

1 **The Terephthalate Probe for Hydroxyl Radicals: Yield of 2-**  
2 **Hydroxy Terephthalic acid and Transition Metal**  
3 **Interference**

4  
5 David H. Gonzalez<sup>1</sup>, Xiaobi M. Kuang<sup>1</sup>, John A. Scott<sup>1,2</sup>, Gisele Olimpio de la  
6 Rocha<sup>1,3</sup>, and Suzanne E. Paulson<sup>1\*</sup>

7 <sup>1</sup>Department of Atmospheric and Oceanic Sciences, University of California,  
8 Los Angeles

9 <sup>2</sup>Department of Chemistry and Biochemistry, University of California, Los  
10 Angeles

11 <sup>3</sup>Instituto de Química, Universidade Federal de Bahia, Bahia, Brazil

12  
13

14 **Abstract**

15 Hydroxyl radicals ( $\cdot\text{OH}$ ) are key players in chemistry in surface waters, clouds  
16 and aerosols. Additionally,  $\cdot\text{OH}$  may contribute to the inflammation  
17 underlying adverse health outcomes associated with particulate matter  
18 exposure. Terephthalate is a particularly sensitive probe for hydroxyl  
19 radicals, with a detection limit as low as 2 nM. However, there is uncertainty  
20 in  $\cdot\text{OH}$  quantification using this method, and potential for interference from  
21 fluorescent compounds and from some transition metals. Terephthalate  
22 reacts with  $\cdot\text{OH}$  to form a fluorescent product, 2-hydroxylterephthalic acid  
23 (hTA), with a moderate dependence on pH and temperature. However, there

24 is disagreement in the literature on the yield of the fluorescent product ( $Y_{\text{hTA}}$ ),  
25 which introduces a large uncertainty in the quantification of OH. Additionally,  
26 TA and similar organic probes are known to complex Cu(II) at high  
27 concentrations, thus if this reaction is important at lower concentrations,  
28 Cu(II) could reduce apparent hTA formation, and reduce activity of Cu(II) in  
29 target samples. Using a pH 3.5 dark ferrous Fenton system to generate  $\cdot\text{OH}$   
30 radicals, we find that  $Y_{\text{hTA}} = 31.5 \pm 7\%$ . This is about double the recent  
31 literature value measured, but in excellent agreement with earlier  
32 measurements. Additionally, we find that interactions between Cu(II) and  
33 hTA are small enough to be ignored at Cu(II) concentrations below  $\sim 50 \mu\text{M}$ .

#### 34 **Introduction**

35  $\cdot\text{OH}$  plays an important role in various atmospheric and surface water  
36 processes. Aerosol aging by  $\cdot\text{OH}$  can modify chemical composition  
37 (Shrivastava et al. 2008) cloud condensation nuclei (CCN) activity (Shilling et  
38 al. 2007) hygroscopic properties (Suda et al. 2014), and optical properties of  
39 aerosols (Kim and Paulson 2013). Hydroxyl radical also plays an important  
40 role in the chemistry of surface waters (Lindsey and Tarr 2000, Goldstone et  
41 al. 2002) degradation of drugs after release into the environment (Rosenfeldt  
42 and Linden 2004) in oxidative stress in marine organisms (Lesser 2006) and  
43 in waste water treatment (Fernandez-Castro et al. 2015). Inhalation of fine  
44 particulate matter has shown correlation with adverse health impacts,  
45 including asthma, cardiovascular diseases, pulmonary inflammation, lung  
46 cancer and mortality (Brook et al. 2010, Beelen et al.). While the

47 mechanism(s) by which ambient particles impact health is not yet  
48 completely understood, a hypothesized cause under active investigation is  
49 oxidative stress, mediated by reactive oxygen species (ROS) (Bates et al.  
50 2015).

51 A direct measurement of hydroxyl radical in aqueous solutions is  
52 difficult due to its low concentrations, short lifetime and chemical and  
53 physical similarity to the aqueous solvent. Chemical probes such as benzene  
54 (Faust and Allen 1993), nitrobenzene (Zepp et al. 1992), benzoate (Jung et  
55 al. 2006), and terephthalate (TA) (Matthews 1980, Fang et al. 1996, Saran  
56 and Summer 1999, Snyrychova et al. 2007, Page et al. 2010, Charbouillot et  
57 al. 2011) have been used to quantify OH. These methods depend on  
58 fluorescence (2-hydroxyterephthalic acid) or UV absorption (benzene  
59 derivatives) of oxidation products. Additional approaches such as electron  
60 paramagnetic resonance are also available (Shi et al. 2003).

61 Of the hydroxyl radical probes, terephthalate has several advantages.  
62 Due to its symmetric configuration, the ·OH reaction with terephthalate  
63 results in only one ring- preserving product, 2-hydroxyterephthalic acid (hTA,  
64 Fig. 1). Furthermore, 2-hydroxyterephthalic acid is strongly fluorescent  
65 (Armstrong et al. 1963) facilitating detection limits as low as ~2 nM (SI Tab.  
66 S1), compared to 30 nM for benzoate (Shen and Anastasio 2012). Further, TA  
67 is more soluble, has a more stable fluorescent product and is less susceptible  
68 to pH changes compared to several other ·OH probes (Son et al. 2015).

