Supplementary Materials for:

Insights into the photoproduction sites of hydroxyl radicals by dissolved organic matter in natural waters

Luni Sun,[†] Jianguo Qian,[‡] Neil V. Blough,[§*] and Kenneth Mopper[†*]

[†]Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, Virginia 23529, United States

[‡]Department of Chemistry, Washington State University, Pullman, Washington 99164-4630, United States

[§]Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742-3281, United States

*Correspondence authors:

E-mail: neilb@umd.edu.

E-mail: kmopper@odu.edu.

Chemicals:

The following chemicals were used: phenol (purity grade >99 %, Sigma), benzene (HPLC grade, Sigma), sodium benzoate (99.5 %, Sigma), salicylic acid (99%, Fisher), 3-hydroxybenzoic acid (99%, Acros), 4-hydroxybenzoic acid (99%, Sigma), 2,3-dihydroxybenzoic acid (99%, Sigma), 2,6-dihydroxybenzoic acid (98%, Aldrich), 2,4-dihydroxybenzaldehyde (98 %, Aldrich), 2,5-dihydroxybenzoic acid (99%, Fluka), 2,4-dihydroxybenzoic acid (98%, TCI), ferric chloride (99%, Sigma), 1,10-phenanthroline (99%, Aldrich), potassium oxalate (99%, Baker), 3-Amino-

2,2,5,5,-tetramethyl-1-pyrrolidinyloxy free radical (3-ap) (Sigma), fluorescamine (99%, Fisher), sodium nitrite (99.7%, Fischer), methane (UHP grade, Matheson), H_2O_2 (35 % w/w, Acros), dimethyl sulfoxide (B&J), methanol (HPLC grade, Acros) and acetonitrile (HPLC grade, EMD). The acetonitrile was dried with anhydrous sodium sulfate (99%, Sigma), which was dried at 200 °C about 4 hours prior to use. Ultra-pure water (Milli-Q water, >18 $M\Omega cm^{-1}$, Millipore) was used for solution preparation. The buffer solutions were as follows: pH 4.5~5.5 (5 mM acetate buffer), pH 6~7 (5 mM phosphate buffer), pH 8~9 (5 mM borate buffer). Potassium ferrioxalate used for actinometry was prepared by adding three parts 1.5 M potassium oxalate to one part 1 M ferric chloride. The resulting precipitate was recrystallized three times with Milli-Q water and dried in a vacuum oven.

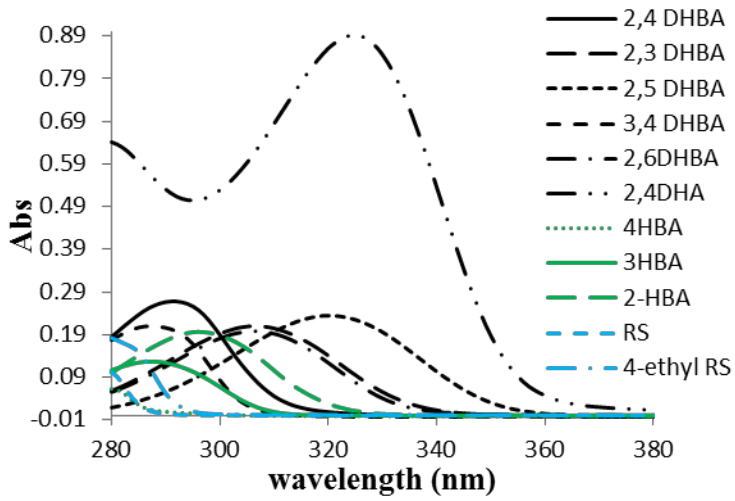

Fig. S1. Absorbance spectra of 20 µM model compounds at pH ~7 measured by an Agilent 8453 diode array spectrophotometer with a 3 cm quartz cuvette. NOTATION: DHBA-dihydroxybenzoic acid, HBA - hydroxybenzoic acid, DHA – dihydroxybenzaldehyde, RS-resorcinol.

