Competition between copper and iron for humic ligands in estuarine waters

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ABSTRACT

We determined the concentration of iron- and copper-binding humic substances (Fe-HS and Cu-HS) in estuarine waters along with the concentrations of iron- and copper-complexing ligands (L_{Fe} and L_{Cu}). Suwannee River humic acid (SRHA) was used as a humic standard. The complex stability of Fe with salicylaldoxime (SA) was calibrated for salinities between 4 and 35 and fitted to linear equations to enable Fe speciation in estuarine waters: $K'_{Fe'SA} = -2.98 \times 10^4 \times Sal + 4.60 \times 10^6$ and $\log B'_{Fe'SA2} = -1.41 \times \log Sal + 12.85$. The concentration of Cu-HS in waters from the Mersey estuary and Liverpool bay was less than the overall ligand concentration ($[Cu\text{-}HS]/L_{Cu} = 0.69 \pm 0.05$) suggesting that a second ligand was of importance to Cu complexation. The concentration of Fe-HS was virtually equal to the total ligand concentration for Fe ($[Fe\text{-}HS]/L_{Fe} = 0.95 \pm 0.16$) confirming that humics are responsible for Fe complexation in these waters. The concentration of HS determined from Fe-HS was within 4% of that found from Cu-HS, confirming that the same substance is detected. The average complex stability ($\log K'_{Fe'L}$) was 11.2 ± 0.1, the same as for $\log K'_{Fe'\text{-}SRHA}$. Copper additions demonstrated competition between Cu and Fe for the HS-type ligands. This competition was used to determine the complex stability for the Cu-HS species, giving a value of 10.6 ± 0.4 for $\log K'_{Cu'HS}$, which is nearly a unit less than the complex stability, $\log K'_{Cu'L} = 11.4 \pm 0.2$, found for all Cu ligands (the HS and the unknown ligand combined). The competition affects the complexation of both metals with HS-type ligands. Extrapolation of the concentration of Fe-HS to an ocean salinity of 35 gives a residual level of 0.05 mg HS L^{-1}, equivalent to an Fe-binding ligand concentration of 1.5 nM. If HS-type ligands are confirmed to be ubiquitous in coastal or ocean waters, competition reactions could be of importance to the bioavailability of both metals to marine microorganisms.

1. Introduction

Iron (Fe) and copper (Cu) occur complexed with organic matter in waters from estuarine and oceanic origin (Buck et al., 2007; Campos and van den Berg, 1994; Gledhill and van den Berg, 1994; Muller and Batchelli, 2013; Rue and Bruland, 1995; Sander et al., 2014; van den Berg, 1995) in spite of competition by the major cations that occur at concentrations typically 10^6 times greater. Metal complexation is important because it affects the metal geochemistry and bioavailability. The main removal pathway of freshly added metals in estuarine and coastal waters is by scavenging with suspended particulate matter (SPM) (Achterberg et al., 1999; Ellwood et al., 2008; Li et al., 1984), in addition to biological uptake in ocean waters (Balistrieri et al., 1981). Dissolved complexation reactions are in competition with the removal processes (Turner et al., 1998; van den Berg et al., 1987). Complexation also affects availability to microorganisms leading to feedback reactions, as exemplified by releases of exopolysaccharides from marine bacteria (Hassler et al., 2011), and other ligands (Eldridge et al., 2004; Weaver et al., 2003). Importantly, the solubility of Fe is enhanced by organic complexation (Schlosser and Croot, 2009) causing the element to remain in solution allowing more time for uptake by microorganisms.

Copper (Cu) speciation in seawater is dominated by organic complexation (Bruland et al., 2000; Buck and Bruland, 2005; Kogut and Voelker, 2003). Thiols have been identified as one type of Cu-binding ligands (Dupont et al., 2004; Laglera and van den Berg, 2003; Le Gall and van den Berg, 1998) and humic substances (HS) are likely another ligand (Kogut and Voelker, 2001; Muller and Batchelli, 2013; Shank et al., 2004; Xue and Sigg, 1999). Cu-binding ligands (Skrabal et al., 1997) and thiols (Chapman et al., 2009) have been shown to emanate from pore-waters into shallow surface waters. Cu-HS species have recently been shown to occur in estuarine waters (Whitby and van den Berg, 2014).

