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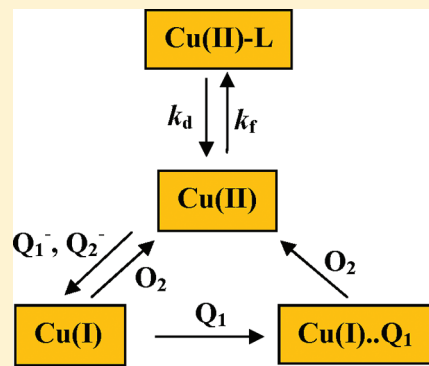
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Kinetics of Cu(II) Reduction by Natural Organic Matter

A. Ninh Pham,[†] Andrew L. Rose,[‡] and T. David Waite^{*,†}[†]School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW, Australia 2052[‡]Southern Cross GeoScience, Southern Cross University, Lismore, NSW 2480, Australia

S Supporting Information

ABSTRACT: The kinetics of Cu(II) reduction by Suwannee River fulvic acid (SRFA) at concentrations from 0.25 to 8 mg L⁻¹ have been investigated in 2 mM NaHCO₃ and 0.7 M NaCl at pH 8.0. In the absence of oxygen, SRFA reduced Cu(II) to Cu(I) in a biphasic manner, with initial rapid formation of Cu(I) followed by a much slower increase in Cu(I) concentration over time. When present, oxygen only had a noticeable effect on Cu(I) concentrations in the second phase of the reduction process and at high [SRFA]. In both the absence and presence of oxygen, the rate of Cu(I) generation increased with increasing [SRFA]. At 8 mg L⁻¹ [SRFA], nearly 75% of the 0.4 μM Cu(II) initially present was reduced to Cu(I) after 20 min, although the yield of Cu(I) relative to [SRFA] decreased at [SRFA] > 1 mg L⁻¹. Two plausible kinetic modeling approaches were found to satisfactorily describe the experimental data over a range of [SRFA]. Despite some uncertainty as to which approach is correct, common features of both approaches were complexation of Cu(II) by SRFA and reduction of Cu(II) by two different electron donor groups within SRFA: a relatively labile electron donor (with a concentration of 1.1 × 10⁻⁴ equiv of e⁻ (g of SRFA)⁻¹) that reduced Cu(II) relatively rapidly and a less labile donor (with a concentration of 3.1 × 10⁻⁴ equiv of e⁻ (g of SRFA)⁻¹) that reduced Cu(II) more slowly.



1. INTRODUCTION

Copper is required for the normal functioning of humans, animals, plants, and almost all microorganisms,¹ but excessive copper concentrations can be extremely toxic.² In natural waters, the redox transformation between cuprous copper (Cu(I)) and cupric copper (Cu(II)) plays a critical role in the speciation, transport and bioavailability of this element.³ The more thermodynamically stable Cu(II) redox state is largely complexed by dissolved organic matter in natural waters and thus not immediately bioavailable.^{4,5} The toxicity of copper is often related to the concentration of aquo free copper (Cu²⁺) rather than that of total dissolved copper.² Although organic complexation of Cu(I) is generally considered unimportant due to the fact that Cu(I) has stringent stereochemical requirements,⁶ thiols,⁷ and sulfides⁸ have recently been reported to form strong complexes with Cu(I). At circumneutral pH, Cu(I) is oxidized to Cu(II) with a half-time of less than a minute under freshwater conditions⁹ but on a slower time scale of several minutes in seawater due to stabilization of Cu(I) by high concentrations of chloride.¹⁰ The oxygenation of Cu(I) species results in the formation of superoxide (O₂⁻) and, following disproportionation of this species, hydrogen peroxide (H₂O₂). Cu(II) can be reduced to Cu(I) in sunlit surface waters by reaction with photogenerated O₂⁻ and H₂O₂, and through the direct photolysis of Cu(II) complexes.³

Humic substances (HS), a heterogeneous class of naturally occurring high-molecular-weight organic compounds, are ubiquitous in all soils, sediments, and natural waters¹¹ and have been long recognized for their ability to complex metals.¹² HS can also act as electron shuttles between microorganisms

and oxidized metals species^{11,13} or, directly, as electron donors^{14–16} and electron acceptors in anaerobic microbial respiration.^{11,17} In environmental systems, HS can exist in multiple redox states with the oxidized state typical of oxic surface waters whereas the reduced state may be formed in anoxic bottom waters.¹⁸ Recent studies,^{19–21} however, have identified the presence of reduced functional groups in HS even under oxygenated conditions. A variety of redox potentials ranging from 0.32 V (pH 7.0)²² to 0.78 V (pH 5)²³ have been reported, although these are not easily determined experimentally due to the presence of multiple redox-active functional groups. Recent studies by Aeschbacher and co-workers²⁴ have revealed that reducible moieties in humic acids that have been previously electrochemically reduced to different redox states cover a wide range of apparent standard reduction potentials (*E*_h) from +0.15 to -0.3 V at pH 7.

A number of functional groups have been identified in HS, of which carboxyl and phenolic groups are most abundant.²⁵ The redox activity of HS, however, has been particularly attributed to quinone–hydroquinone moieties (under reducing conditions)^{23,26–28} and phenolic moieties (under oxic conditions)^{23,24} though other redox-active groups including nitrogen- and sulfur-containing functional groups²⁹ and other aromatic structures³⁰ have also been suggested to be involved in HS-

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mediated redox processes. Reduction of several metals including Hg(II), Fe(III) and As(V) by HS has been previously documented^{21,31–36} with half-times, typically on the order of days, found to be a function of HS origin, concentration, and pH. Although there is general consensus on the involvement of quinone moieties in the early rapid stage of metal reduction, other redox active entities may contribute to redox transformations of metals at longer time scales, possibly with varying degrees of contribution as the reaction proceeds.³⁷ Additionally, except for recent work by Gu and co-workers,³³ the effect of metal complexation by HS has not been considered in previous studies of metal reduction by HS.

In this paper, we present evidence that HS, exemplified here by Suwannee River fulvic acid (SRFA), are capable of rapidly reducing Cu(II) to Cu(I) under conditions typical of many natural waters. In addition, kinetic modeling that takes into consideration the various redox reactions of copper species and their complexation by SRFA has been employed to describe the reduction kinetics of Cu(II) by SRFA. The role of different redox active pools within HS and thermodynamic characteristics of the system are also discussed.

2. EXPERIMENTAL METHODS

2.1. Chemicals. All solutions were prepared using 18 M Ω cm ultrapure Milli-Q water (Millipore). Analytical grade chemicals were purchased from Sigma-Aldrich (or as otherwise stated) and used without further refinement. Copper(I) chloride (CuCl, anhydrous beads, >99.99%) was kept in an airtight desiccator at all times to minimize oxidation of the reagent. All glassware was soaked in 10% w/v HCl for at least one week before use. Stock solutions were kept in dark bottles, covered in foil and refrigerated (at 4 °C) when not in use. All studies were performed at a controlled room temperature of 22 \pm 0.6 °C. Experiments were conducted in darkness with the reactor covered in foil for the duration of the reaction.

All solutions were prepared in 0.7 M NaCl, buffered by 2 mM NaHCO₃ and pH adjusted to 8.0 by adding 1 M HCl or NaOH. All pH measurements were made using a Hanna HI9025 pH meter combined with a glass electrode and Ag/AgCl reference. The pH electrode was calibrated on the NBS scale using NIST-traceable buffer solutions (pH 4.01, 7.01 and 10.01).

Cu(I) stock solutions (0.5 μ M) were prepared daily according to the method described previously.⁹ Cu(II) stock solutions (0.4 μ M) were prepared weekly by dissolving an appropriate amount of copper(II) chloride in a 10 mM HCl solution. Stock solutions of SRFA Standard I (2 g L⁻¹) from the International Humic Substances Society (IHSS) were prepared weekly in Milli-Q water. Deterioration of SRFA (potentially due to oxygenation of hydroquinone moieties) at low pH (pH \sim 4), 4 °C and in darkness during one week of storage was assumed to be negligible.

2.2. Experimental Measurements. Studies of Cu(II) reduction by SRFA under anoxic conditions were undertaken by sparging solutions with a gas mixture of 327 ppm CO₂ in argon for 1 h before the addition of Cu(II) and then during the course of experiments at a constant gas flow rate to prevent the intrusion of oxygen. Cu(I) concentrations were determined spectrophotometrically using the bathocuproine (BC) method.^{9,38} In brief, a peristaltic pump was used to continuously draw from both the experimental solution and a bathocuproine solution (containing 0.05 mM BC and 0.25 mM EDTA) via different tubes. The two solutions were combined at a mixing

tee junction positioned immediately before a 1 m path length liquid waveguide capillary cell (LWCC Type II, World Precision Instruments). Reaction of Cu(I) with BC resulted in a stable Cu(I)–BC₂ complex, which was measured colorimetrically at 484 nm using an Ocean Optics spectrophotometry system (consisting of a broadband Tungsten Halogen lamp and a USB4000 spectrophotometer). The absorbance was baseline corrected at a reference wavelength of 690 nm. The spectrophotometer was zeroed for each run using a Cu(I)-free control solution to account for the absorbance of the background solution. EDTA (ethylenediaminetetraacetate) was added to the BC solution to bind Cu(II), thereby preventing any BC-induced reduction of Cu(II). A negligible concentration of Cu(I) was produced in the absence of SRFA. Disproportionation of Cu(I) (to form Cu(0) and Cu(II)) and reduction of Cu(I) by SRFA was shown to be negligible under the conditions investigated here (Figure S1 in the Supporting Information).

