Speciation of Cu in seawater by using CLE-CSV with multi-detection windows

*Hajime Obata[1], Kuo Hong Wang[1], Taejin Kim[1], Toshitaka Gamo[1]

1.Atmosphere and Ocean Research Institute, University of Tokyo

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. On the other hand, at high concentrations in seawater, Cu^{2+} is known to be toxic for marine phytoplankton. Therefore, many phytoplankton and bacterial species have the ability to release Cu-complexing ligands to decrease the concentration of free Cu^{2+} and reduce its toxicity. As a result, at the eutrophic surface waters, most of Cu form complexes with organic ligands.

For the Cu speciation study in the ocean, competitive ligand equilibrium/cathodic stripping voltammetry (CLE/CSV) is frequently applied. However, some problems have been proposed on the CLE/CSV methods recently. One problem is concerning on “detection window”, which is defined by the conditional stability constant and concentration of the competitive ligands. To measure the conditional stability constants and concentrations of main ligands (usually two ligands) accurately, we have to apply the CLE/CSV method with multi detection windows for the speciation. In this study, we determined the total dissolved Cu concentrations and estimated Cu speciation in seawater by using the CLE/CSV method with multi detection windows 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 (2015/06/25 - 2015/07/06). The samples were collected in low-density polyethylene bottles through a 0.2 μm-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^{o}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^{o}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 μM SA and 1 μM SA were used as the competing ligand for each of the two titrations, respectively.

III. Results and Discussion

Total dissolved Cu concentrations ranged from 0.47 to 4.65 nM. In surface waters with low salinities, higher concentrations of Cu were observed, which can be attributed to the freshwater discharge with high Cu concentrations from Yangtze River. Two classes of ligands were found in the surface waters in this study. The concentration of the stronger ligand, L_1, ranged from 3.6 nM to 11.2 nM, with log K values of 13 –14.1, whereas for the weaker ligand, L_2, the concentrations were in the range of 25.6 nM to 47.6 nM, with log K values of 11.7 –12.2. The variation of the strong ligands suggests that these ligands were biologically produced *in situ* by marine microorganisms.

Keywords: ocean, Cu, organic ligand

