

## Distribution and speciation of copper in seawater of East China Sea and its surrounding areas

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### I. Introduction

Copper is an essential micronutrient for all living organisms as it plays an important role in electron transfer in many life-supporting systems, and is present in many enzymes and proteins. However, at high concentrations in seawater,  $\text{Cu}^{2+}$  is known to be toxic to marine microorganism. Therefore, many phytoplankton and bacterial species have the ability to release Cu-complexing ligands to decrease the concentration of  $\text{Cu}^{2+}$  and reduce its toxicity. As a result, at the eutrophic surface waters, more than 99% of Cu are complexed with organic ligands. Hence, in this study, we determined the total dissolved Cu concentrations, Cu speciation parameters and  $\text{Cu}^{2+}$  concentrations at 15 stations in the East China Sea and its surrounding areas.

### II. Sampling and Methods

Seawater samples were collected using acid-cleaned, Teflon-coated X-type Niskin samplers mounted on conductivity-temperature-depth carousel multi-sampling system (CTD-CMS) onboard R/V Shinsei Maru during KS-15-6 cruise (June-July 2015) and R/V Hakuho Maru during KH-15-3 cruise (October 2015). The samples were collected in low-density polyethylene bottles through a 0.2  $\mu\text{m}$ -pore size filter. Samples for total Cu analysis were acidified to a pH of less than 1.8 using ultrapure HCl, and stored. Another set of samples, for CLE/CSV analysis, was frozen at  $-18^\circ\text{C}$  immediately after sampling. The samples were brought back to the laboratory and analyzed using CLE-CSV with salicylaldoxime (SA) as the competing ligand (Campos and van den Berg, 1994).

Samples used for total dissolved Cu were placed under UV radiation for 60 minutes to destroy all organic ligands prior to analysis. Frozen samples for Cu speciation analysis were allowed to thaw for 24 hours at  $4^\circ\text{C}$ , and then placed at room temperature for 4-8 hours. 10mL of sample, borate buffer, and a known concentration of Cu were added into two sets of 10 Teflon vials, left for at least 2 hours to allow the natural ligands to equilibrate with the added Cu, and the competing ligand, SA, was then added into the solution. The vials were then left to equilibrate overnight before analysis. 5  $\mu\text{M}$  SA and 1  $\mu\text{M}$  SA were used as the competing ligand for each of the two titrations, respectively.

### III. Results and Discussion

The highest concentration of total dissolved Cu was found at the surface (10m) of Stn.05, where  $[\text{Cu}] = 4.65\text{nM}$  and the lowest concentration was at Stn.13 ( $[\text{Cu}] = 0.47\text{ nM}$  at 100m). Surface waters at Stn.03, Stn.04 and Stn.05 have relatively low salinities when compared to those of other stations, and this can be attributed to the freshwater discharge from Yangtze River, which is likely a major source of copper into the East China Sea (Koshikawa et al., 2007; Abe et al., 2003). Two classes of ligands were found in the surface waters in this study. The concentration of the stronger ligand,  $L_1$ , ranged from 0.63 nM to 6.11 nM, with an average log K value of around 14, whereas for the weaker ligand,  $L_2$ , the concentrations were in the range of 4 nM to 27 nM, with an average log K value of around 12.3.  $\text{Cu}^{2+}$  concentrations remain constant at all stations ( $\sim 10^{-14}\text{ M}$ ) despite the large fluctuations in total Cu concentrations. The large ligand pool had probably buffered against changes in Cu concentration in seawater.

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