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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, logK′ =19–22) also weak Fe-binding ligands (P) existed with an α value (binding potential=K′·[P]) varying between 1011.1 and 1011.9. 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 4.3×10−4 s−1. The rate constants of the strong organic ligand varied between kd =1.5×10−3–17×10−2 s−1 and k=2.2×108–2.7×109 M−1 s−1. The dissociation rate constant of freshly amorphous Fe-hydroxide was found to be between 4.3×10−4 and 3.7×10−3 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 Fe(TAC)2 varied between 0.1×108 and 3.6×108 M−1 s−1, the dissociation rate constant between 0.2×10−5 and 17×10−5 s−1 for both S=26 and S=10. The conditional stability constant of Fe(TAC)2 (KFe(TAC)2) varied between 22 and 23.4 for S=10 and S=26 more or less equal to that known from the literature (logKFe(TAC)2=22.4; [Croot, P.L., Johansson, M., 2000. Marine Chemistry 103 (2007) 30–45 www.elsevier.com/locate/marchem

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Determination of iron speciation by cathodic stripping voltammetry in seawater using the competing ligand 2-(2-Thiazolyazo)-p-cresol (TAC). Electroanalysis, 12, 565–576.) However, at $S=0.3$ the log$\beta_{\text{Fe(TAC)}}$ 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 $\beta_{\text{Fe(TAC)}}$ is known.

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 (Crook 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; Crook and Johansson, 2000; Boye...
et al., 2001, 2003), the Fe complexation characteristics of the Scheldt estuary were determined here by means of a kinetic study.

We sampled water in two size fractions (<0.2 μm and <1 kDa) at three different salinities representing three specific zones in order to establish the dissociation and formation rate constant of dissolved Fe-binding ligands: (a) upstream of the high turbidity zone, where terrestrial organic matter is present in high concentrations (S=0.3); (b) the zone where high primary production of plankton blooms generate fresh organic matter (S=10); (c) the zone with predominantly coastal marine organic matter (S=26).

2. Methods

2.1. Sampling, filtration and measurement of dissolved Fe

In April 2002, samples were taken during a cruise on the ship Navicula (Royal-NIOZ) in the estuary of the river Scheldt in the south of the Netherlands (Fig. 1). A torpedo towed alongside the ship was used to pump (Teflon diaphragm pump, Almatec A-15, Germany, driven by a compressor, Jun-Air model 600-4B, Denmark) water from 1 to 2 m depth via acid-washed braided PVC tubing to an over-pressurized class 100 clean container. The samples were filtered inline using 0.2 μm polycarbonate filter-cartridges (Sartorius Sartobran filter capsule 5231207H8). Salinity was measured with a simple TS meter.

Samples to characterise the dissolved organic Fe-binding ligands were collected from three stations in the Scheldt estuary at S=0.3, upstream of Antwerp, at S=10 near Hansweert and at S=26 where the river outlet enters the North Sea (Fig. 1). Part of these samples was ultra-filtrated using an acid-cleaned Amicon SP60 cartridge (<1 kDa fraction) and a peristaltic pump of Watson Marlow (604S/R), enabling filtration of large sample volumes. Samples for the determination of dissolved Fe (<0.2 μm and <1 kDa) were immediately acidified to pH=2 with concentrated 3× quartz-distilled (3xQD) HNO3 and stored at room temperature. Dissolved Fe in samples at high salinity (S=26) was measured with flow injection analysis (FIA) (de Jong et al., 1998). Dissolved Fe in samples of medium and

Fig. 1. The estuary of the river Scheldt in the southwest of The Netherlands. The three sampling sites are indicated by arrows.
low salinity (0.3 and 10) was directly measured by graphite furnace atomic absorption spectroscopy GFAAS (Perkin Elmer). Samples taken for the characterisation of the dissolved organic ligands were frozen immediately preventing chemical reactions to take place; only during thawing of the samples that precipitation of Fe could happen. Although the possibility of Fe-precipitation cannot be ruled out, we assume, as was done by Kuma et al. (1996), that the initial concentration of Fe-hydroxides is $[\text{FeX}]=0$ at $t=0$.

2.2. Complexation characterisation

2.2.1. Equipment

Determination of the organic speciation of iron in seawater was performed using Competing Ligand Exchange–Adsorptive Cathodic Stripping Voltammetry (CLE–ACSV). The 2-(2-Thiazolylazo)-p-cresol (TAC) was used as competing ligand (Croot and Johansson, 2000). All solutions were prepared using 18.2 MΩ nanopure water. The equipment consisted of a μAutolab voltameter (Ecochemie, The Netherlands), 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.

The chemicals used were a 0.01 M stock solution of TAC in 3xQD methanol, an 1 M boric acid (Suprapur, Merck) in 0.3 M 3xQD ammonia (Suprapur, Merck) and a 1 M boric acid (Suprapur, Merck) in 0.3 M 3xQD ammonia (Suprapur, Merck) (extra cleaning by the addition of TAC after which TAC was removed with a C18 SepPak column) to buffer the samples to a pH of 8.05 (Boye et al., 2003) and a 10⁻⁵ M Fe(III) stock solution acidified with 0.012 M HCl (3xQD). The borate buffer was adapted to samples of differing salinities and pH’s, at $S=26$ the final concentration in the samples was 5 mM borate buffer. The final TAC concentration was 10 μM unless otherwise stated.

The concentration $\text{Fe(TAC)}_2$ in the samples was measured using the following procedure: (i) removal of oxygen from the samples for 200 s with dry nitrogen gas, a fresh Hg drop was formed at the end of the purging step, (ii) a deposition potential of $–0.40$ V was applied for 30–60 s according to the sample measured, the solution was stirred to facilitate the adsorption of the Fe (TAC)$_2$ to the Hg drop, (iii) at the end of the adsorption period the stirrer was stopped and the potential was scanned using the differential pulse method from $–0.40$ to $–0.90$ V at 19.1 mV s⁻¹ and the stripping current from the adsorbed Fe(TAC)$_2$ recorded.

