Supporting Information for

Ligand-Enhanced Reactive Oxidant Generation by Nanoparticulate Zero-Valent Iron and Oxygen

*Christina R. Keenan and David L. Sedlak**

Department of Civil and Environmental Engineering

University of California at Berkeley

Berkeley, California 94720

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Figures S1-S8 and Table S1

* Corresponding author e-mail: sedlak@ce.berkeley.edu; telephone: (510) 643-0256; fax: (510) 642-7483.

Ferrous and Total Iron Measurements. A modified ferrozine method (*1-2*), was used to determine the concentration of filterable Fe(II), total filterable iron, and total iron in experiments without EDTA. The $Fe^{III}EDTA$ complex was measured directly by UV absorption at 258 nm (ε_{258} = 9,300 M^{-1} cm^{-1}; *3*) in most EDTA experiments. EDTA was in excess relative to Fe in all experiments and Fe was present as Fe(III). To measure filterable Fe, a 2-mL aliquot of filtered sample was added to 1 mL of formate buffer (0.005 M sodium formate and 0.015 M formic acid, pH 3.3). Total iron was determined by adding 2 mL of acidified sample (pH 3) to 1 mL of formate buffer. Total EDTA was measured by UV absorption at 258 nm after adding 2 mL of acidified sample to 1 mL of buffer and 150 µL of 1 mM ferric chloride. When benzoic acid was used as a probe compound, it was necessary to separate $Fe^{III}EDTA$ from benzoic acid because their UV spectra overlap (λ_{max} = 258 nm and 255 nm, respectively). In this case, the $Fe^{III}EDTA$ complex was measured by HPLC as described previously (*4-5*), omitting the drying and redissolution steps. For both $Fe^{III}EDTA$ methods, the standard curves were linear with regression coefficients >0.9990 and detection limits of 5 µM.

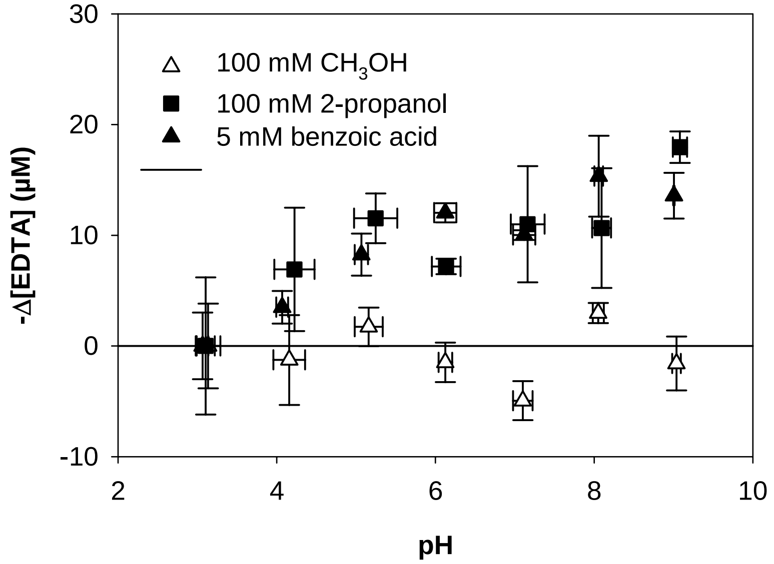

Figure S1. EDTA transformation in the presence of 100 mM CH_3OH, 100 mM 2-propanol, and 5 mM benzoic acid (t = 60 min) as measured by the difference in initial and final [EDTA].