The complex stability is a function of the stability constant (K'_{CuL}), which is conditual upon side-reactions of the ligand with competing cations, and the ligand concentration. Natural waters containing ligands of various sources (terrestrial, break down products of plant materials, and in-situ produced by microorganisms), contain a mixture of ligands that form strong as well as weak complexes, that can be crudely subdivided into ligand classes. Log K'_{CuL} values vary between ligand

classes, typically ranging from log K′$_{Cu'L}$ = 8–10 for weak ligands (L2 type) (Donat et al., 1994; Moffett et al., 1990) to as high as log K′$_{Cu'L}$ = 15 for strong ligands (L1 type) (Bundy et al., 2013) (these constants were converted to the Cu′ scale using a value for α$_{Cu'}$ of ~20 valid for pH 8 seawater (Whitby and van den Berg, 2014)). Suwannee River humic acid (SRHA) gives a log K′$_{Cu'SRHA}$ = 10.7 in seawater (Kogut and Voelker, 2001; Whitby and van den Berg, 2014). Estuarine waters have been reported to have ligands for Cu with a complex stability of log K′$_{Cu'L}$ ranging from 11–16 (Muller and Batchelli, 2013) encompassing that of HS but also several thiol compounds (Dryden et al., 2007).

The speciation of iron (Fe) is, like Cu, dominated by organic complexation and it tends to occur >99% complexed with organic matter in sea (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; van den Berg, 1995) and estuarine waters (Batchelli et al., 2010; Rijkenberg et al., 2006). Siderophores (low-molecular weight, high-affinity Fe(III)-binding ligands secreted by bacteria) (Macrellis et al., 2001; Mawji et al., 2011; Velasquez et al., 2011) and humic substances (Laglera and van den Berg, 2009) have been reported as Fe-binding ligands. Certain natural ligands, such as domoic acid, are known to be complexed with both copper and iron in seawater (Rue and Bruland, 2001) suggesting that metal competition could play a role. It has been suggested that Fe uptake by Pseudo-nitzschia is regulated by both domoic acid and copper (Wells et al., 2005), which could possibly be explained by competition reactions.

Speciation measurement is generally by cathodic stripping voltammetry (CSV) making use of competition between an added ligand, which forms an electroactive complex, and natural complexing matter. Using this technique the concentration and complex stability of natural complexing ligands of Cu and Fe have been determined in estuarine (Buck et al., 2007; Gerringa et al., 2007), coastal (Buck and Bruland, 2005; Muller and Batchelli, 2013; Sander et al., 2014) and ocean waters (Buck et al., 2012; Rue and Bruland, 1995; van den Berg, 1995). Competition between the metals for ligands occurring in natural waters has not been demonstrated though competition has been shown between Fe, Cu (Whitby and van den Berg, 2014), Al and Co for complexation with Suwannee River humic substances (SRHA and SRFA) added to seawater (Yang and Van den Berg, 2009).

It is possible to determine specific ligands in seawater on the basis of the specific CSV response of their metal species. This has been used to identify Cu binding thiols (Al-Farawati and Van Den Berg, 2001; Le Gall and van den Berg, 1993), Cu and Fe binding humic substances (Laglera et al., 2007; Whitby and van den Berg, 2014), and various sulphur species (Luther and Ferdelman, 1993; Rozan et al., 2000).

Using the ligand competition method it has not been possible to investigate competition between metals for natural complexing ligands because the added competing ligand affects the speciation of all metals. Here we make use of the signal for specific ligands (humic substances present in the seawater) to investigate competition between Cu and Fe for these ligands in estuarine and coastal waters. Concentrations of copper and iron binding ligands were determined separately using ligand competition techniques and from the signal for Cu-HS and Fe-HS.

