

## INTRODUCTION

### Background

The lower Cape Fear River is vital to southeastern North Carolina for several reasons. Citizens and industries in the Cape Fear region use the river not only as a consumable resource, but also as a sink for waste waters, both treated and untreated. The river also hosts two important shipping terminals: the Port of Wilmington, one of the state's two commercial ports, and the Military Ocean Terminal Sunny Point (MOTSU), a military shipping terminal near Southport at the river's terminus. Point sources and runoff water associated with agriculture, shipping, industry, and municipal development ultimately drain into the Cape Fear River. Anthropogenic contaminants associated with these activities can potentially degrade water quality and have deleterious effects on the Cape Fear estuarine ecosystem.

Two of these potential contaminants are copper (Cu) and zinc (Zn), which are widely used in numerous products associated with human and industrial activity. Zinc is a key component of paint pigments, is added to animal feed and fertilizers, is present in anti-fouling hardware for ships, and is the metal used for galvanization (Gupta and Karuppiah, 1996; Comber et al. 2002; Heijerick et al., 2002). Copper is present in feeds and fertilizers, wood preservatives, water tubing, and anti-fouling paints for ship and boat bottoms (Seligman and Zirino, 1998). Metals such as Cu and Zn occur naturally at low dissolved concentrations and are necessary trace nutrients for native biota. However, at higher concentrations these metals can be toxic to organisms such as phytoplankton (Sunda and Guillard, 1976; Brand et al., 1983; Brand et al., 1986) which form the base of the food chain and support higher trophic levels in estuaries and the ocean.

Numerous studies have demonstrated the importance of metal speciation in controlling the toxicity, bioavailability, and geochemical behavior of trace metals such as Cu and Zn in estuarine and oceanic waters (see Bruland et al., 1991 and Donat and Bruland, 1995; and references therein). Speciation of a metal is defined as its distribution among various organic and inorganic forms, including inorganically complexed, organically complexed, and free hydrated ionic forms (Donat and Bruland, 1995). In many studies of estuarine waters, dissolved Cu speciation is dominated by at least two classes of organic ligands: a very strong class ( $L_1$ ) which usually exists at relatively lower concentrations but with a large conditional stability constant (with respect to free  $Cu^{2+}$  ion,  $K'$ ) of  $10^{11}$  to  $10^{15}$ ; and relatively weaker classes ( $L_2, L_3$ ) with generally higher concentrations but smaller values of  $K'$  ( $10^8 - 10^{10}$ ) (Apte et al. 1990; Moffett et al. 1990; Donat et al. 1994; Moffett, 1995). This large degree of complexation leads to virtually all total dissolved Cu (>99.9%) existing as relatively strong Cu-organic complexes in most estuarine and marine waters.

Zinc speciation in estuarine waters is less well known, primarily because there are fewer methods to characterize Zn-organic complexes in natural waters. However, in estuarine waters, one or two classes of ligands have been detected. These ligand classes have values of  $K'$  of  $10^{7.4}$  to  $10^{9.4}$  with concentrations of 40 to 160 nM (van den Berg and Dharmvanij, 1984; van den Berg et al. 1986, 1987; Muller and Kester, 1991; Gardner, 1999). Calculations of organically-complexed Zn in estuaries range widely between 1 and 95%, depending on ligand strength and concentration.

The exact sources of Cu- and Zn-complexing ligands, which constitute usually  $\leq 0.1\%$  of the total pool of dissolved organic carbon (DOC), are not well characterized. In

general, these ligands are composed of various colloidal or dissolved fractions of DOC, including phytoplankton or bacterial exudates and their degradation products (Anderson et al., 1984; Seritti et al., 1986; Kerner and Geisler, 1995; Moffett and Brand, 1996; Gordon et al., 2000) and humic substances (Kogut and Voelker, 2001).

