

## Proposal for a SCOR Working Group: **Organic Ligands – The Key Control on Trace Metal Biogeochemistry in the Ocean**

### **Abstract**

The trace metals iron (Fe), copper (Cu), nickel (Ni), cobalt (Co), cadmium (Cd) and zinc (Zn) are essential micronutrients to marine phytoplankton and control primary productivity in up to half of the open ocean from tropical to polar regions. Consequently, they exert a major influence on the global carbon cycle and play a key role in controlling the world's climate. However, the availability of these metals to the biota is governed by speciation, whereby trace metals are bound by organic ligands. Organic ligands are defined as molecules that can bind to and form a complex with trace metals. In the ocean trace metals are overwhelmingly bound (90 to 99.999%) to organic ligands. Metal-binding ligands are ubiquitous in the ocean yet the composition and source of these ligands remains largely unknown. Over the past three decades, advances in analytical techniques have led to consensus on accuracy and precision, and dramatically improved our knowledge on the global and regional distributions of trace metals. In contrast, our understanding of trace metal-binding ligands and their pivotal biogeochemical functions remains at a comparatively early stage. *To date, we do not know the exact composition, source and provenance of metal-binding ligands, which is hindering further advances in the field of trace metal biogeochemistry.*

The proposed working group would focus on advancing our understanding of trace metal-binding organic ligands in the oceans, and over a 4-year period the group will (1) summarize published results and generate a ligand database to confirm the nature of the most pressing research questions; (2) establish a ligand intercalibration programme, and evaluate key analytical issues with currently employed methodologies to establish whether they need to be improved, supplemented or eventually replaced; (3) debate the nature of sampling strategies for both laboratory and field experiments that are needed to enhance our understanding of the links between the provenance, fate, distribution, chemistry and biological function of ligands; (4) recommend future approaches to ligand biogeochemistry including the decade-long GEOTRACES field efforts (i.e. both regional surveys and process studies) and the need for rapid incorporation of this research into biogeochemical models. In addition, the working group will also establish a ligand biogeochemistry webpage and promote this forum for discussion of ideas and results by our members soliciting input from both the trace metal and modelling communities. This interdisciplinary webpage will provide a platform to propose special sessions on trace metal-binding ligands at international meetings such as Ocean Sciences and EGU.

### **Rationale**

Understanding the role of metal-binding ligands in oceanic biogeochemistry is extremely important, as these ligands control the bioavailability of trace metals, thus influencing global elemental cycles such as carbon and nitrogen. To a large extent, we simply do not understand the role or chemical structure of metal-binding ligands in the oceans and we cannot, therefore, predict how they, and hence trace metal cycles, will respond to projected global alteration of continental aridity (dust supply), ocean acidification, and oceanic oxygen minimum zones due to a changing climate.

It is timely to focus on the issue of trace metal-binding ligands as it is now more than a decade since 'The Biogeochemistry of Fe' (SCOR WG 109) was established, which led to a seminal publication on iron biogeochemistry that concluded with key questions for future research. This resulted in dramatic advances in analytical capability (e.g. production of an iron standard) and quantification of iron sources and sinks. However, a key question relating to the composition, source and biological role of metal-binding ligands has yet to be addressed and is the focus of this proposal. In addition, a SCOR-sponsored international programme, GEOTRACES, was launched in late 2009. The decade-long GEOTRACES programme aims to determine the distributions of trace metals using ocean section cruises through all ocean basins. A core measurement on these sections is metal-binding ligands. Knowledge of metal-binding ligands is essential to understand their control on trace metal bioavailability and phytoplankton growth in the ocean. Furthermore,

as these ligands are inextricably linked to trace metal cycling, it is critical to determine how best to incorporate metal-ligands with trace metal data in global ocean models. For example, results from models of Fe biogeochemistry fluctuate dramatically depending upon the ligand data chosen (Parekh *et al.* 2005). Therefore, to ensure that GEOTRACES benefits from understanding the role of metal-binding ligands, it is important that this SCOR WG is established as soon as possible, to both better help in interpretation of data on trace metals and ligands and to inform sampling and analytical strategies. This will also allow us to target a GEOTRACES process study designed to study ligand dynamics at a site that may be used as a natural laboratory.

