Marine Chemistry 177 (2015) 706–719

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Organic speciation of dissolved iron in estuarine and coastal waters at multiple analytical windows

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ARTICLE INFO

Article history:
Received 4 March 2015
Received in revised form 5 October 2015
Accepted 2 November 2015
Available online 9 November 2015

Keywords:
Iron speciation
Estuarine
Coastal waters
Voltammetry
CLE–CSV
Multiple analytical windows (MAWs)
Humic substances (HS)
Dissolved organic carbon (DOC)
Principal coordinate analysis (PCoA)

ABSTRACT

Here we use cathodic stripping voltammetry with competitive ligand exchange (CLE–CSV) to determine the speciation of Fe in samples from the Mersey River estuary and Liverpool Bay in the presence of salicylaldoxime (SA). Multiple analytical windows (MAWs) were obtained by varying the concentration of SA. Data fittings from individual titrations were compared to simultaneous analysis of all windows using KINETEQL Multiwindow Solver (KMS) giving good agreement. Individual and MAW titrations agreed and demonstrated the presence of only one ligand dominating in all samples. The ligand concentration behaved non-conservatively with increasing salinity, and was in excess of the iron concentration throughout the salinity range tested. The ligand concentration co-varied with that of iron-binding humic substances (HS). Measurement of the composition of dissolved organic carbon (DOC) using 2-dimensional fluorescence scans indicated the presence of terrestrial as well as microbial sources of organic matter in the estuary. The fraction of HS in the DOC amounted between 21 and 46%.

1. Introduction

Iron (Fe) is an essential micronutrient for marine phytoplankton as it controls primary productivity in large regions of the open ocean; consequently it has a major influence on the global carbon cycle and climate (Boyd and Ellwood, 2010). The availability of this trace metal to biota is dependent on its speciation (Brand et al., 1983). The inorganic complexation of iron in natural waters is well known (Hudson et al., 1992). It is well established that iron is >99% bound to organic ligands in the ocean (Rue and Bruland, 1995; van den Berg, 1995) however the composition and source of these ligands remain largely unknown (ligand soup) (Hunter and Boyd, 2007). Possible Fe-binding ligands are siderophores and exopolymer saccharides, heme and porphyrins (Gledhill and Buck, 2012; Hassler et al., 2011; Hunter and Boyd, 2007; Ibisanmi et al., 2011; Velasquez et al., 2011). Other possibilities include degradation products released during the decomposition of organic matter, bacterial degradation of sinking particles and cell lysis products, photolysis ligand products of some high-affinity marine siderophores and bioremineralization products like humic substances (HS), which have been suggested as weaker ligands (Hunter and Boyd, 2007; Poorvin et al., 2011; Wells et al., 2013).

Competitive ligand exchange–cathodic stripping voltammetry (CLE–CSV) is commonly used for metal complexation study. CLE–CSV measures the presence of natural metal complexing ligands because of the suppression of the response of the metal with an added competing ligand (AL). Several competing ligands with known stability constants for Fe such as 1-nitroso-2-naphthol (1N2N) (Gledhill and van den Berg, 1994; van den Berg, 1995), salicylaldoxime (SA) (Abualhaija and van den Berg, 2014; Rue and Bruland, 1995), 2-(2-thiazolylazo)-p-cresol (TAC) (Croot and Johansson, 2000) and 2,3-dihydroxynaphthalene (DHN) (van den Berg, 2006) have been used to determine the iron speciation.

