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Determination of Complexing Capacity of Ligands in Natural Water

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ABSTRACT: Most of the trace metals in natural waters are believed to exist in complexed or chelated forms with the miscellaneous organic ligands of both natural and pollutants origin which regulate the availability of these metals in the system . Such a mechanism maintains a reservoir of metals ready for biological uses. The abundance of complexing ligands in a body of water thus determines the complexing capacity of the water and hence its regulating capability. The measurement of complexing capacity will add a new parameter to the chemistry of trace metals in the aquatic environment, especially in areas of biological uptake and toxicological studies (6,7). Such information is also pertinent in bioassay work where the knowledge of the possible forms of the metals after being added to a system is important. The complexation properties of some drinking waters for U(VI), Al(III) and Cu(II) are determined by ligand titration (LT) with the metal ions, using a new method for monitoring, i.e. the sorption of metal ion on complexing resins. The concentration of the free metal ion in solution is evaluated from the concentration of sorbed metal ion and from the quantity K^* , which is the ratio of the concentration of the metal ion sorbed on the resin to the concentration of free metal ion in solution, and can be independently evaluated.

KEYWORDS: complexing, ligands, water, concentration, metal, capacity, drinking

I. INTRODUCTION

The presence of organic ligands (L) whose conditional stability constants (K'_{ML}) are strong enough to allow them to form complexes with copper has been reported in oceanic waters. However, there is no general agreement on the distributional characteristics of such strong ligands in the water column. We present that these inconsistencies are derived from not only different analytical methods employed for their detection but also different oceanographic conditions. In particular, the nature and quantities of detectable natural ligands are affected by what kind of form the ligands are present in situ in different marine environments, that is, chemical speciation of natural ligands (ligand speciation), which depends strongly on the variations in concentrations of coexisting trace metals.[1]

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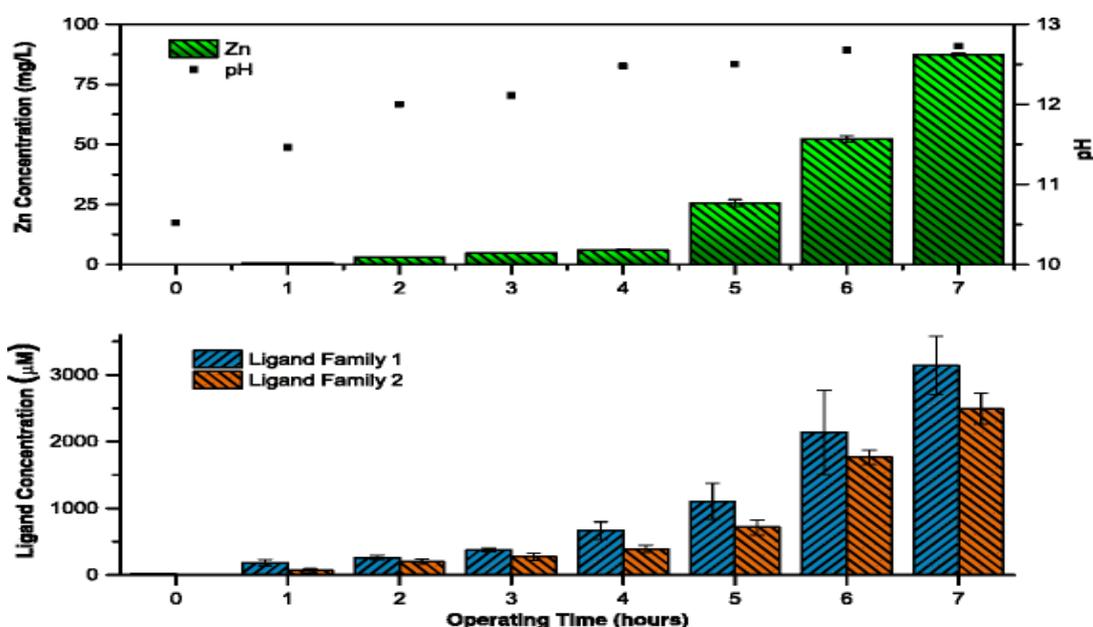


Fig.1. Complexing capacity of electroplating rinsing baths—a twist to the resolution of two ligand families of similar strength

