## HULIS Enhancement of Hydroxyl Radical formation from Fe(II):

Kinetics of Fulvic Acid-Fe(II) Complexes in the Presence of Lung Anti-Oxidants.

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> Supporting Information Information on materials and cleaning process Input parameters for Minteq Modeling of Fe(II) and SRFA OH production from BBA in SLF Information on interference of SRFA on TA assay Kinetic data for Fe(II) and SRFA-Fe(II) system Sensitivity of kinetic model to k<sub>14</sub> Contains 7 pages, 8 figures, 3 tables

## Materials

SRFA Standard I (International Humic Substances Society), TA (TCI, 99%), TAOH (Aldrich, 97%), Ferrozine (Aldrich, 97%), FeSO<sub>4</sub>•5H<sub>2</sub>O (Arcos, 99%), NaCl (EMD, 99%), sodium phosphate dibasic (Acros, 99%), potassium phosphate monobasic (Acros, 99%), ascorbate sodium salt (Sigma, 99%), urate sodium salt (Sigma, 99%, L-glutathione reduced (Sigma, 99%) and citrate tribasic sodium salt (Sigma-Aldrich, 99%) and 2,2,2-trifluoroethanol (Arcos, 99%) were used as received. SRFA standard I is a purified material and contains less than 1% inorganic ash and background transition metal contaminants are negligible.

## **Cleaning Process**

A rigorous cleaning process was followed for vessels. After each use, each vessel was washed with warm water and soap, and then rinsed deionized (18 M $\Omega$  DI) water (3×), ethanol (3×), and finally DI water (3×), soaked in a 1 M nitric acid bath overnight, rinsed with DI water and air dried. Acid baths were replaced after tow uses and kept covered to avoid dust deposition. All analytical solutions were prepared with chelex-treated 18 M $\Omega$  DI water.

Species	Concentration (mg/L)					
Cl	4041					
PO4 <sup>3-</sup>	950					
Citrate	57.6					
Na <sup>+</sup>	3006					
K <sup>+</sup>	86.02					
$Fe^{2+}(x10^{-2})$	.558, 1.395, 2.79, 5.58					
SRFA	0, .005, .010, .015, .02					
pH = 7.4						

**Table S1**. Concentration inputs for Visual MINTEQ speciation calculations.

Ionic Strength set to 0.17 M

								Ratio of	% active
			$\mathbf{Q}_1$			$Q_2$		DOM to	DOM that is
Species	logK1	<b>n</b> <sub>1</sub>	(mmol/g)	logK <sub>2</sub>	n <sub>2</sub>	(mmol/g)	b	DOC	FA
Proton	2.34	0.66	5.88	8.6	0.76	1.86	0.57	2	100
Fe	6	0.25		36	0.19				

**Table S2**. Input parameters for SRFA using NICA-Donnan model.

K-equilibrium constant. Q- Binding site concentration per mass of SRFA.  $Q_1$  and  $Q_2$  indicated carboxylate and phenolic binding sites respectively. n-Non-ideality parameter. b-Donnan volume parameter.

System	[OH] Production µM
500 nM Fe(II)	$.55 \pm .02$
$BBA^*$	$3.4 \pm 0.1$
$BBA^* + 500 \text{ nM Fe(II)}$	$5.0 \pm 0.1$

Table S3. OH generated at two hours from Fresno BBA and 500 nM Fe(II) extracted in SLF.

Errors denote  $\pm 1\sigma$  of three measurements. \*9.5 µg/mL HULIS present in solution (upper limit).

## Figures





**Figure S2.** 2 hour OH production rates from 500 nM Fe(II) as a function of SRFA concentration, calculated data in figure 2. Filled points indicate the average of three measurements while the unfilled point indicate the average of two. Error bars denote  $\pm 1\sigma$ . The dashed line is a linear fit of the first four points.



**Figure S3.** OH production at two hours from varying [SRFA] and 500 nM Fe(II) in phosphate buffer (absent from anti-oxidants)





**Figure S4**. Ratio of OH produced at two hours per Fe(II) in solution as a function of [Fe(II)]. Different curves represent differing amounts of SRFA.



**Figure S5.** Number of reduction cycles in the first two hours as a function of [SRFA]. Data estimated by multiplying [OH]/[Fe(II)] ratio by 3.



**Figure S6.** OH produced at two hours from 10  $\mu$ g/mL SRFA mixed with Fe(II) (blue circles) and Fe(II) + 1  $\mu$ M H<sub>2</sub>O<sub>2</sub> (orange circles) as a function of [Fe(II)]<sub>i</sub>. Each filled data point represents the average of three measurements and error bars denote  $\pm 1\sigma$ .



**Figure S7.** OH produced at two hours from 15  $\mu$ g/mL SRFA mixed with Fe(II) and Fe(II) + 1  $\mu$ M H<sub>2</sub>O<sub>2</sub> as a function of [Fe(II)]<sub>i</sub>. Each filled data point represents the average of three measurements and error bars denote ±1 $\sigma$ . Lines are best fits of the data.



**Figure S8.** OH produced at two hours from Fe(II) and as a function of  $[Fe(II)]_I$ . Each filled data point represents the average of three measurements and error bars denote  $\pm 1\sigma$ . Lines are best fits of the data. Solid line indicates model fit with  $k_{14} = 0.3 \text{ M}^{-1} \text{s}^{-1}$ .