

THE ROLE OF BENTHIC MACROFAUNA IN INFLUENCING FLUXES AND
SPECIATION OF DISSOLVED ZINC AND COPPER IN ESTUARINE SEDIMENTS

Kenneth A. MacGillivray

A Thesis Submitted to the
University of North Carolina at Wilmington in Partial Fulfillment
Of the Requirements for the Degree of
Master of Science

Department of Chemistry

University of North Carolina at Wilmington

2002

Approved by

Advisory Committee

_____ Chair

Accepted by

Dean, Graduate School

TABLE OF CONTENTS

ABSTRACT	iii
ACKNOWLEDGEMENTS	v
DEDICATION	vi
LIST OF TABLES	vii
LIST OF FIGURES	viii
INTRODUCTION	1
Background	1
Goals	6
METHODS	7
Sediment and Water Collection from the Estuary	7
Core Incubation Experiments	9
Total Dissolved Metal Determinations	11
Copper and Zinc Speciation Experiments	15
RESULTS AND DISCUSSION	18
Fluxes of Total Dissolved Metals and Ligands	18
Cu- and Zn-Complexing Ligand Fluxes.....	27
Role of Bioturbation in Fluxes in Cape Fear Estuary.....	32
Characterization of Cu and Zn Ligands	33
Role of Benthic Fluxes and Cape Fear Estuary.....	34
SUMMARY	36
REFERENCES CITED	37

ABSTRACT

Sediment flux experiments were carried out for sediment and water samples collected on April 23, 2001 and June 26, 2001 from a site in the lower CFR estuary. Benthic fluxes were determined for total dissolved copper (Cu) and zinc (Zn) and the ligands that bind these metals. Benthic fluxes of total dissolved Cu (TDCu) ranged from 130 to -180 $\text{nmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, where a negative flux represents the migration of a species from the sediment into the overlying water. The copper-complexing ligand fluxes ranged from 590 to -1030 $\text{nmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. Total dissolved Zn (TDZn) fluxes ranged from 56 to -300 $\text{nmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ and the Zn-complexing ligand fluxes ranged from 1220 to -980 $\text{nmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. Fluxes of both TDCu and TDZn were several times lower than the concentration of metal-binding ligands, suggesting that both Cu and Zn are largely complexed when they flux from sediments. There were no significant differences ($\alpha = 0.05$) between the two seasons in the fluxes of TDZn and Zn- and Cu-complexing ligands. However, fluxes of TDCu were significantly greater in April than in June.

The role of bioturbation in influencing benthic fluxes of these chemical species was also investigated using *Streblospio benedicti*, an opportunistic species common in the lower Cape Fear estuary. The presence of these polychaetes did not significantly affect fluxes of metals or ligands in any of the experiments.

Speciation analysis using competitive ligand equilibration – cathodic stripping voltammetry revealed that Cu was bound by a single strong class (L_1) whose K_{cond} ranged from $10^{13.5}$ to $10^{14.5}$, a result consistent with studies of Cu in this and other estuaries. Zn speciation analyses revealed qualitatively that there are two separate ligand classes

responsible for binding dissolved zinc. The conditional stability constants of the two ligand classes are too close in value ($\sim 10^{7.5}$) to compute values for each ligand class.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Stephen Skrabal, for being a knowledgeable, generous, and patient mentor. He has made this project possible by sharing his time, expertise, and good humor when I needed it most. To adequately thank him would require more space than is available here.

I would also like to thank Dr. Robert Whitehead for his advice about instrumentation, research methods, and careers in academia. His guidance inside and outside the lab is appreciated. Thanks also go out to Dr. Robert Kieber, who as my committee member and graduate program coordinator helped me to accomplish my goals in graduate school.

Special thanks are in order for Dr. Ned Martin, Dr. Pamela Seaton, and Dr. James Kiddle, three unofficial mentors who convinced me that I was capable of graduate work at the M.S. level and beyond.

I would like to thank my fellow graduate students for their support and cooperation, especially Chris Shank, Kristie Lieseke and Cliff Smith. Their willingness to share ideas and laboratory facilities is appreciated.

My family and friends, especially Brendan Doyle, provided necessary perspective during times of duress.

Finally, I would like to acknowledge the love and support of Bethany Pridgen, who reminded me on many occasions that life can be fun and exciting outside the chemistry lab as well as inside it.

DEDICATION

This thesis is dedicated to my parents, Ken and Una MacGillivray. Their faith, patience, optimism, and wisdom helped replenish my well whenever it ran dry.

LIST OF TABLES

Table	
Page	
1. Instrumental parameters and reagent concentrations used in the total dissolved metal concentrations of Cu and Zn	14
2. Instrumental parameters and reagent concentrations used in the CLE-CSV titrations of Cu and Zn	17
3. Total dissolved copper concentrations and fluxes for the (a) April 23, 2001 experiment and the (b) June 26, 2001 experiment.....	20
4. Concentrations of (a) total dissolved copper and (b) Cu-complexing ligand in selected estuarine environments.....	21
5. Comparison of TDCu and TDZn fluxes for different estuarine environments.....	22
6. Total dissolved zinc concentrations and fluxes for the (a) April 23, 2001 experiment and the (b) June 26, 2001 experiment.....	25
7. Concentrations of total dissolved Zn and Zn-complexing ligand in selected estuarine environments.....	26
8. Copper ligand concentrations and fluxes for the (a) April 23, 2001 experiment and the (b) June 26, 2001 experiment.....	29
9. Zinc ligand concentrations and fluxes for the (a) April 23, 2001 experiment and the (b) June 26, 2001 experiment.....	31

LIST OF FIGURES

Figure	Page
1. Illustration of the estuarine box model	5
2. Map showing the channel marker 35 (M-35) sampling site	8
3. Diagram of apparatus used in core incubation experiments.....	10
4. Concentration of total dissolved copper vs. time for six cores during (a) the April 23, 2001 and (b) the June 26, 2001 sediment flux experiments.....	19
5. Concentration of total dissolved zinc vs. time for six cores during (a) the April 23, 2001 and (b) the June 26, 2001 sediment flux experiments.....	24
6. Concentration of copper-binding ligands vs. time for six cores during (a) the April 23, 2001 and (b) the June 26, 2001 sediment flux experiments.....	28
7. Concentration of zinc-binding ligands vs. time for six cores during (a) the April 23, 2001 and (b) the June 26, 2001 sediment flux experiments.....	30