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Dissolved iron distribution and organic complexation in the coastal waters of the East China Sea

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ABSTRACT

The distribution of total dissolved iron and organic ligands in the coastal waters of the East China Sea, especially in the Yangtze River estuary, was investigated using competitive ligand equilibration–adsorptive cathodic stripping voltammetry (CLE–ACSV) with 2,3-dihydroxynaphthalene (DHN) as the competing ligand.

The seasonal variation of total dissolved iron (D-Fe) and its organic ligands (L_t) were observed in spring and autumn. The average D-Fe concentration in both surface and bottom waters in spring was higher than that in autumn. With respect to the horizontal distribution of D-Fe and L_t content, the highest values were observed in the estuary stations located in the Yangtze River Estuary and the Hangzhou Bay area and the lowest values were observed in offshore stations. The average surface D-Fe concentration of estuary stations in spring and autumn was 39.4 ± 26.6 (the standard deviation) nmol/L and 20.5 ± 11.0 nmol/L, respectively. The average bottom D-Fe concentrations of estuary stations in spring and autumn were 76.1 ± 58.6 nmol/L and 78.5 ± 39.0 nmol/L, respectively.

Higher surface L_t concentrations were observed during the spring. The average surface L_t concentrations of estuary stations in spring and autumn were 40.0 ± 26.8 and 23.2 ± 7.8 nmol/L, respectively. The concentration of D-Fe and L_t in the bottom water was higher than that observed in surface water and exhibited less seasonal variability. Strong ligands were observed in spring estuary surface water. The average surface $\log K'_{FeL}$ values in spring and autumn were 12.9 ± 0.8 and 11.7 ± 0.5, respectively. The total ligand concentration in this study was generally in excess of the dissolved iron, particularly in autumn at offshore stations. Higher excess organic ligand concentrations were also generally observed in the upper water column compared to bottom waters in autumn.

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1. Introduction

Iron (Fe) is an essential trace element for the growth of phytoplankton in the marine environment. Approximately 40% of the global oceans (Moore et al., 2002), including the north Pacific Ocean (Martin and Fitzwater, 1988), the equatorial Pacific Ocean (Coale et al., 1996; Rue and Bruland, 1997) and the Southern Ocean (Tréguer and Jacques, 1993) are high-nutrient low chlorophyll (HNLC) regions, where the growth of phytoplankton is limited by the low concentration of bio-available iron (Boyd et al., 2004; Coale, 2004). The concentration of iron in the open oceans influences atmospheric CO_2 content and hence global climate. Iron is also a limiting factor for the growth of marine phytoplankton in coastal regions (Bruland et al., 1991; Johnson et al., 1999), therefore, it might influence the competition between phytoplankton species. Because iron is a transition metal, and the standard redox potential for $Fe(OH)_3/Fe^{2+}$ is −0.236 V (Widdel et al., 1993), iron can function as an electron mediator during specific metabolic processes; for example, iron influences N_2 fixation during photosynthesis and plays an important role during the oxygen removal reaction. Iron is the fourth most abundant element on the earth; however, because the dominant redox species of iron is Fe(III), the theoretical thermodynamic concentration in seawater is approximately 1.0×10^{-11} mol/L (Liu and Millero, 2002). Iron concentrations in the open oceans range from 0.09 to 0.77 nmol/L (Rue and Bruland, 1995), which is significantly greater than the thermodynamically estimated dissolved iron (D-Fe) concentration. Over 99% of D-Fe is strongly complexed by organic Fe-binding ligands (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Wu and Luther, 1995; Öztürk et al., 2003; Ibisanmi et al., 2011; Kondo et al., 2012). These organic Fe-binding ligands increase the solubility of D-Fe and prevent oxyhydroxide precipitation, which would decrease Fe bioavailability (Rich and Morel, 1990; Hutchins et al., 1999). In addition, organic ligands significantly increase the residence time of D-Fe within the euphotic zone (Boye et al., 2003; Fan, 2008). In the absence of ligands in seawater, the solubility of Fe(III) hydroxide is approximately 0.15–0.20 and 0.07–0.09 nmol/L in coastal seawater

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and open ocean water, respectively (Kuma et al., 1996). Therefore, it is crucial to measure the concentration of dissolved organic Fe-binding ligands in estuaries and the coastal environment.

