



Copper binding by terrestrial versus marine organic ligands in the coastal plume of River Thurso, North Scotland



François L.L. Muller*, Silvia Batchelli

Environmental Research Institute, University of the Highlands and Islands, Castle Street, Thurso KW14 7JD, UK

ARTICLE INFO

Article history:

Received 7 June 2013

Accepted 20 August 2013

Available online 29 August 2013

Keywords:

coastal waters

colloids

copper speciation

cross-flow filtration

humic acids

ABSTRACT

It is generally assumed that terrestrial humic matter contains a high density of metal complexing ligands spanning a wide range of stability constants. From equilibrium modelling it would be anticipated that carboxyl groups, which are known to be abundant in humic matter, should be capable of binding Cu quantitatively in humic-rich estuarine systems such as the river plume outflow of River Thurso, on Scotland's north coast, where concentrations along the full mixing gradient typically range for Cu: 1–25 nM and for DOC (Dissolved Organic Carbon): 150–1500 μ M. Using a combination of reverse and forward titrations monitored by adsorptive cathodic stripping voltammetry (ACSV), we show that terrestrial humic substances were the likely source of high-affinity (class 1), low abundance ligands (1–4 nM) found throughout the coastal plume, but that weaker (class 2), more abundant ligands (90–170 nM) appeared to be produced largely *in situ*, probably as a biological response to Cu inputs into the estuary. Conditional stability constants for Cu-binding were respectively $\log K_1' = 14.9$ – 15.9 and $\log K_2' = 11.8$ – 12.6 . Class 2 ligands were evenly distributed between the low and high molecular weight fractions of dissolved organic matter (DOM), both in March and May. Class 1 ligands were more abundant in the low molecular weight fraction in March, but not in May. The latter could be related to seasonal differences in the nature of peatland derived organic matter carried by River Thurso. Since class 1 ligands (terrestrial, humic) were saturated with Cu throughout the plume, it effectively fell upon class 2 ligands (marine, biological) to control Cu speciation in Thurso Bay, in particular keeping the free Cu concentration $[Cu^{2+}]$ within a relatively narrow range ($10^{-13.6}$ M to $10^{-12.4}$ M). On the other hand, class 1 ligands were responsible for solubilising small amounts of Cu derived from this peatland catchment and effectively transporting Cu, in dissolved and colloidal forms, to the ocean.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Copper is an essential micronutrient for all living organisms as it plays an important role in electron transfer in many life supporting systems (oxidative enzymes and energy transfer) and is present in many enzymes and proteins (Da Silva and Williams, 1991). Its importance for biological systems and active geochemistry meant that it received a great deal of attention early on and was the first one for which the influence of organic complexation in coastal and oceanic surface waters became fully appreciated (Kremling et al., 1981; Mills et al., 1982; Hanson and Quinn, 1983). Culture studies (Sunda and Huntsman, 1995; Gerringa et al., 1995a, b; Moffett and Brand, 1996) and observations in the field (Coale and Bruland, 1990; Croot et al., 2000) have helped establish that the complexing ligands have a biological origin. It is now widely recognised that

most phytoplankton and bacterial species have the ability to release Cu-complexing ligands and thus dramatically alter the chemical speciation of Cu, mostly to reduce its toxicity. This is because, essential though Cu may be, it occurs in seawater at concentrations that would be toxic to most cyanobacteria and prokaryotic organisms if it were not for the ability of these organisms to lower its bioavailability through the formation of strong organic complexes (Whitfield, 2001). Culture and field studies have shown that both prokaryotes and eukaryotes are capable of releasing ligands with stability constants (measured under seawater ionic composition and pH) of 10^{12} – 10^{15} (Croot, 2003; Muller et al., 2003, 2005) while eukaryotes (notably dinoflagellates) can also release ligands with stability constants (K') of 10^9 – 10^{12} (Croot et al., 2000). Macroalgae also release exudates identified in the literature as metal ligands. Their binding constants towards Cu seem to vary among green algae species from 10^7 to 10^9 (Andrade et al., 2010) while some brown macroalgae have been found to exude ligands with K' values of 10^{10} to 10^{12} (Gledhill et al., 1999; Murray et al., 2013).

* Corresponding author.

E-mail address: francois.muller@uhi.ac.uk (F.L.L. Muller).

This compelling body of evidence that marine micro- and macroorganisms produce Cu-binding ligands does not rule out the possibility that other types of organic ligands, e.g. terrestrial humic substances, may significantly alter Cu speciation—particularly in coastal regions of freshwater influence (Shank et al., 2004; Waelles et al., 2005, 2008; Takata et al., 2012) or near the sediment–water interface (Skrabal et al., 1997; De la Rosa et al., 2011). Indeed, it is likely that the pool of Cu-binding ligands in estuarine and coastal regions comprises a mixture of a wide range of ligands including humic and fulvic substances as well as biological exudates. Until now, most studies have focused either on the ligands derived from external sources (land, sediments) and referred to as allochthonous, or those produced *in situ* by the biota and referred to as autochthonous. Little is known about the relative contribution of the two sources of ligands to the speciation and cycling of Cu in estuarine and coastal environments. Furthermore, comparison among different published studies using competitive ligand equilibration techniques is seriously complicated by the fact that the detected ligands tend to fall in different classes of K' values, depending on the analytical window of the chosen technique. This artefact can be addressed by employing a “multiple analytical windows” approach (Moffett et al., 1997; Muller et al., 2001; Ndungu, 2012) so that both weaker and stronger ligands are represented and a meaningful picture of Cu speciation is obtained. In practice, this means conducting at least two competitive ligand titrations on each water sample, as was done in the present study. A reverse titration with a strong synthetic ligand detects the strongest, already occupied Cu-binding sites by pulling out the copper from its strongest natural complexes (Santos-Echeandía et al., 2008). A forward titration is then carried out with Cu in the presence of a fixed concentration of the added synthetic ligand, such that it establishes a balanced competition with the naturally occurring ligands.