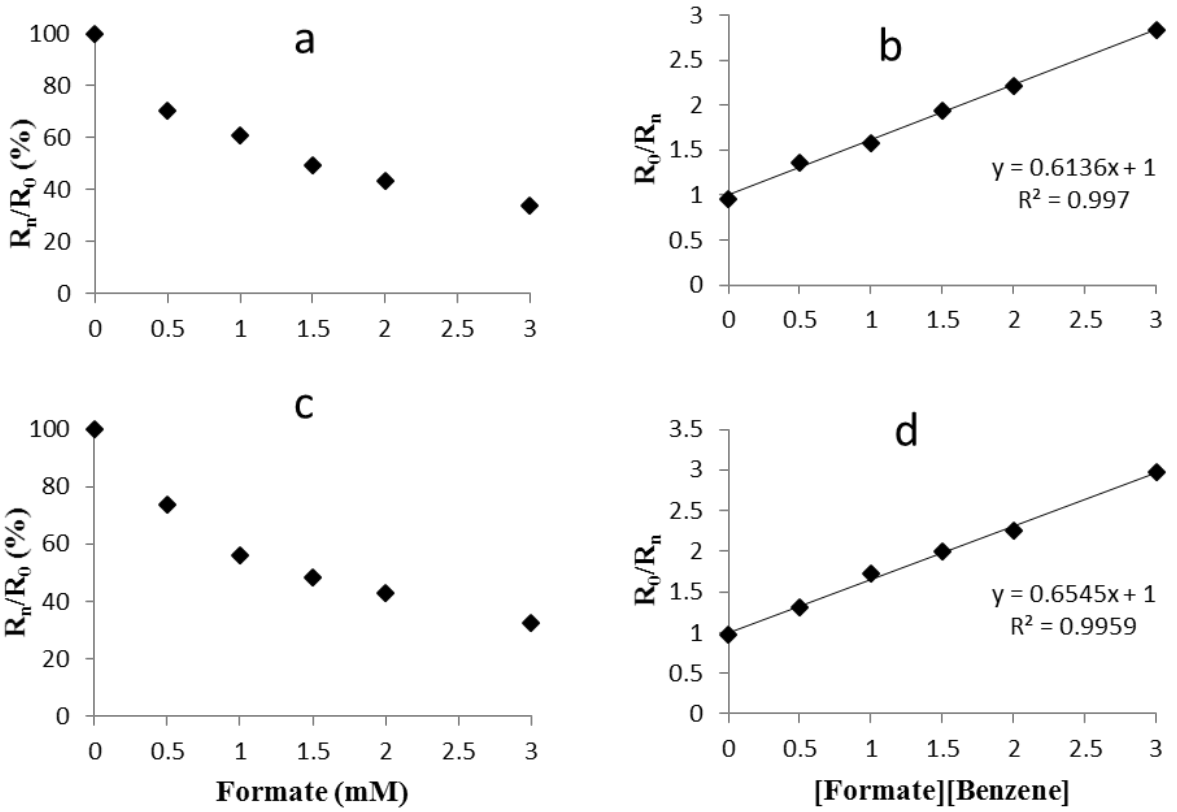

Fig. S2. (a) The effect of formate concentration on phenol relative formation rate R_n/R_0 (%); (b) R_0/R_n vs. [formate]/[benzene] using 2,4- DHBA as the •OH source and benzene as the probe; (c) The effect of different formate concentrations on phenol relative formation rate R_n/R_0 (%); (d) R_0/R_n vs. [formate]/[benzene]) using H_2O_2 as the •OH source and benzene as the probe. R_n is the photoproduct formation rate at a given competitor concentration; R_0 is the photoproduct formation rate with no competitor added.