Concentrations of H₂O₂ were measured using the Amplex Red method.³⁹ In brief, Amplex Red (AR) is oxidized by H₂O₂, resulting in the formation of highly fluorescent resorufin, which emits light at 587 nm upon excitation at 563 nm allowing the amount of H₂O₂ in a solution to be quantified. The fluorescence emitted was determined using a fluorometer (Ocean Optics). EDTA was also used to bind Cu(II) thereby preventing Cu(II) from potentially interfering with the method, although no such interference has been previously reported. SRFA at low concentrations (0.25–8 mg L⁻¹) had a negligible effect on resorufin fluorescence (Figure S2, Supporting Information). Generation of H₂O₂ due to dark oxygenation of hydroquinones in SRFA in the absence of Cu(II) was slow (at a rate of \sim 1.6 pM s⁻¹, Figure S3, Supporting Information) and assumed to contribute negligibly to the total [H₂O₂] produced in the system over the duration of the experiments.

2.3. Speciation and Kinetic Modeling. Cu(I) and Cu(II) speciation was calculated with the program MINEQL+.⁴⁰ Kinetic models were fitted to the experimental data over a range of experimental conditions using the program Kintek Explorer.⁴¹

3. RESULTS AND DISCUSSION

3.1. Cu(II) Reduction by SRFA in the Absence of Oxygen. In the absence of O₂, SRFA reduced Cu(II) to Cu(I) in a biphasic manner, with initial rapid formation of Cu(I) followed by a much slower increase in Cu(I) concentration over time (Figure 1). Similar biphasic behavior was observed by Palmer and von Wandruszka³⁷ in studies of arsenate reduction by humic acids, with the initial fast phase of reduction ascribed to reaction with quinoid-centered redox entities. In a similar manner, rapid Cu(I) production is thus most likely associated with Cu(II) reduction by quinone moieties present in the SRFA. The much slower process is possibly related to the presence of nonquinone redox sites of a similar nature to those proposed to be present in fulvic acid by Ratasuk and Nanny.²⁷ These nonquinone entities may include thiols and disulfides,²⁷ nitrogen- and sulfur-containing functional groups,²⁹ and/or carbohydrate-rich fractions.³⁰

3.1.1. Initial Phase of Rapid Cu(I) Formation. At the lower SRFA concentrations examined (0.25, 0.5, and 1 mg L⁻¹), the initial concentration of Cu(I) that was rapidly formed was approximately linearly proportional to the SRFA concentration, with the transfer of \sim 0.1 mequiv of e⁻ (g of SRFA)⁻¹ (Figure 1). However, although the initial yield of Cu(I) formed still

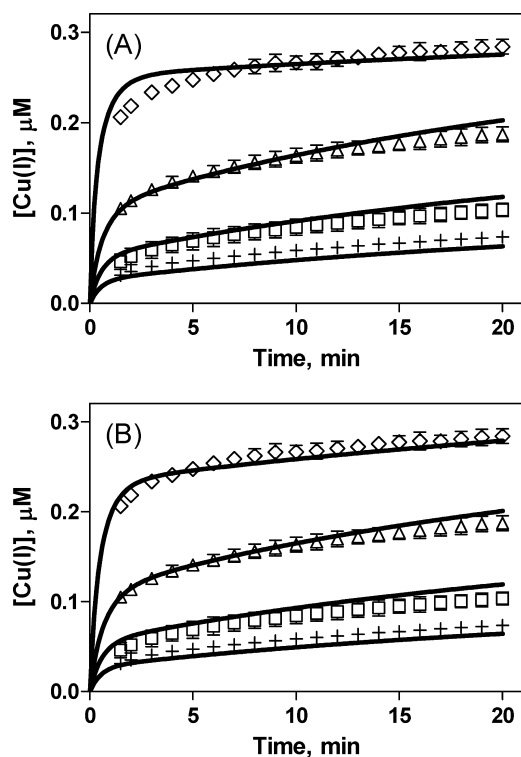


Figure 1. Kinetics of Cu(I) formation under deoxygenated conditions in solutions of 0.7 M NaCl and 2.0 mM NaHCO₃ at pH 8.0 initially containing 0.4 μM Cu(II) in the presence of (+) 0.25 mg L⁻¹ SRFA, (□) 0.5 mg L⁻¹ SRFA, (Δ) 1 mg L⁻¹ SRFA, or (◇) 4 mg L⁻¹ SRFA. Error bars are standard errors from triplicate measurements and lines represent model fits. Model fits are shown using either (A) the one-ligand class model or (B) the two-ligand class model.

increased at the highest concentration of SRFA examined under these conditions (4 mg L⁻¹), only ~0.06 mequiv of e⁻ (g of SRFA)⁻¹ was transferred, yielding initial rapid reduction of only ~250 nM Cu(II) to Cu(I). This indicates that the initial formation of Cu(I) was not simply due to a reaction between an electron donating group and the total Cu(II) added, as a linear relationship between SRFA concentration and Cu(I) initial yield and formation rate would also be expected to apply at higher SRFA concentrations in this case. Because it is unlikely that the nature of the electron donating groups would vary substantially with SRFA concentration over the relatively small concentration range examined, this observation strongly implies that complexation of Cu by SRFA influences the kinetics of Cu(I) production in this system. Cu(I) added to SRFA solutions was fully recovered by the BC method (see section 3.2), implying that any Cu(I) complexes formed would probably be too weak to account for these observations, and further implying that complexation of Cu(II) by SRFA is most likely responsible for the decrease in initial yield of Cu(I) formed.

Cu(II) complexation by SRFA has been previously studied in detail, with several studies of the Cu(II) binding capacity of SRFA undertaken under varying conditions (Table 1). The study of Cabaniss and Shuman⁴² was undertaken at [Cu]_T from 100 nM to 100 μM over a wide pH range (~5–9), whereas the other three studies were undertaken at lower [Cu]_T around pH 8 only. Despite some differences in the experimental matrix and modeling approach (e.g., the number of ligand groups modeled), the studies carried out at lower [Cu]_T all inferred

the presence of low concentrations of relatively strong Cu(II)-binding ligands. In contrast, the Cabaniss and Shuman⁴² study determined a larger number of more abundant, relatively weak Cu(II)-binding ligands, presumably because, at the relatively high [Cu]_T used, any strong Cu(II)-binding ligands present at low concentrations would have been completely bound by Cu(II) at Cu(II) concentrations below the “analytical window” of the method employed. Conversely, the studies conducted at lower [Cu]_T would have been unable to determine the presence of more abundant, weaker Cu(II)-binding ligands due again to the “analytical window” employed.

Because 1 mg L⁻¹ SRFA resulted in the initial rapid reduction of >100 nM Cu(II) to Cu(I), whereas 4 mg L⁻¹ SRFA resulted in the initial rapid reduction of <300 nM Cu(II), at least 100 nM Cu(II) must have been complexed into a form that was not able to be rapidly reduced during this initial period. It is clear from Table 1 that even if complex equilibrium was rapidly attained within this initial period, none of the strongest Cu(II)-binding ligands identified by Xue and Sigg,⁴³ Yang and van den Berg,¹² or Kogut and Voelker⁴⁴ is capable of binding sufficient Cu(II) to explain the experimental observations in this study because of their low concentrations. The first ligand identified by Cabaniss and Shuman⁴² is also incapable of binding sufficient Cu(II) due to its weak binding strength, despite its high concentration. Of the remaining ligands, all but the weaker Cu(II)-binding ligand identified by Xue and Sigg⁴³ would effectively bind the entire [Cu]_T in the presence of 4 mg L⁻¹ SRFA if the complex rapidly equilibrated with inorganic Cu(II). This suggests two possible scenarios to explain the experimental data:

- (i) Rapid binding of Cu(II) with a ligand similar to the weaker Cu(II)-binding ligand identified by Xue and Sigg to yield a nonreducible (or very slowly reducible) complex. The remaining pool of rapidly reducible Cu(II) could then be inorganic Cu(II) or a second, weaker still organic complex, perhaps of the type identified by Cabaniss and Shuman.⁴²
- (ii) Complex formation on a time scale similar to that of Cu(II) reduction, such that not all Cu(II) would be organically complexed when the initial rapid reduction stage was complete. In this case, reduction of inorganic Cu(II) must be responsible for the initial Cu(I) production, although the existence of multiple complex types would also be possible.

