

TABLE OF CONTENTS

ABSTRACT	iv
ACKNOWLEDGEMENTS	vi
DEDICATION	vii
LIST OF TABLES	viii
LIST OF FIGURES	ix
INTRODUCTION	1
Background	1
The Role of Sediments	3
EXPERIMENTAL	4
Study Location	4
Sampling	4
Total Dissolved Zn	8
Zn Speciation Determinations	9
Speciation Calculations	11
Flux Calculations	14
Humic Substances Extractions	14
RESULTS AND DISCUSSION	15
Total Dissolved Zn and Zn-Complexing Ligands	15
Role of Humics as Zn-Complexing Ligands	28
Benthic Fluxes	31
Total Dissolved Zn Fluxes	31
Zn Ligand Fluxes	34

Comparison of Zn and Cu Speciation and Fluxes	36
Characterization of Zn Ligands	38
CONCLUSIONS.....	41
REFERENCES	43

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⁻² d⁻¹. 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.

LIST OF TABLES

Table	Page
1. Voltammetric analyzer settings for the analysis of Zn speciation	12
2. Concentrations of (a) total dissolved Zn and (b) Zn-complexing ligands from bottom water at time point T0 from Station 1 and Station 2 at each sampling time (ND = non-detectable)	16
3. Concentrations of TDZn and Zn-complexing ligands in selected estuarine environments.....	18
4. Summary of salinity, DOC, and river flow of Station 1 and Station 2 during each sampling time	22
5. Total dissolved Zn fluxes for individual core measurements at Station 1 and Station 2 at each sampling date. Negative values indicate a flux into the sediment. Positive values indicate flux out of the sediment. Non-statistically significant fluxes are represented as “0” net flux. n = number of cores per sampling site. p = level of significance.....	32
6. Fluxes for TDZn and Zn-complexing ligands in different estuarine systems. Negative values indicate a flux into the sediment. Positive values indicate flux out of the sediment.	33
7. Zn-ligand fluxes for individual core measurements at Station 1 and Station 2 at each sampling date. Negative values indicate a flux into the sediment. Positive values indicate flux out of the sediment. Non-statistically significant fluxes are represented as “0” net flux. n = number of cores per sampling site. p = level of significance.....	35
8. Zn-ligand and Cu-ligand fluxes for individual core measurements at Station 1 and Station 2 for each sampling date. Negative values indicate a flux into the sediment. Positive values indicate flux out of the sediment. Non-statistically significant fluxes are represented as “0” net flux. n = number of cores per sampling site	37

LIST OF FIGURES

Figure	Page
1. Map of the Cape Fear estuary showing the two sampling sites, Station 1 and Station 2.....	5
2. Relationship between TDZn and Zn-complexing ligands from bottom waters at both sampling stations at all sampling times. There is no statistically significant correlation between the two parameters ($p > 0.05$)	19
3. Relationship between TDZn and Zn-complexing ligands from bottom waters at (a) Station 1 (no significant correlation; $p > 0.05$) and (b) Station 2 (significant correlation; $p \leq 0.01$)	20
4. Relationship between DOC concentrations and salinity from bottom waters at both sampling stations at all sampling times (significant correlation; $p \leq 0.001$)	23
5. Relationship between (a) TDZn and (b) Zn-complexing ligands and DOC from bottom waters at both sampling stations at all sampling times. Both plots show no statistical significance ($p > 0.05$).....	25
6. Relationship between DOC concentrations and river flow, showing a statistically significant correlation ($p \leq 0.01$).....	26
7. Relationship between (a) TDZn and (b) Zn-complexing ligands and river flow from bottom waters at both sampling stations at all sampling times. Both plots show no statistical significance ($p > 0.05$)	27
8. Titration curves in the (a) presence and (b) absence of C_{18} extracted humic substances (20 mg/L) in UV-irradiated diluted seawater (salinity = 10)	29
9. Titration curve showing complexation of Cu in a 19.5 mg/L solution of humic substances (extracted from the CFE) in UV-irradiated diluted seawater (salinity = 12). Data from Shank (2003)	30
10. Typical titration curve in the (a) presence and (b) absence of Zn-complexing ligands. (a) October 2001, Station 1, Time point T5. (b) June 2002, Station 2, Time point T5.....	39
11. Typical Ruzic-van den Burg linearization of a titration curve indicating the presence of one Zn-complexing organic ligand. Cape Fear estuary, March 2002, Station 2, Timepoint T0.....	40