69 Accurate quantification of  $\cdot\text{OH}$  with the terephthalate probe requires  
70 knowledge of the yield of the fluorescent product, hTA, per molecule of  $\cdot\text{OH}$   
71 reacted. A handful of prior studies have quantified the  $\cdot\text{OH}$  formation yield,  
72 each with a different source of hydroxyl radicals: Matthews (1980) used  
73 radiolysis; Charbouillot et al. (2011) used photolysis of nitrate and  $\text{H}_2\text{O}_2$  (Fig.  
74 1), Page et al. (2010) used photolysis of nitrite and Mark et al. (1998) used  
75 sonication of water. Page et al. (2010) and Mark et al. (1998) but did not  
76 show data or indicate a pH for their measurements. The Matthews (1980)  
77 (30.5 - 35% increasing as pH increased from 2 - 9), Mark et al. (1998) and  
78 Page et al. (2010) (both 35% at unspecified pH) measurements are nearly  
79 double those of Charbouillot et al. (2011) (14 - 23% increasing as pH  
80 increased from 4 - 7.5). As both the high (Son et al. 2015, An et al. 2016,  
81 Batista et al. 2016, Gonzalez et al. 2017) and low (Huang et al. 2013,  
82 Paušová et al. 2015, Li et al. 2016, Tafer et al. 2016) values have been taken  
83 up in the literature, we attempt to address the discrepancy.

84 The hTA yield has also been found to depend on  $\text{O}_2$  concentration in  
85 the sample (Matthews 1980; Saran and Summer 1999); all yields discussed  
86 here are for aqueous solutions in equilibrium with air at one atmosphere.  
87 Charbouillot et al. (2011) found that the hTA yield is not influenced by ionic  
88 strength, ammonium or sulfate ions within the 0.25 - 2 mM range studied,  
89 but that the yield has a fairly strong temperature dependence; the yield  
90 increases by about a factor of 2 between 278 and 303 K at pH 5.4.

91 The discrepancy between the measurements of Matthews (1980), Page  
92 et al., (2010) and Charbouillot et al. (2011) were suggested by Page et al.  
93 (2012) suggested to be due to the photolysis light source used by  
94 Charbouillot et al. (2011) also photolyzing hTA, reducing its apparent yield.

95 While previously unrecognized by the community using TA as a probe  
96 for hydroxyl radicals, formation of metal-terephthalate complexes at high  
97 concentrations are well known, including with Cu(II), Co(II), Fe(II), Mn(II) and  
98 Ni(II) (Acheson and Galwey 1967, Sherif 1970, Rabu et al. 2001, Carson et al.  
99 2009). This presents the possibility that metal interactions with TA might  
100 impact the outcome of the assay, either by changing the ability of metals to  
101 contribute to chemistry that leads to formation of  $\cdot\text{OH}$  or by reducing metal  
102 ion availability in solution.

103 Here, we report a new measurement of the hTA yield, using a different  
104 source of OH. Because of the substantial discrepancy between the published  
105 datasets, and because there is little data available for the yield of hTA under  
106 acidic conditions relevant to water in the atmosphere, such as cloud, fog and  
107 rain water (Falconer and Falconer 1980) we measure  $Y_{\text{hTA}}$  at pH 3.5 using a  
108 dark ferrous Fenton system to generate OH. Further, due to its abundance in  
109 the atmospheric samples (Wang et al. 2010) here we examine the ability of  
110 Cu(II) to interfere with the hTA assay.

111

## 112 **Materials and Methods**

### 113 **Materials**

114 Disodium terephthalate (TA) was purchased from TCI America. 2-  
115 hydroxy terephthalic acid (hTA) was purchased from Apollo Sci. Methanol  
116 (HPLC grade) and sulfuric acid (reagent grade), Chelex<sup>®</sup> 100 sodium form  
117 (50-100 dry mesh), uric acid (>99%), sodium Citrate tribasic  
118 dihydrate (>99%), L-ascorbic acid (BioXtra, >99%), L-glutathione reduced  
119 (>98%), ethylenediaminetetraacetic acid (EDTA), horseradish peroxidase  
120 type II, para-hydroxyphenyl acetic acid, potassium hydrogen phthalate, H<sub>2</sub>O<sub>2</sub>  
121 (30%) and FeSO<sub>4</sub> (>98%) were purchased from Sigma-Aldrich. Sodium  
122 phosphate dibasic and potassium phosphate monobasic were purchased  
123 from Acros Organics. Ferrozine (4,4'-[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]  
124 dibenzenesulfonate) was purchased from Fluka Analytic. Hydrophilic  
125 Lipophilic Balance cartridges were purchased from Waters (Oasis, 10mg). All  
126 materials were used as received.

127 A rigorous cleaning process was followed for all glass and Teflon  
128 containers. After each use, the glass/plastic ware was washed with warm  
129 water and soap, then rinsed in deionized (18 MΩ DI) water (3×), ethanol  
130 (3×), and finally DI water (3×). The vessels were then soaked in a 1 M nitric  
131 acid bath overnight, rinsed with DI water (3x) and air dried. Nitric acid baths  
132 were replaced after being used twice.

133 Stock solutions were prepared with 18 MΩ DI water after further  
134 purification by passing through a Chelex column to remove trace metals. pH  
135 was measured with a bench top pH meter (HANNA instruments, HI 3220),  
136 calibrated daily. Stock solutions of hTA (10<sup>-3</sup> M) and Fe(II) (5.1 mM) were

137 wrapped in foil; hTA was kept refrigerated for a few months and Fe(II) was  
138 prepared daily and refrigerated. Dissolved oxygen was present in all  
139 solutions as solutions were in contact with air and were not degassed.

