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Seasonal survey of copper-complexing ligands and thiol compounds in a heavily utilized, urban estuary: Elizabeth River, Virginia

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Abstract

Concentrations of thiol compounds, copper-complexing ligands, and total dissolved copper were followed over the course of 1 year (October 2002 until September 2003) in the Elizabeth River, Virginia to evaluate seasonality. Copper-complexing ligand concentrations were determined by competitive ligand equilibration-adsorptive cathodic stripping voltammetry (CLE/ACSV). Thiol detection was carried out by high performance liquid chromatography (HPLC) and calibration using a suite of nine thiol compounds (cysteine, glutathione, mercaptoacetic acid, 2-mercaptoethanesulfonic acid, 2-mercaptoethanol, 2-mercaptopropionic acid, 3-mercaptopropionic acid, mercaptosuccinic acid, and monothioglycerol). Total dissolved copper concentrations reached a January low of 13.1 nM to a June high of 24.7 nM and were found to vary seasonally with higher concentrations occurring from June to September. With a low of 26 nM during April to a high of 56 nM in October, copper-complexing ligand (average log K'_{CuL} of 12.0 ± 0.2) concentrations displayed a similar seasonal pattern to that of total dissolved copper. Free cupric ion concentrations remained below 1.5 pM for a majority of the year except during March, April, and December when values reached pM levels greater than 1.5. Six of the nine thiol compounds surveyed were detected in the Elizabeth River samples and ranged in concentration from below detectable concentrations (<5 nM) to individual highs ranging from 25.3 to168.5 nM. The thiol compound concentrations displayed a clear seasonality fluctuating at below detection limits during November to February then increasing with increasing surface water temperatures from March to July. CLE/ACSV was used to assess whether or not the suite of thiol compounds detected by HPLC could contribute to the copper-complexing ligand pool. Conditional stability constants for each one of six thiol standards (average log $K'_{\mathrm{CuL}} \sim 12.1 \pm 0.5$) were found to be statistically equivalent to the naturally occurring copper-complexing ligands (average log $K'_{\mathrm{CuL}} \sim 12.0 \pm 0.2$). This suggests that these thiol compounds could act as copper-complexing ligands in natural samples and could contribute to the copper-complexing ligand pool detected by CLE/ACSV. This study involving seasonality of copper-complexing ligands and thiols in an industrialized, urban estuary underscored several points that have to be substantiated in future research efforts including copper-complexing ligands sources and the role that thiol compounds as well as other unidentified organic compounds play in the copper-complexing ligand pool.

Keywords: Copper; Trace metals; Copper speciation; Organic ligands; Thiols; USA, Virginia, Elizabeth River

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1. Introduction

In some estuaries, contamination by metal pollution is of concern because some metals are harmful to organisms at relatively low levels. For example copper, although a

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nutrient metal, at elevated concentrations can cause a toxic response in bacteria (Sunda and Ferguson, 1983), phytoplankton (Brand et al., 1986), crab larvae (Sanders et al., 1983), and copepod larvae (Sunda et al., 1987). Copper speciation studies have shown that the dissolved copper in most natural waters is predominately organically complexed (Coale and Bruland, 1990; Moffett et al., 1990). By dominating the copper speciation, organic complexation may control copper's bioavailability (by controlling Cu^{2+} activity), its reactivity with suspended particles, and ultimately govern its biogeochemical cycling in seawater (Coale and Bruland, 1988, 1990; Moffett et al., 1990; Donat and van den Berg, 1992; Donat et al., 1994).

Sources of organic copper-complexing ligands in seawater are not well known, however, compelling laboratory and field data suggest that marine microorganisms produce strong organic metal binding ligands (Moffett et al., 1990; Gordon et al., 1996, 2000; Moffett and Brand, 1996; Croot, 2003; Dryden et al., 2004). Studies have shown that autotrophic picoplankton (the <2 μm component of the phototrophic planktonic microflora), specifically the cyanobacteria *Synechococcus* spp., produce an extracellular copper chelator with binding characteristics comparable to the strong ligands, L_1, in the water column (Moffett et al., 1990; Bruland et al., 1991; Moffett and Brand, 1996; Gordon et al., 1996, 2000). Other studies have shown that heterotrophic marine bacteria and fungi can produce dissolved, high-affinity copper ligands (Schreiber et al., 1990; Stein and Gessner, 1989; Gordon et al., 1996, 2000). Sources for organic copper-complexing ligands not produced directly by marine organisms also exist in coastal environments. Estuarine sediment porewaters, sewage effluents, and estuarine and coastal humic substances have been examined as potential sources of organic copper-complexing ligands (Skrabal et al., 1997; Sedlak et al., 1997; Kogut and Voelker, 2001; Voelker and Kogut, 2001). Skrabal et al. (1997) found that ligands in estuarine sediment porewaters had binding characteristics similar to the water column strong copper-complexing ligands, L_1. Kogut and Voelker (2001) used Suwannee River humic acid and fulvic acid to demonstrate that terrestrial humic substances may make up a significant fraction of the L_1 strength copper-complexing ligands in coastal systems. To date whether or not the majority of the strongest organic copper-complexing ligands, L_1, are of planktonic or nonplanktonic origin is unknown.

Although the chemical nature and complete chemical characteristics of the copper-complexing ligands in natural waters remains unknown, preliminary studies are investigating known copper-complexing compounds and copper-complexing functional groups. Laglera and van den Berg (2003), Tang et al. (2001), Leal et al. (1999), and Leal and van den Berg (1998) have investigated thiol compounds and suggested they might constitute a major part of the natural copper-complexing ligand pool.

As uncertainties still surround the origins of copper-complexing ligands and their chemical identities, it is difficult to predict possible seasonal changes these compounds might undergo. However, seasonal studies may elucidate the origins of the copper-complexing ligands if biological data is collected simultaneously. Only recently, Croot (2003) collected seasonal ligand and biological data in a relatively pristine fjord off the coast of Sweden. Croot (2003) found that copper speciation appeared to by driven by the seasonal abundance of the cyanobacterium *Synechococcus*. Unlike Croot (2003), the work presented in our study examined an anthropogenically impacted estuary and investigated seasonal changes in copper-complexing ligand concentrations and thiol concentrations over an annual cycle. The aim of this study was to ascertain whether any correlations exist between copper-complexing ligands and marine microorganism abundances as well as concentrations of thiol compounds and copper-complexing ligands. The anthropogenically impacted study site is located in the Elizabeth River, Virginia bound by the cities of Chesapeake, Norfolk, Portsmouth, and Virginia Beach. Located in the Hampton Roads area of Virginia, the Elizabeth River is a three-branched estuary located on the southern shore of the James River and is the Chesapeake Bay's southernmost tributary. Over 300 years of shipping, civilian and military shipbuilding, and manufacturing have discharged pollutants like polycyclic aromatic hydrocarbons (PAHs), heavy metals, and pesticides into the Elizabeth River leaving a legacy of contaminated sediments and reasons for concern about the biological effects and ultimate fate of these pollutants (deFur and Foersom, 2000; Huggett et al., 1984; Hargis et al., 1984).

2. Materials and methods

2.1. Sample collection and handling

Surface water samples for this study were collected from the Elizabeth River at the Old Dominion University (ODU) sailing pier (Fig. 1). The ODU sailing pier is located slightly east of the main stem of the Elizabeth River at the mouth of the Lafayette River with depth of slightly more than 2 m at high tide. To maximize the water column between the surface and the sediment all samples were collected during the peak of high tide and spring tide. Samples were collected monthly for 1 year to allow