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Kinetic study reveals weak Fe-binding ligand, which affects the solubility of Fe in the Scheldt estuary

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Abstract

The chemistry of dissolved Fe(III) was studied in the Scheldt estuary (The Netherlands). Two discrete size fractions of the dissolved bulk (<0.2 μm and <1 kDa) were considered at three salinities ($S=26$, 10 and 0.3).

Within the upper estuary, where fresh river water meets seawater, the dissolved Fe concentration decreases steeply with increasing salinity, for the fraction <0.2 μm from 536 nM at $S=0.3$ to 104 nM at $S=10$ and for the fraction <1 kDa from 102 nM to 36 nM Fe. Further downstream, in the middle and lower estuary, this decrease in the Fe concentration continues, but is far less pronounced. For all samples, the traditionally recognised dissolved strong organic Fe-binding ligand concentrations are lower than the dissolved Fe concentrations.

Characteristics of dissolved Fe-binding ligands were determined by observing kinetic interactions with adsorptive cathodic stripping voltammetry. From these kinetic experiments we concluded that apart from the well-known strong Fe-binding organic ligands (L, $\log K'=19$–22) also weak Fe-binding ligands (P) existed with an α value (binding potential$=K'\cdot[\mathrm{P}]$) varying between $10^{11.1}$ and $10^{11.9}$. The presence of this relatively weak ligand explained the high concentrations of labile Fe present in both size fractions in the estuary. This weak ligand can retard or prevent a direct precipitation after an extra input of Fe.

The dissociation rate constants of the weak ligand varied between 0.5×10^{-4} and $4.3\times10^{-4}\ \mathrm{s}^{-1}$. The rate constants of the strong organic ligand varied between $k_\mathrm{d}=1.5\times10^{-3}$–$17\times10^{-2}\ \mathrm{s}^{-1}$ and $k_\mathrm{f}=2.2\times10^{8}$–$2.7\times10^{9}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. The dissociation rate constant of freshly amorphous Fe-hydroxide was found to be between 4.3×10^{-4} and $3.7\times10^{-3}\ \mathrm{s}^{-1}$, more labile or equal to the values found by Rose and Waite [Rose, A.L., Waite, T.D., 2003a. Kinetics of hydrolysis and precipitation of ferric iron in seawater. Environ. Sci. Technol., 37, 3897–3903.] for freshly precipitated Fe in seawater.

Kinetic rate constants of Fe with the ligand TAC (2-(2-Thiazolylazo)-*p*-cresol) were also determined. The formation rate constant of $\mathrm{Fe(TAC)_2}$ varied between 0.1×10^{8} and $3.6\times10^{8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, the dissociation rate constant between 0.2×10^{-5} and $17\times10^{-5}\ \mathrm{s}^{-1}$ for both $S=26$ and $S=10$. The conditional stability constant of $\mathrm{Fe(TAC)_2}$ ($\beta_{\mathrm{Fe(TAC)_2'}}$) varied between 22 and 23.4 for $S=10$ and $S=26$ more or less equal to that known from the literature ($\log\beta_{\mathrm{Fe(TAC)_2'}}=22.4$; [Croot, P.L., Johansson, M., 2000.

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Determination of iron speciation by cathodic stripping voltammetry in seawater using the competing ligand 2-(2-Thiazolylazo)-*p*-cresol (TAC). Electroanalysis, 12, 565–576.]). However, at $S=0.3$ the $\log\beta_{\mathrm{Fe(TAC)}_2}'$ was 25.3, three orders of magnitude higher. Apparently the application of TAC to samples of low salinity can only be done when the correct $\beta_{\mathrm{Fe(TAC)}_2}'$ is known.

Keywords: Iron; Ligand; Estuary; Fe species; Kinetic rate constants

1. Introduction

Fe is essential for phytoplankton growth and it is known to be limiting the primary production in the open ocean as well as in coastal areas (Hutchins et al., 1998). Dissolved organic ligands increase the solubility of Fe in marine and estuarine waters. In this study we estimate the influence of dissolved ligands on the solubility and reactivity of Fe in the Scheldt estuary. Since the nature of organic ligands changes from terrestrial to marine environments, large solubility changes of the metals can be expected across salinity gradients (Baeyens et al., 1998b).