#### 140 **Fluorescence Spectroscopy and quantification of hTA**

141 hTA fluorescence intensity was measured in single wavelength mode  
142 at excitation/emission wavelengths of 310/420 nm with a Lumina  
143 Fluorescence Spectrometer (Thermo Scientific). For the purposes of the  
144 measurements carried out here, hTA calibration curves were prepared in pH  
145 3.5 or 7.4 solutions at hTA concentrations of 50, 100, 500 and 800 nM. An  
146 EEM scan of hTA fluorescence recorded performed with 10 nm excitation and  
147 emission slit widths, 5 nm intervals scanning at 60 nm/s with 10 ms  
148 integration time (SI Fig. S1). A  $10^{-3}$  M Stock solution of hTA in milli-Q water  
149 (18 M $\Omega$ ) was prepared using an acid cleaned Teflon bottle which was  
150 wrapped in aluminum, and stored in the refrigerator. A 5-point calibration  
151 was performed prior to each experiment.

#### 152 **Quantification of Fe(II)**

153 Fe(II) was quantified with the ferrozine method (Stookey 1970) using a  
154 liquid waveguide capillary cell (LWCC-3100, World Precision Instruments  
155 Inc.), a UV-Vis light source (AvaLight-DHS, Avantes) and UV-Vis spectrometer  
156 (AvaSpec 2048L, Avantes). The Fe(II)-ferrozine complex has a maximum  
157 absorbance at 562 nm ( $A_{562}$ ). To account for instrument drift and solution  
158 turbidity, the absorbance at 700 nm ( $A_{700}$ ) was subtracted from  $A_{562}$ . Aliquots  
159 were analyzed by adding 10  $\mu$ L of 5.1 mM ferrozine to 2.0 mL aliquots. Fe(II)

160 calibration curves are made by preparing a stock solution of 2 mM Iron  
161 Sulfate (Sigma-Aldrich) at pH 3.5 and diluting to between 0.012 and 0.75  $\mu$ M  
162 Fe(II).

### 163 **Quantification of H<sub>2</sub>O<sub>2</sub>**

164 Quantification of aqueous H<sub>2</sub>O<sub>2</sub> was performed using a High  
165 Performance Liquid Chromatograph equipped with a fluorescence detector  
166 (Shimadzu RF-10AXL detector) (Arellanes et al. 2006). The eluent, water with  
167 0.1 mM EDTA adjusted to pH 3.5 with 0.1 N sulfuric acid, was delivered at 0.6  
168 mL/min to a C18 guard column. H<sub>2</sub>O<sub>2</sub> elutes at 0.5 min, after which it is  
169 mixed with a fluorescent reagent containing horseradish peroxidase and  
170 para-hydroxyphenyl acetic acid (POHPAA). The peroxidase enzyme catalyzes  
171 a reaction between H<sub>2</sub>O<sub>2</sub> and POHPAA to form a fluorescent dimer, which is  
172 detected at the  $\lambda_{\text{ex}}/\lambda_{\text{em}}$  320/400nm. The solution is mixed with ammonium  
173 hydroxide (30%) to increase its fluorescence intensity prior to detection. The  
174 HPLC was calibrated at least weekly with 10<sup>-8</sup> to 10<sup>-6</sup> M standards prepared  
175 from a 0.3% stock solution, titrated with sodium thiosulfate to determine the  
176 concentration.

### 177 **Oxidation of TA via a Ferrous Fenton System**

178 Experiments to derive hTA yields were carried out as follows. Triplicate  
179 samples of 4.44-4.77  $\mu$ M FeSO<sub>4</sub> and 5.38-6.00  $\mu$ M H<sub>2</sub>O<sub>2</sub> (SI Tab. S2) were  
180 mixed with excess terephthalate (~500  $\mu$ M, 100-fold excess) in 60 mL Teflon  
181 bottles and allowed to react in the dark with gentle shaking (25 rpm,  
182 Heidolph Rotamax) at 20° C. FeSO<sub>4</sub> was added last as to initiate the Fenton



183 reaction. The resulting solution was monitored in triplicate for H<sub>2</sub>O<sub>2</sub>, Fe(II)  
184 and hTA every 20 minutes for 2 h. Initial concentrations of H<sub>2</sub>O<sub>2</sub> and Fe(II) are  
185 shown in SI Tab. S2. Blanks consisted of TA in pH 3.5. Aliquots were diluted  
186 by 5 - 10x to fall within the ranges of detection for Fe(II) and H<sub>2</sub>O<sub>2</sub>. At μM  
187 concentrations, the system is sensitive to trace contaminants, including  
188 metals and organics, which can change ·OH formation chemistry and/or the  
189 ability of terephthalate to scavenge all available OH, thus rigorous cleaning,  
190 dust exclusion and high purity reagents were critical for these experiments.

191 A 54-reaction chemical kinetics model (SI Tab. S3) including reactions  
192 describing Fenton chemistry, acid-base equilibria, iron sulfate chemistry and  
193 odd oxygen free radical chemistry was developed to derive hTA yields.  
194 Concentrations as a function of time were calculated from initial  
195 concentrations using FACSIMILIE (MCPA Software, UK).

