The effect of dissolved natural organic matter on the rate of removal of ferrous iron in fresh waters

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Abstract The ease of removal of iron in water treatment is determined principally by the form of iron present. If iron is complexed to natural organic matter (NOM) and present in dissolved form, it is quite difficult to remove by conventional deep-bed filtration methods while if present as particulate iron oxyhydroxides it is readily removed. A major source of iron in reservoirs is the benthic sediments which, on becoming anoxic, release ferrous iron (Fe(II)) to the water column. This Fe(II) may either bind to NOM and be retained in dissolved form or may form inorganic hydroxyl complexes which oxidize to Fe(III) species which typically precipitate rapidly. In this paper, we report on studies of the kinetics of Fe(II) removal from solution in the presence and absence of the IHSS standard Suwannee River Fulvic Acid (SRFA). Oxidation of inorganic Fe(II) by oxygen is negligible at low pH but addition of organics changes the kinetics of removal of Fe(II) remarkably, reducing the half life of Fe(II) from hours to minutes. Increasing the concentration of SRFA also enhances the degree of Fe(II) removal. Experimental results obtained over a wide range of conditions are successfully described using a kinetic model which accounts for the transformations between Fe(II) and Fe(III) species.

Keywords Iron complexation; iron oxidation; kinetics; natural organic matter; pH

Introduction
Release of elements such as iron and manganese from benthic lake sediments to the overlying water column is a critical determinant of lake water quality. These elements may reach concentrations in the water column which create problems in treated water supplies and play critical roles in the cycling of other elements (particularly phosphorus). Manganese (Mn(II)) oxidizes abiotically very slowly at the pH typical of most natural waters and may pass through water treatment plants in this form unless powerful oxidants such as potassium permanganate or chlorine dioxide are added to induce formation of particulate Mn(III,IV) oxyhydroxides. Ferrous iron (Fe(II)) behaves somewhat differently in that it generally oxidizes more rapidly than manganese but may be retained in solution as ferric complexes bound to natural organic matter (NOM). These complexes may pass through the treatment plant and, like manganese, be subsequently precipitated in the distribution system. A critical factor determining whether iron forms easily filtered particulate ferric oxyhydroxides or much more troublesome dissolved iron-NOM complexes is the rate of formation and dissociation of Fe(II)-NOM complexes as these rates determine the proportion of iron present in inorganic compared to organic forms (Rose and Waite, 2003a).

In recent studies, Rose and Waite (2002) have developed a detailed kinetic model to describe the oxidation of Fe(II) in the presence and absence of the International Humic Substances Society (IHSS) standard Suwannee River Fulvic Acid (SRFA) by extension of the well-documented Haber-Weiss model. They concluded that, at nanomolar Fe(II) concentrations typical of marine waters, the critical reactions are the oxidation of Fe(II) and its complexes by oxygen and the complexation of Fe(II) by organic matter.

In this study, we have investigated the oxygenation kinetics of Fe(II) at micromolar
concentrations typically found in natural lake waters in the presence of SRFA at different pHs. The kinetics of Fe(II) removal was modeled in order to evaluate the changes in the oxidation and complexation rate constants with pH. The presence of ferrous and ferric complexes over time was also determined.

**Experimental section**

All solutions were prepared using 18 MΩ Milli-Q water and chemicals were used as received. pH adjustments were performed using high purity 30% w/w HCl and 52% w/w NaOH (Fluka puriss p.a plus).

Fe(II) stock solutions (2.5 mmol L⁻¹) were prepared weekly using Fe(NH₄SO₄)₂.6H₂O (Ajax Chemical), acidified with 0.4 mmol L⁻¹ HCl to prevent oxidation by ambient oxygen and also to avoid significant pH change when added to the sample matrix.

Ferrozine stock solutions of 0.1 mol L⁻¹ were prepared by dissolving 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p' disulfonic acid, monosodium salt hydrate (Fluka) in Milli-Q water. A Suwannee River fulvic acid stock solution of 2 g L⁻¹ (on a dry ash-free basis), supplied by IHSS was also prepared by dissolving standard SRFA in Milli-Q water. All stock solutions were refrigerated in the dark at 4°C when not in use. Because ferrozine and SRFA stock solutions are highly acidic, pH was adjusted when adding stocks to working solutions.