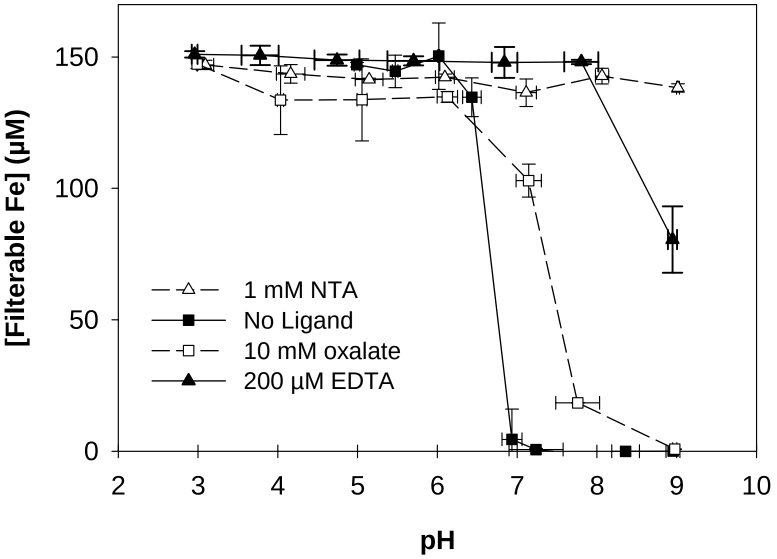

Figure S2. Dissolved Fe in 150 µM Fe(II) in 100 mM CH_3OH at 60 min. Data for no ligand, 10 mM oxalate, 1 mM NTA, and 200 µM EDTA. Initial pH as indicated.

