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Sources of strong copper-binding ligands in Antarctic Peninsula surface waters

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ABSTRACT

Copper-binding organic ligands were measured during austral winter in surface waters around the Antarctic Peninsula using competitive ligand exchange-adsorptive cathodic stripping voltammetry with multiple analytical windows. Samples were collected from four distinct water masses including the Antarctic Circumpolar Current, Southern Antarctic Circumpolar Current Front, Bransfield Strait, and the shelf region of the Antarctic Peninsula. Strong copper-binding organic ligands were detected in each water mass. The strongest copper-binding ligands were detected at the highest competition strength in the Antarctic Circumpolar Current, with an average conditional stability constant of $\log K^{cond}_{CuL,Cu^{2+}} = 16.00 \pm 0.82$. The weakest ligands were found at the lowest competition strength in the shelf region with $\log K^{cond}_{CuL,Cu^{2+}} = 12.68 \pm 0.48$. No ligands with stability constants less than $\log K^{cond}_{CuL,Cu^{2+}} = 13.5$ were detected in the Antarctic Circumpolar Current at any competition strength, suggesting a shelf source of weaker copper-binding ligands. Free, hydrated copper ion concentrations, the biologically available form of dissolved copper, were less than 10^{-14} M in all samples, approaching levels that may be limiting for some types of inducible iron acquisition.

1. Introduction

Copper (Cu) plays an important role in phytoplankton growth. Cu can be both a micronutrient and a toxicant for phytoplankton in the ocean and this role is dependent on its speciation and concentration. The most bioavailable form of dissolved Cu is considered to be the inorganic free, hydrated Cu^{2+} ion (hereafter referred to simply as Cu^{2+}; Sunda and Lewis, 1978), while the majority of dissolved Cu in the oceans is strongly chelated by a heterogeneous pool of organic ligands (van den Berg, 1987; Moffett and Dupont, 2007; Coale and Bruland, 1988). The extent of the organic complexation of Cu causes Cu^{2+} concentrations to remain extremely low in most open ocean environments, generally less than 10^{-13} M, with elevated levels in contaminated coastal regions (Moffett et al., 1997; Moffett and Dupont, 2007; Buck and Bruland, 2005). Most Cu research has, thus, focused on these anthropogenically influenced areas, since concentrations as low as 10^{-11} M can be toxic to some phytoplankton, particularly to small cells like the cyanobacteria *Synechococcus* (Brand et al., 1986). However, Cu has also been shown to be an important micronutrient, especially for diatoms such as *Thalassiosira oceanica* when using inducible iron (Fe) uptake that requires multi-Cu oxidases (Peers et al., 2005; Maldonado et al., 2006). This implies that Cu requirements may be heightened in some Fe-stressed regions of the ocean, especially high nutrient low chlorophyll regions (HNLC) such as the Southern Ocean (Maldonado et al., 2006; Annett et al., 2008; Peers et al., 2005, Peers and Price, 2006).

The Antarctic Peninsula is an important ecological region in the Southern Ocean and serves as an ideal setting to study Cu along a natural gradient. The Antarctic Peninsula is a site of mixing between a low Fe, relatively low chlorophyll "blue water zone" to the west and naturally Fe-enriched water masses influenced by the peninsula to the east. In this region, the southern portion of the mesotrophic Antarctic Circumpolar Current (ACC) sweeps south and is mixed with shelf-influenced water masses as it becomes bathymetrically constrained by the Shakelton Fracture Zone, here called the Southern ACC Front (SACCF). Water from the Bransfield Strait (BS), moving between the continent and the Shetland Islands, also mixes with the SACCF along the bathymetry. This mixing causes an input of Fe and other nutrients to the shelf and the ACC, and has been hypothesized to be the cause of numerous large-scale summer blooms that can be seen down-stream (Selph et al., 2013; Measures and Hatta, 2013). Cu in particular may be mixed into the waters surrounding the Antarctic Peninsula from Cu-enriched sediments or upwelling of Upper Circumpolar Deep Water (UCDW) (Nolting et al., 1991; Loscher, 1999). This distinct circulation and the resulting natural

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gradients in Fe and productivity are unique for studying sources of Cu and organic ligands to this region of the Southern Ocean.

Although Fe and its organic speciation have been studied extensively, very little Cu speciation data exists in the open ocean despite the influence of organic Cu-binding ligands on Cu^{2+} concentrations and phytoplankton growth. The Southern Ocean is relatively understudied with respect to Cu and its organic speciation (Boyle et al., 1977; Capodaglio et al., 1994, 1998; Corami et al., 2005; Frache et al., 2001). Previous Cu speciation studies in this region have employed a common electrochemical approach to speciation analyses, competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV). This approach involves titrating the natural organic ligands in a sample with added Cu, and then adding a well-characterized electroactive ligand to compete with the natural ligands for the added Cu (Campos and van den Berg, 1994). The concentrations as well as the conditional stability constants of naturally occurring pools of organic ligands (usually distinguished as stronger, L_1 or weaker, L_2) can then be determined. Previous studies in both the northern Pacific (Coale and Bruland, 1988) and the Sargasso Sea (Moffett, 1995) have hypothesized that Cu organic speciation is dominated by strong complexation in the surface ocean due to production of strong Cu-chelators by cyanobacteria and diatoms, as seen in culture studies under toxic conditions (Moffett and Brand, 1996; Dupont et al., 2004). This is supported by the remarkably similar stability constants ($\log K^{cond}_{CuL,Cu^{2+}} = 14-16$) of Cu-binding ligands measured in culture to those measured in seawater by CLE-ACSV in field studies. These strong Cu-binding ligands observed in culture studies (Moffett and Brand, 1996; Dupont et al., 2004; Wiramanaden et al., 2008) are thought to be the main source of strong Cu ligands in seawater. Weaker Cu ligands also exist in seawater and have been hypothesized to be comprised mostly of thiols (Dupont et al., 2006) and humics (Laglera and van den Berg, 2009), and are thought to have an estuarine or sediment source (Donat et al., 1994; Skrabal et al., 1997; Chapman et al., 2009). Some weaker Cu ligands may also be degradation products (i.e., photochemical) of strong Cu ligands in the euphotic zone (Laglera and van den Berg, 2006). However, few of these ligand sources have been studied in the open ocean despite their importance on Cu cycling and bioavailability. Attempts to infer sources and sinks of Cu-binding ligands have also been complicated in the past due to variations in analytical approach to CLE-ACSV, which can result in marked differences in perceived conditional stability constants (Bruland et al., 2000).