The Fe bound by TAC after equilibration overnight (>15 h) is defined as labile Fe with respect to TAC.

2.2.2. Characterisation of the dissolved ligands

2.2.2.1. Equilibrium titrations. Equilibrium titrations were executed to get information about the strong dissolved organic Fe-binding ligands in the samples. Aliquots of 15 ml were spiked with Fe(III) until final concentrations between 0 and 50–200 nM (depending on $S$) and allowed to equilibrate overnight (>15 h) with 5 mM borate buffer and depending on the experiment 1, 5, 10 or 20 μM TAC. The kinetic experiments were performed using 10 μM TAC. Since the strong organic Fe-binding ligands were saturated with Fe using 10 μM TAC, the conditional stability constant $K'$ could not be calculated. The total concentration of L was taken as the intercept of the straight titration line (TAC=10 μM) with the x-axis. The thus obtained values were used in the kinetic experiments as concentrations for the strong ligand L.

2.2.2.2. Kinetic experiments. To determine the dissociation and formation rate constants for the dissolved Fe-species a slightly modified method was used as described by Wu and Luther (1995). Instead of 1-nitroso-2-naphtol (NN), TAC was used as competing ligand (Croot and Johansson, 2000). The Fe or TAC is added to the sample and the changes imposed by these additions are followed with time until equilibrium is reached. All reactions considered are assumed to go via inorganic Fe (Fe'). Direct formation of one complex of Fe out of another complex of Fe is ignored; that is, it is assumed to exist only via dissociation from one complex followed by the formation of the other complex. The frozen samples were thawed directly before the kinetic experiments.

To determine the formation rate constants for the binding and precipitation of Fe, 20 nM of Fe is added at $t=0$ to 250 ml seawater and 15 sub-samples were taken in time. After the removal of oxygen, TAC (10 μM) was added to the sample. An extra 30 s of nitrogen bubbling was employed to remove the last traces of oxygen and an Fe(TAC)$_2$ deposition period of 90 s defined the measured labile Fe in these samples. The observed decrease in labile Fe with time is explained by the formation of Fe complexes and by the precipitation of Fe-hydroxides (FeX) (Fig. 2A, B).

To determine the dissociation rate constants of the naturally complexed-Fe, 10 μM TAC was added to the seawater forcing the dissociation of the natural dissolved Fe-complexes. The subsequent increase of the concentration Fe(TAC)$_2$ with time reflects the dissociation of natural Fe complexes on the one hand
and the formation of Fe(TAC)_2 on the other hand (Fig. 2C, D).

2.3. Modelling

In order to formulate a model for the calculation of rate constants, some general assumptions have to be made. The inorganic speciation of Fe is described by: inorganic Fe=[Fe']=10^{10}\cdot[Fe^{3+}] \quad (Hudson et al., 1992). We use the solubility depending on temperature and salinity by the following equation according to Liu and Millero (2002):

\[
\log \text{Fe}^{\text{III}} = -10.53 + 322.5/T - 2.524 I^{0.5} + 2.921 I 
\]

with \( I \) = ionic strength=19.922S/(1000−1.005S).

The maximum Fe' concentration ([Fe'_eq]) with respect to the solubility product (\( K_{SO} \)) of amorphous Fe-hydroxides, FeX, is according to (1): 0.19 nM Fe' at \( S=26 \) (log\( K_{SO} = 4.28 \)), 0.1 nM Fe' at \( S=10 \) (log\( K_{SO} = 4.03 \)) and 0.25 nM Fe' at \( S=0.6 \) (log\( K_{SO} = 4.39 \)).

2.3.1. Model 1: Addition of Fe

Titration analyses (10 \( \mu M \) [TAC]) showed that the Fe-binding ligand sites were saturated with Fe. Thus upon addition of 20 nM Fe, labile Fe should decrease to form Fe-hydroxides. We assume that the short presence of TAC in the sample does not influence the concentrations of either natural FeL or Fe-hydroxides.

Precipitation of Fe-hydroxides alone could not model the data. Since the labile Fe concentration was too high to fit the above-mentioned assumption (solubility product permitted 0.19–0.25 nM dissolved labile Fe), the presence of a relatively weak ligand called P was assumed. This is discussed extensively in Results and discussion. Furthermore, it is implicitly assumed that FeP dissociates within 120 s in the presence of 10 \( \mu M \) TAC. The hypothesis needs to be tested that the measured labile Fe accordingly contains [Fe']+[FeP]. Moreover, as the FeL and FeP all have been defined as having the simple 1:1 coordination, the outcomes on P and L are seen as indicative only. Henceforth the free form of the constituents is annotated with a prime ([L']).
The reactions, which take place after addition of Fe can be described by,

\[ [\text{FeL}] \xrightarrow{k_1}{k_2} [\text{Fe}'] + [L'] \quad (2) \]

\[ [\text{FeP}] \xrightarrow{k_3}{k_4} [\text{Fe}'] + [P'] \quad (3) \]

The parameters \( k_{d1} \) and \( k_{d3} \) are the dissociation rate constants \( (s^{-1}) \) and \( k_{r2} \) and \( k_{r4} \) are the formation rate constants \( (s^{-1}) \) of FeL and FeP, respectively (Fig. 3).

\[ [\text{Fe(OH)}_3]_4 + 3[H^+] \xrightleftharpoons[k_i]{k_f} [\text{Fe}'] + 3[H_2O] \quad (4) \]

Where \( k_d \) denotes the dissolution rate constant and \( k_i \) the precipitation rate constant. For Eq. (4) we can assume, according to Rose and Waite (2003a), \( K = 1/K_{SO} = k_i/k_d \) at equilibrium.