Kinetics Figures

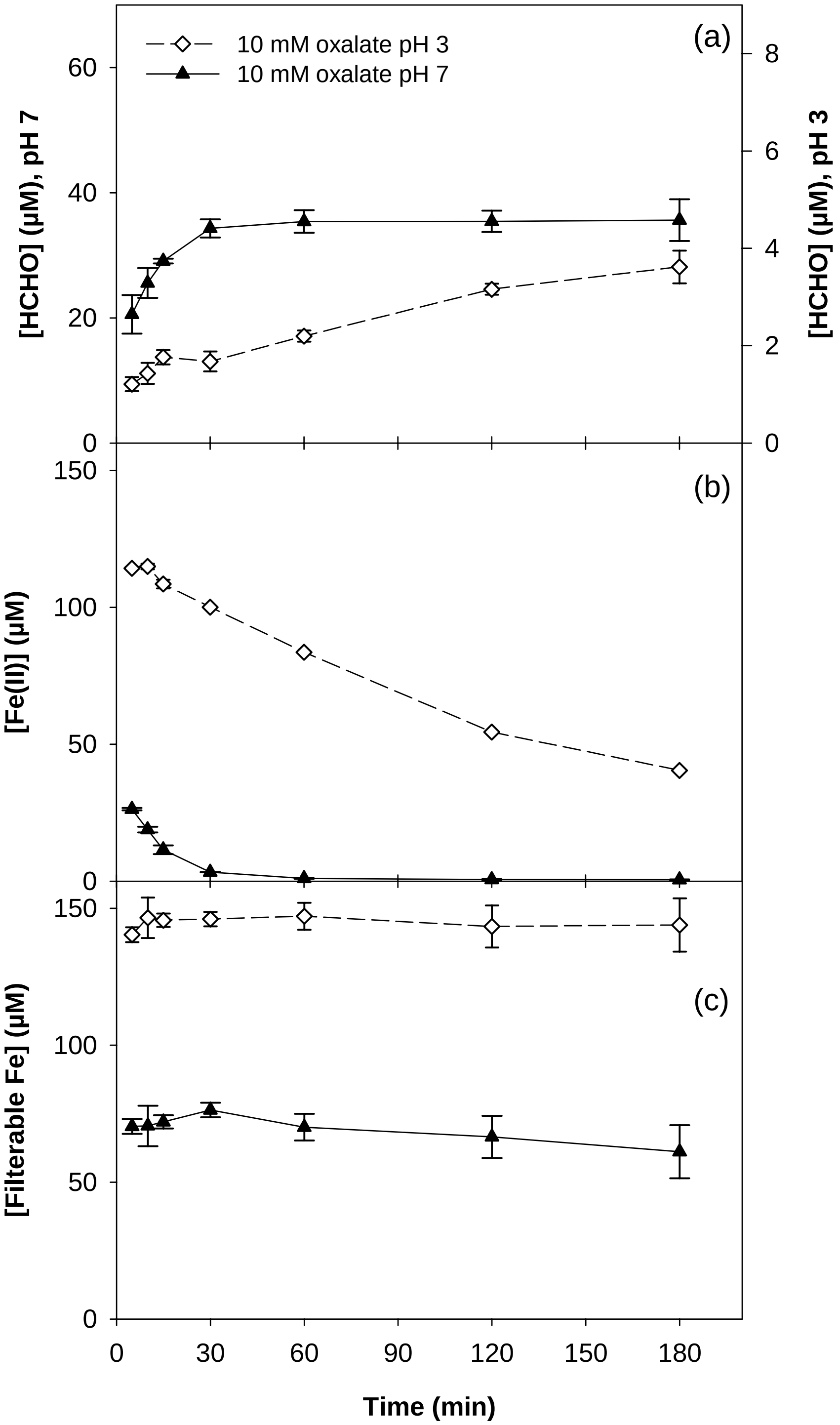

Figure S3. Kinetics of (a) HCHO production, (b) Fe(II) oxidation, and (c) Fe dissolution in 150 µM nZVI and 10 mM oxalate at pH 3 and 7.

