). The decrease in TDCu fluxes from Sta. M from March to June 1995 indicates increasing Cu uptake into insoluble sulfide phases (Huerta-Diaz and Morse 1992) due to increasing sulfide production as the rate of sulfate reduction increased during this period (Burdige and Homstead 1994; Marvin 1995). The TDCu fluxes are within the range of fluxes summarized by Rivera-Duarte (1995) for a number of estuarine and coastal systems ($-6,500$ to $11,300$ $\text{nmol m}^{-2} \text{d}^{-1}$), with 73% of the measurements in the range of ± 300 $\text{nmol m}^{-2} \text{d}^{-1}$). The variability in the fluxes we report is quite small relative to that reported by Kuwabara et al. (1996) over a 2-week period in San Francisco Bay ($-4,200$ to $1,100$ $\text{nmol m}^{-2} \text{d}^{-1}$), which may be attributable to differences in pollutant loading and biogeochemical characteristics between

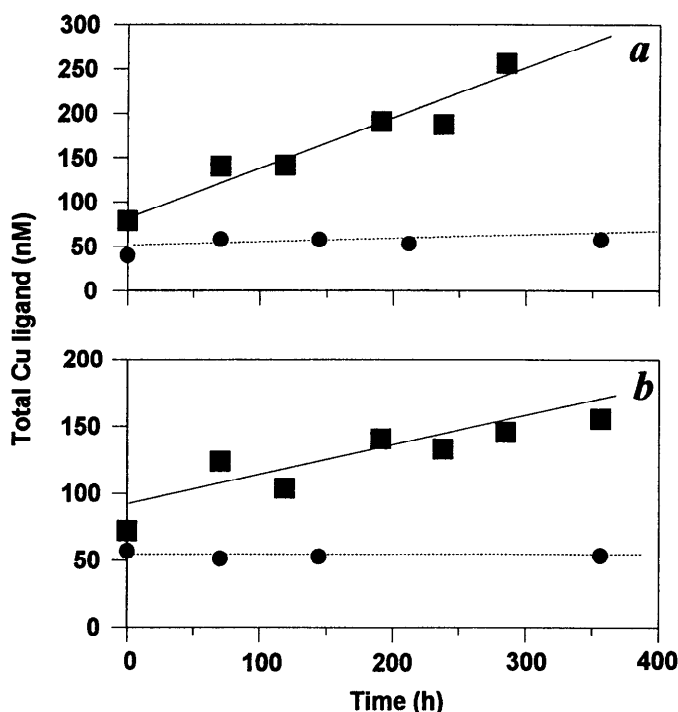


Fig. 4. Core incubation results for Sta. M (a) and Sta. S (b), June 1995. Symbols and lines are the same as in Fig. 3.

the two systems. We will present a detailed discussion of the biogeochemistry of Cu and Cu-complexing ligands in Chesapeake Bay sediments, including comparisons to other systems, in a separate publication.

In both seasons, we detected a flux of Cu-complexing ligands (expressed as a total of all ligand classes) from sediments to the overlying waters, which exceeded the flux of TDCu by 3- to >40-fold (Table 1). These data suggest that any Cu fluxing from the sediments is likely to be organically complexed. The total ligand fluxes are a small fraction (0.05–0.2%) of the DOC flux. Total dissolved sulfide, which can form soluble complexes with Cu and might be expected to flux out of anoxic sediments (as at Sta. M), was measured at the conclusion of the June 1995 experiment. The sulfide concentrations (Sta. M, 52 nM, Sta. S, 11 nM) constitute no more than ~10–30% of the total ligand concentrations (Sta. M, 170 nM, Sta. S, 110 nM). Thus, although sulfide also forms complexes with Cu, particularly in waters overlying anoxic sediments (such as Sta. M), we find that organic ligands must account for the bulk of the total ligand flux.

We are currently trying to quantify more completely the concentrations and strengths of the various ligand classes fluxing out of Bay sediments. Preliminary results using competitive ligand (8-hydroxyquinoline) equilibration, coupled with adsorptive cathodic stripping voltammetry (Donat 1994; Donat et al. 1994) on water samples from core incubation experiments in June and October 1995, suggest that a significant fraction (perhaps up to 50%) of the total ligand pool fluxing out of the sediments is very strong, with K' values of $\sim 10^{15}$. Previous field and laboratory observations suggest that strong Cu-complexing ligands (with $K' > 10^{13}$) may be produced by cyanobacteria such as the ubiquitous

coastal and oceanic species, *Synechococcus* (Moffett et al. 1990; Moffett and Brand 1994). On the basis of our preliminary experiments, the K' of the strong ligand class fluxing from Chesapeake Bay sediments is consistent with that of the strong ligand class found in the overlying waters, although the relative importance of the sediment source and the phytoplankton source remains to be determined and may vary among different ocean regimes. Thus, sediments are a significant, but previously unrecognized, source of Cu-complexing ligands to the overlying waters.

In most oceanic surface waters, levels of the strong ligand class (L_1) are sufficient to completely complex all TDCu and control its speciation (Moffett and Zika 1987; Coale and Bruland 1988; Sunda and Huntsman 1991; Donat and van den Berg 1992; Sunda and Hanson 1987). However, concentrations of L_1 can be less than TDCu concentrations in estuarine and coastal waters, such as Chesapeake Bay (Donat 1994) and South San Francisco Bay (Donat et al. 1994). In such cases, Cu complexation becomes more important with weaker ligand classes (i.e. L_2 , L_3) than with L_1 . Thus, the relative proportions of the different ligand classes control the overall speciation of Cu in such environments.

Addition of Cu-complexing ligands in relatively shallow estuarine and coastal waters by sediment–water exchange may strongly influence the biogeochemistry and cycling of dissolved Cu in the overlying water columns. Given an average concentration of Cu-complexing ligands of 75 nM (Donat 1994) and water residence time of 9–12 months in Chesapeake Bay (A. Valle-Levinson pers. comm.), we calculate that benthic fluxes could supply 10–50% of the standing stock of ligands in the water column. Depending on the time scales over which these ligands are degraded in the water column, relative to physical processes that transport them out of the estuary to the coastal ocean and perhaps the open ocean, this benthic flux of Cu-complexing ligands may play an important role in the oceanic cycles of Cu and Cu-complexing ligands. We are currently studying the lifetimes of these ligands in Bay waters.

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