\( K_{SO} = [\text{Fe}^{3+}]/[H^{+}]^3 \)

\[ [\text{FeL}]_{eq} = k_{d*}/k_6 \text{ with } k_{d*} = k_d[H^{+}]^3 \text{ or Fe and } [\text{FeL}]_{eq} \text{ being the maximum dissolved inorganic Fe when equilibrium is reached with the solid Fe(OH)_3 (varying between 0.19 and 0.25 nM, depending on the salinity). Fe(OH)_3, the inorganic side reaction of Fe is assumed to be } 10^{10}, \text{ the pH is constant at 8, thus } k_{d*} = 10^{14} k_d s^{-1}. \text{ Eq. (4) can be rewritten as,} \]

\[ [\text{FeX}]/k_5 = k_6 \quad (4a) \]

with \( k_5 = k_{d*} \) and \( k_6 = k_d/[\text{FeL}]_{eq}. \)

Total [L] is known or deduced from the titration analysis as explained above. Total dissolved [Fe] is measured and an extra 20 nM Fe is added at \( t=0 \) as [Fe']. The parameter \( k_5 \) is the dissociation rate constant \( (s^{-1}) \) and \( k_6 \) is the formation rate constant \( (s^{-1}) \) of the precipitate FeX (Fig. 3). Thus, the changes in concentrations of all species are defined by the following set of equations,

\[ d[[\text{Fe}']/dt = k_{d1}[\text{FeL}] + k_{d3}[\text{FeP}] + k_{d5} - k_{r2}[\text{Fe}'][L'] - k_{r4}[\text{Fe}'][P'] - k_{r6}[\text{Fe}'] \quad (5) \]

\[ d[[\text{FeL}]'/dt = k_{r2}[\text{Fe}'][L'] - k_{d1}[\text{FeL}] \quad (6) \]

\[ d[[\text{L}']/dt = k_{r1}[\text{FeL}] - k_{r2}[\text{Fe}'][L'] \quad (7) \]

\[ d[[\text{FeP}]/dt = k_{r4}[\text{Fe}'][P'] - k_{d3}[\text{FeP}] \quad (8) \]

\[ d[[\text{P}']/dt = k_{d3}[\text{FeP}] - k_{r4}[\text{Fe}'][P'] \quad (9) \]

\[ d[[\text{FeX}]/dt = k_{r6}[\text{Fe}'] - k_{d5} \quad (10) \]

A concentration for total P was chosen as: \( [P]=3* [\text{Fe}_{\text{diss}}] \), \( [\text{Fe}_{\text{diss}}] \) denoting the dissolved Fe concentration. Calculations were also executed using a constant P concentration with salinity. For a constant P (P=1000 nM, results not shown) the fitted \( k_{d3} \) values and the \( \alpha \) factor of FeP remained the same as for the assumption \( [P]=3* [\text{Fe}_{\text{diss}}], \) the fitted \( k_{d4} \) values were smaller by a factor: \( 3* [\text{Fe}_{\text{diss}}]/1000 \).

We used four different models to describe the data, once in which \( k_{d5} \) (and consequently also \( k_6 \) via \( [\text{FeL}]_{eq} = k_{d5}/k_6 \) was fitted (model 1A), once with literature values for \( k_{d5} \) (model 1B) and twice without considering FeL (model 1Ca fitting \( k_{d5} \) and model 1Cb using a value from the literature for \( k_{d5} \)). For models 1B and 1Cb we chose from the literature \( k_{d5} = 0.3 \times 10^{-4} s^{-1} \) as found by Rose and Waite (2003a) for the dissolution of freshly precipitated amorphous Fe (1 min of aging).

Since the strong ligands L were saturated with Fe, when the extra 20 nM of Fe was added, formation (reaction (2)) was not occurring and therefore the rate constants \( k_{d1} \) and \( k_{r2} \) could only be fitted with large uncertainties. Therefore model 1C assumed [FeL] did not change with time due to the addition of 20 nM of Fe. The concentration of FeL was subtracted from the total Fe concentration and Eqs. (5)–(10) were changed into,

\[ d[[\text{Fe}']/dt = k_{d3}[\text{FeP}] + k_{d5} - k_{r4}[\text{Fe}'][P'] - k_{r6}[\text{Fe}'] \quad (5A) \]

\[ d[[\text{FeP}]/dt = k_{r4}[\text{Fe}'][P'] - k_{d3}[\text{FeP}] \quad (8) \]

\[ d[[\text{P}']/dt = k_{d3}[\text{FeP}] - k_{r4}[\text{Fe}'][P'] \quad (9) \]

\[ d[[\text{FeX}]/dt = k_{r6}[\text{Fe}'] - k_{d5} \quad (10) \]
Together with the boundary conditions, (5)–(10) were used to solve either five \((k_1\sim k_5)\) (model 1A) or four rate constants \((k_1\sim k_4)\) (model 1B). Models 1Ca and 1Cb used Eqs. (5A), (8), (9) and (10) to calculate three \((k_3\sim k_5)\) or two \((k_3\sim k_4)\) rate constants, depending on the assumptions of \(k_{d5}\) (models 1A and 1B, respectively). \(k_6\) is related to \(k_{d5}\) following (4). Modelling was done using Scientific software (Micromath Scientific software) and the calculations were performed using a least squares fit.

To check whether realistic values were calculated for \(k_{d1}\) and \(k_{d2}\) in models 1A and 1B, the starting values were always the same, \(1.39 \times 10^{-2}\) and \(1.39 \times 10^8\), respectively. These values result in \(\log K_{FeL} = 10\). Ligands with a \(\log K' = 10\) dissociate in the presence of TAC (10 \(\mu\)M) as used in the equilibration titration. Since the titrations resulted in straight lines the model was forced to fit values of \(k_{d1}\) and \(k_{d2}\) that result in higher \(\log K'\) values.