It is unclear from the literature which scenario would seem most reasonable. On the basis of an Eigen–Wilkins mechanism of complex formation, Cu(II) is expected to undergo rapid complexation, with rate constants around 10¹⁰ M⁻¹ s⁻¹ at pH 8 due to its extremely fast rate of water loss.⁴⁴ However, the limited measurements of the kinetics of Cu(II) complexation by HS have determined much lower values: Lin et al.⁴⁵ observed two phases of Cu(II) complexation by SRFA at pH 6, with rate constants of 5 × 10³ and ~10⁶ M⁻¹ s⁻¹, and similar results were obtained by Wu et al.⁴⁶ using a fulvic acid extract from a Canadian bog at pH 7, and by Louis et al.⁴⁷ in natural river water samples. Similarly, slow Cu(II) binding by synthetic macrocyclic ligands has also been observed, and the mechanism rationalized in terms of Eigen–Wilkins theory.⁴⁸

3.1.2. Second Phase of Slower Cu(I) Formation. It is clear from analysis of the initial rapid phase of Cu(I) formation that Cu(II) complexation by ligands within SRFA should occur in some manner. Regardless of whether inorganic Cu(II) or a

Table 1. Literature Studies of Cu(II) Complexation by SRFA

authors	[Cu] _T (M)	[SRFA] _T (mg L ⁻¹)	pH	matrix	method	Cu(II) binding group	[L] _T (mol (g of SRFA) ⁻¹)	log K _{Cu²⁺} ^a	log K _{Cu(II)} ^b	[Cu ^{II} L] _{eq} with 400 nM [Cu] _T in 4 mg L ⁻¹ SRFA (nM) ^c
Cabaniss and Shuman ⁴²	10 ⁻⁷ to 10 ⁻⁴	1.9, 3.8, 19, 38 ^d	5.14, 7.00, 8.44	5–100 mM NaClO ₄	titration with Cu(II) selective electrode	L ₁	2.6 × 10 ^{-3d}		3.90 ^e	30
						L ₂	1.0 × 10 ^{-4d}		9.49 ^f	390
						L ₃	5.8 × 10 ^{-4d}		7.36 ^f	390
						L ₄	7.6 × 10 ^{-5d}		8.52 ^f	300
						L ₅	5.0 × 10 ^{-3d}		5.95 ^f	380
Xue and Sigg ⁴³	10 ⁻⁸ to (2 × 10 ⁻⁷)	6	8.0	10 mM KNO ₃	titration with CLE-CSV	L ₁	4.4 × 10 ^{-6d}	14.1 ^e	12.7 ^g	18
						L ₂	4.1 × 10 ^{-5d}	11.7 ^e	10.3 ^g	160
Yang and van den Berg ¹²	<10 ⁻⁶ to 10 ⁻⁵	6	8.1	seawater	titration with CLE-CSV	L ₁	1.8 × 10 ⁻⁵	10.0 ^e	9.1 ^h	72
Kogut and Voelker ⁴⁴	0 to (2 × 10 ⁻⁷)	1.0	8.2	seawater	titration with CLE-CSV	L ₁	2.1 × 10 ⁻⁶	13.2 ^e	12.3 ^h	8.4
						L ₂	1.8 × 10 ⁻⁴	10.4 ^e	9.5 ^h	400

^aConditional stability constants with respect to Cu²⁺ and the conditional speciation of L under the given conditions. ^bConditional stability constants with respect to total inorganic Cu(II) and the conditional speciation of L in 0.7 M NaCl. ^cEquilibrium concentration of Cu^{II}L calculated from [L]_T and log K_{Cu(II)} with [Cu]_T = 400 nM and [SRFA] = 4 mg L⁻¹ using the analytical equation:

$$[\text{Cu(II)L}]_{\text{eq}} = \frac{1}{2} \left(\frac{1}{K_{\text{Cu(II)}}} + [\text{L}]_{\text{T}} + [\text{Cu}]_{\text{T}} - \sqrt{\left(\frac{1}{K_{\text{Cu(II)}}} + [\text{L}]_{\text{T}} + [\text{Cu}]_{\text{T}} \right)^2 - 4[\text{Cu}]_{\text{T}}[\text{L}]_{\text{T}}} \right)$$

^dValues reported by the authors in terms of grams of C were converted to units in terms of grams of SRFA based on 0.5244 g of C per g of SRFA.²⁵ ^eAs reported by the authors. ^fpH-dependent values reported by the authors were adjusted to pH-independent values at pH 8.0. ^glog K_{Cu²⁺} were converted to log K_{Cu(II)} values using the ratio [Cu(II)]/[Cu²⁺] = 27 in seawater at pH 8.1,¹² assuming that the same value is approximately correct at pH 8.0 in 10 mM KNO₃. It was further assumed that log K_{Cu(II)} values in 10 mM KNO₃ were approximately equal to those in 0.7 M NaCl. ^hlog K_{Cu²⁺} were converted to log K_{Cu(II)} values using the ratio [Cu(II)]/[Cu²⁺] = 27 in seawater at pH 8.1,¹² and assuming that Ca²⁺ and Mg²⁺ present in seawater decrease log K_{Cu(II)} values in seawater by ~0.5 log units around pH 8⁴² relative to those in 0.7 M NaCl at the same pH.

readily reducible organic Cu(II) complex is the substrate, the linear relationship between the yield of Cu(I) during this initial phase and SRFA concentration (when [SRFA] is ≤1 mg L⁻¹) implies that this initial yield is stoichiometrically limited by the pool of kinetically labile electron donors available (e.g., hydroquinones and other polyphenolic-rich moieties), which we denote hereafter by Q₁⁻. Consequently, the second phase of slower Cu(I) formation appears to be mediated by a second pool of less labile electron donors (e.g., nonquinone redox groups), which we denote hereafter by Q₂⁻. Based on the observed stoichiometry of initial Cu(I) production, the concentration of Q₁⁻ is ~0.1 mequiv of e⁻ (g of SRFA)⁻¹; however, it is more difficult to constrain the concentration of Q₂⁻ from the data in Figure 1 alone, because Cu(I) production was still occurring when experiments were concluded after 20 min. Crude estimation of Q₂⁻ indicated that in the presence of 1 mg L⁻¹ SRFA, almost 0.2 μM Cu(I) was produced within 20 min (Figure 1), requiring the transfer of 0.2 mequiv of e⁻ (g of SRFA)⁻¹ to Cu(II) within this time period. The total quantity of electrons transferred to Cu(II) (EDC) substantially exceeded the reducing capacity of native SRFA of ~0.06 mequiv of e⁻ (g of SRFA)⁻¹ at pH 7.0 reported by Jiang and Kappler⁴⁹ (assuming Standard SRFA 1S101F was used in their study with 0.5244 g C per g of SRFA). Aeschbacher and co-

workers²⁰ more recently measured the electron accepting capacity (EAC) of SRFA (type 2S101F) to be 0.67 mequiv of e⁻ (g of SRFA)⁻¹ using a mediated electrochemical reduction method and suggested that the electron carrying capacity (ECC) reported by Ratasuk and Nanny,²⁷ and others that used Fe³⁺ as a reductant^{21,49,50} may have been underestimated because equilibrium between Fe(III)–citrate/K₃[Fe(CN)₆] and the HS (after treatment with Pd) may not have been reached (with the process potentially taking hours to days to reach completion instead of the 15 min allowed). When a correction factor of 5.6 (derived by comparing the results of studies from Aeschbacher et al.²⁰ and Ratasuk and Nanny²⁷) was applied to the value reported by Jiang and Kappler,⁴⁹ the true reducing capacity of SRFA could be as much as 0.36 mequiv of e⁻ (g of SRFA)⁻¹, which was close to that determined here. In addition, the higher pH used in this study (i.e., pH 8.0) compared to that used by others would result in a lower SRFA redox potential and thus enhanced reducing capacity of the system.⁵¹ We therefore use this value as an estimate for the total concentration of redox sites in SRFA when attempting to model the experimental data at pH 8.0.