Using published data from observations in the laboratory and the field, we provide limits to the ranges of conditional stability constants of organic ligands for copper, zinc and cadmium that are detectable by the extensively used direct metal-titration method. For example, our model indicates that organic ligands for copper with $\log K'_{CuL(Cu)} > 12.4$ in surface water and with $\log K'_{CuL(Cu)} > 9.9$ in deep water might not have been detected because stronger ligands had formed complexes[2] with ambient metals in situ at a station in the North Pacific. The estimation suggests that there is a basinscale difference in speciation of natural organic ligands and, moreover, that this difference influences metal speciation. It is postulated that comparisons of the occurrence and levels of organic ligands might not be possible among spatially and temporally different observations without reconciliation of the effects of speciation of the ligands, even if an identical method is used in every case.[3]

The characterization of metal forms in natural aquatic environments has become an important and attractive subject for research in the past decade. Metal speciation is required when assessing biological impact because bioavailability and toxicity seem to be directly related to the concentration of the metal ion species only.[4]

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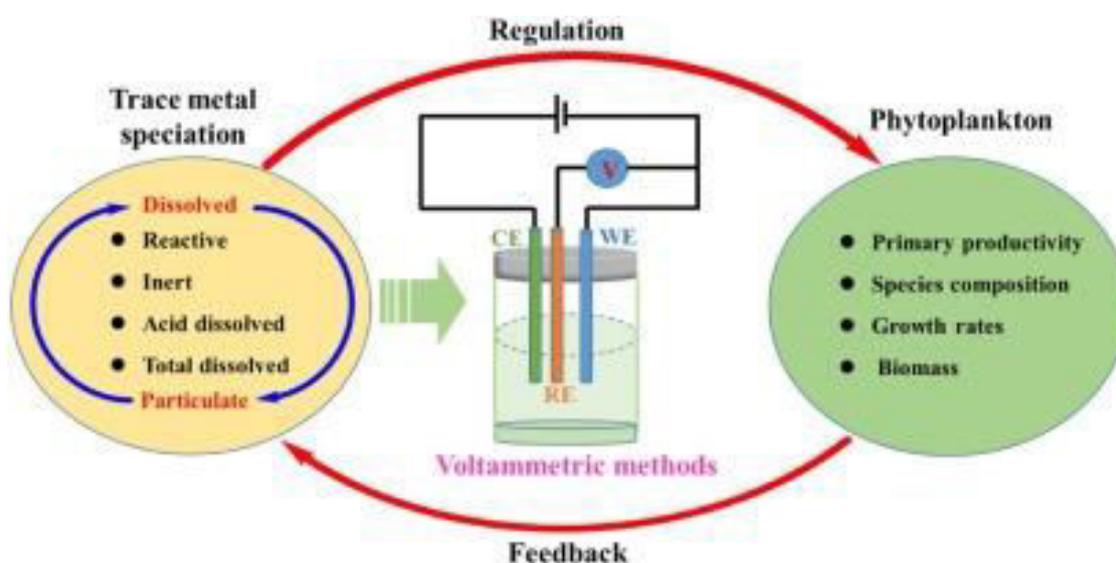


Fig.2. Voltammetric methods for speciation analysis of trace metals in natural waters

The chemical and phase speciation of trace elements is an important aspect of their biogeochemical cycles in natural waters. Microorganisms can modify the speciation of trace metals by excreting metal-binding ligands. It has been shown that a number of trace metals are bound by biogenic ligands in open ocean surface seawater) and in estuarine water. However, the chemical properties of these ligands, e.g., their structure, elemental composition, and functional groups, are not well known. Furthermore, the specific manner in which these organic ligands[5] affect the biogeochemistry and bioavailability of trace metals in aquatic environments is still a matter of contention because of difficulties in the determination of their concentrations as well as their chemical speciation. Copper is one of the most extensively studied trace metals in natural waters. [6]It has been reported that the strong organic ligands (L1) are mostly responsible for Cu complexation in open ocean surface waters whereas the weaker ligands (L2) can dominate Cu speciation in coastal waters. In waters with high phytoplanktonic activities, the strong specific ligands dominate at low Cu concentrations, whereas fulvic or humic substances, a major portion of bulk organic matter in fresh water.[7]