2.3.2. Model 2: Addition of TAC

In another experiment no Fe was added, only 10 \(\mu\)M TAC as competing ligand. The changes in [Fe(TAC)\(_2\)] were followed until equilibrium was reached. An extra reaction had to be taken into account for model 2,

\[
[\text{Fe(TAC)}_2] \xrightarrow{k_{d7}} \text{[Fe']} + 2[\text{TAC}']
\]

with two new rate constants \(k_{d7}\) and \(k_{d8}\). Adding (12) and (13) to (4)–(10) in the model gives,

\[
d[\text{Fe(TAC)}_2]/dt = k_7\text{[Fe'][TAC]}^2 - k_{d7}\text{[Fe(TAC)}_2]
\]

\[
d[\text{TAC}']/dt = k_{d7}\text{[Fe(TAC)}_2] - k_8\text{[Fe'][TAC]}^2
\]

We removed (10) from the model, since precipitation of Fe in the presence of high concentrations of TAC is not possible (Fig. 4). As a result (5) was changed into (5B),

\[
d[\text{Fe'}/dt = k_{d1}\text{[FeL]} + k_{d3}\text{[FeP]}
\]

\[
+ k_{d7}\text{[Fe(TAC)}_2] - k_{d2}\text{[Fe'][L']} - k_{d4}\text{[Fe'][TAC'][2]}
\]

Model 2 uses (5B–9), (12) and (13) in two variations.

Model 2A: the rate constants \(k_1\sim k_4\) from model 1A were used to fit the rate constants \(k_{d7}\) and \(k_{d8}\) of Fe(TAC\(_2\)).

Model 2B: the rate constants \(k_{d3}\) and \(k_{d4}\) from model 1Ca were used to fit rate constant \(k_{d1}\), \(k_{d2}\), \(k_{d7}\) and \(k_{d8}\).

The program Scientist was used to fit the data.

3. Results and discussion

3.1. Dissolved Fe

Data on dissolved Fe from the Scheldt estuary are scarce (Van den Berg et al., 1987; Nolting et al., 1999; Herzl, 1999). Nolting et al. (1999) presented dissolved Fe concentrations from 1978, which were much higher than the values found in this work. Their Fe concentrations ranged from 50 nM at \(S=30\), via 300 nM at \(S=10\) to >1 \(\mu\)M at \(S=1\). This is more than twice higher than our data (Table 1). Van den Berg et al. (1987) measured comparable Fe concentrations as Nolting et al. (1999), ranging from 400 nM at \(S=10\) to 30 nM at \(S=27\). For a large part the higher dissolved Fe concentrations are due to a higher organic load during the 1970–80s, exemplified by the oxygen depletion reached up to \(S=15\) (Duinker et al., 1983). Dissolved and colloidal Fe concentrations from 1993 to 1997 are presented by Herzl (1999). She found mean dissolved Fe concentrations in the upper estuary (\(S=0.3\)) of 524 nM and near Vlissingen (\(S=30\)) a mean Fe concentration of 28 nM.

The dissolved Fe concentrations decrease very steeply in the upper estuary due to flocculation and possibly oxidation (Sholkovitz, 1976; Duinker et al., 1983; Zwolsman and van Eck, 1993; Herzl, 1999) followed by a more gradual decrease at higher salinities (Table 1). The soluble Fe fraction <1 kDa is 3 to 6 times smaller than the total dissolved Fe (<0.2 \(\mu\)M) fraction, suggesting a high content of colloidal Fe (1 kDa<colloidal Fe<0.2 \(\mu\)M) in the estuary. Herzl (1999) filtered Scheldt water over two size fractions <0.45 \(\mu\)M and <0.05 \(\mu\)M. She found that almost all dissolved Fe was <0.05 \(\mu\)M. Only during high river discharge high Fe
concentrations were measured that ranged between 0.45 and 0.05 μm. However, Kuma et al. (1998) found that most Fe in estuaries is in the colloidal fraction, which is similar to our findings. This is in line with results from Galveston Bay where 80% of dissolved Fe was >1 kDa (Wen et al., 1999), similar to the Venice Lagoon (Martin et al., 1995) and other estuaries (Powell et al., 1996).

### 3.2. Complexation characteristics of Fe

#### 3.2.1. [L] and \(K'\) estimated by titration with Fe after equilibration of the samples

Titrations (10 μM [TAC]) showed that the concentrations of organic Fe-binding ligands in both size fractions, <0.2 μm and <1 kDa, and at all three salinities (\(S=26, 10\) and 0.3) are slightly lower than the concordant dissolved Fe concentrations (Table 1A). The titrations resulted in straight lines and not in curves (Fig. 5). The ligand concentration L was taken as the intercept of the straight titration line with the x-axis. In all samples, the Fe-binding ligand sites were saturated with Fe. At \(S=26\), 1.5 times more Fe than ligand was present and at the other salinities 1.1 times more Fe than ligand (Table 1A).

Titrations of samples from both size fractions showed high Fe concentrations with respect to TAC. Because these high Fe concentrations exceeded the solubility product of the Fe-hydroxides ([\(Fe_{eq}^+\])=0.19–0.25 nM; Liu and Millero, 2002), the existence of a weaker ligand group was expected in both size fractions.

![Fig. 5. Results from the titration method, according to the equilibrium approach, for samples \(S=0.3\) (A) using different concentrations of TAC and \(S=26\) (B).](image-url)
For samples from $S=0.3$ and $S=26$, in the fraction $<0.2\,\mu m$, other detection windows than 12.4 were applied. Titrations of a sample from $S=0.3$ showed straight lines at all detection windows applied ($DW=10.4–12.8$, TAC=1–20 $\mu M$, respectively). The change in DW hardly changed the obtained concentration of L or the labile Fe concentration with respect to TAC (Fig. 5A). However, the titration of a saline sample ($S=26$) did show curvature when a lower detection window was applied (Fig. 5B; $DW=11.8$, [TAC]=5 $\mu M$). The log $\mathcal{K}$ value of the organic Fe-binding ligands at $S=26$ with DW=11.8 is 19.6 and the ligand concentration 38.8 nEq of M Fe. However, the estimated errors are large (Table 1B).