The technical specifics of CLE-ACSV can have important effects on the concentration and strength of the Cu-binding ligands detected (Bruland et al., 2000). In particular, the competition strength of the added ligand is an important consideration and has been shown to have an effect on the strength and concentration of Cu-binding ligands measured in the field (Bruland et al., 2000; Buck and Bruland, 2005). Thus, competition strength, or analytical window, should be considered when studying particular classes of ligands, strong or weak. Stronger ligands (operationally referred to herein as having $\log K^{cond}_{CuL,Cu^{2+}} > 13.5$) are generally detected by methods employing higher concentrations of the added ligand, while weaker ligands ($\log K^{cond}_{CuL,Cu^{2+}} \leq 13.5$, herein) are generally detected by methods using weaker competition strengths. The differences in the analytical window employed for Cu speciation studies by CLE-ACSV have generally made data interpretation difficult between laboratories and Cu complexation comparisons between sites nearly impossible. Data evaluation techniques incorporating multiple analytical windows can prove extremely insightful, but are not common in most studies (van den Berg and Donat, 1992; Sander et al., 2011). A few studies have employed multiple analytical windows (MAW) to fully probe the continuum of Cu-binding ligands in seawater (Campos and van den Berg, 1994; Moffett et al., 1997; Buck and Bruland, 2005). The MAW approach enables a more complete view of Cu complexation and, hence, bioavailability. These studies are unique in that they elucidate the importance of detecting the full range of stronger to weaker Cu-binding ligands, which have been shown to have important effects on Cu bioavailability (Buck and Bruland, 2005).

In this study, dissolved Cu and Cu organic speciation was determined in Antarctic Peninsula surface waters during austral winter. In order to probe sources of Cu and ligands to these surface waters, CLE-ACSV was employed using the MAW approach to fully characterize the range of Cu-ligands present in these waters.

2. Experimental

2.1. CLE-ACSV theory

CLE-ACSV is an electrochemical method that utilizes the competition between a well-characterized added ligand and the natural ligands in a sample in order to determine the thermodynamic stability of the ambient ligands. Previous studies have employed a variety of added ligands, which govern the analytical window or the competition strength of the method, and consequently the type of ligands detected, whether stronger or weaker (Campos and van den Berg, 1994; Moffett et al., 1997; Buck and Bruland, 2005; Moffett and Dupont, 2007). The competition strength of the added ligand, in this case salicylaldoxime (SA), determines the range of binding strengths that can be detected in a given sample. The competition strength is represented by the side reaction coefficient, $\alpha_{Cu(SA)_x}$, defined as

$$\alpha_{Cu(SA)_x} = \frac{[Cu(SA)_x]}{Cu^{2+}} = \beta_2^{cond}[SA]^2 + K_1^{cond}[SA] \quad (1)$$

where β_2^{cond} and K_1^{cond} are the conditional stability constants of the $Cu(SA)_2$ and $Cu(SA)^+$ complexes (SA-labile Cu species). Both β_2^{cond} and K_1^{cond} have been experimentally determined at different salinities (Campos and van den Berg, 1994) according to $\log \beta_2^{cond} = 15.78-(0.53 \log(\text{salinity}))$ and $\log K_1^{cond} = 10.12-(0.37 \log(\text{salinity}))$, and can therefore be considered as constants. All $\alpha_{Cu(SA)_x}$ determined in this study were determined using this salinity relation as described by Campos and van den Berg (1994). The competition strength, then, is simply a function of the added ligand concentration. Only at high added ligand concentrations (> 2.5 μM SA) the $Cu(SA)^+$ species is insignificant, and Eq. (1) can be simplified to

$$\alpha_{Cu(SA)_2} = \beta_2^{cond}[SA]^2 \quad (2)$$

where analytical window is simply related to the square of the added ligand concentration. Eq. (1) was employed in this study, using a range of concentrations of SA from 1 to 25 μM and the resulting analytical window ranging from approximately 1000–644,000. A variety of ligand stability constants can be detected when a range of competition strengths are employed (see Bruland et al., 2000; Buck and Bruland, 2005; Hudson et al., 2003; Sander et al., 2011). It also allows subtle distinctions to be made between different ligand pools, and potentially ligand sources.

At each titration point, assuming inorganic complexation is negligible, the mass balance between all Cu species is given by

$$[Cu_T] = [CuL] + [Cu(SA)_x] + [Cu^{2+}] \quad (3)$$

where $[Cu_T]$ is the total dissolved Cu in the sample, [CuL] is the Cu bound by organic ligands. $[Cu(SA)_x]$ is proportional to the sensitivity and the peak height at each titration point, and $[Cu^{2+}]$ is the free, hydrated form of Cu. The sensitivity is determined by internal calibration, from the linear portion at the end of the