II. OBSERVATIONS

Organic ligands form strong complexes with many trace elements in seawater. Various metals can compete for the same ligand chelation sites, and the final speciation of bound metals is determined by relative binding affinities, concentrations of binding sites, uncomplexed metal concentrations, and association/dissociation kinetics. Different ligands have a wide range of metal affinities and specificities. However, the chemical composition of these ligands in the marine environment remains poorly constrained, which has hindered progress in modeling marine metal speciation. In this study, we detected and characterized natural ligands that bind copper (Cu) and nickel (Ni) in the eastern South Pacific Ocean with liquid chromatography tandem inductively coupled plasma mass spectrometry (LC-ICPMS), and high-resolution electrospray ionization mass spectrometry (ESIMS).[8]

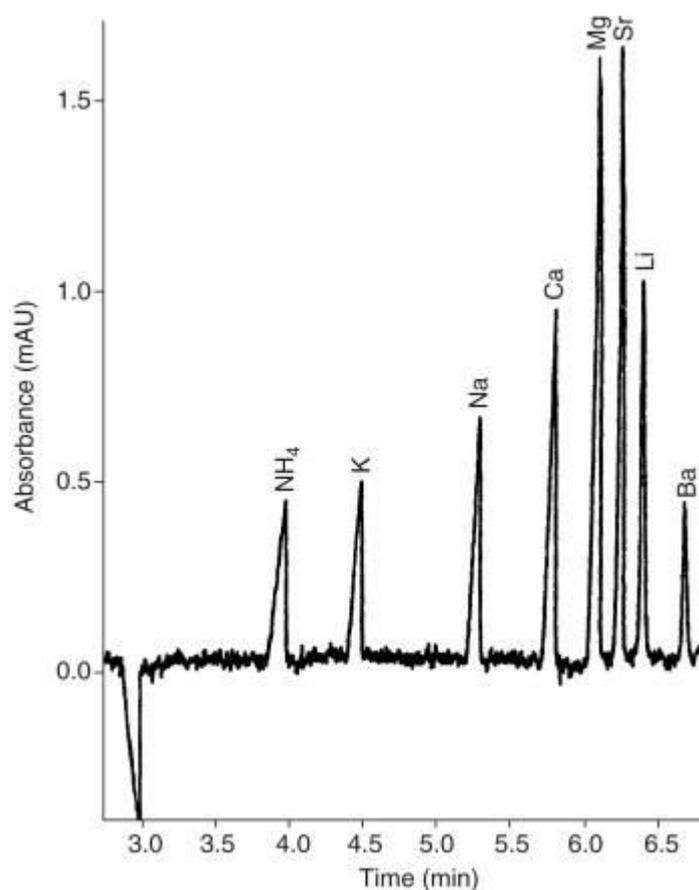


Fig.3. Complexation

Dissolved Cu, Ni, and ligand concentrations were highest near the coast. Chromatographically unresolved polar compounds dominated ligands isolated near the coast by solid phase extraction. Offshore, metal and ligand concentrations decreased,[9] but several new ligands appeared. One major ligand was detected that bound both Cu²⁺ and Ni²⁺. Based on accurate mass and fragmentation measurements, this compound has a molecular formula of [C₂₀H₂₁N₄O₈S₂+M]⁺ (M = metal isotope) and contains severalazole-like metal binding groups. Additional lipophilic Ni complexes were also present only in oligotrophic waters, with masses of 649, 698, and 712 m/z (corresponding to the ⁵⁸Ni metal complex).[10] Molecular formulae of [C₃₂H₅₄N₃O₆S₂Ni]⁺ and [C₃₃H₅₆N₃O₆S₂Ni]⁺ were determined for two of these compounds. Addition of Cu and Ni to the samples also revealed the presence of additional compounds that can bind both Ni and Cu.[11]