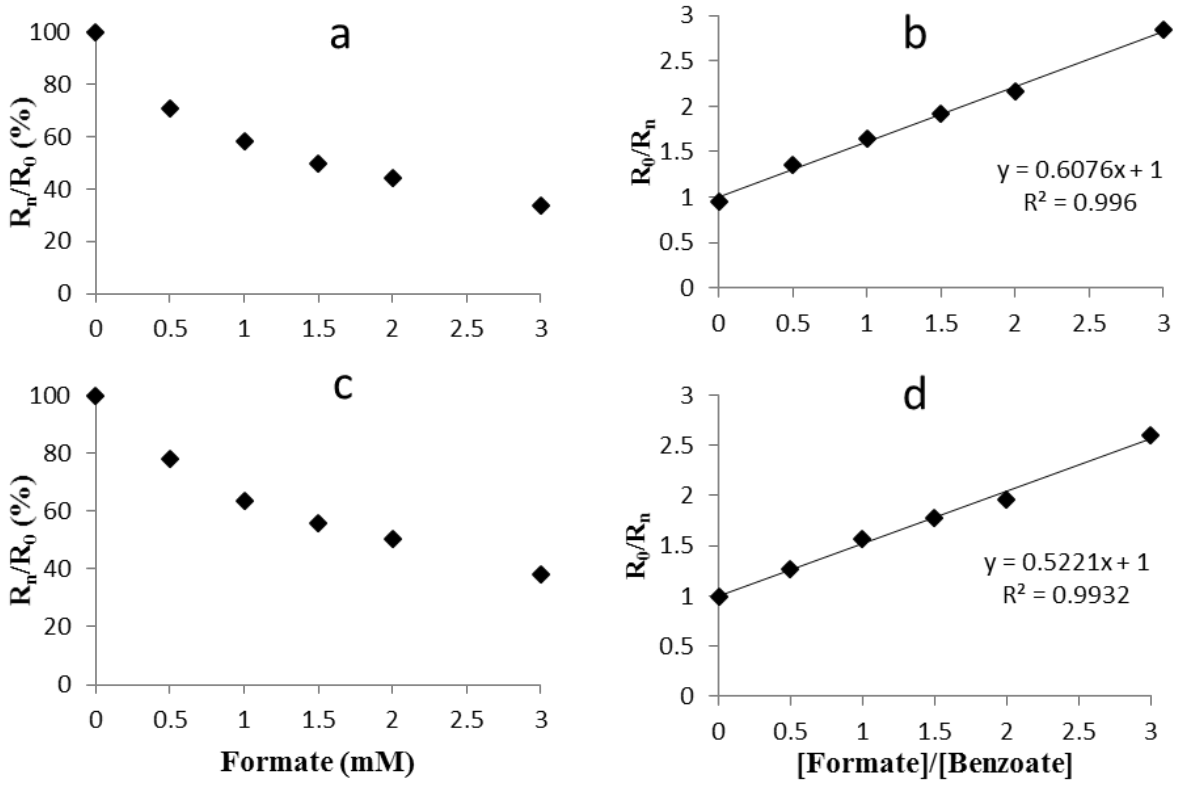

Fig. S3. (a) The effect of formate concentration on salicylic acid (SA) relative formation rate R_n/R_0 (%); (b) R_0/R_n vs. [formate]/[benzoate] using 2,4- DHBA as the •OH source and benzoate as the probe; (c) The effect of formate concentration on SA relative formation rate R_n/R_0 (%); (d) R_n/R_0 vs. [formate]/[benzoate]) using H_2O_2 as the •OH source and benzoate as the probe.