3.2. Cu(II) Reduction by SRFA in the Presence of Oxygen. Oxygen had no discernible effect on the rate of the initial rapid reduction of 0.4 μM added Cu(II) (Figure 2) but

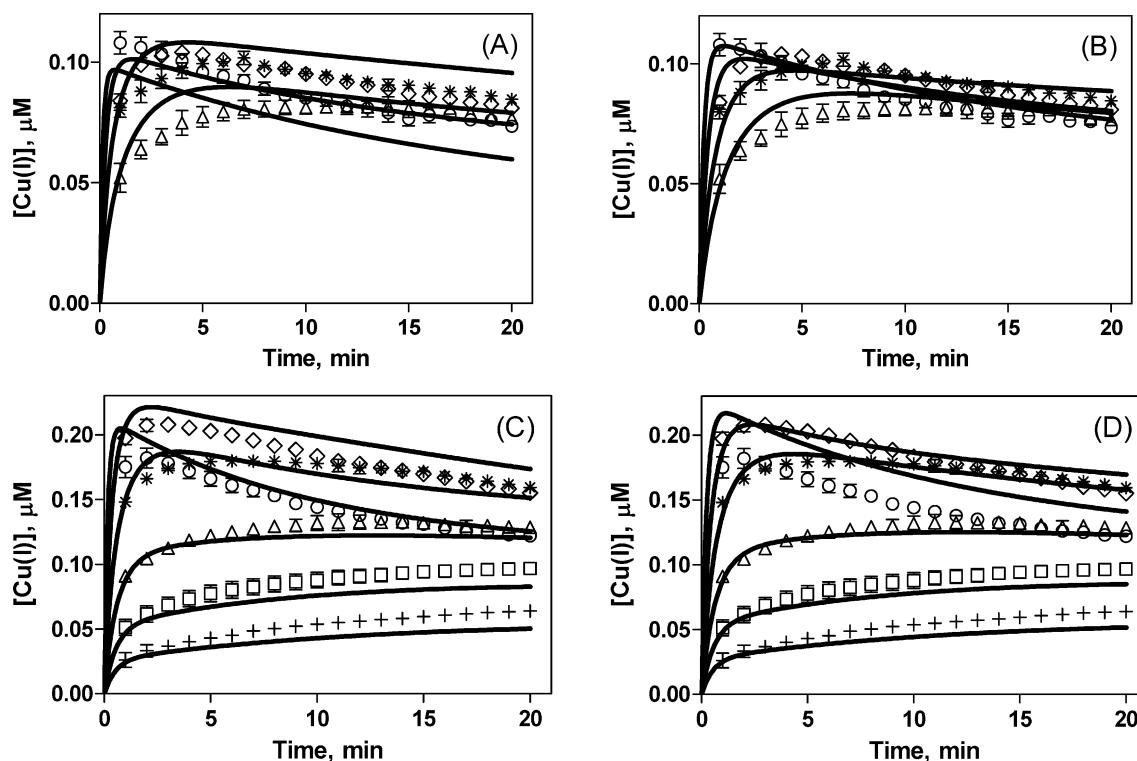


Figure 2. Kinetics of Cu(I) formation under oxygenated conditions in solutions of 0.7 M NaCl and 2.0 mM NaHCO₃ at pH 8.0 initially containing (A) and (B) 0.2 μM Cu(II) or (C) and (D) 0.4 μM Cu(II) in the presence of (+) 0.25 mg L⁻¹ SRFA, (□) 0.5 mg L⁻¹ SRFA, (Δ) 1 mg L⁻¹ SRFA, (*) 2 mg L⁻¹ SRFA, (◇) 4 mg L⁻¹ SRFA, or (○) 8 mg L⁻¹ SRFA. All solutions were initially saturated with O₂ ([O₂]₀ = 243 μM). Error bars are standard errors from triplicate measurements and lines represent model fits. Model fits are shown using either (A) and (C) the one-ligand class model or (B) and (D) the two-ligand class model. Not all SRFA concentrations were examined under the different experimental conditions shown in each panel.

became important later in the reduction process at higher SRFA concentrations. Comparing the kinetics of Cu(I) accumulation in the absence and presence of oxygen, it is evident that the oxidation of Cu(I) is almost negligible at the lowest SRFA concentrations (0.25 and 0.5 mg L⁻¹ SRFA) but is substantial at higher SRFA concentrations. Furthermore, the net rate of Cu(I) accumulation during the later stages of experiments is negative (i.e., Cu(I) concentrations decay) only at higher SRFA concentrations in the presence of oxygen, despite the relatively similar (positive) Cu(I) accumulation rates at all SRFA concentrations at corresponding times in the absence of oxygen (Figure 1). This suggests that higher concentrations of SRFA promoted Cu(I) oxidation in the presence of oxygen. As the SRFA-mediated redox transformation of 0.4 μM copper progressed in the presence of O₂, nanomolar concentrations of H₂O₂ were produced (Figure 3).

To further constrain the interactions between Cu(I) and SRFA in the presence of oxygen, we also examined the oxygenation of Cu(I) added directly to solutions containing SRFA. As shown in Figure 4, SRFA had no major effect on Cu(I) oxidation kinetics over a range of SRFA concentrations. However, 4 and 8 mg L⁻¹ SRFA had a slight effect on the oxidation of 0.2 μM Cu(I) (Figure 4A). This contrasts strongly with the effect of SRFA on Fe(II) oxidation kinetics, which are rapidly accelerated at pH 8 by even relatively low SRFA concentrations.⁵²

The differing effects of SRFA concentration on rates of Cu(I) oxidation in the system where copper was added initially as Cu(II) (Figure 2) or Cu(I) (Figure 4) indicates that a species

able to accelerate Cu(I) oxidation is formed during the oxidation of SRFA. This could be either due to formation of additional oxidants, potentially including the oxidized Q groups in SRFA or some other organic moiety, or due to formation of a more readily oxidized Cu(I) complex between Cu(I) and some ligand in the oxidized SRFA. In contrast, the relatively small effect of SRFA on Cu(I) oxidation kinetics in the latter experiment implies either that Cu(I) does not form complexes with unreacted SRFA⁶ or that any complexes formed are minor species that do not oxidize at an appreciable rate.

3.3. Model for Cu(II) Reduction by SRFA. A model (reactions 1–6, Table 2) developed for the oxygenation of inorganic Cu(I) and the reduction of Cu(II) by H₂O₂ (details described in the Supporting Information) was used as a basis for developing a more comprehensive model which incorporated the interactions of Cu(II) with SRFA (reactions 7–18, Table 2). On the basis of our previous conclusions, the simplest model for Cu(II) reduction by SRFA also requires the formation of at least one type of organic complex, the reduction of Cu(II) by at least two different electron donor groups (Q₁⁻ and Q₂⁻), and promotion of Cu(I) oxidation by an organic moiety formed during the oxidation of SRFA.

Model fits of the two different scenarios described above are shown in Figures 1–4. In both models, the same concentrations of Q₁⁻ (1.1 × 10⁻⁴ equiv of e⁻ (g of SRFA)⁻¹) and Q₂⁻ (3.1 × 10⁻⁴ equiv of e⁻ (g of SRFA)⁻¹) were used. The total EDC of 4.2 × 10⁻⁴ equiv of e⁻ (g of SRFA)⁻¹ is in reasonable agreement with the value determined by Jiang and Kappler⁴⁹ after application of a correction factor. This consistency suggests that, despite other uncertainties, the concentration

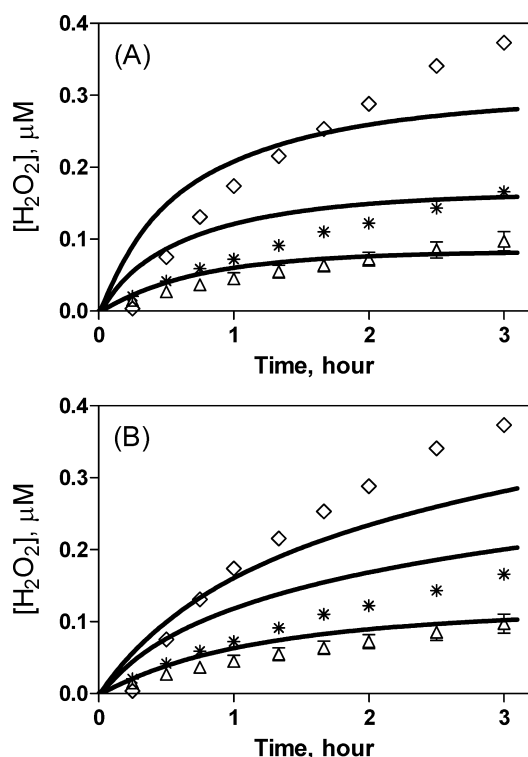


Figure 3. Production of H_2O_2 in solutions of 0.7 M NaCl and 2.0 mM NaHCO_3 at pH 8.0 initially containing $0.4 \mu\text{M}$ Cu(II), $243 \mu\text{M}$ O_2 and (Δ) 1 mg L^{-1} SRFA, ($*$) 2 mg L^{-1} SRFA, or (\diamond) 4 mg L^{-1} SRFA. Error bars are standard errors from triplicate measurements and lines represent model fits. Model fits are shown using either (A) the one-ligand class model or (B) the two-ligand class model.

and reactivity of these electron donor groups is well constrained in this model. We additionally assumed that Q_1 is capable of forming a weak complex with Cu(I) (reaction 14), which promotes the oxidation of Cu(I) to Cu(II) (reaction 15) in the presence of O_2 . Although this assumption is highly speculative, inclusion of this process was necessary to accurately reproduce the measured concentrations of Cu(I) at high SRFA concentrations when Cu(II) was added to SRFA in the presence of oxygen while maintaining consistency with the insignificant effect of SRFA on Cu(I) oxidation kinetics when Cu(I) was added to SRFA. Other obvious mechanisms by which Cu(I) oxidation might be accelerated by high concentrations of partially oxidized SRFA, such as formation of additional Cu(I) oxidants, were not able to quantitatively reproduce the observed effect at high [SRFA] in the presence of oxygen. The assumption that O_2^- reacts rapidly with oxidized Q_1 and Q_2 in both models (reactions 17 and 18) also accords with reported literature values for reaction rates of oxidized quinones with O_2^- .⁵³