Given the need for a multidisciplinary solution to this problem, a SCOR working group, consisting of analytical chemists, biogeochemists, and modelers is the best mechanism to focus the international scientific expertise on metal-binding ligands. Appropriate scientific expertise will be assembled from different countries and an international working group will help develop this topic in developing nations. Other organizations cannot ensure that the activity is suitably interdisciplinary, involve scientists from a wide range of countries, while helping train young scientists. The results of this WG will be presented during a symposium and published in a special issue of a journal or book and a report to SCOR.

### **Background**

A short background is provided here to summarize the issues that have motivated us to propose a working group on metal-binding ligands.

In the decade since the seminal publication from the SCOR WG on ‘The Biogeochemistry of Fe’ (Turner & Hunter 2001), and the inextricable links between Fe and Fe-binding ligands presented in that book, there has been a considerable increase in publications focusing on Fe speciation as well as those for other trace metals, albeit to a lesser extent. It appears that Fe, Cu, Ni, Co, Cd and Zn are all bound to various extents by organic ligands and these metal-binding ligands are ubiquitous in the ocean. Metal-binding ligands appear to facilitate bioavailability and uptake of the trace metals Fe and Co, while those binding Cu, Ni, Cd and Zn sequester and decrease the bioavailability. While there are some known biological sources of metal-binding ligands, such as for Fe and Cu, the sources and identities of most ligands remain unknown.

At present we indirectly measure the binding capacity (i.e., the ligand concentration and binding strength, termed *stability constant*) of the metal of interest by means of a metal-ligand titration with electrochemical detection (e.g. Croot & Johansson 2000). Most ligand data published to date either describes the distribution of ligands binding to a specific trace metal in a specific water mass, or characterizes the ligand produced by one specific organism grown in a laboratory culture. Only recently, and supported through analytical advances, research has focused on determining the link between the binding strength of ligands in natural seawater and the biota that may be producing the metal-complexing ligands. For example, siderophores, produced by bacteria for iron acquisition have been shown to have similar stability constants as Fe-binding ligands in surface waters and have been measured in seawater (Mawji *et al.* 2008). While most focus has been on Fe, and to some extent on Cu, very little is known about the composition and sources of other essential trace metal-binding ligands. What is known is that metal-binding ligands are typically present everywhere in the water column for many elements, suggesting that they are either highly recalcitrant, and/or a result of passive biological production *in-situ* (i.e., remineralization). For example, the bioremineralization of sinking particles was shown to produce iron-binding ligands (Boyd *et al.* 2010), humic substances can bind Fe and may be the source of some Fe-binding ligands in the deep ocean (Lagerla & van den Berg, 2009), while zooplankton grazing on phytoplankton also releases Fe-binding ligands (Sato *et al.* 2007). In addition, hydrothermal input of organic ligands to the deep ocean may be much larger than previously thought (Sander *et al.* 2007) and has only just been incorporated into models (Tagliabue *et al.* 2010). Further, the ubiquitous presence of metal-binding ligands would seem to indicate that at least some of these ligands are not metal-specific. While this has not been directly assessed to date in the field, compiling published data would allow some insights into this issue. This is crucial as recent evidence

suggests that Fe availability depends on Cu availability (Peers *et al.* 2005), with the bioavailability of both metals governed by organic complexation; similar synergistic behavior between other trace metals may also be important. Thus, an over-arching question is: ***What is the composition, source and fate of metal-binding ligands?***

Currently, in the absence of structural characterization of the ligands, conditional stability constants provide the only means to distinguish between different metal-ligand complexes in the ocean. Measured metal-binding ligands are typically reported in terms of ligand classes, with L<sub>1</sub> used for stronger ligands and L<sub>2</sub> for weaker ligands. The distinction between these ligand classes has proven useful in discussions of sources and roles of these ligands, but the distinction remains an operational definition that varies between analysts and is strongly dependent on the method used and hence the analytical window applied. Therefore, we need to investigate the distinction between L<sub>1</sub> and L<sub>2</sub> ligands and ***Determine how to best define these ligand classes.*** In addition, intercalibration studies have just started for Fe and Cu-binding ligands and need to be completed for the remaining trace metals. The data acquired using ligand titrations needs to be intercompared and examined in detail to ensure that the numbers for the concentration [L] and stability constants (log K') of measured ligands are valid.