### 196 **Interference of Cu(II) with the hTA assay**

197 EEM scans were performed to probe fluorescence of terephthalate and  
198 Cu(II) complex, if any. The potential reduction of hTA fluorescence intensity  
199 by Cu(II) was probed by adding 1 μM to 250 μM of Cu(II) to 800nM hTA, and  
200 measuring fluorescence using the single-wavelength scan mode after 2  
201 hours. Additionally, H<sub>2</sub>O<sub>2</sub> formation from 20 μM Cu(II) with different  
202 concentrations of TA (0.5 to 10mM) was measured every 30 minutes for 2  
203 hours. 20 μM of Cu(II) was chosen because in aqueous solutions at pH 3.5  
204 this concentration produces significant amounts of H<sub>2</sub>O<sub>2</sub> in the dark (this  
205 work, SI Fig. S2).

206

## 207 **Results**

### 208 **Hydroxyterephthalate Yield**

209 Fig. 1 shows experimental data (symbols) and model best fit (lines) for  
210 the average of three experiments; error bars show the standard deviation of  
211 nine measurements at each time point (three replicates from each of three  
212 experiments). The model is most sensitive to the rate constant for Fe(II)  
213 reacting with H<sub>2</sub>O<sub>2</sub> to make ·OH and co-products (the Fenton reaction,  $k_{15}$  in SI  
214 Tab. S3). Most published rates for this reaction fall within the range 55 -76 M<sup>-1</sup>  
215 s<sup>-1</sup> (Zuo and Hoigne 1992, De Laat and Le 2005). The best fit between the  
216 model and the measured H<sub>2</sub>O<sub>2</sub> and Fe(II) was obtained using 76 M<sup>-1</sup>s<sup>-1</sup> for the  
217 Fenton reaction. This results in mean square errors (MSEs) of 4.3 and 3.1 %  
218 for Fe(II) and H<sub>2</sub>O<sub>2</sub>, respectively (Fig. 1). We then adjusted the yield of hTA  
219 ( $Y_{\text{hTA}}$ ) to minimize the MSE between the model and the average concentration  
220 of hTA, and found a best-fit  $Y_{\text{hTA}} = 31.5 \pm 7\%$ , with an MSE of 0.24%.  
221 Altering  $Y_{\text{hTA}}$  does not affect the modeled Fe(II) and H<sub>2</sub>O<sub>2</sub> concentrations. The  
222 error bars for the yield were derived by finding the best fit  $Y_{\text{hTA}}$  for  $\pm 1 \sigma$  of  
223 the measured hTA concentrations (Fig. 1). At pHs above 4, formation of iron  
224 hydroxide and iron sulfate precipitates increase (De Laat and Le 2005),  
225 compromising the utility of the Fe(II)/H<sub>2</sub>O<sub>2</sub> system as an ·OH source, so we  
226 were not able to measure  $Y_{\text{hTA}}$  at higher pHs.

227 Fig. 2 summarizes reported measurements of hTA yields as a function  
228 of pH. Our results are in excellent agreement with the results of Matthews

229 (1980) and about double those of Charbouillot et al. (2011). Some of the  
230 difference is explained by the temperature dependence reported by  
231 Charbouillot et al. (2011) (above). Differences in the temperature of this  
232 work (293 K) and Charbouillot et al. (2011) (288 K) would suggest a  
233 difference of about 20% (Matthews et al. (1980) did not report a  
234 temperature. To generate  $\cdot\text{OH}$  radicals, Matthews (1980) used radiolysis,  
235 while Charbouillot et al. (2011) photolyzed either nitrate or  $\text{H}_2\text{O}_2$  using a  
236 1000 W xenon lamp ( $\lambda > 300$  nm). In a separate study, Page et al. (2010)  
237 reported that the UV absorption spectrum for hTA contains a weak  
238 absorption between 275 - 365 nm, with a slight pH dependence.  
239 Wavelengths below 365 nm were observed to cause some decomposition of  
240 hTA, leading the researchers to conclude that nitrate photolysis could not be  
241 used to probe hTA formation (Page et al. 2012). Charbouillot et al. (2011)  
242 had good agreement between their results using nitrate or  $\text{H}_2\text{O}_2$  as the  $\cdot\text{OH}$   
243 source, but since they used the same lamp, similar degradation of hTA likely  
244 occurred. We conclude that the Matthews (1980) yields, together with this  
245 work and Page et al. (2010) are correct and recommend a yield of 35% for  
246 pHs above 9, decreasing monotonically to 30.5% at pH 2 with the expression  
247  $Y_{\text{hTA}} (\%) = 30 + 0.43 \times \text{pH}$ , and possibly decreasing more below pH 2.

#### 248 **Potential interference of Cu(II) with hTA assay**

249 We performed several experiments to explore the potential for Cu(II) to  
250 interfere with TA of hTA, and vice-versa. At high concentrations,  
251 terephthalate and Cu(II) in water at pH3.5 rapidly form a blue precipitate

252 (Carson et al. 2009). However, mixtures of 1 – 250  $\mu\text{M}$  Cu(II) and 10 mM TA  
253 did not produce an observable precipitate (this study), and further did not  
254 exhibit fluorescence in EEM scans. Next, we investigated if TA changes Cu(II)  
255 reactivity by investigating the effect of added TA on the formation of  $\text{H}_2\text{O}_2$   
256 from 200  $\mu\text{M}$  Cu(II). The results indicate a decrease in  $\text{H}_2\text{O}_2$  formation that,  
257 while statistically significant at the  $p < 0.5$  level (SI Fig. S2s), was very slight;  
258 over the TA concentration range of 0.5 to 10 mM, the decrease was less than  
259 2%.