The concentration of iron complexed with organic ligands is difficult to measure directly because there is a gradient of many different kinds of organic compounds that bind Fe to varying degrees in seawater. Therefore, indirect measurements such as competitive ligand equilibration–adsorptive cathodic stripping voltammetry (CLE–ACSV) are used to determine the concentration of iron-complexing organic ligands and the complexation capacity of Fe(III) with natural ligands (Worsfold et al., 2014). The competitive ligands used for these studies include 1-nitroso-2-naphthol (NN) (Gledhill and van den Berg, 1994), 2-(2-thiazolylazo)-p-cresol (TAC) (Croot and Johansson, 2000), salicylaldoxime (SA) (Rue and Bruland, 1995) and 2,3-dihydroxynaphthalene (DHN) (van den Berg, 2006). Previous field studies have indicated that Fe-binding ligand concentrations vary greatly between coastal and open ocean waters. In open ocean waters, the concentrations of organic Fe-binding ligands ($[L_t]$) are quite low, for instance, 0.37–1 and 1.3–2.8 nmol/L for the stronger and weaker ligand class, respectively (Rue and Bruland, 1995); however, coastal water contains higher ligand concentrations, for instance, 4.3–526 nmol/L (Powell and Wilson-Finelli, 2003; Gerringa et al., 2007) was found.

The peak reduction current from titration has been calculated using linear (Ružić, 1982; Van den Berg, 1982; Cheize et al., 2012) or non-linear (Gerringa et al., 1995; Hudson et al., 2003; Wu and Jin, 2009) mathematical solutions, and the total ligand concentration ($[L_t]$) and the conditional stability constant (K'_{FeL}, commonly expressed as $\log K'_{FeL}$) (Gerringa et al., 2014) are determined. Linear fitting and non-linear fitting have been performed using the Langmuir isotherm model. For linear fitting, iterative correction of sensitivity (S) is performed, whereas S is included as a parameter for non-linear fitting (Laglera et al., 2013). The linear method is generally considered an oversimplification (Gerringa et al., 2014), and it is not practical to perform at least 3 titrations per sample for ligand saturation; therefore, titration data are generally fitted using non-linear methods (Laglera et al., 2013). Recent field studies have differentiated organic Fe-binding ligands into two classes: the stronger ligand class (L_1, $\log K_1'$) ranges between 11.1 and 13.9, and the weaker ligand class (L_2, $\log K_2'$) ranges between 9.7 and 11.95 (Rue and Bruland, 1995, 1997; Cullen et al., 2006; Buck et al., 2007; Ibisanmi et al., 2011; Gledhill and Buck, 2012). Compared to deep waters, surface waters generally have higher ligand concentrations and stronger stability constants (Bruland et al., 2001; Hunter and Boyd, 2007; Gledhill and Buck, 2012).

The East China Sea (ECS) is one of the biggest marginal seas in the western Pacific Ocean and is located in the area of 26–31°N, 121–126°E (Fang et al., 2009). Two main rivers, the Yangtze and Qiantang Rivers, enter the ECS. The Yangtze River has a watershed of 1.8×10^6 km^2 and is the third largest river in the world, with a sediment load of 5×10^{11} kg/year in the 1990s (Zhang et al., 1994; Müller et al., 2008). Anthropogenic activity generated elevated concentrations of dissolved Fe in the Yangtze and Qiantang Rivers, resulting in their deposition in estuaries and the ECS (Fang et al., 2009; Pan and Wang, 2012). In addition, the ECS is strongly influenced by the interaction between the China Coastal Current, Taiwan Warm Current and the Kuroshio Current (Liu et al., 2007), as well as the Asian monsoon and Asian dust storms (Uematsu et al., 2010; Li et al., 2014). On the other hand, according to annual reports from the State Oceanic Administration (SOA) of China, harmful algal blooms (HABs) occur in the ECS area every spring and summer (SOA, 2013). The current system and algal blooms influence the content of D-Fe and L_t in the ECS during different seasons. Based on these factors influencing the ECS, we determined the distribution of D-Fe and L_t in the ECS, mainly in the inner shelves. We examined the impact of diluted water from the Yangtze and Qiantang Rivers, anthropogenic activity, current, and HABs on changes in the dissolved iron concentration and speciation along the Chinese seacoast. To date, the ECS data here represent the first study of the distributions and seasonal variation of Fe-binding ligands.