In the one-ligand class model, Cu(II) is complexed by one dominant binding group L_2 where both the binding concentration $[\text{L}_2]_0 = 4.0 \times 10^{-5} \text{ mol (g of SRFA)}^{-1}$ and the stability constant of the complex $K = k_8/k_{-8} = 1.4 \times 10^9 \text{ M}^{-1}$ are similar to the properties of the ligand binding group reported in the Yang and van den Berg study¹² (Table 1). The association rate constant for the $\text{Cu}^{\text{II}}\text{L}_2$ complex of $k_8 = 2.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ is in reasonable accord with literature values for complexation of Cu(II) by SRFA.^{45–48}

In the two-ligand class model, Cu(II) is complexed by two dominant binding groups within SRFA: L_1 (strong) with a

concentration of $5.9 \times 10^{-5} \text{ mol (g of SRFA)}^{-1}$ and L_2 (weak) with a concentration of $1.9 \times 10^{-4} \text{ mol (g of SRFA)}^{-1}$. The stability constants of the strong ligand group $\log K_{\text{L}_1} = \log k_7/k_{-7} = 13.4$ and weak ligand group $\log K_{\text{L}_2} = \log (k_8/k_{-8}) = 11.6$ (Table 2) are reasonably similar to those reported in previous studies with low concentrations of Cu(II)^{12,43,44} (Table 1). Although unbound Cu(II) and the weak complex $\text{Cu}^{\text{II}}\text{L}_2$ can be reduced by both Q_1^- and Q_2^- at reasonable rates, the strong complex $\text{Cu}^{\text{II}}\text{L}_1$ is proposed to be unreactive with Q_1^- , Q_2^- , and O_2^- . Thus at higher [SRFA], more Cu(II) would be expected to be present as $\text{Cu}^{\text{II}}\text{L}_1$ and, because this species is relatively inert, the extent of initial Cu(I) generation relative to total [SRFA] would decrease, as observed.

The kinetic models (Table 2) fit the Cu(I) data reasonably over the range of experimental conditions investigated, as shown in Figures 1, 2, and 4. However, the models provide a relatively poor description of H_2O_2 production, particularly in the presence of 4 mg L^{-1} SRFA (Figure 3). (It should be noted that variation in the concentration of H_2O_2 from 0 to $0.1 \mu\text{M}$ has a negligible effect on the quality of fits in Figures 1, 2, and 4). This suggests that processes other than those included in the relatively simple models developed here may affect the transformations of O_2^- and H_2O_2 . For example, quinones may react with H_2O_2 ,⁵⁴ whereas phenoxyl-type radicals that have been suggested to be present in HS^{SS} may act as a sink for O_2^- that does not produce H_2O_2 ,⁵⁶ as proposed to occur during sunlight-induced photolysis of SRFA under conditions similar to those used in the present work.⁵⁷ It is also possible that a low concentration of H_2O_2 was generated due to the slow oxygenation of hydroquinone moieties present in the SRFA (Figure S3, Supporting Information). We have not included such reactions in the model presented here to avoid unnecessary uncertainty; however, such processes may require further attention in future work to better constrain the redox behavior of HS such as SRFA under typical environmental conditions.

3.4. Limitations of the Proposed Kinetic Models.

Despite the reasonable fit of the two models to the experimental data over a range of [SRFA], the reaction mechanisms employed are almost certainly simplistic representations of the complex interaction between SRFA and redox active metals and, as such, some uncertainty exists with regard to both the veracity of the modeling approaches used and the derived constants. The simplest model that assumes the presence of one ligand binding group would appear practical if one considered the major binding sites for Cu(II) were largely attributed to carboxylate moieties in SRFA at neutral pH.⁵⁸ On the other hand, in the two ligand class model, the assumption that SRFA contains two types of binding sites that form complexes of 1:1 stoichiometry with Cu(II) would seem reasonable given that carboxyl (with $\text{pK}_a \sim 3.8$) and phenolic ($\text{pK}_a \sim 8.6$) functional groups are most abundant in SRFA²⁵ and representation of the Cu(II)-binding ability of SRFA in terms of these groups has been found to satisfactorily describe its complexation behavior previously.^{12,44} However, this is clearly an oversimplification, as fulvic acids are recognized to contain a complex array of binding sites.⁵⁹ In addition, as a number of redox active functional groups are present in fulvic acids with each possessing a different characteristic E_h and concentration, the use of Q_1^- and Q_2^- as representatives for their redox properties is also an oversimplification.

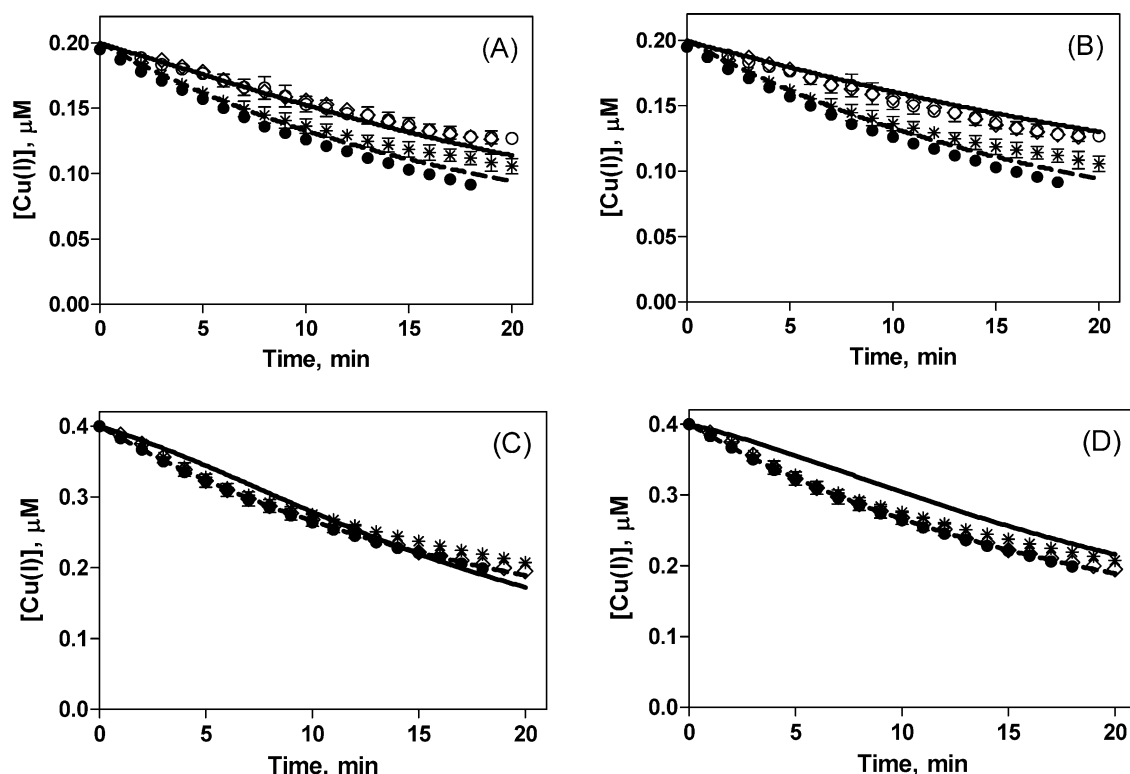


Figure 4. Kinetics of Cu(I) oxygenation in 0.7 M NaCl and 2.0 mM NaHCO₃ at pH 8.0 in the presence of (●) no SRFA, (*) 2 mg L⁻¹ SRFA, (◇) 4 mg L⁻¹ SRFA, or (○) 8 mg L⁻¹ SRFA. (A) and (B) [Cu(I)]₀ = 0.2 μM; (C) and (D) [Cu(I)]₀ = 0.4 μM. All solutions were initially saturated with O₂ ([O₂]₀ = 243 μM). Error bars are standard errors from triplicate measurements. Dashed lines represent model fits for oxygenation of inorganic Cu(I) and solid lines represent model fits for Cu(I) oxygenation in the presence of SRFA; fits at 2 and 4 mg L⁻¹ SRFA in panels (A) and (B) and 2 mg L⁻¹ SRFA in panels (C) and (D) are omitted for clarity. Model fits are shown using either (A) and (C) the one-ligand class model or (B) and (D) the two-ligand class model.

We have also assumed that the Cu(II)-binding capacity of SRFA is not affected by its oxidation even though oxidation of HS may, at least in theory, affect complexation properties by providing additional binding sites and/or altering the binding affinities of existing functional groups. However, if quinone moieties are the major groups involved with electron transfer as expected^{17,27} and carboxylate and/or phenolic groups are the major binding sites for Cu(II), oxidation of hydroquinones to semiquinones and/or semiquinones to quinones is unlikely to affect total Cu(II) binding site concentrations. Consistent with this assumption, Maurer and co-workers⁶⁰ found that electrochemical reduction of humic acid only increased the amount of proton-reactive sites by 15%. It is also possible that reducing conditions may be created during argon sparging with resultant increase in the concentration of reduced quinone sites. However, the fact that (i) similar initial concentrations of Cu(I) were generated in the absence and presence of O₂ (Figures 1 and 2) and (ii) removal of O₂ would prevent the oxidation of hydroquinone moieties in SRFA suggest that argon sparging did not significantly modify the redox behavior of SRFA in this work.