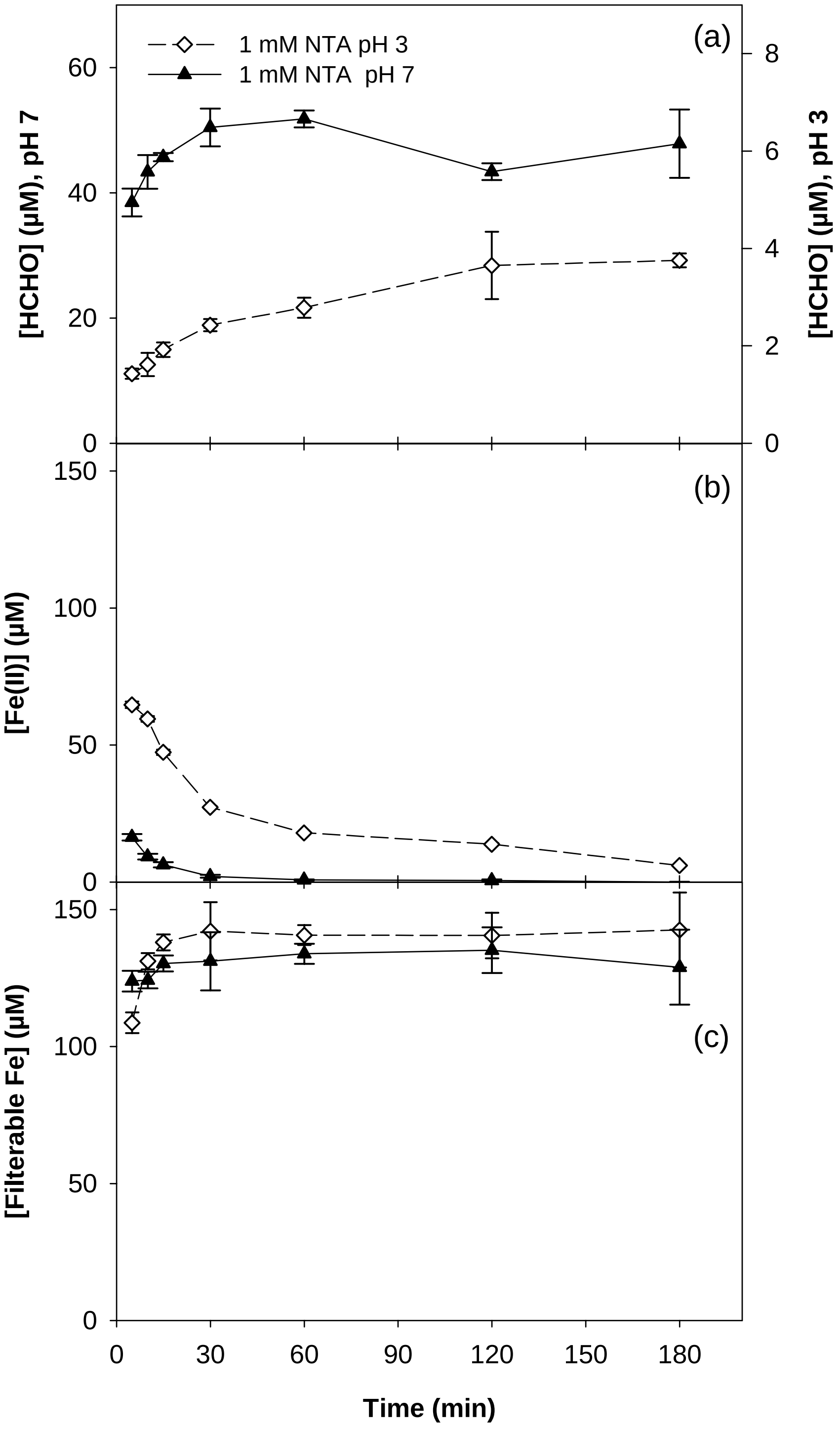

Figure S4. Kinetics of (a) HCHO production, (b) Fe(II) oxidation, and (c) Fe dissolution in 150 μM nZVI and 1 mM NTA at pH 3 and 7.

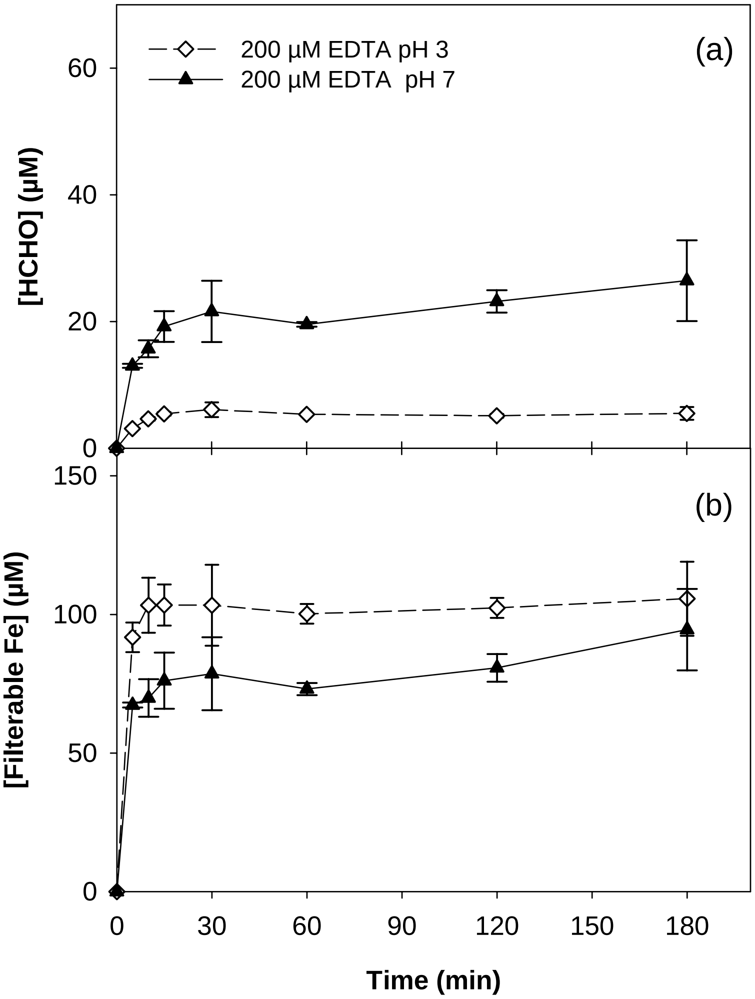

Figure S5. Kinetics of (a) HCHO production and (b) Fe dissolution in 150 µM nZVI and 200 µM EDTA at pH 3 and 7.

Speciation Figures: Equilibrium calculations were performed using the software MINEQL+ with the stability constants provided in the database. Additional equilibrium constants for the oxalate species were used (*6*). All solids were considered for Fe(II) calculations and only ferrihydrite was included for Fe(III) calculations. All figures were corrected for ionic strength.

