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Spatial variability of total dissolved copper and copper speciation in the inshore waters of Bermuda

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ABSTRACT

Total dissolved copper (Cu) and Cu speciation were examined from inshore waters of Bermuda, in October 2009 and July–August 2010, to determine the relationship between total dissolved Cu, Cu-binding ligands and bioavailable, free, hydrated Cu^{2+} concentrations. Speciation was performed using competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV). Mean total dissolved Cu concentrations ranged from 1.4 nM to 19.2 nM, with lowest concentrations at sites further from shore, consistent with previous measurements in the Sargasso Sea, and localized Cu enrichment inshore in enclosed harbors. Ligand concentrations exceeded dissolved [Cu] at most sites, and $[Cu^{2+}]$ were correspondingly low at those sites, typically $<10^{-13}$ M. One site, Hamilton Harbour, was found to have [Cu] in excess of ligands, resulting in $[Cu^{2+}]$ of $10^{-10.7}$ M, and indicating that Cu may be toxic to phytoplankton here.

In natural waters, dissolved copper exists as several chemical species, collectively described as either the labile inorganic species (Cu′) or the comparatively inert, organic copper–ligand complexes (CuL_i; where *i* denotes ligand class). At modern seawater pH of ~8.2, inorganic copper is predominantly complexed as copper carbonate (~78%), with ~7% in the form of the free hydrated copper ion, Cu^{2+} (Morel and Hering, 1993), referred to hereafter simply as Cu^{2+}. In the absence of Cu-binding organic ligands, total dissolved copper is equal to Cu′, and Cu^{2+} is easily calculable from basic parameters (Byrne et al., 1988). However, the speciation of Cu in seawater is governed by its chelation with organic ligands, with dissolved Cu typically ⩾90% complexed to ambient strong Cu-binding ligands in the surface ocean (Buckley and van den Berg, 1986; Coale and Bruland, 1988; Moffett et al., 1990; Donat and van den Berg, 1992; Moffett, 1995; Moffett and Dupont, 2007; Buck et al., 2012). The natural Cu-binding ligands measured in seawater are characterized by their conditional stability constants, $K^{cond}_{CuL_i,Cu^{2+}}$, where *i* denotes ligand class, with L_1 representing a stronger ligand class and L_2, L_3, etc., denoting progressively weaker ligand classes. For copper, two ligand classes are typically reported, although values of log $K^{cond}_{CuL_1,Cu^{2+}}$ and log $K^{cond}_{CuL_2,Cu^{2+}}$ show considerable overlap (van den Berg, 1984; van den Berg et al., 1987; Coale and Bruland, 1988; Moffett, 1995; Bruland et al., 2000).

The impact of dissolved Cu on marine microorganisms is not singular; Cu can be either growth limiting or toxic depending on its concentration and speciation. The bioavailability of dissolved Cu in the marine Environment is best represented by $[Cu^{2+}]$ in the presence of Cu-binding ligands, which is not necessarily proportional to the total dissolved Cu concentration, [Cu] (Sunda and Guillard, 1976; Anderson and Morel, 1978). Marine organisms show varying toxicity thresholds to $[Cu^{2+}]$, with Cu^{2+} concentrations as low as 10^{-11} M inhibiting growth of several phytoplankton groups (Brand et al., 1986). Thus, while Cu is an important micronutrient (Manahan and Smith, 1973), especially

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in iron-limited environments (Peers et al., 2005; Peers and Price, 2006; Maldonado et al., 2006; Guo et al., 2010), elevated Cu concentrations generate concern for toxicity in urban influenced environments.

The Sargasso Sea is characterized as an oligotrophic system dominated by cyanobacteria populations in surface waters (Waterbury et al., 1979; Chisolm et al., 1988; Lomas and Moran, 2011), which are especially sensitive to Cu toxicity (Brand et al., 1986). Cu speciation studies conducted in the Sargasso Sea, largely in the region of the Bermuda Atlantic Time-series Station (BATS) just south of Bermuda, have found Cu speciation dominated by Cu-binding ligands in surface waters (Moffett et al., 1990; Moffett, 1995). However, in some parts of the water column, including the mixed layer, Cu-binding ligands were not in excess of dissolved Cu, which resulted in Cu^{2+} concentrations approaching or even exceeding 10^{-11} M (Moffett et al., 1990; Moffett, 1995). The distribution of cyanobacteria species in these waters has been shown to reflect this variability, with the abundance of Cu-sensitive species inversely correlated with Cu^{2+} concentrations (Mann et al., 2002).