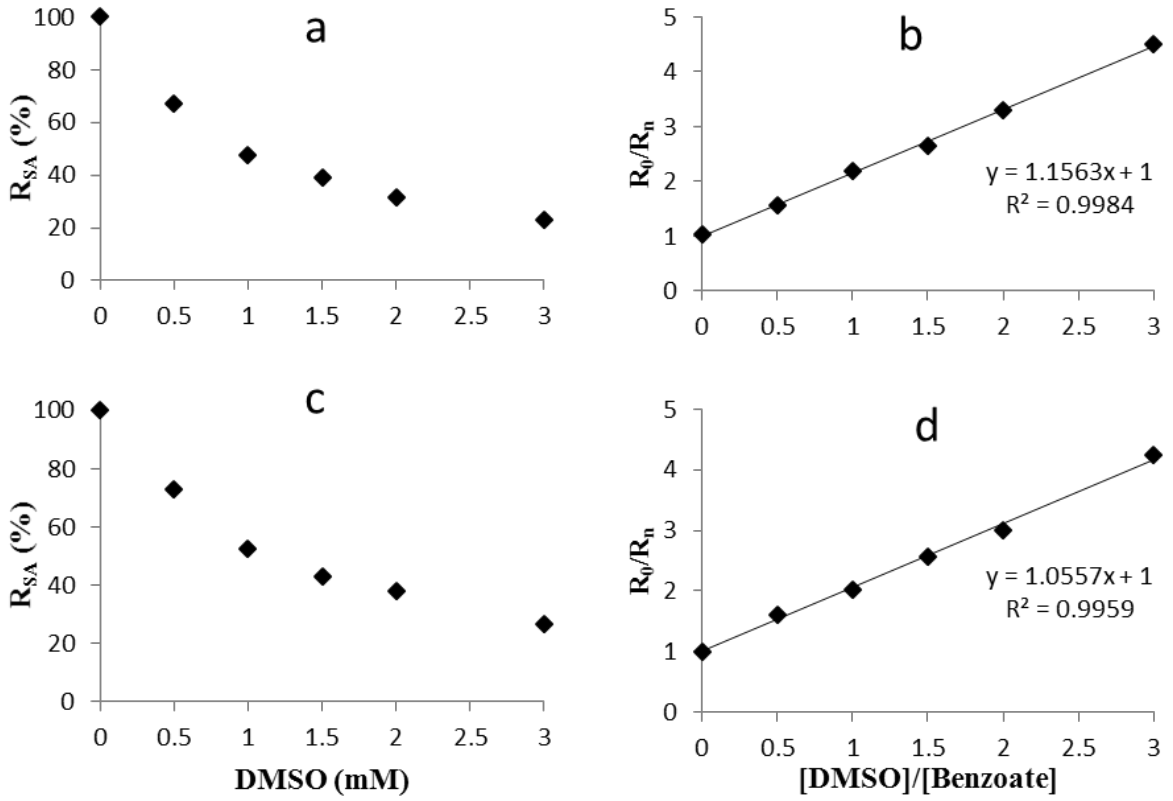

Fig. S4. (a) The effect of DMSO concentration on SA relative formation rate R_n/R_0 (%); (b) R_0/R_n vs. [formate]/[benzoate] using 2,4-DHBA as the •OH source and benzoate as the probe; (c) The effect of DMSO concentration on SA relative formation rate R_n/R_0 (%); (d) R_n/R_0 vs. [formate]/[benzoate]) using H_2O_2 as the •OH source and benzoate as the probe.

