Copper speciation: from estuaries to open ocean

Supervisors: Dr. Pascal Salaün, Prof. Stan van den Berg and Prof. George Wolff (UoL).
Contact: salaun@liverpool.ac.uk

COLLABORATION PARTNERS: Dr. Cédric Garnier (Université de Toulon, France), Dr. Dario Omanović (Ruđer Bošković Institute, Zagreb, Croatia)

Introduction

There are a number of reasons to study the chemical speciation of copper in marine waters. On one hand, copper is a micronutrient required in a number of cellular processes that are key for phytoplankton growth [1]. A lack of it will affect the biological community. On the other hand, it is a toxic element and impacts phytoplankton communities in harbours/estuaries [2] and possibly in the Mediterranean [3]. In addition, copper and iron have recently been shown to share the same organic ligands [4]. A possible effect of increased levels of Cu can thus be a decrease of the bioavailable pool of iron by favoring its dissociation leading to precipitation and scavenging. In view of the importance of iron in limiting primary productivity in vast areas of the oceans, understanding copper speciation might also shed lights into iron speciation. Finally, with increasing pCO₂ and decreasing pH (ocean acidification problem), there are strong concerns about the potential Cu toxicity due to a predicted increase in bioavailable levels.

Copper is described as a “hybrid element”. In surface waters, it presents a nutrient-like profile while in deeper waters, it presents the characteristics of a scavenged element. Copper bioavailability is strongly ruled by its chemical speciation, i.e. the distribution of its chemical species. It is now well established that copper speciation is highly governed by organic complexation with up to 99.9% of copper being bounded to organic complexes. This complexation buffers the free metal ion (the ion that is non-complexed, highly reactive and bioavailable) and keeps it at low levels. Without such complexation, the abundance and the structure of phytoplankton communities would be very much different.

While concentrations in open ocean and coastal waters range from 300 pM to several 10s of nM, concentration of free Cu²⁺ as low as 10 pM (10⁻¹¹ moles per litre) has been shown to be toxic to cyanobacteria. This level is now cited as the “critical threshold” although it is species dependent, and might be much higher/smaller for other organisms (e.g. fish). Although the role of complexation is crucial in shaping our marine environment, there are a lot of unknowns regarding even the most basic questions: what are the identities of these ligands, where do they come from and what are their biogeochemical pathways?

Figure 1: Dissolved Cu concentrations in the North Atlantic (www.egeotracess.org) ranges between 0.5 and 3 nmol.kg⁻¹.
Answers to these questions are hampered by the difficulty of analysing low levels of copper and low levels of highly heterogeneous complexing matter. There are only few analytical methods that have sufficient sensitivity to gain insights into the Cu complexation parameters. One of the most powerful techniques is by titration of the excess ligand with added Cu and measuring the electrochemical signal. The experimental data is modelled assuming the presence of 1 or 2 ligands, allowing the determination of stability constants, ligand, metal-organic complex and free metal ion concentrations. Recently we developed the pseudo-polarography at solid gold electrode [6], the technique for Cu speciation in coastal waters at its ambient concentration.

**Project summary**

The objectives of the project are:

- Constrain the pseudopolarographic and titration technique using model ligands (e.g. NTA, EDTA, glutathione, humic substances) at the gold electrode together with recent modeling capabilities (PROSECE/ProMCC, Garnier) [5, 6];
- Characterise the chemical speciation of Cu in marine waters. Complexing parameters (ligand concentrations and stability constant) will be obtained by titrations and complemented by other techniques such as the pseudopolarographic technique;
- Study the competition between Fe and Cu in open ocean waters;
- Study the impact of ocean acidification on copper speciation [7].

The novelty of this project in comparison to existing studies is the use of novel techniques such as the pseudopolarography [8] in complement of the titration technique. Levels and quality of DOC will be measured and correlated to complexation parameters. Samples will be collected from: 1- the Mersey estuary and/or Toulon Bay (France) where Cu concentrations range from several hundreds of nM down to less than 15 nM within a few kilometers [2]; 2- the pristine Krka estuary (Croatia) where strong salinity and Cu depth gradients are observed within the well-marked halocline 1-2 meters [5]; 3- cruises of opportunities on research vessels at the shelf-edge and at open sea.

The PhD student will be trained in marine analytical chemistry, marine biogeochemistry and electrochemistry. She/He will gain valuable field experience during e.g. research cruise(s) and will have the opportunity to spend time in the collaborating partner laboratory in Toulon (France) and/or Zagreb (Croatia). This project is well suited to students with a background in chemistry, geochemistry and/or environmental sciences and having an interest in oceanography and marine chemistry. Knowledge of electroanalysis is not required as the student will be trained during his first year.

**References**