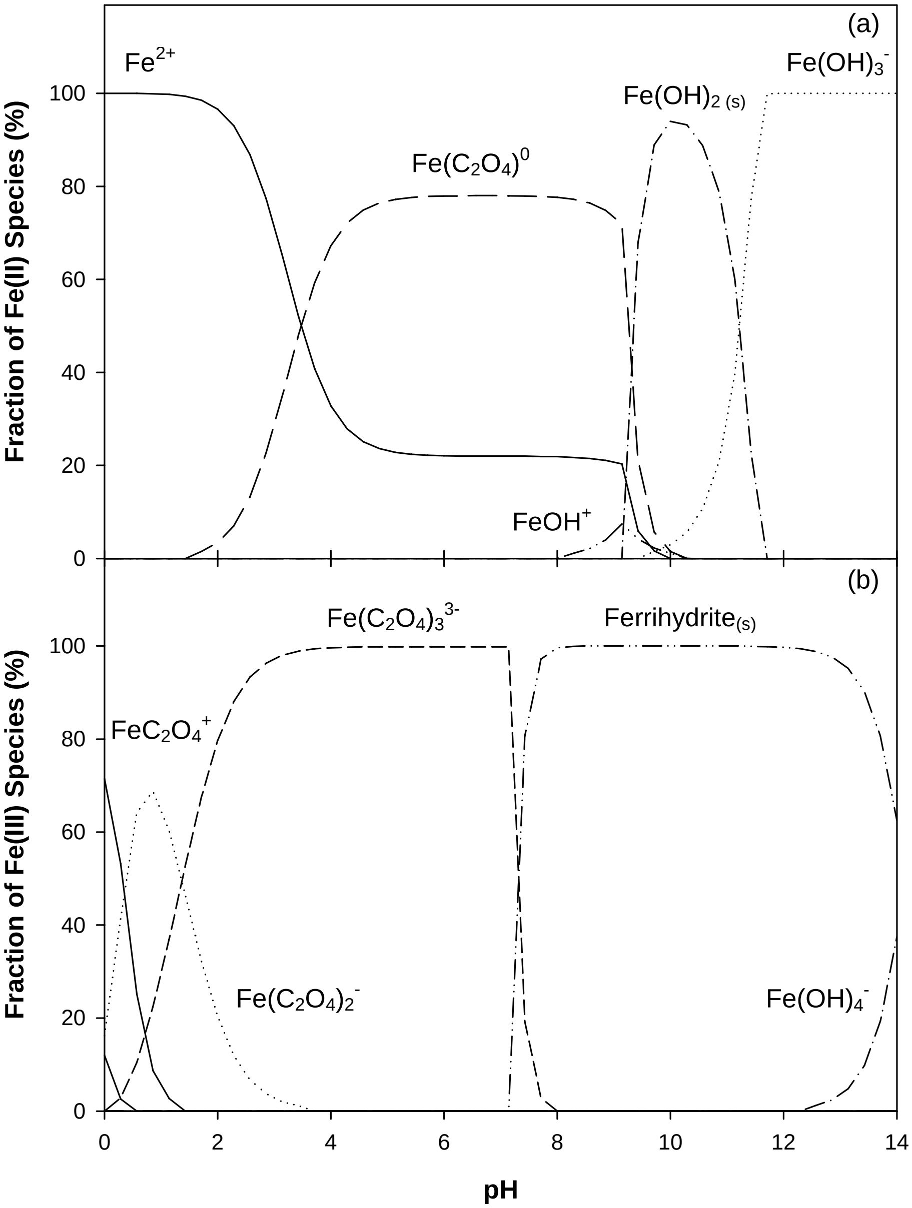

Figure S6. Speciation of (a) ferrous and (b) ferric species in 10 mM oxalate.