Solutions were buffered using 10 mmol L⁻¹ MES (for pH 6.0 and pH 6.5), 10 mmol L⁻¹ MOPS (for pH 7.0) and 10 mmol L⁻¹ HEPES (for pH 7.5 and pH 8.0). These buffers are reported to be non-complexing agents and effectively control pH at low concentrations (King, 1998; Kandegedra and Rorabacher, 1999). The measured pH varied by no more than ±0.05 over the course of experiments.

Fe(II) was measured colorimetrically using ferrozine as a color complexing agent. Ferrozine was chosen because of its ability to react rapidly with Fe(II) to form a stable purple colored complex with maximum absorbance at 562 nm. Additionally, FZ has not been shown to bind Fe(III) (Pullin and Cabaniss, 2001) and is commercially available.

Fe(II) was introduced to a solution containing SRFA in buffered solutions. By mixing FZ reagent with the sample immediately before the flowcell cuvette (using a peristaltic pump), only the unbound Fe(II) is able to react with the FZ prior to measurement of absorbance. Calibration was performed by the standard addition of known concentrations of Fe(II) to the sample solution and correlating the recorded absorbance signal with the corresponding Fe(II) concentration. This linear relationship was used to determine the concentration of Fe(II) over time.

The model was developed from that previously described by Rose and Waite (2002). While some rate constants in this model are available from literature, others were determined by fitting the model to the experimental data using our own software based on that developed by Stefan Hug (EAWAG, Switzerland), which combines the kinetics program ACUCHEM (Braun et al., 1988) with MATLAB (Mathworks).

**Results and discussion**

In general, the oxidation of Fe(II) by oxygen in the absence of organic matter is kinetically slow at low pH, with the half life of Fe(II) in the order of hours at pH 7.0. At pH 8.0 however, Fe(II) is rapidly oxidized with a half life of only a few minutes. The rapid oxidation kinetics is due to the changes in ferrous iron speciation, particularly due to the increase in the concentrations of highly reactive species such as FeCO₃²⁻, Fe(CO₃)(OH)⁻ and Fe(OH)₂⁰ (Millero et al., 1987; King, 1998).

The oxidation kinetics of Fe(II) at pH 8.0 was observed to be faster than reported in the previous study in seawater by Rose and Waite (2002). In seawater, the rapid formation of
FeCl\(^+\) and FeSO\(_4\)\(^-\), which are less reactive with oxygen, may reduce the overall rate of Fe(II) oxidation (Millero and Izaguire, 1989).

In the presence of SRFA, the rate of removal of Fe(II) was observed to increase markedly.

As shown in Figure 1, while it takes hours to oxidize inorganic Fe(II) at pH 6.0, addition of 10 mg L\(^{-1}\) SRFA reduced the half life of Fe(II) in solution to the order of minutes. A similar effect was observed at pH 7.0 but less effect of organics was seen at pH 8.0. Increasing the concentration of SRFA also enhanced the removal rate (Figure 2).

To provide insight into the mechanism of Fe(II) removal, a set of reactions has been developed based on the previous Rose and Waite (2002) kinetic model in which some of the critical reactions are identified empirically by fitting to the experimental data. The full reaction scheme with rate constants at pH 7.0 is shown in Table 1.

Figure 3 and Figure 4 show model outcomes and experimental data in the presence of 2 mg L\(^{-1}\) SRFA and 4 mg L\(^{-1}\) SRFA respectively.
Sensitivity analysis of the model has shown that at pH 6.0 and in the presence of 10 mg L–1 SRFA, removal of Fe(II) due to oxidation of inorganic Fe(II) by oxygen is negligible (kox1 = 0.035 mol–1 L–1 s–1). The dominant reactions are a complexation of Fe(II) by SRFA (with a rate constant kf = 0.07 (g L –1)–1 s–1), oxidation of this complex by oxygen (kox2 = 3.2 mol–1 L–1 s–1) and the dissociation of Fe(II)-SRFA (kd = 1.4 × 10–3 s–1).