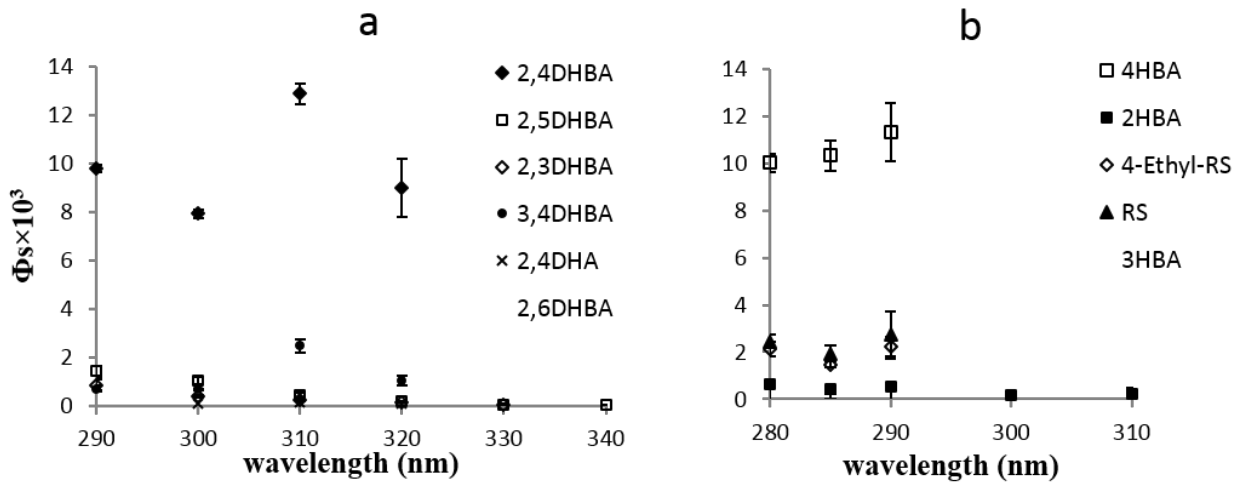

Fig. S5. Quantum yields (Φs) for 20 μM of model compounds using benzene as the probe at wavelengths 290-340 nm at pH 7. Φs were not shown for the wavelengths where the compounds have low absorbance ($<5\times10^{-3}$), or •OH production is undetectable. NOTATION: DHBA-dihydroxybenzoic acid, HBA - hydroxybenzoic acid, RS-resorcinol, DHA-dihydroxybenzaldehyde. The large error bars in the case of 2,4DHBA and 4HBA were due to low absorbance at the longer wavelengths.

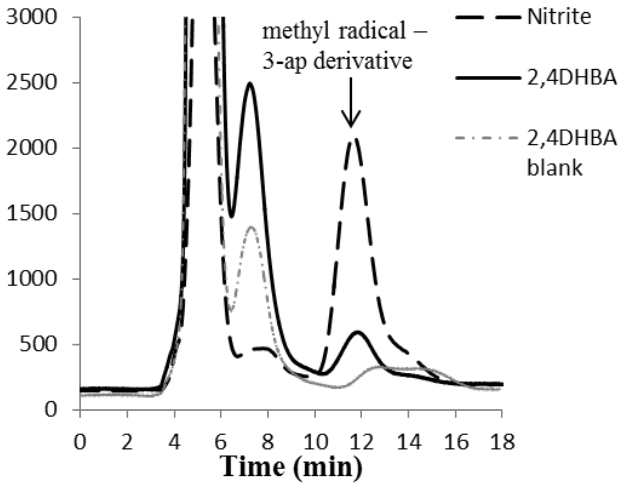

Fig. S6. HPLC chromatogram showing the production of the fluorescent methyl radical – 3-ap fluorescamine derivative. The "2,4-DHBA blank" represents a 2 hour irradiation of 2,4-DHBA without methane but in the presence of 3-ap. The peak was verified by irradiation of 10 µM nitrite in the presence of 10 mM DMSO.

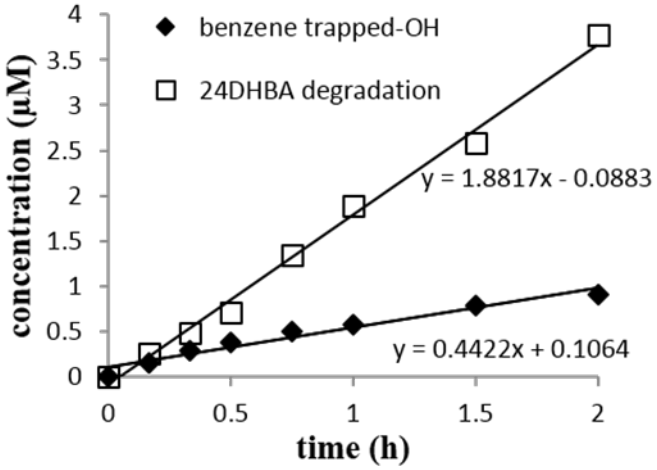

Fig. S7. (a) 2,4-DHBA degradation vs. benzene trapped-OH during a 2 h irradiation. The 2,4-DHBA degradation concentration was obtained by HPLC. The slopes are the 2,4-DHBA degradation and •OH formation rates ($\mu M h^{-1}$).