Bermuda is a small, densely populated, remote group of islands located in the Sargasso Sea, more than 1000 km off the coast of North Carolina. Previous studies in the inshore waters of Bermuda have documented elevated concentrations of Cu in sediments (Jickells and Knap, 1984; Jones, 2010 and 2011) and the water column (Jickells and Knap, 1984; Jones, 2007 and 2010). Dissolved Cu contamination in Bermuda arises from a variety of sources, including antifouling paint leachate and particles, industrial effluent, runoff from roads, and metal leaching from waste materials (Jickells and Knap, 1984; Flood et al., 2005; Jones, 2007; Jones, 2010; Jones, 2011). Local harbors adjacent to urban areas, like Hamilton Harbour and St. George's Harbour, have some of the highest concentrations of Cu contamination in sediments, likely reflecting a combination of boating activities and associated leaching of Cu from antifouling paints, surface runoff, and reduced mixing with the adjacent open ocean (Jickells and Knap, 1984; Jones, 2011). Castle Harbour has been examined for potential metal contamination, as it is the location of a metal waste dump, or "seafill", though it has been shown to have lower Cu concentrations in the water column and sediments than the more urbanized sites in Bermuda (Jickells and Knap, 1984; Flood et al., 2005).

Here we report total dissolved (defined as <0.4 μm) Cu concentrations and dissolved Cu speciation of surface samples collected from a suite of inshore sites across the Bermuda platform, in October 2009 and July–August 2010 (provided in Table 1 and mapped in Fig. 1). An electrochemical technique was employed to determine total dissolved Cu and Cu speciation (Campos and van den Berg, 1994; Buck and Bruland, 2005; Buck et al., 2012). This is the first report of dissolved Cu speciation, Cu^{2+} concentrations and corresponding Cu bioavailability from the inshore waters of Bermuda.

Samples were collected from approximately 0.5 m in depth by dipping bottles over the bow of a small boat, while facing into the water current to avoid contamination from the vessel. Contamination was further minimized with the use of sleeve guards and gloves, and by inserting bottles closed, then opening them underwater to fill. All bottles, filters and containers used in sampling and processing were acid-cleaned and conditioned with Milli-Q (>18 MΩ cm) prior to use. Sample bottles were rinsed three times with sample prior to filling. Samples were collected into 2.5 L polycarbonate bottles (Nalgene), and were kept in coolers in the dark until returned to the trace metal clean lab at the Bermuda Institute of Ocean Sciences. Samples were filtered within 2 h of their return through acid-cleaned 0.4 μm polycarbonate track etched filters (Whatman), positioned in a PTFE vacuum filtration ring (Savillex), into 500 mL fluorinated high-density polyethylene bottles (Nalgene). Several samples were taken from within Castle Harbour, from 16 sites in 2009 and from 3 tidal cycles (low, ebb and high) at 6 sites in replicate in 2010. All samples were either analyzed within 2 weeks or were frozen for storage at −20 °C. Frozen samples were thawed prior to analysis and analyzed within two days of thawing. Salinity was measured at sampling sites using a YSI conductivity probe. For a qualitative estimate of turbidity

Table 1
Sampling sites, dates and locations.

#	Sampling Site	Date	Latitude (°N)	Longitude (°W)
1	North Channel	25 Oct 2009; 17 Aug 2010	32.3753	−64.6821
2	St Georges Harbour	25 Oct 2009; 17 Aug 2010	32.3384	−64.7152
3	Castle Harbour	9 Oct 2009	32.3097	−64.7823
4	Castle Harbour	9 Oct 2009	32.2887	−64.7830
5	Castle Harbour	9 Oct 2009	32.4160	−64.7429
6	Castle Harbour	9 Oct 2009	32.3197	−64.8277
7	Castle Harbour	9 Oct 2009	32.3591	−64.6996
8	Castle Harbour	9 Oct 2009	32.3587	−64.7003
9	Cave, Castle Harbour	29 Sept 2009	32.3559	−64.7057
10	Castle Harbour	29 Sept 2009	32.3616	−64.6949
11	Castle Harbour	29 Sept 2009	32.3614	−64.6888
12	Castle Harbour	29 Sept 2009	32.3467	−64.6884
13	Castle Harbour	14 Oct 2009	32.3433	−64.7073
14	Castle Harbour	14 Oct 2009	32.3603	−64.6963
15	Castle Harbour	14 Oct 2009	32.3593	−64.7001
16	Castle Harbour	14 Oct 2009	32.3526	−64.6906
17	Castle Harbour	14 Oct 2009	32.3593	−64.7000
18	Castle Harbour	14 Oct 2009	32.3581	−64.7034
19	Castle Harbour	15 Jul 2010; 10–14 Aug 2010	32.3615	−64.6948
20	Castle Harbour	15 Jul 2010; 10–14 Aug 2010	32.3612	−64.6952
21	Castle Harbour	15 Jul 2010; 10–14 Aug 2010	32.3604	−64.6950
22	Castle Harbour	15 Jul 2010; 10–14 Aug 2010	32.3598	−64.6972
23	Castle Harbour	15 Jul 2010; 10–14 Aug 2010	32.3589	−64.7003
24	Castle Harbour	15 Jul 2010; 10–14 Aug 2010	32.3598	−64.7000
25	Harrington Sound	25 Oct 2009; 17 Aug 2010	32.3597	−64.6970
26	Tynes Bay	25 Oct 2009; 17 Aug 2010	32.3597	−64.6964
27	Hamilton Harbour	25 Oct 2009; 17 Aug 2010	32.3625	−64.6952
28	Long Island	17 Aug 2010	32.2875	−64.8214
29	Dockyard	25 Oct 2009; 17 Aug 2010	32.3630	−64.6942