Influence of ocean acidification on the complexation of iron and copper by organic ligands in estuarine waters

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ABSTRACT

The uptake of anthropogenic atmospheric CO_2 by the oceans causes a shift in the carbonate chemistry system which includes a lowering of pH; this process has been termed ocean acidification. Our understanding of the specific effects of ocean acidification on chemical speciation of trace metals, in particular on organic–metal interactions, is limited. In this study we have experimentally determined the effects of changing pH from 8.3 to 6.8 (on the NBS scale) on the speciation of iron and copper in estuarine waters. Our experimental results indicated that complexation of iron and copper would decrease and inorganic iron and copper concentrations increase, as pH decreased, although it was not possible to confidently quantify changes in speciation at lower pH due to constraints of the analytical technique. In addition to our experimental approach, we used a non-ideal competitive adsorption (NICA)–Donnan model to determine the chemical speciation of iron and copper as a function of pH. The NICA–Donnan model was optimised in order to produce similar metal binding characteristics to those observed in our sample across the pH range examined in our study. The model allowed for simultaneous modelling of solubility and organic complexation. Model results indicated that a decrease in iron and copper binding by organic matter at lower pH, coupled with increased solubility (for iron), resulted in a 3 fold increase in inorganic iron concentration and a 6 fold increase in inorganic copper concentration at pH of 7.41 compared to a pH of 8.18 (expressed on the total scale). This compared to a 10 fold increase in inorganic iron concentration, and a 5 fold increase in inorganic copper concentration, obtained at pH 8.18, when the dissolved organic carbon (DOC) concentration was halved. Variability in DOC might thus be expected to have a greater impact on metal speciation in seawater, than projected variability in pH resulting from increases in atmospheric CO_2. Our study therefore suggests that increases in the concentrations of the more bioavailable inorganic iron and copper species in estuarine waters resulting from increased pCO_2 are likely to occur, but that such changes will be moderate in magnitude.

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1. Introduction

The world's oceans play a key role in the global carbon cycle and take up about one quarter of the anthropogenic CO_2 emissions, which are estimated at 10 Pg C per year (Canadell et al., 2007). As a consequence of the oceanic CO_2 uptake, the accumulation in the atmosphere of this important greenhouse gas is reduced, thereby buffering the effects of climate change (Le Quere et al., 2009). The increase in the amount of CO_2 dissolved in the oceans changes the carbonate chemistry system and thereby lowers pH and carbonate ion concentrations (Orr et al., 2005). This process is termed ocean acidification. The increase in atmospheric CO_2 from pre-industrial (280 µatm) to current levels of ca.

400 µatm (Myhre et al., 2013) has resulted in a decrease in average surface ocean pH of ca. 0.1 unit (Caldeira and Wickett, 2003). In case CO_2 emissions are not successfully curtailed in future, surface ocean pH is projected to decrease by a further 0.3 units by the end of the current century, to an average of ca. 7.8 in the year 2100 (Representative concentration pathway 8.5; Gattuso et al., 2014). A further reduction to ca. 7.5 is a possibility in following centuries (Caldeira and Wickett, 2003). The hydrogen ion concentration will more than double (increase by 130%) in case of a pH reduction by 0.4 units. The present rate of surface ocean pH change is ca. 0.015–0.02 pH units per decade (Byrne et al., 2010; Orr et al., 2005; Santana-Casiano et al., 2007), and consequently will result in larger and more rapid pH changes over the next several centuries than experienced over the last 20 million years and perhaps longer (Caldeira and Wickett, 2003; Raven et al., 2005). The projected changes in the marine carbonate system will likely have profound biological consequences for oceanic and near-coastal ecosystems within the coming

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decades and centuries (Guinotte and Fabry, 2008) with anticipated detrimental effects on marine calcifiers (Fabry, 2008), corals (Hoegh-Guldberg et al., 2007), mollusks (Gazeau et al., 2013) and crustaceans (Whiteley, 2011), making it more difficult to build and maintain skeletons, tests, and shells of calcium carbonate (Doney, 2006). The effects of ocean acidification on coccolithophore calcification are not fully resolved and a topic of much debate (Iglesias-Rodriguez et al., 2008; Riebesell et al., 2000; Young et al., 2014) with reported species specific responses to ocean acidification (Langer et al., 2006). Furthermore, our understanding on the effects of ocean acidification on non-calcifying marine organisms, ecosystem diversity and biogeochemical processes is only just emerging (Gattuso et al., 2013; MacGilchrist et al., 2014; Raven et al., 2005; Richier et al., 2014).

The observed changes in carbonate chemistry have potential consequences for the chemical speciation of trace metals. The effects on inorganic metal speciation can be modelled with some level of accuracy, e.g., with the use of the ionic Pitzer interaction model (Millero and Pierrot, 2007; Millero et al., 2009; Pitzer, 1991). The strongest effects of ocean acidification on inorganic metal speciation is for metals that form strong complexes with carbonates (e.g., copper and rare earth elements) and or hydroxides (e.g., iron and aluminium), whereas metals that are mainly in the free ionic form (e.g., manganese) or those that form strong complexes with chlorides (e.g., silver and cadmium) are not strongly affected. In contrast, the effects of a decrease in pH on metal complexation by natural organic ligands in seawater are largely unclear (Millero et al., 2009; Shi et al., 2010). The aim of this study is to determine the effects of ocean acidification on trace metal speciation in seawater, with particular emphasis on metal–organic interactions. For this purpose, we have conducted metal complexation measurements with natural seawater under different pH conditions for iron and copper, and have complimented this with non-ideal-competitive adsorption modelling of complexation by dissolved organic matter for these elements. In our study we have employed a pH range between 8.3 and 6.8 for experimental work (measured on the NBS scale), and between 8.2 and 7.4 for modelling, which relates to atmospheric CO_2 concentrations ranging between ca. 200 and 10,000 ppm and ca. 280 and 2000 ppm, respectively (Caldeira and Wickett, 2003).