260 Fig. 3 shows the reduction in fluorescence intensity of 800 nM hTA with  
261 added Cu(II) in both pH3.5 and phosphate buffer. The result showed that  
262 significant reduction ( $>10\%$ ) of hTA intensity occurs only at concentration  
263 above about 50  $\mu\text{M}$  of Cu(II) (Fig. 3), a high concentration relative to copper  
264 concentrations in many environmental extracts (e.g., Wang et al. 2010). We  
265 conclude that under most conditions, Cu(II) does not interfere with the TA  
266 assay, or vis-versa.

267

## 268 **Conclusions**

269 The terephthalate method for quantification of hydroxyl radical is a  
270 robust, straightforward method under most conditions, and it can often be  
271 used with a stand-alone fluorescence spectrometer without the need for prior  
272 separation. To calculate the  $\cdot\text{OH}$  concentration, the yield of hTA from the  $\cdot\text{OH}$   
273 reaction with TA is required; best estimates of this yield are 35% at pH 9 or  
274 above, decreasing monotonically to 31% at pH = 2. The potential for direct

275 interactions between TA and soluble metals such as Cu (II) should be  
276 considered if target samples contain high (high  $\mu\text{M}$  - mM range)  
277 concentrations of metals.

278

## 279 **Acknowledgements**

280 This material is based upon work supported by the U.S. National Science  
281 Foundation under Grant No. 443956-PA-22671. The views and opinions  
282 expressed in this manuscript are those of the authors. We gratefully  
283 acknowledge Messrs. Yu Zhong, Zane Karl and Kevin Huynh and Christopher  
284 Cala for their valuable assistance in the laboratory.

285

## 286 **References**

- 287 Acheson, R. and A. Galwey (1967). The thermal decomposition of nickel  
288 terephthalate and nickel salts of other carboxylic acids. J. Chem. Soc. A:  
289 Inorg. Phys. Theor. **1**: 1174-1178.
- 290 An, J., G. Li, T. An and X. Nie (2016). Indirect photochemical transformations  
291 of acyclovir and penciclovir in aquatic environments increase ecological  
292 risk. Env. Tox. Chem. **35**(3): 584-592.
- 293 Arellanes, C., S. E. Paulson, P. M. Fine and C. Sioutas (2006). Exceeding of  
294 Henry's Law by Hydrogen Peroxide Associated with Urban Aerosols. .  
295 Envir. Sci. Tech. **40** (16): 4859-4866.
- 296 Armstrong, W. A., R. A. Facey, D. W. Grant and W. G. Humphreys (1963). A  
297 tissue-equivalent chemical dosimeter sensitive to 1 rad. Can. J. Chem.  
298 **41**(6): 1575-1577.
- 299 Bates, J. T., R. J. Weber, J. Abrams, V. Verma, T. Fang, M. Klein, . . . A. G.  
300 Russell (2015). Reactive Oxygen Species Generation Linked to Sources of  
301 Atmospheric Particulate Matter and Cardiorespiratory Effects. Env. Sci.  
302 Tech. **49**(22): 13605-13612.
- 303 Batista, A. P. S., A. C. S. C. Teixeira, W. J. Cooper and B. A. Cottrell (2016).  
304 Correlating the chemical and spectroscopic characteristics of natural  
305 organic matter with the photodegradation of sulfamerazine. Water Res.  
306 **93**(Supplement C): 20-29.

307 Beelen, R., O. Raaschou-Nielsen, M. Stafoggia, Z. J. Andersen, G. Weinmayr,  
308 B. Hoffmann, . . . G. Hoek (2014). Effects of long-term exposure to air  
309 pollution on natural-cause mortality: an analysis of 22 European cohorts  
310 within the multicentre ESCAPE project. Lancet **383**(9919): 785-795.

311 Brook, R. D., S. Rajagopalan, C. A. Pope, J. R. Brook, A. Bhatnagar, A. V. Diez-  
312 Roux, . . . J. D. Kaufman (2010). Particulate Matter Air Pollution and  
313 Cardiovascular Disease. An Update to the Scientific Statement From the  
314 American Heart Association **121**(21): 2331-2378.

315 Carson, C. G., K. Hardcastle, J. Schwartz, X. Liu, C. Hoffmann, R. A. Gerhardt  
316 and R. Tannenbaum (2009). Synthesis and structure characterization of  
317 copper terephthalate metal-organic frameworks. Eur. J. Inorg. Chem.  
318 **2009**(16): 2338-2343.

319 Charbouillot, T., M. Brigante, G. Mailhot, P. R. Maddigapu, C. Minero and D.  
320 Vione (2011). Performance and selectivity of the terephthalic acid probe  
321 for (OH)-O-center dot as a function of temperature, pH and composition of  
322 atmospherically relevant aqueous media. J. Photochem. Photobiol. a-  
323 Chem. **222**(1): 70-76.

324 De Laat, J. and T. G. Le (2005). Kinetics and modeling of the Fe (III)/H<sub>2</sub>O<sub>2</sub>  
325 system in the presence of sulfate in acidic aqueous solutions. Env. Sci.  
326 Tech. **39**(6): 1811-1818.

327 Falconer, R. and P. Falconer (1980). Determination of cloud water acidity at a  
328 mountain observatory in the Adirondack Mountains of New York State.  
329 Journal of Geophysical Research: Oceans **85**(C12): 7465-7470.