Over the last 10 years there has been an increasing tendency to track compositional changes in DOM, including metal and ligand content, as a function of its molecular weight (MW). For instance, a recent study on ultrafiltered dissolved organic matter (DOM) from the St Lawrence estuary revealed that various functional groups tended to be associated with different MW fractions (Landry and Tremblay, 2012). Therefore cross-flow ultrafiltration should provide a complementary tool to unravel the different types of metal binding sites. In this study, we used cross-flow filtration (CFF) in an attempt to differentiate Cu-binding ligands not only in binding strength but also in molecular weight and to help untangle the

contributions of different sources (terrestrial vs. marine) to the ligand pool. We refer to HMW DOM as ‘colloidal’ and to LMW DOM as ‘truly dissolved’ or ‘soluble’.

We chose the River Thurso plume as a natural laboratory for examining the role played by terrestrial humic substances on Cu speciation in the coastal marine environment. The River Thurso drains an area of 400 km² situated and at the eastern edge of the Flow Country, which is by far the largest contiguous area of blanket bogs (4000 km²) in the British Isles. As such, it produces small, organic rich plumes in the adjoining marine environment. Earlier work has shown that the residence time of freshwater in the estuary proper is typically very short and that both DOC and Fe concentrations exhibit a conservative mixing behaviour (Batchelli et al., 2009, 2010). In this work we focused on the high salinity region of the plume in early and late spring. Conceptually, this is a region where the dominant mixing mechanisms are shear mixing and wind mixing and which provides a direct link to neighbouring coastal waters. As a result, the distribution and cycling of Cu between HMW and LMW DOM in this region is key to understanding Cu export pathways to the coastal ocean.

2. Material and methods

2.1. Salinity profiling, sampling and prefiltration of plume water

Coastal seawater samples were collected in Thurso Bay from the research vessel ERI Aurora during two surveys, on 17 March and 25 May 2009, conducted within the last 2 h of the outgoing tide. The river flow measured over the previous 3 days was slightly above ($12.5 \pm 2.3 \text{ m}^3 \text{ s}^{-1}$) and below ($6.6 \pm 1.1 \text{ m}^3 \text{ s}^{-1}$) the long term average, in March and May respectively. More importantly, it remained essentially constant during the typical flushing time of freshwater in Thurso Bay (<24 h). Under these conditions, we have shown that the relationships with salinity of alkalinity, dissolved organic carbon (Batchelli et al., 2009) and total dissolved iron (Batchelli et al., 2010) are all linear. Water sampling was done at four sites (H1–H4 and L1–L4 in March and May, respectively on Fig. 1) across Thurso Bay chosen to cover the high salinity range (30–35 and 23–35, respectively). A pure river water sample for total metal determination was also taken from a footbridge situated about 500 m upstream of the tidal limit. However, it was not used as a source of humic NOM in our speciation measurements as this would have entailed a storage time longer than a week between the sampling date and the start of the experiments. Instead we

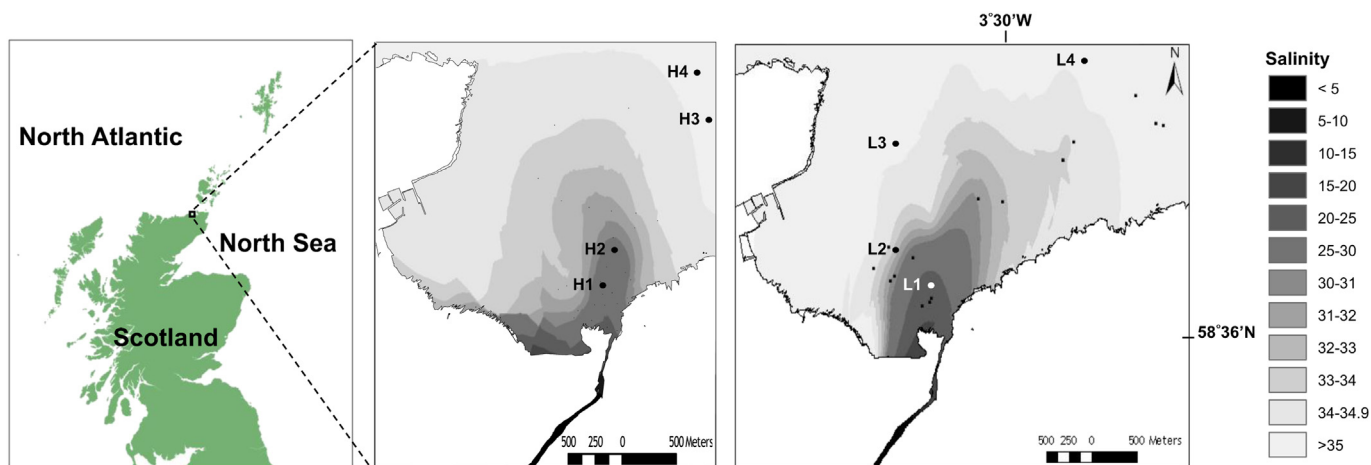


Fig. 1. Location of Thurso Bay, on the north coast of Scotland, and contour maps of salinity measured at the 0.30 m depth horizon on (a) 17 March and (b) 25 May. The sampling sites are designated H1–H4 (17 March) and L1–L4 (25 May), respectively.

Download English Version:

<https://daneshyari.com/en/article/6385034>

Download Persian Version:

<https://daneshyari.com/article/6385034>

[Daneshyari.com](https://daneshyari.com)