3.5. Thermodynamic Considerations Relating to the Reduction of Cu(II) by SRFA. Though it is difficult to rationalize the kinetics of redox reactions on the basis of their thermodynamic properties alone, estimation of the solution redox potentials and of particular redox couples may assist in ascertaining the likely tendency of proposed chemical reactions to occur under the conditions of the system being investigated. Because only 0.4 μM Cu(II) was employed in the current study

and the total EDC in SRFA was ~0.42 mequiv of e⁻ (g of SRFA)⁻¹, the E_h of the solution in the absence of O₂ and in the presence of 4 mg L⁻¹ SRFA was likely determined by the SRFA redox couple(s) and thus can be estimated as follows.

As shown in Figure 1, after the initial rapid reduction of Cu(II) by SRFA, a steady state concentration of Cu(I) of ~0.25 μM was reached after 5 min. Thus the pseudoequilibrium E_h of the system can be estimated from the Cu²⁺/Cu⁺ couple. Speciation calculations based on the Xue and Sigg⁴³ model (Table 1) for Cu(II) (at [Cu(II)]_T = 0.15 μM) using MINEQL + gave [Cu²⁺] = 8.3 × 10⁻¹² M, whereas the concentration of Cu⁺ (with [Cu(I)]_T = 0.25 μM) was calculated to be 1.5 × 10⁻¹² M, assuming organic complexation of Cu(I) was not important. The pseudoequilibrium E_h of the system, assumed to be similar to that of the Cu²⁺/Cu⁺ couple, is given by the Nernst equation:⁶¹

$$\begin{aligned} E_h &= E_{h(\text{Cu}^{2+}/\text{Cu}^+)} \\ &= E_{h(\text{Cu}^{2+}/\text{Cu}^+)}^0 - 0.059 \log \frac{[\text{Cu}^+]}{[\text{Cu}^{2+}]} \\ &= 0.197 \text{ V} \end{aligned} \quad (1)$$

where E_h⁰(Cu²⁺/Cu⁺) = 0.153 V (Table S1, Supporting Information).

Thus, E_h of the major SRFA redox couple, which is assumed to be represented by Q/Q⁻, can be calculated by assigning [Q⁻]_{0,T} (in 4 mg L⁻¹ SRFA) = 4.2 × 10⁻⁴ equiv of e⁻ (g of SRFA)⁻¹ × 4 mg of SRFA = 1.7 × 10⁻⁶ equiv of e⁻ L⁻¹ (Table 2). At pseudoequilibrium, after the transfer of 2.5 × 10⁻⁷ equiv

Table 2. Modeled Reactions for Cu(II) Reduction by SRFA^a

no.	reaction	rate constant	
1	$\text{Cu(I)} + \text{O}_2 \rightarrow \text{Cu(II)} + \text{O}_2^-$	$k_1 = 1.5 \pm 0.04 \text{ M}^{-1} \text{ s}^{-1}$	
2	$\text{Cu(I)} + \text{O}_2^- \xrightarrow{2\text{H}^+} \text{Cu(II)} + \text{H}_2\text{O}_2$	$k_2 = (2.0 \pm 0.05) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
3	$\text{Cu(I)} + \text{H}_2\text{O}_2 \xrightarrow{-\text{OH}^-} \text{Cu(II)} + \text{OH}^\bullet$	$k_3 < 100 \text{ M}^{-1} \text{ s}^{-1}$	
4	$\text{Cu(II)} + \text{O}_2^- \rightarrow \text{Cu(I)} + \text{O}_2$	$k_4 = (6.6 \pm 0.7) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	
5	$\text{Cu(II)} + \text{H}_2\text{O}_2 \xrightarrow{-2\text{H}^+} \text{Cu(I)} + \text{O}_2^-$	$k_5 = (4.7 \pm 0.16) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$	
6	$\text{O}_2^- + \text{O}_2^- \xrightarrow{2\text{H}^+} \text{H}_2\text{O}_2 + \text{O}_2$	$k_6 = 6.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	
		One-Ligand Class Model	Two-Ligand Class Model
7	$\text{Cu(II)} + \text{L}_1 \xrightleftharpoons[k_{-7}]{k_7} \text{Cu}^{\text{II}}\text{L}_1$	N/A	$k_7 = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} b, c$ $k_{-7} = 4.0 \times 10^{-4} \text{ s}^{-1} b$
8	$\text{Cu(II)} + \text{L}_2 \xrightleftharpoons[k_{-8}]{k_8} \text{Cu}^{\text{II}}\text{L}_2$	$k_8 = 2.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} b, c$ $k_{-8} = 2.0 \times 10^{-4} \text{ s}^{-1} b$	$k_8 = 4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} b, c$ $k_{-8} = 1.0 \times 10^{-2} \text{ s}^{-1} b$
9	$\text{Cu(II)} + \text{Q}_1^- \rightarrow \text{Cu(I)} + \text{Q}_1$	$k_9 = 8.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} b, c$	
10	$\text{Cu}^{\text{II}}\text{L}_2 + \text{Q}_1^- \rightarrow \text{Cu}^{\text{I}}\text{L}_2 + \text{Q}_1$	N/A	$k_{10} = 8.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} b$
11	$\text{Cu(II)} + \text{Q}_2^- \rightarrow \text{Cu(I)} + \text{Q}_2$	$k_{11} = 1.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} b, c$	
12	$\text{Cu}^{\text{II}}\text{L}_2 + \text{Q}_2^- \rightarrow \text{Cu}^{\text{I}}\text{L}_2 + \text{Q}_2$	N/A	$k_{12} = 1.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} b$
13	$\text{Cu}^{\text{I}}\text{L}_2 \rightarrow \text{Cu(I)} + \text{L}_2$	N/A	$k_{13} = 1.0 \times 10^9 \text{ s}^{-1} d$
14	$\text{Cu(I)} + \text{Q}_1 \rightarrow \text{Cu}^{\text{I}}\text{Q}_1$	$k_{14} = 7.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} b$	
15	$\text{Cu}^{\text{I}}\text{Q}_1 + \text{O}_2 \rightarrow \text{Cu}^{\text{II}}\text{Q}_1^+ + \text{O}_2^-$	$k_{15} = 4.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1} b$	
16	$\text{Cu}^{\text{II}}\text{Q}_1^+ \rightarrow \text{Cu(II)} + \text{Q}_1$	$k_{16} = 1.0 \times 10^9 \text{ s}^{-1} d$	
17	$\text{Q}_1 + \text{O}_2^- \rightarrow \text{Q}_1^- + \text{O}_2$	$k_{17} = 4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} b$	$k_{17} = 8.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} b$
18	$\text{Q}_2 + \text{O}_2^- \rightarrow \text{Q}_2^- + \text{O}_2$	$k_{18} = 7.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} b$	$k_{18} = 8.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} b$

^aCu(I) and Cu(II) represent all inorganic cuprous and cupric species respectively. Q_1^- and Q_1 represent two redox-active groups in SRFA molecules. Reactions of Cu(I) and Cu(II) species with any radical species other than O_2^- , Q_1^- , Q_1 , Q_2^- , or Q_2 were considered to be unimportant and thus not included in the reaction scheme. Rate constants for reactions 1–6 were determined from a kinetic model for the oxygenation of inorganic Cu(I) and reduction of Cu(II) by H_2O_2 (see the Supporting Information). L_2 (in one-ligand class model) and L_1 and L_2 (in two-ligand class model) represent Cu-binding ligand groups. ^bFitting parameter. ^cFitted initial concentrations of ligands and redox active moieties in SRFA were $[\text{L}_2]_0 = 4.0 \times 10^{-5} \text{ mol (g of SRFA)}^{-1}$ (for one-ligand class model); and $[\text{L}_1]_0 = 5.9 \times 10^{-5} \text{ mol (g of SRFA)}^{-1}$, ^{12,44} $[\text{L}_2]_0 = 1.9 \times 10^{-4} \text{ mol (g of SRFA)}^{-1}$ (for two-ligand class model); $[\text{Q}_1^-]_0 = 1.1 \times 10^{-4} \text{ equiv of e}^- \text{ (g of SRFA)}^{-1}$, and $[\text{Q}_2^-]_0 = 3.1 \times 10^{-4} \text{ equiv of e}^- \text{ (g of SRFA)}^{-1}$ in both models. ^dAssigned value as the reaction is expected to be very rapid.

of $\text{e}^- \text{ L}^{-1}$ to Cu(II), $[\text{Q}^-]_{\text{T}} = 1.4 \times 10^{-6} \text{ equiv of e}^- \text{ L}^{-1}$ and $[\text{Q}] = 2.5 \times 10^{-7} \text{ equiv of e}^- \text{ L}^{-1}$. In addition, assuming the half redox reaction of the Q/Q^- couple (with $n_{\text{H}^+}/n_{\text{e}^-} \sim 0.9$ at pH 8²⁴) is described by



then, applying the Nernst equation for the Q/Q^- couple at pH = 8.0, gives

$$E_{\text{h}} = E_{\text{h(Q/Q}^-)}^0 - 0.059 \log \frac{[\text{Q}^-]}{[\text{Q}][\text{H}^+]^{0.9}} = 0.197 \text{ V} \quad (3)$$

resulting in $E_{\text{h(Q/Q}^-)}^0 = 0.666 \text{ V}$.