330 Fang, X. W., G. Mark and C. vonSonntag (1996). OH radical formation by  
331 ultrasound in aqueous solutions .1. The chemistry underlying the  
332 terephthalate dosimeter. Ultrasonics Sonochem. **3**(1): 57-63.

333 Faust, B. C. and J. M. Allen (1993). Aqueous-phase photochemical formation  
334 of hydroxyl radical in authentic cloudwaters and fogwaters. Env. Sci. Tech.  
335 **27**(6): 1221-1224.

336 Fernandez-Castro, P., M. Vallejo, M. F. San Roman and I. Ortiz (2015). Insight  
337 on the fundamentals of advanced oxidation processes. Role and review of  
338 the determination methods of reactive oxygen species. J. Chem. Tech.  
339 Biotech. **90**(5): 796-820.

340 Goldstone, J. V., M. J. Pullin, S. Bertilsson and B. M. Voelker (2002). Reactions  
341 of hydroxyl radical with humic substances: Bleaching, mineralization, and  
342 production of bioavailable carbon substrates. Env. Sci. Tech. **36**(3): 364-  
343 372.

344 Gonzalez, D. H., C. K. Cala, Q. Y. Peng and S. E. Paulson (2017). HULIS  
345 Enhancement of Hydroxyl Radical Formation from Fe(II): Kinetics of Fulvic  
346 Acid-Fe(II) Complexes in the Presence of Lung Antioxidants. Env. Sci.  
347 Tech. **51**(13): 7676-7685.

348 Huang, W., M. Brigante, F. Wu, K. Hanna and G. Mailhot (2013). Effect of  
349 ethylenediamine-N,N'-disuccinic acid on Fenton and photo-Fenton  
350 processes using goethite as an iron source: optimization of parameters for  
351 bisphenol A degradation. Envir. Sci. Poll. Res. **20**(1): 39-50.

352 Jung, H., B. Guo, C. Anastasio and I. M. Kennedy (2006). Quantitative  
353 measurements of the generation of hydroxyl radicals by soot particles in a  
354 surrogate lung fluid. *Atmos. Environ.* **40**(6): 1043-1052.

355 Kim, H. and S. E. Paulson (2013). Real refractive indices and volatility of  
356 secondary organic aerosol generated from photooxidation and ozonolysis  
357 of limonene, alpha-pinene and toluene. *Atmos. Chem. Phys.*, **13**(15):  
358 7711-7723.

359 Lesser, M. P. (2006). Oxidative stress in marine environments: Biochemistry  
360 and physiological ecology. *Annu. Rev. Physiol.* Palo Alto, Annual Reviews.  
361 **68**: 253-278.

362 Li, R., C. Zhao, B. Yao, D. Li, S. Yan, K. E. O'Shea and W. Song (2016).  
363 Photochemical Transformation of Aminoglycoside Antibiotics in Simulated  
364 Natural Waters. *Env. Sci. Tech.* **50**(6): 2921-2930.

365 Lindsey, M. E. and M. A. Tarr (2000). Inhibition of hydroxyl radical reaction  
366 with aromatics by dissolved natural organic matter. *Env. Sci. Tech.* **34**(3):  
367 444-449.

368 Mark, G., A. Tauber, R. Laupert, H.-P. Schuchmann, D. Schulz, A. Mues and C.  
369 von Sonntag (1998). OH-radical formation by ultrasound in aqueous  
370 solution - Part II: Terephthalate and Fricke dosimetry and the influence of  
371 various conditions on the sonolytic yield. *Ultrasonics Sonochemistry* **5**(2):  
372 41-52.

373 Matthews, R. W. (1980). The radiation-chemistry of the terephthalate  
374 dosimeter. *Radiation Res.* **83**(1): 27-41.

375 Page, S. E., W. A. Arnold and K. McNeill (2010). Terephthalate as a probe for  
376 photochemically generated hydroxyl radical. *J. Environ. Monitor.* **12**(9):  
377 1658-1665.

378 Page, S. E., M. Sander, W. A. Arnold and K. McNeill (2012). Hydroxyl Radical  
379 Formation upon Oxidation of Reduced Humic Acids by Oxygen in the Dark.  
380 *Env. Sci. Tech.* **46**(3): 1590-1597.

381 Paušová, Š., J. Krýsa, J. Jirkovský, C. Forano, G. Mailhot and V. Prevot (2015).  
382 Insight into the photocatalytic activity of ZnCr-CO<sub>3</sub> LDH and derived  
383 mixed oxides. *Applied Catalysis B: Environmental* **170-171**(Supplement  
384 C): 25-33.

385 Rabu, P., J. Rueff, Z. Huang, S. Angelov, J. Souletie and M. Drillon (2001).  
386 Copper (II) and cobalt (II) dicarboxylate-based layered magnets: influence  
387 of  $\pi$  electron ligands on the long range magnetic ordering. *Polyhedron*  
388 **20**(11): 1677-1685.

389 Rosenfeldt, E. J. and K. G. Linden (2004). Degradation of endocrine disrupting  
390 chemicals bisphenol A, ethinyl estradiol, and estradiol during UV  
391 photolysis and advanced oxidation processes. *Env. Sci. Tech.* **38**(20):  
392 5476-5483.