In CLE–CSV the selection of the analytical window affects the detection of complexation parameters (Kogut and Voelker, 2001; van den Berg and Donat, 1992), where the window is determined by the complex stability of the competing ligand and the limit of detection. It has been suggested that the metal speciation can be improved by varying the detection window (Pižeta et al., 2015; Sander et al., 2011). It is estimated that natural organic complexes are measured if the α-coefficient of the unknown complex (α_{ML}) is within a decade of either side of the α-coefficient of the competing ligand (α_{MAL}) (Ibisanmi et al., 2011; van den Berg et al., 1990). The effect of varying the detection window has been studied for copper speciation in coastal (van den Berg et al., 1990; van den Berg and Donat, 1992) and estuarine waters (Buck and Bruland, 2005; Sander et al., 2015a) and for iron in seawater (Bundy et al., 2014; Ibisanmi et al., 2011) and estuarine-influenced shelf region

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http://dx.doi.org/10.1016/j.marchem.2015.11.001
0304-4203/

(Bundy et al., 2015). Studies have used TAC (Ibisanmi et al., 2011) and SA (Bundy et al., 2015; Bundy et al., 2014) as competing ligand for Fe speciation analysis.

Other than the detection window, data analysis also has key importance in speciation results. Traditionally, the methods used for the determination of total ligand concentration and stability constants involve the fitting of titration data using linearization (Ružić, 1982; van den Berg, 1982) which is easily implemented in spread-sheet software, and non-linear data fitting can also be used (Gerringa et al., 1995) which may have the advantage to fit more than one ligand to the data. New approaches have also been suggested for simultaneous data-fitting of several detection windows (Hudson et al., 2003; Sander et al., 2015a) and have been used for copper (Sander et al., 2015a; Wells et al., 2013) and iron (Bundy et al., 2015). In a recent intercomparison of CLE–CSV data analysis methods using simulated data, the simultaneous multiwindow analysis based on speciation was shown to produce the most accurate and precise parameters (Pižeta et al., 2015).

CLE–CSV is an electrochemical technique which is useful only in estimating the metal-binding ligand parameters but the technique does not provide any information about the structure or sources of those ambient ligands. Inclusive of other advanced techniques such as fluorescence spectroscopy is complementary for the source identification of those ambient ligands.

Early work on Fe (Boyle et al., 1977; Sholkovitz, 1976; Sholkovitz et al., 1978) across salinity gradients in estuarine systems described the scavenging of Fe (as iron oxyhydroxides) and HS due to co-precipitation at the mixing end of freshwaters and brackish waters, removing more than 90% of the Fe and lowering its concentration from 0.5–10 μmol/l in freshwaters (Nagai et al., 2007) to 1–20 nmol/l range in coastal water (Laglera and van den Berg, 2009). The solubility of inorganic iron in seawater is extremely low (0.01 nmol/l) due to the formation of $Fe(OH)_3$ (Liu and Millero, 1999) which is about ~100 fold less than the concentration of Fe (0.1–0.8 nmol/l in seawater (Johnson et al., 1997; Kuma et al., 1996; Laglera and van den Berg, 2009).

We carried out titrations of iron complexing ligands in estuarine and sea water over multiple detection windows (MAW) by varying the concentration of the added competing ligand (salicylaldoxime). We evaluated the data using conventional data fitting after linearization of individual titrations (Ružić, 1982; van den Berg, 1982), compared this to curve fitting program ProMCC (Omanović et al., 2015), and used a new version of KINETEQL Multiwindow Solver (KMS) (Hudson, 2014), to fit the speciation parameters (L_T and $K'_{Fe'L}$) to the MAW complexometric titrations as a unified dataset for one or more ligands simultaneously. We used recently optimised procedures and stability constants for iron speciation with SA in estuarine waters (Abualhaija and van den Berg, 2014; Abualhaija et al., 2015). The results are compared with earlier single window results (Abualhaija et al., 2015). Background data was obtained on dissolved organic carbon, fluorescent organic matter and humic substances.

2. Materials and methods

2.1. Sampling site and sample collection

The Mersey estuary is located in the north-west of England and extends from Warrington, where it receives freshwater from the River Mersey, to Liverpool Bay (47 km to the west) (Fig. 1). The majority of the freshwater entering the estuary is from the Rivers Mersey and Weaver, which drain a catchment area of approximately 4600 km^2. The estuary has a tidal range of up to 10 m, and the volume of water at high tide (35×10^7 m^3) is 50 times than that at low tide (0.7×10^7 m^3), which means that the estuary is well flushed (Wilson et al., 2005).