This estimated standard redox potential of SRFA solution is in reasonable accord with the range of literature values for the E_{h} of HS.^{22,23,35,62,63} In addition, if the pH dependence of the E_{h} of SRFA solution is assumed to be similar to that of SRHA⁶⁴ ($-0.06 \text{ V}/\Delta\text{pH}$), then

$$E_{\text{h}}(\text{SRFA, pH 8.0}) = 0.666 - 0.06 \times 8 = 0.186 \text{ V} \quad (4)$$

This estimated operating E_{h} of the SRFA solution (at pH 8.0) is reasonably consistent with the value of 0.234 V (at pH 7.0) for

humic acids reported by Osterberg and Shirshova.⁶³ At this relatively low operating E_{h} , SRFA would be expected to be able to reduce Cu(II) to Cu(I) in solution (Table S1, Supporting Information).

If a positive correlation between the kinetics of redox reactions and their E_{h} is assumed (as has been shown by Bauer et al.⁵⁰), then the biphasic manner of Cu(II) reduction kinetics in the absence of O_2 might be qualitatively explained as follows. Because the initial redox potential of the Cu(II)/Cu(I) couple is higher than that of the Q/Q^- couple at pH = 8.0, rapid reduction of Cu(II) would be expected to occur upon addition of Cu(II) to the SRFA solution. However, as the reaction proceeds, the E_{h} of the Cu(II)/Cu(I) couple will decrease while the E_{h} of the Q/Q^- couple will increase. The kinetics of Cu(II) reduction will thus be retarded as the reaction proceeds for two major reasons: (i) the tendency for electron transfer would be expected to decrease (due to the increase in the E_{h} of the dominant Q/Q^- couple), and (ii) as the concentration of the more labile electron donor groups in SRFA decreases (or is exhausted), some potential electron donor groups will no longer be available due to the rise in the E_{h} of the system.

In the presence of oxygen ($[O_2]_0 = 0.243 \text{ mM}^{65}$) and 1 mg L^{-1} SRFA, two independent estimates of the system pseudoequilibrium E_h from both Cu^{2+}/Cu^+ and O_2/O_2^- couples may be deduced (as shown below), particularly as the concentration of $Cu(I)$ attains a steady state of $\sim 0.13 \mu\text{M}$ (Figure 2C). The similarity in these two independent estimates of the system pseudoequilibrium E_h should provide confidence in the model used to predict the concentration of O_2^- (and in the assumption that it is the E_h of the O_2/O_2^- couple rather than O_2/H_2O which is relevant to $Cu(I)$ oxidation).

Speciation calculations based on the Xue and Sigg⁴³ model (Table 1) for $Cu(II)$ species at $[Cu(II)]_T = 0.27 \mu\text{M}$ and 1 mg L^{-1} SRFA using MINEQL+ yield $[Cu^{2+}] = 1.7 \times 10^{-8} \text{ M}$, whereas the concentration of Cu^+ with $[Cu(I)]_T = 0.13 \mu\text{M}$ is calculated to be $7.8 \times 10^{-13} \text{ M}$. The pseudoequilibrium E_h of the system estimated from the Cu^{2+}/Cu^+ couple using eq 1 is then 0.409 V . In addition, a steady state concentration of $[O_2^-]$ of $\sim 10^{-13} \text{ M}$ is predicted by the model in accordance with the steady state concentration of $Cu(I)$ at 1 mg L^{-1} SRFA (Figure S4, Supporting Information), yielding a pseudoequilibrium E_h of the system (based on the O_2/O_2^- couple) of 0.394 V using eq 1 (with $E_{h(O_2/O_2^-)}^0 = -0.16 \text{ V}^{61}$). The similarity of the pseudoequilibrium E_h values of the system calculated independently from both Cu^{2+}/Cu^+ and O_2/O_2^- couples supports the veracity of the model and the predicted O_2^- concentration.

4. CONCLUSIONS AND IMPLICATIONS

We have presented evidence that HS (represented here by SRFA) are capable of rapidly reducing $Cu(II)$ to $Cu(I)$ under conditions typical of natural waters. The reduction of $Cu(II)$ in the absence of oxygen is of a biphasic nature with an initial phase characterized by rapid formation of $Cu(I)$, followed by a second phase with much slower increase in $Cu(I)$ concentration. When present, oxygen only had a noticeable influence on $Cu(I)$ concentrations in the second phase of the reduction process and at high SRFA concentrations. Increase in the [SRFA] increased the rate of $Cu(I)$ generation although at high [SRFA], the yield of $Cu(I)$ formed relative to [SRFA] was less than at low [SRFA].

Two plausible kinetic modeling approaches have been shown to satisfactorily describe the experimental data over a range of [SRFA]: (i) a "one ligand approach" where formation of the complex occurs on a similar time scale to $Cu(II)$ reduction with the reduction of inorganic $Cu(II)$ responsible for the initial $Cu(I)$ production, and (ii) a "two ligand approach" where rapid binding of $Cu(II)$ with the stronger ligand yields a non-reducible (or very slowly reducible) complex with the remaining pool of rapidly reducible $Cu(II)$ being a second, weaker organic complex. In both modeling approaches, reduction of $Cu(II)$ was considered to be induced by two electron donor groups within SRFA, a relatively labile electron donor (with a concentration of 1.1×10^{-4} equiv of e^- (g of SRFA) $^{-1}$) that reduced $Cu(II)$ relatively rapidly and a less labile donor (with a concentration of 3.1×10^{-4} equiv of e^- (g of SRFA) $^{-1}$) that reduced $Cu(II)$ more slowly. Further insight into the most appropriate modeling approach can best be obtained by detailed investigation of the rate of complexation of $Cu(II)$ by HS.

Thermodynamic characteristics of the system have also been estimated to assist in ascertaining the likely tendency of the proposed chemical reactions to occur under the conditions of

the system being investigated. The operating redox potential of SRFA solution of $\sim 0.186 \text{ V}$ clearly indicates that $Cu(II)$ could be reduced to $Cu(I)$ in the system. An estimated pseudoequilibrium E_h of $\sim 0.4 \text{ V}$ under oxic conditions in the presence of 1 mg L^{-1} SRFA is also consistent with model predictions of $[O_2^-]$ under such conditions.

This study highlights the importance of largely overlooked redox interactions between $Cu(II)$ and HS. Because HS is capable of reducing $Cu(II)$ quite rapidly, previous studies of $Cu(II)$ complexation by HS may have inadvertently observed both $Cu(II)$ complexation and reduction. Thus, caution must be applied when literature data on interactions between $Cu(II)$ and SRFA are interpreted. Despite their simplifications and assumptions, the kinetic modeling approaches used here should assist in understanding and predicting the factors controlling copper transformation, speciation, bioavailability and toxicity in aquatic systems.

■ ASSOCIATED CONTENT

● Supporting Information

Text, table, and figures for the following: S1, discussion of the kinetic model for the oxygenation of $Cu(I)$ and reduction of $Cu(II)$ by H_2O_2 ; Table S1, standard reduction potentials for $Cu(II)/Cu(I)$ species; Table S2, modeled reactions for the oxidation of inorganic $Cu(I)$ and reduction of inorganic $Cu(II)$ by H_2O_2 ; Figure S1, examination of the extent of disproportionation of $Cu(I)$ and reduction of $Cu(I)$ by SRFA; Figure S2, H_2O_2 calibration curves in the presence of SRFA; Figure S3, generation of H_2O_2 in the absence of $Cu(II)$ and presence of SRFA; Figure S4, predicted concentrations of superoxide in the presence of O_2 and SRFA; Figure S5, model fit and experimental data for the oxidation of inorganic $Cu(I)$; Figure S6, model fit and experimental data for inorganic $Cu(II)$ reduction by H_2O_2 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +61 2 9385 5059. Fax: +61 2 9313 8341. E-mail: d.waite@unsw.edu.au.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Lewis, A. G.; Cave, W. R. *Ocean. Mar. Biol.* **1982**, *20*, 471–695.
- (2) Sunda, W. G.; Guillard, R. R. L. *J. Mar. Res.* **1976**, *34*, 511–529.
- (3) Moffett, J. W.; Zika, R. G. *Geochim. Cosmochim. Acta* **1988**, *52*, 1849–1857.
- (4) Coale, K. H.; Bruland, K. W. *Deep-Sea Res.* **1990**, *37*, 317–336.
- (5) Coale, K. H.; Bruland, K. W. *Limnol. Oceanogr.* **1988**, *33*, 1084–1101.
- (6) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1972.
- (7) Leal, M. F. C.; Van den Berg, C. M. G. *Aquat. Geochem.* **1998**, *4*, 49–75.
- (8) Al-Farawati, R.; van den Berg, C. M. G. *Mar. Chem.* **1999**, *63*, 331–352.
- (9) Yuan, X.; Pham, A. N.; Xing, G. W.; Rose, A. L.; Waite, T. D. *Environ. Sci. Technol.* **2012**, *46*, 1527–1535.
- (10) Moffett, J. W.; Zika, R. G. *Mar. Chem.* **1983**, *13*, 239–251.