2. Materials and methods

2.1. Seawater samples

In this study, seawater samples were obtained from the ECS in spring (22 March–4 April, 2011) and autumn (21 October–2 November, 2011) during two cruises of the R/V "Dong Fang Hong 2" (Fig. 1). Seawater samples were mainly collected from two transects, designated as P and T. The P transect was located in the area between the Yangtze Estuary and the central ECS. The T transect was located at the southwestern boundary of the East China Sea, which runs from north to south, along the coastal area of the Zhejiang and Fujian provinces. Stations C01 and S01 were located in the Yellow Sea and near Jiangsu Province; stations D01 and D02 were located at the northeastern of Yangtze River estuary (Fig. 1). Based on the relative distance from the mainland and the Yangtze River, the sample stations were classified into three groups: 1) estuary stations at the estuary of the Yangtze and Qiantang Rivers, 2) near-shore stations, which were near land but not in estuary stations, and 3) offshore stations, which were relatively far from land as well as the Yangtze and Qiantang Rivers (Fig. 1).

Seawater samples were collected in acid-cleaned Niskin bottles mounted on a Seabird 911 plus CTD Rosette (General Oceanics Co., USA) and parameters such as temperature, salinity, turbidity and fluorescence were measured simultaneously in the water column at grid stations. Niskin bottles, which were all internal Teflon and sealed internal metal springs, were cleaned by 10% hydrochloric acid (HCl, Suprapur, Merck, Germany) at least 24 h, rinsed with Milli-Q and then sealed in zip lock bags.

After collection, the samples were pressure-filtered through acid-cleaned 47 mm filter-holders loaded with 0.4 μm Nuclepore membranes (Millipore Company, Ireland) (soaked in HCl solution (pH = 2, Suprapur, Merck, Germany) for 24 h followed by a Milli-Q water (purified with a water purification system, Millipore, USA) rinse). The filtered seawater was collected in clean low-density polyethylene (LDPE) sample bottles, acidified to under pH 2 using HCl (Suprapur, Merck, Germany) immediately, and then used to analyze the D-Fe content. Other filtered seawater samples were collected in clean 250 mL LDPE bottles and frozen for subsequent analysis of organically-complexed iron. All procedures were performed in a class-100 clean laminar flow bench.

2.2. Bottle washing and reagents

Sample bottles were immersed in a tank containing 10% HCl mass fraction (Suprapur, Merck) for 3 days, rinsed with Milli-Q water 6 times, and then immersed in another tank of 10% HCl (Suprapur, Merck) overnight, rinsed with Milli-Q, and then filled with MQ water that was acidified using HCl (Suprapur, Merck) to pH value 2. The bottles were then sealed in zip lock bags.

All reagents were made in water that was purified using a Milli-Q system with the resistivity of 18.2 MΩ to produce ultra-high purity water (Millipore, USA). Suprapur hydrochloric acid (HCl, mass fraction 30%) was purchased from Merck Chemicals Ltd (100318, Germany). Ammonium hydroxide was prepared by vapor-phase transfer from reagent-grade concentrated NH_4OH into ultra-high purity H_2O. A stock standard solution of 1000.0 μg/g $Fe(NO_3)_3$ (chromatographically pure, Merck, Germany) was prepared and diluted to 100 μmol/L, 10 μmol/L, and 1 μmol/L (in pH = 2) to obtain the working solutions. The competitive ligand used was 2,3-dihydroxynaphthalene (DHN; chromatographically pure, Merck, Germany), and a stock standard solution of 0.1 mol/L DHN was prepared and diluted to 100 μmol/L. BrO_3^- (0.4 mol/L; BHD, UK)/POPSO (0.1 mol/L; chromatographically

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