The Scheldt estuary can be characterised as a system with strong hydrodynamic and physico-chemical gradients. The mixing zone of fresh- and saltwater extends over a distance of 70 to 100 km (Wollast, 1988). The upper part of the estuary has a high organic and nutrient load. Because most particulate matter is negatively charged, mixing of freshwater and seawater neutralises the surface charges resulting in a flocculation zone between $S=1$–5 (Sholkovitz, 1976; Wollast, 1988; Paucot and Wollast, 1997). Due to the large input of biodegradable organic matter during the summer, anoxia occurs (Duinker et al., 1983; Wollast, 1988). During the 1980s the quality of the estuary has been improved, reducing the nutrient and organic matter load, but still in summer anoxia occurs (Baeyens et al., 1998a; Zwolsman and van Eck, 1993).

The residence time of water in the upper estuary is about 3 months during which non-refractory organic matter of terrestrial origin is almost completely mineralised (Wollast, 1988). The combination of decreasing turbidity at $S>5$ and the large supply of nutrients by the river Scheldt result in phytoplankton blooms during spring and summer. During these periods the organic matter produced within the estuary almost equals the amount of terrestrial organic carbon removed by respiration and sedimentation in the upper estuary (Wollast and Peters, 1978).

Processes influencing metal solubility in the Scheldt estuary have been studied extensively in the past. In the upper estuary at low salinity, where dissolved material flocculates and precipitates due to the increase in salinity, a large part of the dissolved metals in the Scheldt river are removed (Sholkovitz, 1976; Duinker and Nolting, 1978; Herzl, 1999). The concentration of dissolved metals, like Zn, Cd, Mn, Cu and Fe, depends in the first place on the input of metals, but once dissolved it depends on the combination of redox conditions and organic ligand content, whether the metals remain dissolved or not (Duinker and Nolting, 1978; Van den Berg et al., 1987; Zwolsman and van Eck, 1993; Regnier and Wollast, 1993; Gerringa et al., 1996; 2001; Paucot and Wollast, 1997; Rijkenberg et al., 2006a; Rijkenberg et al., 2006b). In the upper estuary, where anoxia can occur, the dissolved Fe concentrations are relatively high (Duinker and Nolting, 1978; Zwolsman and van Eck, 1993). Metals like Zn and Cd easily precipitate as sulphides, since the solubility product of these solid sulphides is low (Emerson et al., 1983; Comans and van Dijk, 1988; Gerringa et al., 2001). In contrast Fe sulphides have a relatively high solubility product and their precipitation is unlikely in the Scheldt estuary, because the dissolved sulphide concentrations are not high enough. Concentration of dissolved organic ligands is thought to determine the concentration of dissolved Fe above the solubility product of solid phases (Van den Berg et al., 1987).

Whitworth et al. (1999) could not explain the behaviour of Fe in the Scheldt estuary with their model considering binding with dissolved organic ligands on the one hand and adsorption on particles without precipitation and flocculation on the other hand. From other studies it is known that high labile Fe concentrations occur in seawater, which cannot be easily explained (Croot and Johansson, 2000; Powell, personal communication, 2004; Boye et al., 2005; Rijkenberg et al., 2006a). The existence of a weak Fe-binding ligand, outside the detection window of the applied method, may constitute a perfect explanation for both “too high” dissolved Fe concentrations in the Scheldt estuary and relatively high labile Fe concentrations. To examine the existence of a weaker Fe-binding ligand group besides the commonly measured strong organic Fe-binding ligands with a conditional stability constant $(K')\approx 10^{21}$ (Gledhill and Van den Berg, 1994; Van den Berg, 1995; Nolting et al., 1998; Croot and Johansson, 2000; Boye