- (11) Lovley, D. R.; Coates, J. D.; Blunt-Harris, E. L.; Phillips, E. J. P.; Woodward, J. C. *Nature* **1996**, *382*, 445–448.
- (12) Yang, R. J.; van den Berg, C. M. G. *Environ. Sci. Technol.* **2009**, *43*, 7192–7197.
- (13) Lovley, D. R.; Blunt-Harris, E. L. *Appl. Environ. Microbiol.* **1999**, *65*, 4252–4254.
- (14) Kappler, A.; Haderlein, S. B. *Environ. Sci. Technol.* **2003**, *37*, 2714–2719.
- (15) Curtis, G. P.; Reinhard, M. *Environ. Sci. Technol.* **1994**, *28*, 2393–2401.
- (16) Dunnivant, F. M.; Schwarzenbach, R. P.; Macalady, D. L. *Environ. Sci. Technol.* **1992**, *26*, 2133–2141.
- (17) Scott, D. T.; McKnight, D. M.; Blunt-Harris, E. L.; Kolesar, S. E.; Lovley, D. R. *Environ. Sci. Technol.* **1998**, *32*, 2984–2989.
- (18) Fulton, J. R.; McKnight, D. M.; Foreman, C. M.; Cory, R. M.; Stedmon, C.; Blunt, E. *Aquat. Sci.* **2004**, *66*, 27–46.
- (19) Peretyazhko, T.; Sposito, G. *Geoderma* **2006**, *137*, 140–146.
- (20) Aeschbacher, M.; Sander, M.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **2010**, *44*, 87–93.
- (21) Bauer, I.; Kappler, A. *Environ. Sci. Technol.* **2009**, *43*, 4902–4908.
- (22) Visser, S. A. *Nature* **1964**, *204*, 581–581.
- (23) Struyk, Z.; Sposito, G. *Geoderma* **2001**, *102*, 329–346.
- (24) Aeschbacher, M.; Vergari, D.; Schwarzenbach, R. P.; Sander, M. *Environ. Sci. Technol.* **2011**, *45*, 8385–8394.
- (25) Ritchie, J. D.; Perdue, E. M. *Geochim. Cosmochim. Acta* **2003**, *67*, 85–96.
- (26) Klapper, L.; McKnight, D. M.; Fulton, J. R.; Blunt-Harris, E. L.; Nevin, K. P.; Lovley, D. R.; Hatcher, P. G. *Environ. Sci. Technol.* **2002**, *36*, 3170–3175.
- (27) Ratasuk, N.; Nanny, M. A. *Environ. Sci. Technol.* **2007**, *41*, 7844–7850.
- (28) Uchimiya, M.; Stone, A. T. *Chemosphere* **2009**, *77*, 451–458.
- (29) Fimmen, R. L.; Cory, R. M.; Chin, Y. P.; Trouts, T. D.; McKnight, D. M. *Geochim. Cosmochim. Acta* **2007**, *71*, 3003–3015.
- (30) Chen, J.; Gu, B. H.; Royer, R. A.; Burgos, W. D. *Sci. Total Environ.* **2003**, *307*, 167–178.
- (31) Alberts, J. J.; Schindle, J.; Miller, R. W.; Nutter, D. E. *Science* **1974**, *184*, 895–896.
- (32) Deiana, S.; Gessa, C.; Manunza, B.; Rausa, R.; Solinas, V. *Eur. J. Soil Sci.* **1995**, *46*, 103–108.
- (33) Gu, B. H.; Bian, Y. R.; Miller, C. L.; Dong, W. M.; Jiang, X.; Liang, L. Y. *Proc. Natl. Acad. Sci.* **2011**, *108*, 1479–1483.
- (34) Palmer, N. E.; Freudenthal, J. H.; von Wandruszka, R. *Environ. Chem.* **2006**, *3*, 131–136.
- (35) Skogerboe, R. K.; Wilson, S. A. *Anal. Chem.* **1981**, *53*, 228–232.
- (36) Tongesayi, T.; Smart, R. B. *Environ. Chem.* **2006**, *3*, 137–141.
- (37) Palmer, N. E.; von Wandruszka, R. *Environ. Sci. Pollut. Res.* **2010**, *17*, 1362–1370.
- (38) Moffett, J. W.; Zika, R. G.; Petasne, R. G. *Anal. Chim. Acta* **1985**, *175*, 171–179.
- (39) Zhou, M. J.; Diwu, Z. J.; PanchukVoloshina, N.; Haugland, R. P. *Anal. Biochem.* **1997**, *253*, 162–168.
- (40) Schecher, W. D.; McAvoy, D. C. *Comput. Environ. Urban Syst.* **1992**, *16*, 65–76.
- (41) Johnson, K. A.; Simpson, Z. B.; Blom, T. *Anal. Biochem.* **2009**, *387*, 20–29.
- (42) Cabaniss, S. E.; Shuman, M. S. *Geochim. Cosmochim. Acta* **1988**, *52*, 185–193.
- (43) Xue, H. B.; Sigg, L. *Aquat. Geochem.* **1999**, *5*, 313–335.
- (44) Kogut, M. B.; Voelker, B. M. *Environ. Sci. Technol.* **2001**, *35*, 1149–1156.
- (45) Lin, C. F.; Houng, L. M.; Lo, K. S.; Lee, D. Y. *Toxicol. Environ. Chem.* **1994**, *43*, 1–12.
- (46) Wu, F. C.; Mills, R. B.; Evans, R. D.; Dillon, P. J. *Anal. Chem.* **2004**, *76*, 110–113.
- (47) Louis, Y.; Garnier, C.; Lenoble, V.; Mounier, S.; Cukrov, N.; Omanovic, D.; Pizeta, I. *Mar. Chem.* **2009**, *114*, 110–119.
- (48) McCann, N.; Lawrance, G. A.; Neuhold, Y. M.; Maeder, M. *Inorg. Chem.* **2007**, *46*, 4002–4009.
- (49) Jiang, J.; Kappler, A. *Environ. Sci. Technol.* **2008**, *42*, 3563–3569.
- (50) Bauer, M.; Heitmann, T.; Macalady, D. L.; Blodau, C. *Environ. Sci. Technol.* **2007**, *41*, 139–145.
- (51) Sachs, S.; Bernhard, G. *Geoderma* **2011**, *162*, 132–140.
- (52) Rose, A. L.; Waite, T. D. *Environ. Sci. Technol.* **2002**, *36*, 433–444.
- (53) Roginsky, V.; Barsukova, T. J. *Chem. Soc., Perkin Trans. 2* **2000**, 1575–1582.
- (54) Nohl, H.; Jordan, W. *Bioorg. Chem.* **1987**, *15*, 374–382.
- (55) Nurmi, J. T.; Tratnyek, P. G. *Environ. Sci. Technol.* **2002**, *36*, 617–624.
- (56) Steenken, S.; Neta, P. Transient Phenoxyl Radicals: Formation and Properties in Aqueous Solutions. In *The Chemistry of Phenols*; Zvi, R., Ed.; John Wiley and Sons Ltd.: West Sussex, England, 2003; pp 1107–1152.
- (57) Garg, S.; Rose, A. L.; Waite, T. D. *Geochim. Cosmochim. Acta* **2011**, *75*, 4310–4320.
- (58) Manceau, A.; Matynia, A. *Geochim. Cosmochim. Acta* **2010**, *74*, 2556–2580.
- (59) van Leeuwen, H. P.; Buffle, J. *Environ. Sci. Technol.* **2009**, *43*, 7175–7183.
- (60) Maurer, F.; Christl, I.; Kretzschmar, R. *Environ. Sci. Technol.* **2010**, *44*, 5787–5792.
- (61) Morel, F. M. M.; Hering, J. G. *Principles and applications of aquatic chemistry*; Wiley: New York, 1993.
- (62) Wilson, S. A.; Weber, J. H. *Chem. Geol.* **1979**, *26*, 345–354.
- (63) Osterberg, R.; Shirshova, L. *Geochim. Cosmochim. Acta* **1997**, *61*, 4599–4604.
- (64) Aeschbacher, M.; Graf, C.; Schwarzenbach, R. P.; Sander, M. *Environ. Sci. Technol.* **2012**, *46*, 4916–4925.
- (65) Mel'nichenko, N. A.; Koltunov, A. M.; Vyskrebentsev, A. S.; Bazhanov, A. V. *Russ. J. Phys. Chem. A* **2008**, *82*, 746–752.