2. Experimental

2.1. Equipment

Voltammetric apparatus was a μAutolab-III potentiostat (Ecochemie, Netherlands) connected to a hanging mercury drop electrode (HMDE, Metrohm 663VA). The reference electrode was Ag/AgCl with a 3 M KCl salt bridge, and the counter electrode was a glassy carbon rod. The stirrer was a rotating PTFE rod. GPES software was used to control the instrument. Apparatus used for Cu detection used nitrogen for oxygen removal, whereas apparatus used for Fe and Fe-speciation was pressurised using air (Abualhaija and van den Berg, 2014) in order to ensure that the concentration of dissolved oxygen (DO) was constant

during the measurements. The software was changed to discard 2 mercury drops (instead of 4) between scans. Water used for rinsing and dilution of reagents (MQ) was purified by reverse osmosis (Millipore) and deionisation (Milli-Q). Glass and PTFE voltammetric cells used for total metal determination were cleaned using 0.1 M HCl and rinsed with deionised water followed by UV-digested sample before measurements. Vessels used for titrations were MQ-rinsed about once a week but were not normally rinsed between titrations to minimise de-conditioning. pH measurements (Metrohm models 605 and 827) were calibrated against pH 7 and pH 4 standards on the NBS pH scale. The reference section of the combined pH electrode was filled with 3 M KCL. Total dissolved metal concentrations were determined by CSV after 1 h UV-digestion of acidified samples (20 μL 50% HCl (10 mL)$^{-1}$) either in 30-mL PTFE-capped quartz sample tubes using a 125-W UV system (fitted with a high-pressure mercury vapour lamp) (Van Den Berg, 2014) or in the voltammetric cell with a horizontal UV lamp. pH neutralisation was by addition of ammonia and borate pH buffer. UV absorbance of dissolved humic matter was measured on a Jenway 7315 spectrophotometer set to 355 nm in polystyrene cells of 1 cm path length. Background correction was against UV seawater. The absorbance of each station was compared to a calibration curve of HA standards to quantify the HS in samples, similar to that used for chromophoric dissolved organic matter (CDOM) (Chanudet et al., 2006; Hong et al., 2005; Laglera et al., 2007).

2.2. Reagents

Cu and Fe standard solutions were atomic absorption spectrometry standard solutions (BDH SpectrosoL grade) diluted with MQ water; HCl was added to a pH of 2. Typically 20 mL was prepared of these solutions, which were stable and were replaced only when the level ran low. An aqueous stock solution containing 0.1 M salicylaldoxime (SA) was prepared in 0.1 M HCl. Reference humic and fulvic acid used for calibrations were Suwannee River HA (International Humic Substances Society (IHSS) Standard II 2S101H) and FA (IHSS standard II 2S101F), which were dissolved in MQ water to a concentration of 0.1 g L^{-1} and stored in the dark at 4 °C when not in use. 1 M sodium bicarbonate (Sigma Aldrich) in MQ water was diluted to 2 mM and used to dilute seawater to lower salinity. A pH buffer containing 1 M boric acid (Aristar grade) and 0.35 M ammonia (MOS grade, Fisher Scientific) was UV-irradiated for 45 min to remove organic contaminants. A bromate stock solution containing 0.4 M potassium bromate (Fisher Scientific) was used for the determination of Fe-binding HS. Contaminating metals were removed from the buffer and bromate solutions by overnight equilibration with 100 μM MnO$_2$ (van den Berg, 1982) and then filtered (0.2 μM inorganic membrane, Whatman); 100 μL of the buffer in 10 mL seawater gave a pH$_{NBS}$ of 8.18.

All sample containers were cleaned in 3 steps: first by soaking for 1 week in 1% detergent in warm MQ-water, followed by soaking for 1 week in 1 M HCl (Analar grade), and finally by soaking at least 1 week in 0.1 M HCl (Analar grade). Containers were then rinsed in MQ-water and stored partially filled with 0.01 M HCl (high-purity grade).

2.3. Sample collection and storage

Samples from the Mersey Estuary and Liverpool Bay (Irish Sea) were collected using a peristaltic pump. The water inlet tubing was held away from the vessel, the RV Marisa, (May 2013 and April 2014) and the water was used to first rinse (3×) and then fill a 5-L high-density polyethylene (HDPE) container at each station. The suspended matter was allowed to settle overnight in the laboratory and the supernatant water was filtered through an in-line 0.2 μM filtration cartridge (Sartobran, Whatman) using a peristaltic pump, and stored in the dark at 4 °C in 0.5 L HDPE bottles.