Addition of SRFA greatly influences the removal of Fe(II) due to its capacity to complex iron. If the oxidation of inorganic Fe(II) is relatively slow then the rate of complexation of Fe(II) by organics could be a dominant process. While complex formation and oxidation of the complex by ambient oxygen are responsible for the initial rapid removal of Fe(II) from the system, dissociation of this weak complex accounts for its slower removal in the later stages. The presence of organics is seen to have less effect at pH 8.0 due to the rapid oxidation of inorganic Fe(II) by oxygen at this pH.

Similar to the kinetics of oxidation of inorganic Fe(II) by oxygen which changed enor-

**Table 1** Model reactions and rate constants at pH 7.0

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate constant (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe(II) + O2 = Fe(III) + O2^-</td>
<td>0.12 mol–1 L–1 s–1</td>
</tr>
<tr>
<td>2</td>
<td>Fe(II) + O2^- = Fe(III) + H2O2</td>
<td>1.0 × 10^5 mol–1 L–1 s–1 (a)</td>
</tr>
<tr>
<td>3</td>
<td>Fe(II) + H2O2 = Fe(III) + OH^- + OH^-</td>
<td>2.6 × 10^5 mol–1 L–1 s–1</td>
</tr>
<tr>
<td>4</td>
<td>Fe(II) + OH^- = Fe(III) + OH^-</td>
<td>5.0 × 10^5 mol–1 L–1 s–1 (b)</td>
</tr>
<tr>
<td>5</td>
<td>Fe(III) + O2^- = Fe(II) + O2</td>
<td>1.5 × 10^8 mol–1 L–1 s–1 (a)</td>
</tr>
<tr>
<td>6</td>
<td>Fe(II) + L = Fe(II)L</td>
<td>0.64 (g L–1)^–1 s–1</td>
</tr>
<tr>
<td>7</td>
<td>Fe(II)L + O2 = Fe(III)L + O2^-</td>
<td>2.6 mol–1 L–1 s–1</td>
</tr>
<tr>
<td>8</td>
<td>Fe(II)L + O2^- = Fe(III)L + H2O2</td>
<td>1.0 × 10^5 mol–1 L–1 s–1</td>
</tr>
<tr>
<td>9</td>
<td>Fe(II)L + H2O2 = Fe(III)L + OH^- + OH^-</td>
<td>2.6 × 10^5 mol–1 L–1 s–1</td>
</tr>
<tr>
<td>10</td>
<td>Fe(II)L + OH^- = Fe(III)L + OH^-</td>
<td>5.0 × 10^6 mol–1 L–1 s–1</td>
</tr>
<tr>
<td>11</td>
<td>Fe(II)L = Fe(II) + L</td>
<td>3.2 × 10^3 s–1</td>
</tr>
<tr>
<td>12</td>
<td>Fe(III) + L = Fe(III)L</td>
<td>1.0 × 10^4 (g L–1)^–1 s–1</td>
</tr>
<tr>
<td>13</td>
<td>Fe(III)L + O2^- = Fe(II)L + O2</td>
<td>1.5 × 10^8 mol–1 L–1 s–1</td>
</tr>
<tr>
<td>14</td>
<td>Fe(III)L + L = Fe(III) + L</td>
<td>1.0 × 10^8 s–1</td>
</tr>
<tr>
<td>15</td>
<td>O2^- + O2^- = H2O2</td>
<td>3.1 × 10^3 mol–1 L–1 s–1 (c)</td>
</tr>
</tbody>
</table>

Note: (1) For simplicity, H2O is omitted in the reactions
(2) L denoted for SRFA ligand
(3) Rate constants for the complexation of Fe(II) and Fe(III) are given in (g L–1)^–1 s–1 as this eliminates the unknown variable of organic molecular weight.
(a) Rush and Bielski (1985)
(b) King et al. (1995)
(c) Zafiriou (1990)