393 Saran, M. and K. H. Summer (1999). Assaying for hydroxyl radicals:  
394 Hydroxylated terephthalate is a superior fluorescence marker than  
395 hydroxylated benzoate. *Free Radical Res.* **31**(5): 429-436.

396 Shen, H. and C. Anastasio (2012). A comparison of hydroxyl radical and  
397 hydrogen peroxide generation in ambient particle extracts and laboratory  
398 metal solutions. Atmos. Environ. **46**: 665-668.

399 Sherif, F. G. (1970). Heavy metal terephthalates. Indust. Eng. Chem. Prod.  
400 Res. Dev. **9**(3): 408-412.

401 Shi, T. M., R. P. F. Schins, A. M. Knaapen, T. Kuhlbusch, M. Pitz, J. Heinrich  
402 and P. J. A. Borm (2003). Hydroxyl radical generation by electron  
403 paramagnetic resonance as a new method to monitor ambient particulate  
404 matter composition. J. Env. Monitor. **5**(4): 550-556.

405 Shilling, J. E., S. M. King, M. Mochida and S. T. Martin (2007). Mass spectral  
406 evidence that small changes in composition caused by oxidative aging  
407 processes alter aerosol CCN properties. J. Phys. Chem. A **111**(17): 3358-  
408 3368.

409 Shrivastava, M. K., T. E. Lane, N. M. Donahue, S. N. Pandis and A. L. Robinson  
410 (2008). Effects of gas particle partitioning and aging of primary emissions  
411 on urban and regional organic aerosol concentrations. Journal of  
412 Geophysical Research-Atmospheres **113**(D18): 16.

413 Snyrychova, I., P. Kos and E. Hideg (2007). First application of terephthalate  
414 as a fluorescent probe for hydroxyl radicals in thylakoid membranes.  
415 Photosynthesis Res. **91**(2-3): 307-307.

416 Son, Y., V. Mishin, W. Welsh, S.-E. Lu, J. Laskin, H. Kipen and Q. Meng (2015).  
417 A Novel High-Throughput Approach to Measure Hydroxyl Radicals Induced  
418 by Airborne Particulate Matter. Int. J. Env. Res. Public Health **12**(11):  
419 13678.

420 Stookey, L. L. (1970). Ferrozine---a new spectrophotometric reagent for iron.  
421 Analytical Chemistry **42**(7): 779-781.

422 Suda, S. R., M. D. Petters, G. K. Yeh, C. Strollo, A. Matsunaga, A. Faulhaber, . .  
423 . S. M. Kreidenweis (2014). Influence of Functional Groups on Organic  
424 Aerosol Cloud Condensation Nucleus Activity. Env. Sci. Tech. **48**(17):  
425 10182-10190.

426 Tafer, R., M. Sleiman, A. Boulkamh and C. Richard (2016).  
427 Photomineralization of aqueous salicylic acids. Photoproducts  
428 characterization and formation of light induced secondary OH precursors  
429 (LIS-OH). Water Res. **106**: 496-506.

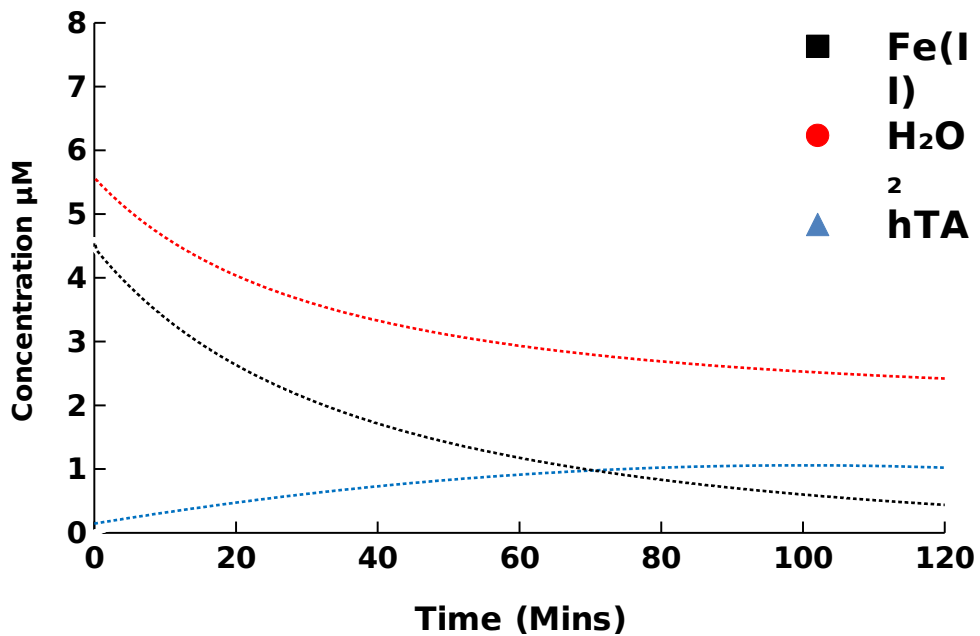
430 Wang, Y., C. Arellanes, D. Curtis and S. E. Paulson (2010). Probing the Source  
431 of Hydrogen Peroxide Generation by Coarse Mode Aerosols in Southern  
432 California. Env. Sci. Tech. **44**: 4070-4075.

433 Zepp, R. G., B. C. Faust and J. Hoigne (1992). Hydroxyl radical formation in  
434 aqueous reactions (pH 3-8) of iron (II) with hydrogen peroxide: the photo-  
435 Fenton reaction. Env. Sci. Tech. **26**(2): 313-319.

