## **Supporting Information**

## Complexation of Iron and Copper in Ambient Particulate Matter and its Effect on the Oxidative Potential Measured in a Surrogate Lung Fluid

Jinlai Wei, Haoran Yu, Yixiang Wang, Vishal Verma\*

University of Illinois at Urbana-Champaign, Urbana, IL 61801

Supporting Information			
Number of pages	6		
Number of figures	6		
Number of tables	2		

\*Corresponding author Assistant Professor Vishal Verma, Ph.D. Department of Civil & Environmental Engineering University of Illinois at Urbana-Champaign 205 N. Mathews Ave, Room 3230D Urbana, IL USA 61801 Phone: (217) 265-6703 Cell: (213) 590-9213 Email: <u>vverma@illinois.edu</u>

Sampling Season	Sample	Start Date	End Date	Sampling
	ID			duration
Spring, 2017 (March – April)	S1	03/19/2017	03/21/2017	48 hours
	S2	03/21/2017	03/23/2017	
	<b>S</b> 3	03/23/2017	03/25/2017	
	<b>S</b> 4	03/25/2017	03/27/2017	
	S5	03/27/2017	03/29/2017	
	<b>S</b> 6	03/29/2017	03/31/2017	
	<b>S</b> 7	03/31/2017	04/02/2017	
	<b>S</b> 8	04/03/2017	04/05/2017	
	<b>S</b> 9	04/09/2017	04/11/2017	
	S10	04/11/2017	04/13/2017	
Summer, 2017 (July – August)	S11	07/07/2017	07/10/2017	
	S12	07/10/2017	07/13/2017	72 hours
	S13	07/13/2017	07/16/2017	
	S14	07/17/2017	07/20/2017	
	S15	07/20/2017	07/23/2017	
	S16	07/23/2017	07/26/2017	
	S17	07/27/2017	07/30/2017	
	S18	07/30/2017	08/02/2017	
Fall, 2017 (October – November)	S19	10/15/2017	10/18/2017	
	S20	10/18/2017	10/21/2017	
	S21	10/21/2017	10/24/2017	
	S22	10/24/2017	10/27/2017	72 hours
	S23	11/01/2017	11/04/2017	
	S24	11/04/2017	11/07/2017	
	S25	11/07/2017	11/10/2017	
Winter, 2018 (December – February)	S26	12/04/2017	12/07/2017	
	S27	12/12/2017	12/15/2017	
	S28	02/02/2018	02/05/2018	72 hours
	S29	02/13/2018	02/16/2018	
	<b>S</b> 30	02/25/2018	02/28/2018	

Table S1 Details of the ambient  $PM_{2.5}$  sampling

Reaction	Reaction	Rate coefficient/cm <sup>3</sup> s <sup>-1</sup>
number		
1	$Asc + Fe^{3+} \rightarrow Asc \cdot + Fe^{2+}$	$k_1 = 1.1 \times 10^{-19}$
2	$\mathrm{Fe}^{2+} + \mathrm{O}_2 \rightarrow \mathrm{Fe}^{3+} + \mathrm{O}_2^{-}$	$k_2 = 5.2 \times 10^{-21}$
3	$\mathrm{Fe}^{2+} + \mathrm{O_2}^- + 2\mathrm{H}^+ \longrightarrow \mathrm{Fe}^{3+} + \mathrm{H_2O_2}$	$k_3 = 3.1 \times 10^{-14}$
4	$\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH} + \mathrm{OH}^{-}$	$k_4 = 4.3 \times 10^{-18}$
5	$Asc + Cu^{2+} \rightarrow Asc + Cu^{+}$	$k_5 = 1.4 \times 10^{-18}$
6	$Cu^+ + O_2 \rightarrow Cu^{2+} + O_2^-$	$k_6 = 6.9 \times 10^{-20}$
7	$Cu^+ + HO_2 \cdot + H^+ \rightarrow Cu^{2+} + H_2O_2$	$k_7 = 5.8 \times 10^{-15}$
8	$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + \cdot OH + OH^-$	$k_8 = 2.4 \times 10^{-20}$

Table S2. Primary rate constants related to ROS generation in SLF mediated by Fe and Cu<sup>76</sup>



Figure S1. Improvement in the extraction efficiency of ambient Fe(II) with an increasing fraction of methanol in the PM extract. Sample S4 was used for these tests. Error bars denote standards deviation  $(1\sigma)$  of the triplicate analysis.



Figure S2. Calibration curve for Ferrozine method



Figure S3. Calibration curve for Bathocuproine method



Figure S4. Calibration curve for the measurement of hydrogen peroxide with 5 times, 10 times, 15 times diluted SLF and without SLF. All calibration equations and  $R^2$  values are shown in the figure except for 5 times SLF. Calibration was performed by replacing the sample from H<sub>2</sub>O<sub>2</sub> solutions (0.05, 0.1, 0.5, 1 and 2  $\mu$ M). Note, due to possible inhibitory effect of thiol groups on horseradish peroxidase, different concentrations of SLF were tried. Apparently, the calibrations with 5 and 10 times diluted SLF were not acceptable (being significantly different than with no SLF). However, the calibration with 15 times dilution of SLF was almost same as without SLF. Therefore, we chose 15 times dilution of SLF for the measurement of H<sub>2</sub>O<sub>2</sub> generation from samples.



Figure S5. Correlation between the fraction of hydrophobic metal in the water-soluble PM extracts and the ratio of the metal's concentration in 50% methanol over water-soluble extracts.



Figure S6. Blank corrected concentration of  $\cdot$ OH generated by 1µM Fe(II) in SLF over 80 minutes. The slope (6.1 nM/min) denotes the generation rate of  $\cdot$ OH. Error bars denote standard deviation (1 $\sigma$ ) of the triplicate measurements.