At present, the size fractionation of trace elements is operationally defined by filtration whereby the colloidal fraction is typically 0.2-0.02 µm while the truly soluble is < 0.02 µm. Studies for Fe have shown that Fe-binding ligands are predominantly present in the colloidal fraction and that this size range is critical to understanding the variability in dissolved Fe (Bergquist *et al.* 2007). Does this imply that colloidal ligands are more easily scavenged than those in the soluble fraction? The proposed working group will use available speciation data and combined knowledge of the technique to ***Evaluate to what extent the distributions of metals and those of metal-binding ligands are correlated in the oceans.*** Assessing the available data from this perspective will allow additional insight into ligand sources and functions, as well as a framework for incorporating metal-binding ligands into models.

Modelling trace metal distributions is a formidable task at present. A good example is provided by recent attempts to model the Fe cycle where models have to make broad assumptions because of poor knowledge about the speciation of Fe (Boyd *et al.* 2010). Even less is known about the speciation of other trace metals in the oceans, and these are typically left out of models despite their importance in phytoplankton growth. Thus, a primary goal of the proposed working group is to ***Assess how to incorporate metal-binding ligands into biogeochemical models.*** Modellers require knowledge not only on the distribution of metal-binding ligands but also on the speed of reactions between trace metals and these ligands. Both the database and the interactive webpage will help address this issue.

### **Statement of Work/Terms of Reference**

1. To summarize published results on all aspects of metal-binding ligands in the oceans (i.e. distributions, chemical structure, sources, sinks, stability), and generate an organic ligand database for use in biogeochemical models and for those working in the field (including results from ongoing GEOTRACES, SOLAS and CLIVAR efforts).
2. To critically evaluate key analytical issues with currently employed methodologies to establish whether they need to be improved, supplemented or eventually replaced.
3. To debate the nature of sampling strategies for both laboratory and field experiments that are needed to enhance our understanding of the links between the provenance, fate, distribution, and chemistry and biological functions of these organic metal-binding ligands in the oceans.
4. To recommend future approaches to ligand biogeochemistry including ongoing GEOTRACES field efforts (i.e., both regional surveys and process studies).
5. To produce information/material resulting from the outcome of the above points in the form of Website, journal special issue or book and a report to SCOR.

## MEETINGS, WORKSHOPS AND SYMPOSIA:

It is proposed that the first formal meeting of this WG will take place before the Aquatic Sciences Meeting in San Juan, Puerto Rico (Feb. 13-18, 2011). Preliminary communications leading up to this meeting will take place during the preceding year and will lead to identification of additional Associate Members, fine-tuning of the Terms of Reference, and creation of an agenda. During the meeting the WG will set up intercalibration efforts and start work on the format for the database and webpage, which will also act as a forum for information exchange and details of new meetings. Other funding sources for the intercalibration efforts, the workshop and final publication will be determined.

Approximately one year after the first meeting a second meeting and an international workshop on trace metal-binding ligands in seawater will be held. This will allow a nominal one-year period over which to structure the workshop agenda, issue announcements and invitations, secure needed funds, and make other necessary preparations. To keep costs at a minimum this would be in combination with the Ocean Sciences Meeting in Salt Lake City, Utah, USA (Feb. 19-24, 2012) The workshop will provide the opportunity for all Full and Associate members of the WG to discuss all points of the terms of references. Groups will be formed and tasks assigned to work on projects and prepare material to be presented at the special symposia and in the special issue or separate book.

Full members of the WG will meet again in year 3 to determine the progress made by different groups and discuss necessary actions to successfully present at a dedicated symposium in year 4 during the Ocean Science meeting in 2014. That conference would also set the date for the fourth and final meeting during which the WG will be rounding off the results and outcomes and finalize the publications. Separate funding will be sought from EU-GEOTRACES COST Action and other sources for the WG third meeting Place and exact time for this meeting will be decided on but could again be in combination with the Aquatic Sciences Meeting 2013.