Organic-rich estuaries such as the Cape Fear might be expected to contain relatively high concentrations of metal-complexing ligands, given that DOC concentrations typically range from 200-800  $\mu\text{M}$  (Avery et al., 2002). Recent studies in the Cape Fear estuary (CFE) indicate that concentrations of strong ( $L_1$ -type) Cu-complexing ligands (10-100  $\mu\text{M}$ ) are in large excess relative to total dissolved Cu concentrations (5 -10 nM), resulting in >99.9 % of the TDCu existing as strong organic complexes (Shank et al., 2003).

Zinc speciation has never been determined in the CFE. However, O'Connell (1999) determined total dissolved Zn concentrations throughout the lower CF system over various seasons and hydrologic conditions. Concentrations ranged from 20-90 nM in the upper estuary (low salinity) to 15-60 nM in the middle and lower estuary.

Because the organic ligands that complex Cu and Zn have an important influence on their behavior in estuarine systems such as the Cape Fear, an understanding of the source of these ligands is clearly desirable. Most previous work on Cu and Zn speciation in estuaries has focused on concentrations of complexing ligands in surface waters, therefore reflecting primarily riverine and oceanic water column processes. However, previous work has shown that *sediments* can be important sources of ligands to the overlying water column. For example, Skrabal et al. (1997) showed that fluxes from bottom sediments may be a significant source of Cu-complexing ligands to overlying

waters of Chesapeake Bay. Depth profiles of sediment porewaters in Chesapeake Bay show that sediments are a potentially large reservoir of Cu-complexing ligands (Skrabal et al., 2000). Studies in the Cape Fear estuary by Shank et al. (2003) also suggest that benthic fluxes may contribute a small fraction of Cu-complexing ligands to overlying waters. Preliminary studies by van den Berg and Dharmvanij (1984) suggest that sediment porewaters are enriched in Zn-complexing ligands relative to overlying waters. These findings support the assertion that sediments can act as sources of metal-binding ligands. Also, it is well documented that metals such as Cu and Zn that accumulate in sediments underlying a body of water can be a source of metals to the water column (Elderfield et al., 1981; Westerland et al., 1986; Kuwabara et al., 1996). Hence benthic fluxes represent a potentially important source of dissolved Cu and Zn and their complexing ligands to the Cape Fear estuary and estuarine systems in general.

As illustrated in Fig. 1, there are several processes and routes by which metals such as Cu, Zn, and their complexing ligands enter the estuary. This work focuses on the contribution from benthic fluxes. While simple diffusion from sediments arising from concentration gradients can engender fluxes of ligands, metals, or both, it is reasonable to investigate whether or not the biologically-induced disturbance of sediments might also cause such fluxes. The activity of benthic (bottom-dwelling) organisms has been shown previously to affect the sediment-water exchange of nutrients and trace metals such as iron, manganese, and arsenic (Allen, 1982; Riedel et al. 1987, 1997). Numerous benthic organisms inhabit the Cape Fear River estuary sediments (Mallin et al., 1996), and their feeding and burrowing activities may influence fluxes of materials. Across the sediment-water interface.