### 3.2.2. Kinetic characterisation of the dissolved ligands

#### 3.2.2.1. Model 1: Addition of Fe

A decline with time in labile Fe was observed in all samples except for the fresh Fe-precipitates were stable with respect to the conditions of the measurement. Unpublished results in estuarine water from the Wadden Sea also showed, that fresh Fe-precipitates were stable with respect to the 120 s exposure of TAC. Moreover, dissolution by prolonged presence of TAC showed a relatively slow dissolution process. The decrease in labile Fe over time

#### Table 2
Results of model 1 (Fig. 3, Eqs. 5–10); (A) According to model 1A; $k_1$–$k_5$ were fitted; (B) According to model 1B; $k_1$–$k_4$ were fitted; $k_5$ is from Rose and Waite (2003a) of freshly precipitated Fe-hydroxides

<table>
<thead>
<tr>
<th></th>
<th>$S=26$</th>
<th>$S=10$</th>
<th>$S=0.3$</th>
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<tr>
<td></td>
<td>&lt;0.2 $\mu m$</td>
<td>&lt;1 kDa</td>
<td>&lt;1 kDa</td>
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<tr>
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<td>2.06 $\times 10^{-3}$</td>
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<tr>
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<td>1.86 $\times 10^{0}$</td>
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<td>1.33 $\times 10^{0}$</td>
<td>1.02 $\times 10^{0}$</td>
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<tr>
<td>$k_d5$</td>
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<td>3.70 $\times 10^{-3}$</td>
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<tr>
<td>$k_d6$</td>
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<td>3.70 $\times 10^{7}$</td>
</tr>
<tr>
<td>[L]</td>
<td>8</td>
<td>2</td>
<td>95</td>
</tr>
<tr>
<td>[P]</td>
<td>150</td>
<td>40</td>
<td>400</td>
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<tr>
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<td>18.85</td>
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<tr>
<td>Log $\alpha$, FeP</td>
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<td>11.93</td>
</tr>
<tr>
<td>SS</td>
<td>36</td>
<td>6</td>
<td>18</td>
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</tbody>
</table>

Mean values of triplicates for $S=26$ and 10, for $S=0.3$, <1 kDa mean values of duplicates are given. The log $\mathcal{K}$ and log $\alpha$ values are given with respect to [Fe$^{3+}$], the rate constants are given with respect to [Fe$^{3+}$]. [P]=3·[Fe$_{diss}$]. Concentrations of P and L are given in nM, $k_1$ in M$^{-1}$ s$^{-1}$, $k_6$ in s$^{-1}$ and log $\mathcal{K}$ in M$^{-1}$. $k_d$ (s$^{-1}$) is calculated using $[Fe^{eq}]_d=k_d1/k_1=k_d2/k_2$ and (1). SS=sum of squared deviations of the fit to the data.
observed in the samples (with the exception of those from \( S=0.3 \), <0.2 \( \mu M \), Fig. 2A and B) is thus probably due to Fe-hydroxides precipitation, annotated as FeX. However, the data could not be fitted by assuming only precipitation of Fe (results not shown). The decline in labile Fe was too slow, too gradual with time, and the labile Fe concentration near \( t=\infty \) too high (>0.19–0.25 nM). Therefore a relatively weak ligand P was assumed to exist next to the strong organic Fe-binding ligands.

In the samples from \( S=0.3 \), in the fraction <0.2 \( \mu m \) apparently no precipitation took place. Due to high variance in the data of the samples from \( S=0.3 \), the <0.2 \( \mu m \) fraction could not be modelled. Initially, the measured concentrations of labile Fe increased with time after which they remained constant. An increase with time is not the expected result (see for comparison Fig. 2A and B). However, the concentrations were very low with respect to the total dissolved Fe concentration (10 nM compared to 525 nM Fe\(_{\text{diss}}\)). Moreover, at low salinity and high organic matter the chemical analysis was operating at the borders of what is possible. It was decided to discard the data from \( S=0.3 \), <0.2 \( \mu m \).

The data could be successfully modelled assuming the presence of a relatively weak ligand P. The best fits (lowest summed squared deviation of the fit from the data, SS) were achieved when the dissolution of solid Fe was fitted as well (models 1A and 1B, Tables 2A and B). Models 1Ca and 1Cb (Tables 3A and B), in which the strong ligand L was removed from the model, result in almost the same values for \( k_d3 \) and \( k_f4 \) than models 1B and 1Cb. Assumption of a fixed \( k_d5 \) value from Rose and Waite (2003a) gives, apart from higher SS values, more variation in the values between the different samples compared to the results of models 1Ca and 1A, without any clear relation with salinity or size fraction. Moreover, \( k_d3 \) and \( k_f4 \) are higher in models 1Ca and 1A, whereas the ratio (\( K' \)) remains comparable between the two assumptions on \( k_s \). This difference in rate constants is directly due to the different values for \( k_d5 \). Since the formation of Fe-hydroxide is faster in 1B and 1Cb, due to the lower value of \( k_d5 \) from Rose and Waite (2003a), the formation of FeP has to be faster also in order to fit the same data sets.

Rose and Waite (2003a) observed dissolution rate constants that depended on the ageing of the Fe-precipitate. They measured dissolution rate constants of \( 2.3 \times 10^{-4} \) s\(^{-1} \) for freshly precipitated iron and \( 4.6 \times 10^{-6} \) s\(^{-1} \) for precipitates aged during one week. Since the FeX modelled in this research can only be

| Table 3 Results from model 1C (Fig. 3, using Eqs. 5A, 8, 9 and 10) |
|-----------------|-----------------|-----------------|-----------------|
|                 | \( S=26 \)       | \( S=10 \)       | \( S=0.3 \)      |
|                 | <0.2 \( \mu m \) | <1 kDa           | <0.2 \( \mu m \) | <1 kDa           | <1 kDa           |
| \( k_d3 \)      | \( 1.40 \times 10^{-4} \) | \( 1.50 \times 10^{-4} \) | \( 4.30 \times 10^{-4} \) | \( 4.87 \times 10^{-5} \) | \( 9.66 \times 10^{-5} \) |
| \( k_f4 \)      | \( 3.38 \times 10^{-4} \) | \( 9.92 \times 10^{-4} \) | \( 1.02 \times 10^{-5} \) | \( 1.31 \times 10^{-5} \) | \( 1.93 \times 10^{-5} \) |
| \( k_d5 \)      | \( 1.04 \times 10^{-3} \) | \( 1.00 \times 10^{-3} \) | \( 3.65 \times 10^{-3} \) | \( 4.30 \times 10^{-4} \) | \( 3.72 \times 10^{-3} \) |
| \( k_f6 \)      | \( 5.42 \times 10^{-6} \) | \( 5.25 \times 10^{-6} \) | \( 3.65 \times 10^{-7} \) | \( 4.30 \times 10^{-8} \) | \( 1.49 \times 10^{-7} \) |
| \([L]\)         | 8               | 2               | 95              | 30              | 85              |
| \([P]\)         | 150             | 40              | 400             | 180             | 350             |
| \( \log K'_{\text{FeP}} \) | 18.4            | 18.8            | 18.3            | 18.5            | 18.3            |
| \( \log \alpha_{\text{FeP}} \) | 11.5            | 11.4            | 11.9            | 11.7            | 11.8            |
| \( \text{SS} \) | 85              | 85              | 30              | 85              | 85              |