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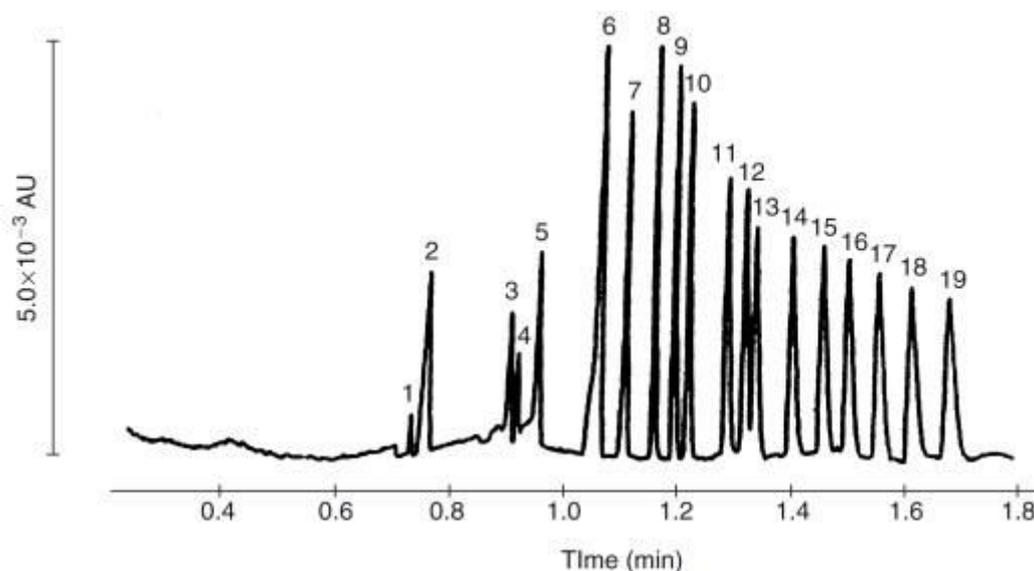
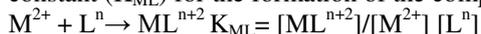


Fig.4. Complexation

Although these specific compounds represent a small fraction of the total dissolved Cu and Ni pool, they highlight the compositional diversity and spatial heterogeneity of marine Ni and Cu ligands, as well as variability in the extent to which different metals in the same environment compete for ligand binding.[12]

III. DISCUSSION

The form or speciation of a metal in natural waters can change its kinetic and thermodynamic properties. For example, Cu(II) in the free ionic form is toxic to phytoplankton, while copper complexed to organic ligands is not toxic. The form of a metal in solution can also change its solubility. For example, Fe(II) is soluble in aqueous solutions while Fe(III) is nearly insoluble. Natural organic ligands interactions with Fe(III) can increase the solubility by 20-fold in seawater. Ionic interaction models that can be used to determine the activity and speciation of divalent and trivalent metals in seawater and other natural elements will be discussed. The model is able to consider the interactions of metals with the major (Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , Br^- , F^-) and minor (OH^- , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , HS^-) anions as a function of temperature (0 to 50 °C), ionic strength [0 to 6 m ($\text{m} = \text{mol kg}^{-1}$)] and pH (1 to 13). Recently, it has been shown that many divalent metals are complexed with organic ligands. [13] Although the composition of these ligands is not known, a number of workers have used voltammetry to determine the concentration of the ligand $[\text{L}^n]$ and the stability constant (K_{ML}) for the formation of the complex [14]



We have added the experimental values of K_{ML} for the formation of complexes of natural organics in seawater of known concentration ($[\text{L}^n]$) with Cu^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} , and Fe^{3+} . The model can be used to examine the competition of inorganic and organic ligands for divalent metals as a function of ionic strength. The importance of organic ligands in controlling the solubility of Fe(III) in seawater will be discussed. New experimental studies are needed to extend the model to higher temperatures and ionic strength.

IV. RESULTS

An automated on-line ion exchange trace enrichment system has been developed to improve the detection limits of flame atomic absorption (AA) spectrophotometry in the determination of trace metals in natural waters. The sample solution is passed through a column of Chelex-100 chelating resin by a carrier buffer stream delivered from a constant

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flow pump. Trace metal ions retained by the Chelex-100 resin in the column are subsequently eluted off the column using complexing agents such as cysteine and EDTA. The variables that affect the performance of the system are studied. The detection limits of the system with flame AA detection are 0.09 $\mu\text{g/L}$ for Cu and Cd and 0.08 $\mu\text{g/L}$ for Mn with a 10-mL sample loop. The trace enrichment system has also been expanded to an automated two-column ion exchange system to study the speciation of trace metals in natural waters. In the two-column system, the sample solution is passed sequentially through a column of Chelex-100 resin and a column of AG MP-1 macroporous anion resin. The Chelex-100 column retains free metal ions and metal ions dissociated from labile metal complexes. The AG MP-1 column retains anionic non-labile metal complexes and metals strongly associated with negatively charged organic matter such as humic acid. The dissolved metal species are classified into three fractions by the proposed measurement scheme. The variables that affect the results obtained by the two-column system are studied using model complexing agents. The measurement scheme is shown to be rapid and simple (about 10 min per sample with a 10-mL sample loop) and is used to determine the speciation of Cu(II), Cd(II) and Zn(II) in natural water samples. The two-column ion exchange system is a versatile tool to study the trace metal complexation in natural waters. The system is used to determine the trace metal complexing capacity and conditional stability constants of synthetic ligands and ligands in natural waters and to study the dissociation kinetics of trace metal complexes in natural waters. The average Cu(II) complexing capacity of a Willamette River water sample is found to be about 4 μM and the conditional stability constant of Cu(II) complexes is about 10^7 at pH 7. The apparent 1st -order dissociation rate constant of Cu-humate complexes is determined to be about 0.3 s^{-1} at pH 6.5.[15]