**Figure 3** Observed and modeled removal of Fe(II) in the presence of 2 mg L–1 SRFA at different pH
(-) model fits, (■) pH 6.0, (▲) pH 7.0, (▲) pH 7.5, (●) pH 8.0

...
mously with increasing pH due to the changes in ferrous iron speciation, the kinetics of complexation of Fe(II) by SRFA also increased substantially with increase in pH. However, the rate of change of organic complexation of Fe(II) with pH is lower than the rate of change of inorganic Fe(II) oxidation by oxygen and it is expected that, at some pH > 8.0, complexation of Fe(II) by organics would be unimportant.

An increase in the complexation rate with increasing pH could be explained by the effect of electrostatic forces. SRFA is a large molecule that consists of a number of functional groups of which carboxylic and phenolic groups are dominant. As the pH increases, the total negative charge of the organic molecules increases due to the effect of greater deprotonation. As a result, the tendency for complex formation between Fe(II) and organics also increases. Increasing pH also slightly increases the concentration of available iron-binding sites on the organic ligand due to the greater deprotonation of functional groups (Ritchie and Perdue, 2002). This increase however may not be sufficient to explain the observed effect of pH on rate of removal of Fe(II).

An additional influence on complexation rates is the change in inorganic Fe(II) speciation with pH. Different inorganic iron species may react at different rates with organic ligands to form complexes, thus the change in Fe(II) speciation may induce an apparent change in the complexation rate constant. Recently, Santana-Casiano et al. (2004) proposed that the apparent change in Fe(II) complexation by the simple organic ligands salicylate and phthalate was entirely due to the change in inorganic speciation of Fe(II) with pH. However, due to the polyelectrolytic nature of natural humic substances such as SRFA in contrast to simple ligands such as phthalate and salicylate, the influence of deprotonation of acidic functional groups on electrostatic interactions between iron and the ligand is probably of much greater importance in the system studied in this work.

The model also provides insight into the relative importance of different iron species in the absence and presence of SRFA.

In the absence of SRFA, the two most important iron species are amorphous iron (oxy)hydroxide (as a result of Fe(III) hydrolysis) and inorganic Fe(II). However, in the presence of SRFA, the ultimate iron species is a dissolved Fe(III)-complex. The concentration of Fe(II)-SRFA rapidly reaches a maximum concentration (e.g. 1.0 µmol L⁻¹ at pH 7.0) then starts to decay, while the concentration of ferric complex gradually increases (Figure 5). Only hydrogen peroxide (a relatively stable end product resulting from the disproportionation of superoxide – a species generated on oxidation of Fe(II)) is present in the nanomolar concentration range, while most of the other reactive species are present in...
much lower concentrations. Ferric precipitation did not occur to any significant extent according to this model though the effect of pH on Fe(III) hydrolysis rate requires further investigation.

**Implications of findings**
This study has confirmed the importance of organics to the removal kinetics of Fe(II) in natural waters at different pH. It also highlights the role of organics in maintaining iron in solution in such systems. Organics can complex Fe(II) and alter its removal rate. At lower pH values (6.0–7.0), complexation of Fe(II) by organics and oxidation of this complex are the dominant processes in Fe(II) removal. At higher pH, however, oxidation of inorganic Fe(II) becomes important and responsible for much of the removal of Fe(II). Organics, on the other hand, still greatly affect the speciation of iron. Instead of being hydrolyzed and precipitating, most of the iron species (at the concentrations considered here) are present in organically complexed forms. Although this model allows accurate prediction of the rates of formation and dissociation of Fe(II)–NOM species and the rate of oxidation of these species, it still requires far more work to be complete. In particular, the rates of formation and dissociation of ferric complexes must be ascertained as must the rates of Fe(III) hydrolysis at different pHs. Once these constants are known with certainty, we will be able to predict the dynamic speciation of iron in raw waters and treatment systems as a function of time.

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**References**