| (B) Results from model 1Cb as in table 2B. \( k_d5 \) according to Rose and Waite (2003a) |
|-----------------|-----------------|-----------------|
|                 | \( S=26 \)       | \( S=10 \)       |
| \( k_d3 \)      | \( 4.09 \times 10^{-5} \) | \( 3.11 \times 10^{-5} \) |
| \( k_f4 \)      | \( 4.02 \times 10^{-4} \) | \( 1.43 \times 10^{-4} \) |
| \( k_d5 \)      | \( 3.50 \times 10^{-5} \) | \( 3.50 \times 10^{-5} \) |
| \( k_f6 \)      | \( 1.84 \times 10^{-5} \) | \( 1.84 \times 10^{-5} \) |
| \([L]\)         | 8               | 2               |
| \([P]\)         | 150             | 40              |
| \( \log K'_{\text{FeP}} \) | 17.9            | 18.7            |
| \( \log \alpha_{\text{FeP}} \) | 11.1            | 11.3            |
| \( \text{SS} \) | 85              | 350             |

Units as in Table 2.
formed during the experiments, it is very fresh. Therefore, it is not surprising that the $k_d$ values found here are between $3.7 \times 10^{-3}$ and $4.3 \times 10^{-4}$ s$^{-1}$ in model 1Ca, comparable and higher, more labile, than found by Rose and Waite (2003a).

It is known that a negative salinity relationship exists for DOC and the total concentration of L in the Scheldt estuary. If P has an organic nature, it is fair to assume that such a relationship also exists for P. Assuming that [P] is related to $\left[ Fe_{\text{diss}} \right]$, a relationship is forced between [P] and S. As mentioned in the Methods section, the values of $K_{Fe(e)}$ and $k_4$ are influenced by the assumption on the concentration of P. As a result only the fitted values of $\alpha$ and $k_3$ are independent of this assumption and can be used for comparison with others.

### 3.2.2.2. Model 2: Addition of TAC

The addition of TAC to the samples introduces two new rate constants, $k_{7}$ and $k_{8}$ (Eqs. (5B), (12) and (13); Fig. 4; Tables 4A and B). Both models, 2A and B, can fit the data very well, although the SS is substantially larger for $S=0.3$, <1 kDa. The results of the parameters of Fe(TAC)$_2$ do not differ between models 2A and 2B. A differentiation in dissociation rate constants exists between the two ligand groups L and P (Tables 3A and 4B). Values vary between $1.5 \times 10^{-3}$ and $17 \times 10^{-3}$ s$^{-1}$ for FeL and between $0.5 \times 10^{-4}$ and $4.3 \times 10^{-4}$ s$^{-1}$ for FeP (considering only model 1Ca for FeP and model 2B for FeL).

The dissociation rate can be translated into half-life times ($t_{1/2}=0.693/k_d$; Stone and Morgan, 1990). The half-life times of the strong ligand thus varies between 40 s and 8.1 min, those of the relatively weak ligand P between 27 min and 3.8 h.

The formation rate constants differ considerably between L and P, with fast formation kinetics for FeL and substantially slower formation kinetics for FeP (Tables 3A and 4B).

The formation rate constant of Fe(TAC)$_2$ is also very fast and varies between $1.14 \times 10^7$ M$^{-2}$ s$^{-1}$ and $34 \times 10^8$ M$^{-2}$ s$^{-1}$ in both variations of the model. The $\beta_{Fe(TAC)}$ varies between $10^{20}$ and $10^{23.4}$, which is close to the value given by Croot and Johansson (2000) of $10^{22.4}$. One model run, performed on a sample of S=0.3, gave a value $\beta_{Fe(TAC)}$ of $10^{25.34}$. This value of $\beta_{Fe(TAC)}$ at S=0.3 is significant higher than the values found at the other salinities. This suggests that the $\beta_{Fe(TAC)}$ is depending on salinity. However, due to a lack of experimental data we cannot firmly secure this.

### 3.3. Assumptions of the model and comparison with literature values

Until now, the method of Wu and Luther (1995) has been applied to open ocean samples with low concentrations of dissolved Fe (<1–2 nM Fe) and low concentrations of relatively strong organic ligands ($\approx 5$ nEq of M

### Table 4

<table>
<thead>
<tr>
<th></th>
<th>$S=26$</th>
<th>$S=10$</th>
<th>$S=0.3$</th>
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<td>&lt;0.2 μm</td>
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<td>&lt;0.2 μm</td>
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<td>($A$)</td>
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<td></td>
</tr>
<tr>
<td>$k_d$</td>
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<td></td>
</tr>
<tr>
<td>$k_d^7$</td>
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<td>$3.25 \times 10^8$</td>
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<td>Log $\beta_{Fe(TAC)}$</td>
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<tr>
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<td>12.59</td>
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<tr>
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</tr>
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<td>$1.73 \times 10^{-6}$</td>
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<td>$k_4$</td>
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<td>Log $\beta_{Fe(L)}$</td>
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<td>22.82</td>
<td>22.68</td>
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<tr>
<td>Log $\beta_{Fe(L)}$</td>
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<td>12.82</td>
<td>12.68</td>
</tr>
<tr>
<td>SS</td>
<td>5.5</td>
<td>0.4</td>
<td>22.5</td>
</tr>
</tbody>
</table>

The $k_d$ is given in M$^{-2}$ s$^{-1}$, the $k_1$ in s$^{-1}$ and the log $\beta_{Fe(TAC)}$ in M$^{-2}$. The log $K$ and log $\alpha$ values are given with respect to $[Fe]$. The $\alpha$ Fe(TAC)$_2$ is $\beta_{Fe(TAC)} \cdot [TAC]^2$. 