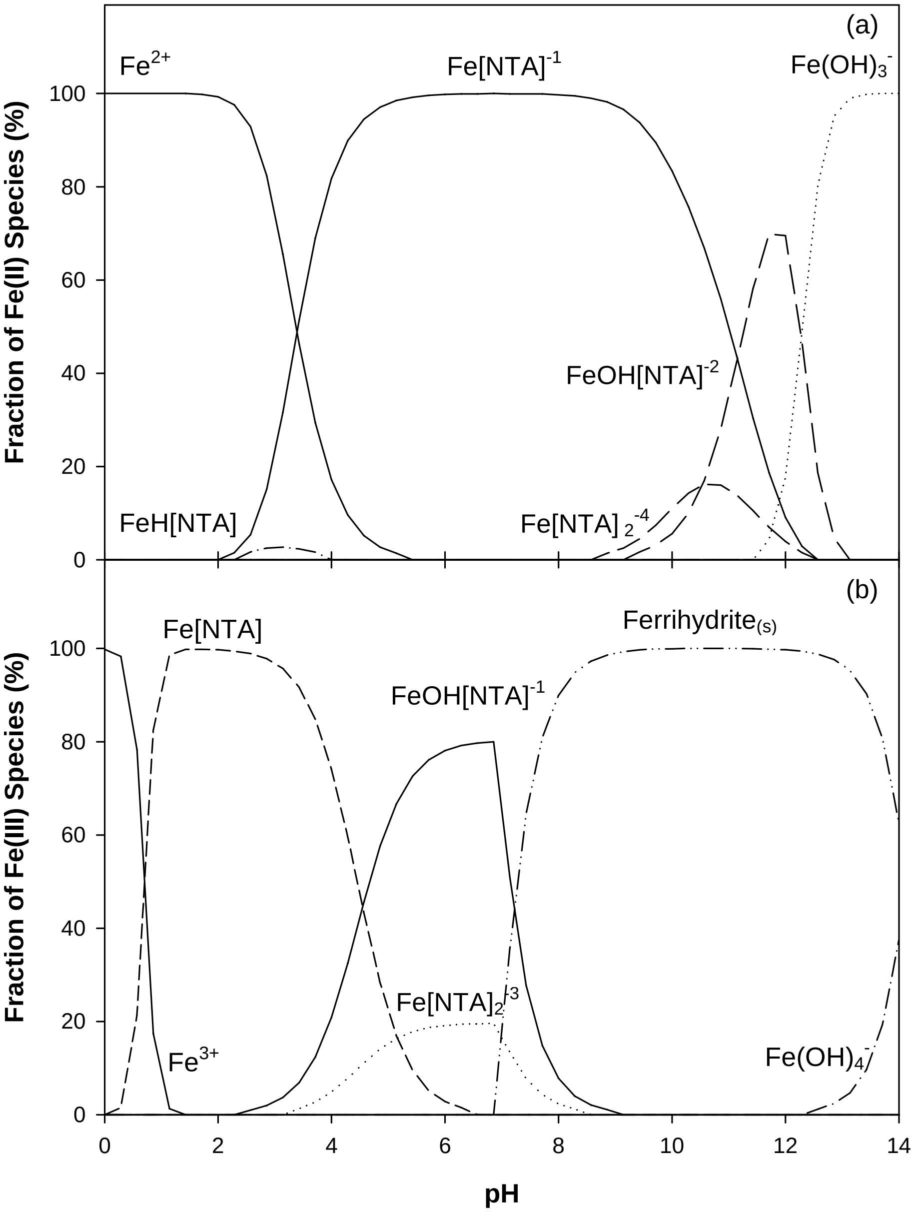

Figure S7. Speciation of (a) ferrous and (b) ferric species in 1 mM NTA.