436 Zuo, Y. and J. Hoigne (1992). Formation of hydrogen peroxide and depletion  
437 of oxalic acid in atmospheric water by photolysis of iron (III)-oxalato  
438 complexes. Env. Sci. Tech. **26**(5): 1014-1022.

439



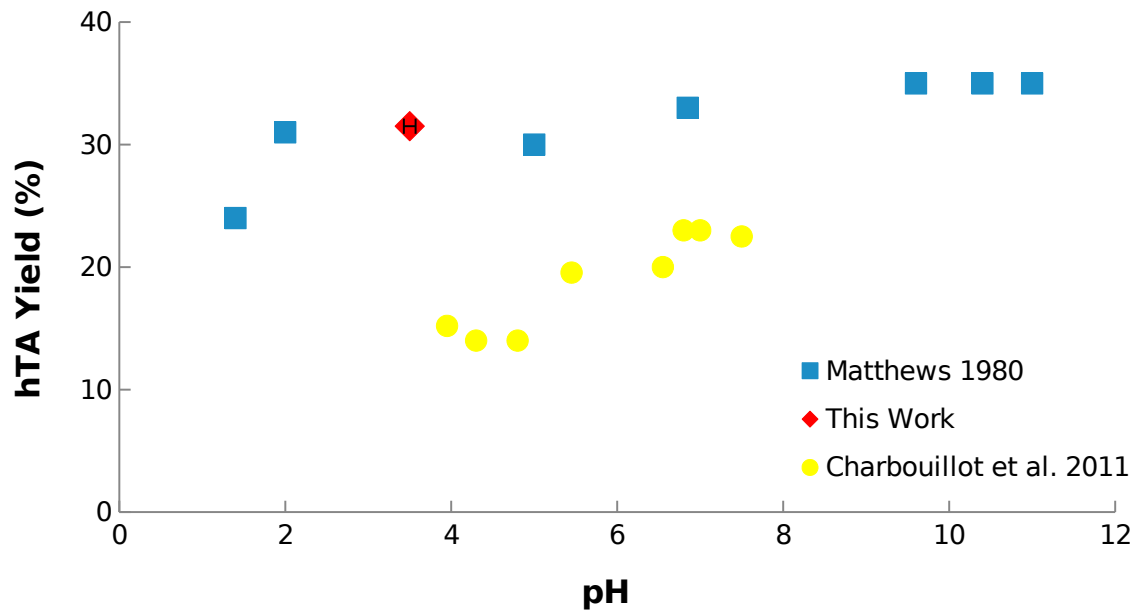


440

441 Figure 1. Concentration profiles of Fe(II), H<sub>2</sub>O<sub>2</sub> and hTA averaged from  
 442 triplicate measurements of three experimental trials. Error bars  
 443 represent  $\pm$  one standard deviation of 9 samples. Dashed lines  
 444 indicate model fit to experimental data. Average initial concentrations  
 445 of Fe(II) and H<sub>2</sub>O<sub>2</sub> were 4.59 and 5.56  $\mu$ M, respectively. The yield of hTA  
 446 is estimated to be  $31.5 \pm 7\%$ .

447

448



449

450 Figure 2. hTA yields as a function of pH. Matthews (1980) did not indicate  
 451 error bars or the experimental temperature; Charbouillot et al. (2011)  
 452 measurements were performed at 288 K; this work was performed at 293  
 453 K. Two other groups (Mark et al. 1998, Page et al. 2010) report values of  
 454 35% at unspecified pH.  
 455

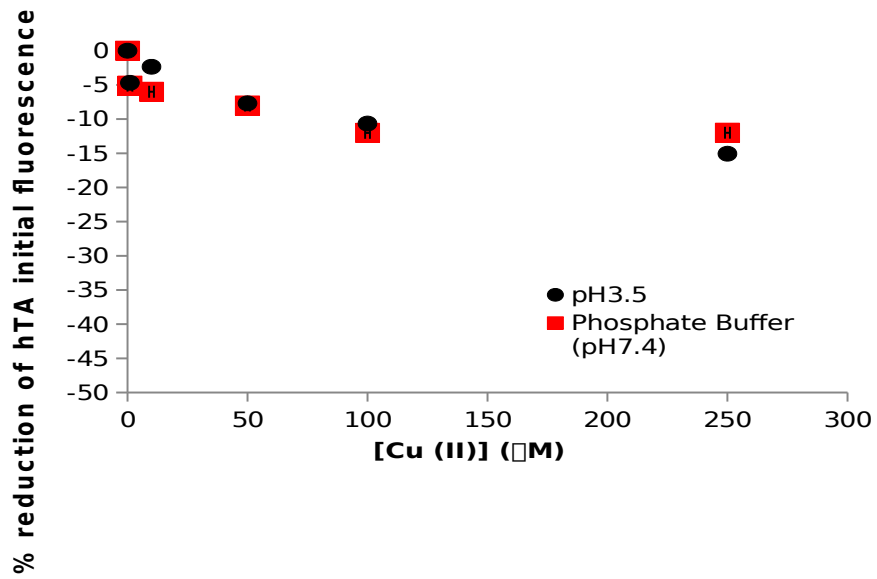
456

457

458

459

460



461

462 Figure 3. Reduction of hTA fluorescence intensity (at Ex/Em of 310/418 nm)

463 by Cu(II).