The results of the parameters of Fe(TAC)$_2$ do...
Fe) (Witter et al., 2000a). The concentrations of Fe and organic matter are much higher in the Scheldt estuary and the salinity is lower and variable. Furthermore, the organic ligands sites of L are saturated with Fe in the Scheldt. Our data cannot be modelled by precipitation of Fe alone and so we assume the existence of a weak ligand class outside the detection window of the titration method. The α values of FeP are substantially lower than those of FeL (Table 4). The α values of FeL and FeP determine the distribution of Fe over these species when equilibrium is reached. The weak ligand is only just outside or at the border of the applied detection window of 10 μM TAC of the equilibration method (Tables 2 and 3). Therefore it is likely that the presence of such weak ligands can influence the determination of the strong ligands.

When constructing the models it was assumed that labile Fe consists of Fe⁺ and FeP, since the dissociation was assumed to be relatively fast. To verify this hypothesis we use the time 120 s of the measurement and mean rate constants from Tables 3A and 4B (kd1 = 7.5 × 10⁻⁷ and kd2 = 1.15 × 10⁹) from Table 4B, kd3 = 1.73 × 10⁻⁴ and kd4 = 5.35 × 10⁴ from Table 3A, [TAC] = 10⁻⁵ M, [Fe⁺] = 20 × 10⁻⁹ M, [Fe(TAC)₂] = 0 at t = 0. For the sake of simplicity we assume equal concentrations of 7.5 nM FeL and FeP and 8 nM total L and 75 nM total P. Fifty-seven times more FeP is dissociated than formed, and 313 times more FeL is formed than dissociated, using (8) and (6), respectively. High labile Fe concentrations can thus be attributed to the dissociation of the relatively weak complex. The measured [Fe(TAC)₂] is due to added Fe⁺ (20 nM) and the dissociating FeP. A maximum of 0.4 nM s⁻¹ Fe(TAC)₂ can be formed (kd8 × [Fe⁺] × [TAC]²) using (12) and the results from Table 4B (mean values of γ = 26 and 10; kd8 = 1.9 × 10⁹).

Nothing is known about the nature of P, whether P is organic is not certain. In an estuary like the Scheldt, rich in organic matter, it is possible that substances binding Fe in the dissolved phase are for a large part organic. Whether P consists of dissolved molecules or colloidal particles is also unknown, however, P is found in both size fractions. If P has a fine colloidal nature then Fe might not be really complexed but adsorbed. In that case the adsorption is reversible and can be described using the theory of the Langmuir isotherm.

Model 2B results in KFe⁺ values, the ratio of kd2 and kd1, in concert with literature values (Gledhill and Van den Berg, 1994; Van den Berg, 1995; Wu and Luther, 1995; Rue and Bruland, 1995, 1997; Nolting et al., 1998; Boye et al., 2001, 2003; Croot et al., 2004) (Table 4B). The calculated formation rate constants of the traditionally known complexed Fe species [FeL] are 100 times faster than the formation rate constants of the model ligands used by Witter et al. (2000a) and those found in surface samples from the NW Atlantic Ocean by Witter and Luther (1998) (Table 5). The dissociation rate constants calculated for FeL by Witter and Luther (1998) and Witter et al. (2000a,b) do compare well with the dissociation rate constant calculated for FeL in this research. Rose and Waite (2003b) studied kinetics of Fe with ligands from terrigenous organic matter from coastal areas. They distinguished two classes, a ligand class with kd values between 3.24 × 10⁻⁴ to 3.4 × 10⁻³ and a ligand class with kd between 10⁻⁶ and 10⁻⁴ s⁻¹ (Table 5). Both these formation and dissociation rate constants are very close to the values found in this research. Since the present research considers estuarine samples, and not open ocean water as was in Witter and Luther (1998) and Witter et al. (2000a), the discrepancies might also be due to the presence of coastal ligands differing from truly marine organic ligands. Another reason of the difference between our results and those of Witter and Luther (1998) and Witter et al. (2000a,b) might be that Witter and Luther (1998) and Witter et al. (2000a,b) measured a mean value of more than one ligand group. Due to the improvement on the calculation

<table>
<thead>
<tr>
<th>Sample</th>
<th>k₁ (M⁻¹ s⁻¹)</th>
<th>k₄ (s⁻¹)</th>
<th>Ref.</th>
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</table>

All rate constants are given with respect to [Fe⁺]. k₁ of FeP depends on the assumed concentration for P; therefore, it is not given in this table (see Tables 2–4). Ref.: 1 = Wu and Luther (1995), 2 = Witter and Luther (1998), 3 = Witter et al. (2000a), 4 = Witter et al. (2000b), 5 = Rose and Waite (2003b), 6 = this research Model 2B, 7 = this research Model 1Ca.
of the method copied from Wu and Luther (1995) we distinguish two ligand groups and therefore the parameters of the strong ligand are not or less influenced by the presence of weaker ligands. The relative high formation and dissociation rate constants are interesting with respect to a recent discussion about the lability of metal complexes in relation to the determination by equilibration titration technique (van Leeuwen, 2001; Town and van Leeuwen, 2005a,b; Van den Berg, 2005; Hunter, 2005). The high rate constants found in this research consolidate the reliability of the equilibration titration technique. The kinetics of the strong ligand is fast enough to reach equilibrium during the overnight waiting period, used in this technique.

It must be kept in mind that most work is done under the assumption of 1:1 stoichiometry for the FeL, whereas it is known that other stoichiometry exists. Gledhill (2001) observed in hydroxamate siderophores 1:2, 2:3 and 2:2 Fe-complexes. The presence of different stoichiometries will definitely influence the values of $k_f$ and $k_d$.

