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## ABSTRACT

Dissolved zinc speciation was determined seasonally in the water column and in benthic flux experiments at two contrasting sites in the Cape Fear estuary (CFE) over a 2 ½ year period. Total dissolved zinc concentrations (TDZn) ranged from non-detectable (ND) to 44 nM in the middle estuary and ND to 61 nM in the lower estuary. Zinc-complexing ligand concentrations, determined using competitive ligand equilibrium - cathodic stripping voltammetry, ranged from 10 to 102 nM in the middle estuary and ND to 67 nM in the lower estuary. One class of Zn-complexing ligands was determined with conditional stability constants ranging from  $10^{7.0}$  to  $10^{9.2}$ , similar to what has been observed in other estuaries. Concentrations of TDZn and Zn-complexing ligands did not fluctuate seasonally in the middle estuary; however there were higher TDZn and Zn-complexing ligands in the lower estuary in the fall compared to spring and winter. Concentrations of both constituents in the middle estuary were greater in the spring and winter compared to the lower estuary. No statistically significant correlations were found between TDZn and Zn-complexing ligands with dissolved organic carbon (DOC). This behavior differs from that observed for Cu-complexing ligands in previous studies of the CFE in which ligands were strongly correlated to DOC. Organically complexed Zn ranged widely from 25 to 84%. In contrast, previous studies showed that concentrations of Cu-complexing ligands were always much greater than total dissolved Cu concentrations and > 99.9 % of Cu was organically complexed.

Statistically significant fluxes of TDZn were observed in 40% of incubated cores of bottom sediments at both sampling stations over all sampling periods. These fluxes of TDZn ranged from -1100 to 1800 nmol m<sup>-2</sup> d<sup>-1</sup>. Only 27% of the cores showed

statistically significant fluxes of Zn-complexing ligands, ranging from -1700 to 2900  $\text{nmol m}^{-2} \text{d}^{-1}$ , where a positive flux represents the movement of the dissolved species from the sediments to the overlying water. The sporadic nature of benthic fluxes of both TDZn and Zn-complexing ligands, combined with the short residence time of water in the CFE, suggests that sediments are not a significant source or at least not a continual source of either constituent to overlying waters of the CFE. However, the ligands that flux out of the sediment are indistinguishable from those in the water column, suggesting that at least a portion of the water column ligands could be derived from sedimentary processes.

Previous studies of Cu speciation in the CFE show that significant benthic fluxes of Cu-complexing ligands did not coincide with fluxes of significant Zn-complexing ligand fluxes. Also, humic substances extracted from Cape Fear freshwater did not detectably complex dissolved Zn. In contrast, previous studies have shown that humic substances from the CFE are very strong Cu complexants. Therefore, the ligands complexed to Zn and Cu are different and their behaviors are decoupled in the Cape Fear estuary.

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## DEDICATION

I would like to dedicate this thesis to my parents, Terry and Trish Lieseke, and to the memory of my grandma, Mary Frances Kelly, who have taught me that with God's love all things are possible.

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