Iron is an essential trace metal, required for a range of physiological processes in phytoplankton, including photosynthesis, respiration, nitrate uptake and nitrogen fixation (Geider and LaRoche, 1994; Hogle et al., 2014). Iron concentrations are very low in seawaters due to the low solubility of the thermodynamically stable redox form of iron (Fe(III), Liu and Millero, 2002). Approximately 99% of iron in seawater is complexed by natural organic ligands (Gledhill and van den Berg, 1994; Rue and Bruland, 1995) and this maintains iron concentrations above the limit set by the solubility of ferric hydroxide in seawater (0.08–0.2 nM, Liu and Millero, 2002) and prevents scavenging. Primary productivity in up to 40% of the world's oceans, the so-called high nutrient low chlorophyll regions, is iron limited with a consequent reduction in the efficiency of the biological carbon pump (Boyd et al., 2007). A decrease in seawater pH has been suggested to result in a higher availability of iron for uptake by marine phytoplankton, as a result of enhanced proton competition for the available iron-binding ligand places (Millero et al., 2009; Raven et al., 2005), and a consequently enhanced ocean productivity and oceanic CO_2 drawdown, resulting in a negative feedback mechanism.

Copper is both an essential micro-nutrient and a toxic element. Copper availability to marine microorganisms is considered to be related to the abundance of ionic copper (Campbell, 1995; Sunda and Guillard, 1976). Copper is an essential element for marine phytoplankton, with the growth of the oceanic diatom *Thalassiosira oceanica* limited at Cu^{2+} concentrations below 10^{-15} M (Sunda and Huntsman, 1995). On the other hand, Cu^{2+} is potentially toxic to cyanobacteria at concentrations as low as 10^{-12} M, and to other algae at higher levels (Brand et al., 1986) which would indicate that it is toxic at typical ambient levels were it not made less available by organic complexation reactions

resulting in more than 99% of copper being complexed (Coale and Bruland, 1988). Whereas, no limitation of primary productivity has been reported in open ocean systems as a result of low copper concentrations, a role of copper in iron uptake by phytoplankton and in nitrogen cycling has been proposed (Jacquot et al., 2013; Maldonado et al., 2006; Peers et al., 2005). In contrast, detrimental effects on marine microbial organisms of enhanced copper concentrations have been reported in perturbed estuarine and coastal systems (Andrade et al., 2006; Braungardt et al., 2007). An increase in free cupric ion concentrations due to ocean acidification would have negative effects on marine ecosystems.

This study has been undertaken in estuarine waters which experience strong natural variability in pH due to strong changes in total alkalinity (TA) and dissolved inorganic carbon (DIC) as a result of freshwater inputs, enhanced primary productivity and respiration. Estuarine systems also receive enhanced inputs of terrestrial organic matter, which has important metal binding capabilities (Buffle et al., 1984). In this study we (1) determined the complexing capacity of our estuarine sample for iron and copper over a pH range of 6.8 to 8.3 (on the NBS scale) by competitive ligand exchange–adsorptive cathodic stripping voltammetry (CLE–ACSV), (2) optimised a non-ideal thermodynamic model of organic matter complexation to fit our determined complexation parameters and (3) modelled the impact of changes in carbonate ion concentration and pH that might result from increased atmospheric pCO_2 on organic matter complexation of iron and copper. In the non-ideal thermodynamic model, we assumed that marine dissolved organic matter (DOM) behaves in a similar way to fulvic acids (FA) as there is considerable evidence that FA type organic material plays an important role in metal complexation in seawater, particularly in estuarine and coastal environments (Batchelli et al., 2010; Hassler et al., 2011b; Laglera and van den Berg, 2009). Furthermore models using humic or FA homologues have been shown to successfully represent metal speciation in the marine environment (Hiemstra and van Riemsdijk, 2006; Kogut and Voelker, 2001; Ndungu, 2012; Stockdale et al., 2011).

2. Experimental

2.1. Sample collection

Seawater for this study was collected in May and August 2008 in Southampton Water, an estuarine system on the English south coast. Surface water (ca. 0.2 m deep) was collected from the bow of a small vessel using a 10 L low density polyethylene bottle (LDPE; Nalgene). The seawater was filtered in-line using a filter capsule (Sartobran 300, Sartorius) with a 0.2 μm cut-off. All LDPE and Polytetrafluoroethene (PTFE) sample bottles (Nalgene) used in this study were cleaned according to a standard protocol (Achterberg et al., 2001). Samples for iron and copper-binding ligand analyses were stored at 4 °C for subsequent analysis. Titrations were performed within a period of one week. Samples for total dissolved iron and copper were acidified to pH 2 (a final concentration of 0.011 M) using ultra clean HCl (Romil UHP grade).

3. Materials and methods

Determination of the iron and copper-complexing ligands in seawater was performed using competitive ligand exchange–adsorptive cathodic stripping voltammetry (CLE–ACSV). The equipment consisted of a potentiostat (PGStat 10 Autolab Ecochemie), a static mercury drop electrode (Metrohm Model VA663), a double-junction Ag/saturated AgCl reference electrode with a salt bridge containing 3 M KCl, and a counter electrode of glassy carbon. De-ionised water (MilliQ, Millipore; >18.2 mΩ cm^{-1}) was used to prepare aqueous solutions. Labile iron and copper concentrations were determined by CLE–ACSV with 1-nitroso-2-naphthol (HNN) for iron (Gledhill and van den Berg, 1994; van den Berg, 1995) and salicylaldoxime (H$_2$SA) for copper (Campos