The kinetic parameters and the conditional stability constant of the ligands L and P do not change with the size fraction and salinity (Tables 3A and 4B). However, the increase in the $\alpha$ factor of the strong ligand with decreasing salinity is evident (Table 4B). Furthermore, $\alpha_{FeL}$ is smaller in the fraction <1 kDa.

It is somewhat surprising that the rate constants and the conditional stability constants of the two ligands L and P do not vary, whilst the ionic strength changes considerably and the character of the organic matter also changes substantially between the river end and the North Sea. However, all over the world seas the same ligand characteristics are found. According to Stone and Morgan (1990) an increase in the ionic strength lowers the reaction rate between a cation and an anion and has little effect on reaction rate when one or both of the reactants are uncharged. Here, we assume that Fe is bound in a 1:1 coordination to the ligand in ionic binding. According to Hering and Morel (1990) the formation rate constant of metal chelation is decreasing with increasing strength for charged metals, although this also depends on the type of complex formation and therefore on the rate-limiting reactions. The dissociation rate constant is related to the formation rate constant through the principle of micro reversibility. Hence, it is proportional to the formation rate constant by division through the conditional stability constant. As the complex is supposed to have no charge and the ionic species are assumed to have a charge of three, the effect on changing activity coefficients is thus higher on the formation rate constant. At $S$=26, 10 and 0.3 the ionic strengths are 0.47, 0.23 and 0.03, respectively. This results, according to the Davies equation, in activity coefficients for ions with a charge of three of 0.0115, 0.056 and 0.21, respectively (Stumm and Morgan, 1996). At $S$=0.3, upstream of the area with maximum turbidity, the organic material has a terrestrial nature. The conditions may differ considerably with more saline water downstream where most of the terrestrial organic matter has already been lost due to flocculation. Therefore, it is quite possible that we cannot compare data from $S$=0.3 with the other data. Although Rose and Waite (2003b) also used organic matter of terrigenous origin, a direct comparison is difficult, because they measured at a constant high salinity in their experiments.

3.4. Consequences for the mobility of Fe in the Scheldt estuary

The $\alpha$ values of FeL (Table 4B) are higher than the $\alpha$ values of the FeP. As the $\alpha$ value of FeL increases with salinity, whilst the $\alpha$ value of FeP remains constant, the difference between the ligands becomes larger with decreasing salinity (Table 3A). As much as 90% of both Fe complexes was dissociated by competition with TAC at $t\approx\infty$ at $S$=26 (both fractions) as well as at $S$=0.3 in the fraction <1 kDa (Fig. 2C). Only 20% of Fe dissociated from organic complexes at $S$=10 (both fractions) and $S$=0.3, <0.2 $\mu$m (Fig. 2D). These results are well explained when the $\alpha$ values of FeL, FeP and Fe(TAC)$_2$ are considered. At $S$=26 and $S$=0.3, <1 kDa, the $\alpha$ values of the ligands L and P are smaller than the $\alpha$ value of Fe(TAC)$_2$ (Tables 3A and 4B). On the other hand, at $S$=10 the $\alpha$ value of FeL is larger than that of Fe(TAC)$_2$ (Tables 3A and 4B).

The strong ligands are saturated in the Scheldt estuary. As a result, the relatively weak ligand and the solubility product determine the inorganic Fe concentration, because the $\alpha$ value of FeP does not change with salinity, whilst the solubility varies only by a factor 2 across the salinity range (Liu and Millero, 2002).

Whitworth et al. (1999) describe the binding constants of several metals on suspended particulate matter in the Scheldt estuary. With these binding constants and those of dissolved organic ligands they can model the competition between ligands and particles and predict the dissolved metal concentration. This is impossible for Fe, because the conditional stability constants for the adsorption of Fe on particles (log$K'_c$=5.1) differ too much from the conditional stability constant of the dissolved organic ligands (log$K'_c$=18–23). They suggest precipitation and flocculation to be
the reason of this gap in conditional stability constants. With our results on the ligand P we fill part of the gap. Ligands like P might be of minor importance in the open ocean where free ligand sites of the strong ligand are abundant. In coastal areas however, or in the open ocean after a sudden input of Fe, the relatively weak ligands like P can become important. High labile Fe and Fe concentrations in excess over the ligand concentrations (Croot and Johansson, 2000; Powell, personal communication, 2004; Boye et al., 2005; Rijkenberg et al., 2006a) can be an indication of the presence of these weak ligands. Since the α value of FeP is close to the detection window of 10 μM TAC, its presence can influence the classical titration measurement.

4. Conclusions

Modelling of the kinetic data of Fe in natural estuarine waters has given new insight in the chemistry and mobility of Fe. A distinction has been made in rate constants between three different Fe species. A strong well-known organic ligand, L, is accompanied by a relatively weak ligand, P, in equilibrium with an amorphous precipitate of Fe-hydroxides. The model calculations have pointed out that excess Fe (with respect to L) was kept in the dissolved phase by the weak ligand P and that the presence of P explained the high concentrations of Fe labile (with respect to TAC) in the estuary.

The formation rate constant of the strong FeL complex is 100 times faster than the model ligands found by Witter et al. (2000b) but comparable to results of Rose and Waite (2003a). The existence of the relatively weak ligand P, outside the detection window of TAC, is not recognized using voltammetric methods. The rate constants also compare well with a weak ligand group detected by Rose and Waite (2003b). The nature of P is unknown. P is found to exist in both size fractions, <0.2 μm and <1 kDa, and the binding with Fe is reversible.

The α factor of the strong ligands increased with decreasing salinity whereas the α factor (with assumed P concentrations related to Fe and thus, indirectly, to salinity) remained constant with salinity.

Care should be taken using TAC as competing ligand in voltammetry at very low salinities. Application of $\beta_{Fe(TAC)}^{2-} = 10^{22.4}$ at $S < 10$ (Croot and Johansson, 2000) would result in an underestimation of the conditional stability constant of the Fe-binding ligands.

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References