## Working Group Membership

The final working group membership is proposed to consist of 10 specialists:

<b>Name</b>	<b>Affiliation</b>	<b>Specialty within the field of trace metal speciation in seawater</b>
Kristen Buck (proposed co-chair)	Bermuda Institute of Ocean Sciences, Bermuda	Organic complexation, expert in electrochemical methods, bioavailability of trace metals
Maeve Lohan (proposed co-chair)	University of Plymouth, United Kingdom	Organic complexation, expert in electrochemical methods, Flow injection analysis
Sylvia Sander (proposed co-chair)	University of Otago, New Zealand	Organic complexation, expert in electrochemical methods, mass spectrometric characterization, hydrothermal systems.
Alessandro Tagliabue	Laboratoire de Science du Climat et de l'Environnement, France	Models of ocean biogeochemistry
Kathy Barbeau	Scripps Institution of Oceanography, USA	Bioavailability and reactivity of different metal species,
Peter Croot	Chemische Ozeanographie Kiel, Germany	Organic complexation, expert in electrochemical methods, bioavailability of trace metals
Martha Gledhill	National Oceanography Centre, Southampton, United Kingdom	Mass spectrometric determination of ligands in Seawater.
Shigenobu Takeda	University of Tokyo, Japan	Interaction between biological oceanographic processes and trace metals
Michael Ellwood	ANU Canberra, Australia	Organic complexation, expert in electrochemical methods and ICP-MS
Rujun Yang	College of Chemistry, Ocean University of China, China	Organic complexation, metal complexation by humics

## Corresponding members

Constant van den Berg (UK), James Moffett (USA), Phil Boyd (NZ), Francois Morel (USA), Barara Sulzenberger (CH), Ken Bruland (USA), Keith Hunter (NZ), Mak Saito (USA), Loes Gerringa (NL),

## **References**

- Bergquist, B.A., Wu, J. *et al.* (2007). Variability in oceanic dissolved iron is dominated by the colloidal fraction. *Geochimica et Cosmochimica Acta* **71**: 2960–2974
- Boyd, P.W., Ibsanmi, E. *et al.* (2010). Remineralization of upper ocean particles: Implications for iron biogeochemistry. *Limnol. Oceanogr.*, **55**: 1271-1288,
- Croot, P. L. & Johansson, M. (2000). Determination of Iron Speciation by Cathodic Stripping Voltammetry in Seawater Using the Competing Ligand 2-(2-Thiazolylazo)-p-crestol (TAC). *Electroanalysis*, **12**: 565-576. GEOTRACES ([www.geotraces.org](http://www.geotraces.org))
- Lagerla, L.M. & van den Berg, C.M.G. (2009). Evidence for geochemical control of iron by humic substances in seawater. *Limnol. Oceanogr.*, **54**: 610-619.
- Mawji, E. & Gledhill, M. *et al.* (2008). Hydroxamate siderophores: occurrence and importance in the Atlantic Ocean. *Environ. Sci. Technol.* **42**: 8675-8680.
- Parekh, P., Follows, M.J. *et al.* (2005). Modelling the global iron cycle. *Glob. Biogeochem. Cycles*, **18**: GB1002, doi:10.1029/2003GB002061.
- Peers, G., Quesnel, S.A. *et al.* (2005). Copper requirements for iron acquisition and growth of coastal and oceanic diatoms. *Limnol. Oceanogr.*, **50**: 1149-1158.
- Sander, S. G., Koschinsky, A. *et al.* (2007). Organic complexation of copper in deep-sea hydrothermal vent systems. *Environmental Chemistry* 4: 81-89.
- Sato M., Takeda, S. *et al.* (2007). Iron regeneration and organic iron(III)-binding ligand production during *in-situ* zooplankton grazing experiment. *Mar. Chem.*, **106**: 471-488.
- SCOR WG 109: [http://www.scor-int.org/Working\\_Groups/wg109front.htm](http://www.scor-int.org/Working_Groups/wg109front.htm) )
- Tagliabue, A., Bopp, L. *et al.* (2010). Hydrothermal contribution to the oceanic dissolved iron inventory. *Nature Geoscience*.
- Turner, D.R. & Hunter, K.A. (2001). The Biogeochemistry of Iron in Seawater. IUPAC Series on Analytical and Physical Chemistry vol 7. John Wiley & Sons, Chichester 396pp.