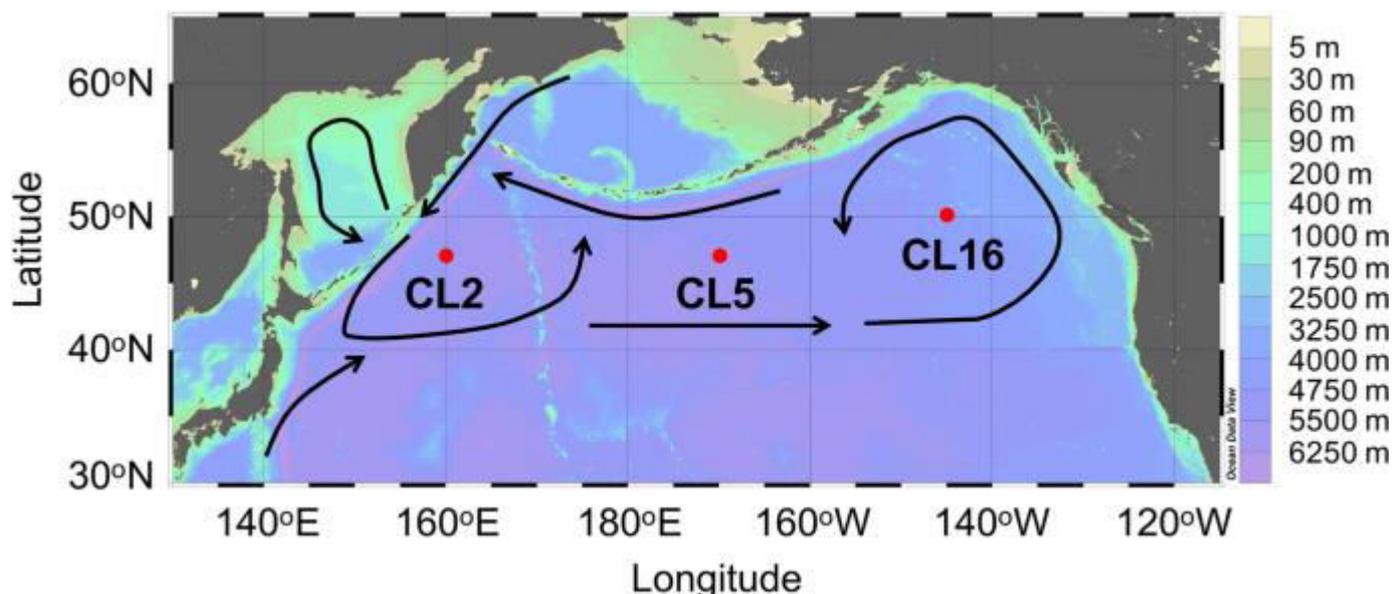


Fig.5. iron binding ligands between eastern and western subarctic pacific

V. CONCLUSION

The speciation of copper plays a strong role in determining bioavailability and toxicity upon copper exposure in marine environments. Specifically, natural organic matter (NOM) can complex with copper, influencing speciation and decreasing bioavailability. The aim of this research was to determine accurate copper speciation values using literature and new techniques and applying the techniques that reflect the most accurate speciation values to investigate the influence of NOM quantity and quality on copper speciation and toxicity. The results from this study will have implications on the development of a marine Biotic Ligand Model (BLM). Free copper was measured using a flow-through ion selective electrode (ISE) system. A published external calibration Cu ISE method showed a wide variability in measured free copper values and so method improvements were investigated. This resulted in the

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development of an internal calibration flow-through ISE method. This new method showed an increase in sample reproducibility and agreed well with modeled free copper values for well defined systems.[15]

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