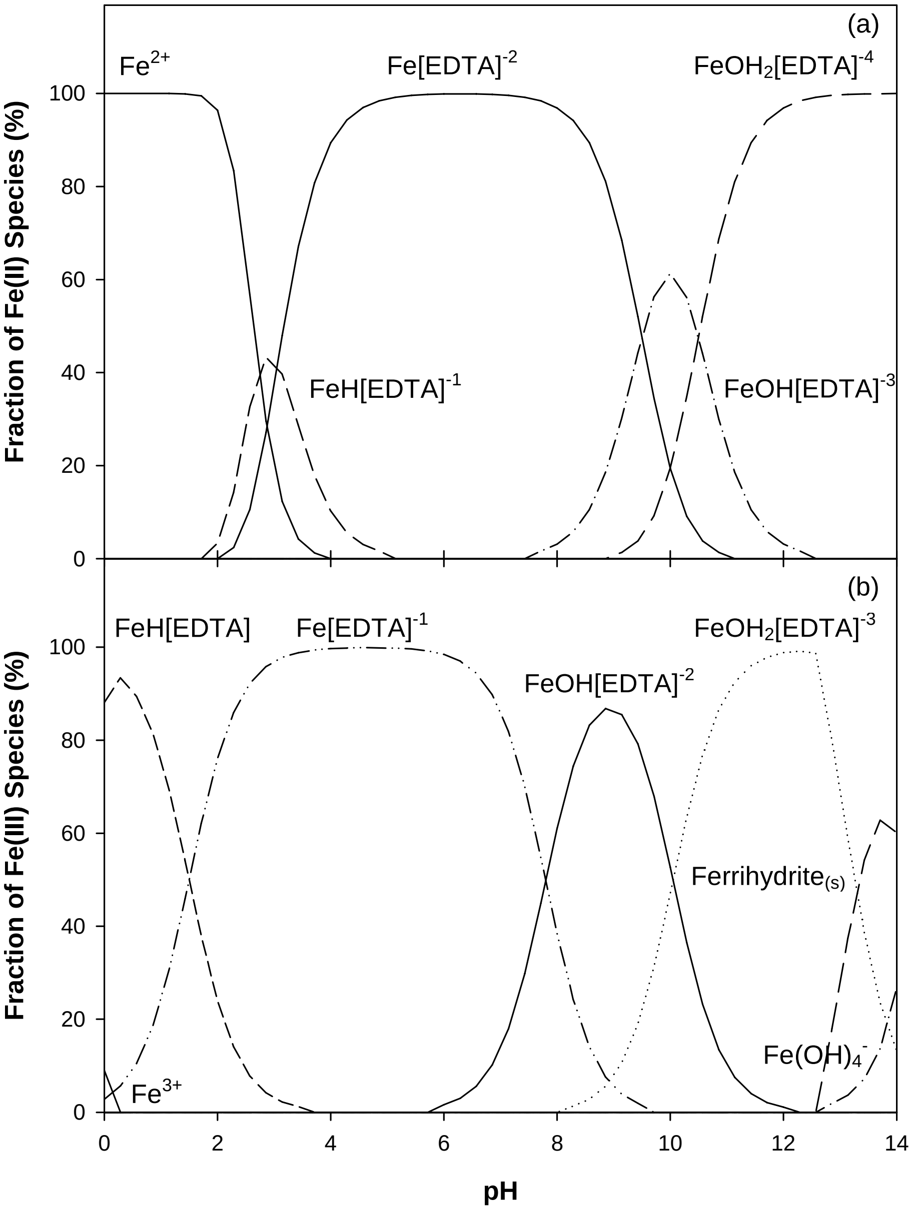

Figure S8. Speciation of (a) ferrous and (b) ferric species in 200 μM EDTA.

Table S1. Selected Published Rate Constants for Reactions of OH· (*7*).

Compound	**k ($M^{-1}s^{-1}$)**
Ethylenediaminetetraacetate ion (H_2EDTA^{2-})	4×10^8
Ethylenediaminetetraacetate ion ($HEDTA^{3-}$)	2×10^9
Nitrilotriacetic acid	2.5×10^9
Nitrilotriacetate	2.1×10^9
Oxalate ion	7.7×10^6
Oxalic acid	1.4×10^6
Acetate	8.5×10^7
Acetic acid	1.6×10^7
Benzoate	4.3×10^9
Benzoic acid	5.9×10^9
Borate	$<1 \times 10^6$
Ethanol	1.9×10^9
Fe(II)	5.0×10^8
Methanol	9.7×10^8
2-propanol	1.9×10^9

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