Six subsurface samples (station 1–station 6) were collected from the Mersey estuary and one from Liverpool Bay (Fig. 1) during two cruises with the Liverpool University research vessel, *RV Marisa*, in May 2013 (estuary) and April 2014 (Liverpool Bay). The hydrographic data for the samples is given in Table 1. Samples were collected from near Pierhead at salinity 18.81 towards the mouth of the estuary with salinity 30.88. The seawater end-member sample was collected from Liverpool Bay at an outgoing tide and had a salinity of 32.2. The average water temperature was 10.7 ± 0.23 °C.

Sample containers (1 l, low-density polyethylene (LDPE) bottles (Nalgene)) were cleaned by soaking in 1% detergent (Citranox, Fischer, UK) (one week), rinsed with milli-Q, soaked in 1 M HCl (two weeks), washed with milli-Q and left filled with 0.1% HCl. 5 l carboys had been used before for sample collection after an initial rigorous cleaning as described for the LDPE bottles. The 5 l carboys were high-density PE (HDPE) and were recycled by rinsing with 0.1 M HCl (reagent grade, Fischer UK) and MQ.

The samples for speciation analysis at MAWs were collected by peristaltic pumping into the 5 l HDPE carboys, which had been rinsed 3 times with the same water before filling. Suspended matter was allowed to settle overnight in the laboratory and the supernatant water was filtered through a 0.2 μm filter (Sartobran cartridge, Whatman) using a vacuum pump and stored in LDPE bottles in the dark at 4 °C until analysis (Batchelli et al., 2010). Separate samples from surface and subsurface (100 mL) were collected for fluorescence analysis, DOC and total dissolved nitrogen (TDN) measurements. For fluorescence analysis, the samples were filtered through pre-combusted GF/F filters (nominal pore size 0.7 mm) in an acid washed glass filtration assembly whereas samples for DOC and TDN were vacuum filtered using 0.2 μm polycarbonate membrane filters. The filtrates were wrapped in aluminium foil, stored in the dark at 4 °C and were analysed within 5 days of samples collection. Sub-samples were used to measure competition between copper and iron for humic ligands using single window iron speciation (5 μM SA) (Abualhaija et al., 2015).

2.2. Reagents

All sample manipulation was done in a Class 100 laminar airflow bench at room temperature. Milli-Q (Millipore U.K) of 18.2 MΩ·cm resistivity was used to prepare reagents and dilutions. Iron solutions of different concentrations were prepared by diluting 1000 ppm atomic absorption standard solutions (BDH, UK) and acidified to pH 2 with HCl. HCl (trace analysis grade) and ammonia (electronic MOS grade) were purchased from Fisher Scientific and were used to adjust the pH. A stock solution of 0.1 M salicylaldoxime (SA) was prepared by dissolving SA in 0.1 M HCl. The SA was 98% purity from Acros organics, Fisher Scientific. The pH buffer contained 1 M boric acid in 0.3 M ammonia in Milli-Q and gave pH 8.15 when added to seawater. Suwannee river HA (Standard II 2S101H) and FA (2S101F) standards were from the International Humic Substances Society (IHSS) and used for calibration. The stock solution contained 0.1 g HS/l in acidified MQ and was stored in the dark at 4 °C. pH measurements were done using a Metrohm model 713 pH meter, and were calibrated against NBS pH buffers 4, 7 and 9.

2.3. Voltammetric equipment

Voltammetric apparatus consisted of a Metrohm 663 VA Stand connected to a μAutolab potentiostat, which was computer-controlled using GPES 4.9 software. A hanging mercury drop electrode (HMDE) was used as working electrode; the reference electrode was Ag|AgCl|3 M KCl, while a glassy carbon rod was used as the auxiliary electrode. The apparatus was pressurised using compressed air at 1 bar; the mercury was filtered approximately every 2 months to remove Hg-oxides. Voltammetric measurements were made using the differential-pulse mode. Each sample was scanned 3 times, and an average value was taken as a peak height. A linear baseline was applied using the peak search function in GPES 4.9 (Metrohm Autolab, NL).