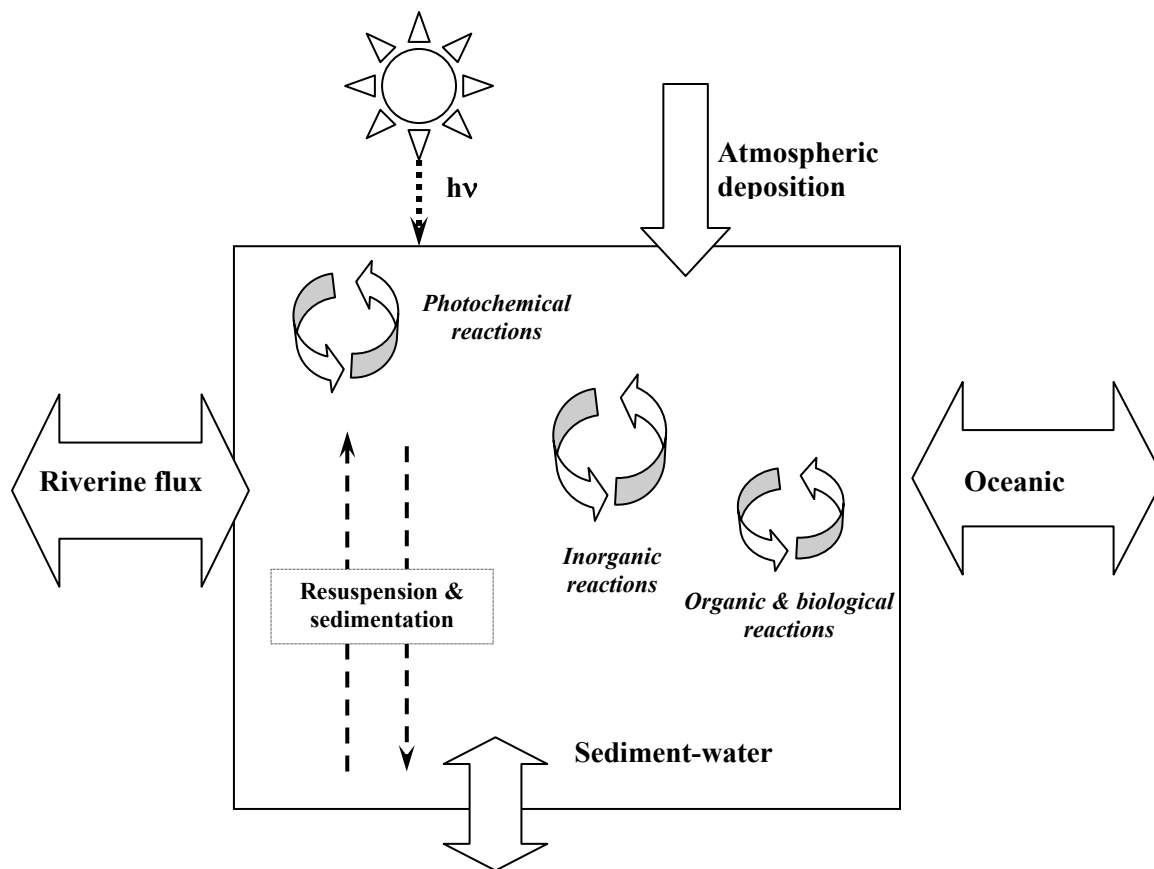


Fig. 1. Illustration of the estuarine box model. This figure shows the possible fates and origins of trace species such as zinc, copper, and metal-complexing ligands.

One such organism is *Streblospio benedicti*, a polychaete common in the Cape Fear River estuary that can quickly alter the topography of the sediment surface. *S. benedicti* is an infaunal organism, typically 20 mm or less in length. It feeds by burrowing into the sediment and then building a feeding tube that extends through the sediment to the overlying water (Levin, 1981, 1984). Levin (1981) reports that the population density of *S. benedicti* in Mission Bay in San Diego, California is 4,000 to 6,000 individuals/m<sup>2</sup>; a similar density of *S. benedicti* often exists in the lower Cape Fear River estuary (oral communication, M. Posey, 2002). This species can be the dominant polychaete in the lower estuary (Posey and Alphin, 2001). The role of this organism in affecting amino acid diagenesis has been investigated previously in Cape Fear sediments (Thomas, 1998). The experiments described in this thesis are the first to explore the possible role that bioturbation may play in sediment fluxes of Cu and Zn and the ligands that bind them.

## Goals

The study presented in this thesis has the following goals:

- Core incubation experiments are performed to determine benthic fluxes for total dissolved Cu, total dissolved Zn, and the ligands that bind these metals.
- Addition of the polychaete *S. benedicti* to incubated cores will determine the effect bioturbation has on benthic fluxes of these two metals and their ligands.
- The concentration of Zn in the Cape Fear River estuary will be measured, and speciation data for Zn will be presented for the first time.