# Humic Acid Extracts Leading to the Photochemical Bromination of Phenol in Aqueous Bromide Solutions: Influences of Aromatic Components, Polarity and Photochemical Activity

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## Text S1

Detailed calculation of formation rate (R) and the quantum yields ( $\Phi$ ) of <sup>3</sup>DOM<sup>\*</sup>, <sup>1</sup>O<sub>2</sub> and <sup>•</sup>OH and solution rates of light absorbance ( $R_{abs}$ ) of the three HA fractions.

Probe compound stock solutions were prepared in Milli-Q water and spiked into water samples containing HA fractions. 2,4,6-Trimethylphenol (TMP), furfuryl alcohol (FFA), and terephthalic acid (TPA) were used to measure <sup>3</sup>DOM<sup>\*</sup>, <sup>1</sup>O<sub>2</sub>, and <sup>•</sup>OH, respectively. In the measurements of <sup>3</sup>DOM<sup>\*</sup> and <sup>1</sup>O<sub>2</sub>, methanol (0.1 M) was added to quench the photogeneration of <sup>•</sup>OH. In the determination of <sup>3</sup>DOM<sup>\*</sup>, an initial concentration of 1 mM TMP was added into the sample. The solutions were sparged with N<sub>2</sub> to remove dissolved oxygen. The degradation rate constant of TMP ( $k_{TMP}$ , s<sup>-1</sup>) was fitted by pseudo-first order kinetics. The initial transformation rate (M s<sup>-1</sup>) of TMP was defined as  $R_{TMP} = k_{TMP}$  [TMP]<sub>0</sub>. The

formation rate of  ${}^{3}\text{DOM}^{*}$  (  $R_{3}$  , M s<sup>-1</sup>) could be obtained from Equation S1 [1,2].

$$R_{TMP} = R_{_{3}}{_{DOM^{*}}} \frac{k_{_{TMP},^{_{3}}DOM^{*}} [TMP]_{_{0}}}{k_{_{TMP},^{_{3}}DOM^{*}} [TMP]_{_{0}} + k_{_{d}}}$$
(S1)

where  $k_{TMP,^3DOM^*}$  is the second-order rate constant between  $^3DOM^*$  and TMP (~  $3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ );  $k_d$  is the

physical quenching constant of <sup>3</sup>DOM<sup>\*</sup> (~ 5.0 × 10<sup>4</sup> s<sup>-1</sup>) [2]. Addition of 1 mM of TMP in this study yielded a scavenging rate of approximately 3 × 10<sup>6</sup> s<sup>-1</sup>, at least 2 orders of magnitude greater than *k*<sub>d</sub>. Thus, the value of  $R_{3_{DOM^*}}$  is approximately equal to  $R_{TMP}$ . Linear plots to determine  $k_{TMP}$  are presented in Figure S2,a.

FFA (50  $\mu$ M initial concentration) was employed to measure the formation rate of <sup>1</sup>O<sub>2</sub> ( $_{R_{1}o_2}$ ,  $_{M}$  s<sup>-1</sup>), which could be determined by the following Equations [1,2]:

$$k_{FFA} = k_{FFA, {}^{1}O_{2}} \frac{R_{{}^{1}O_{2}}}{k_{FFA, {}^{1}O_{2}} [FFA]_{0} + k_{{}^{1}O_{2}}}$$
(S2)

where  $k_{\text{FFA}}$  (s<sup>-1</sup>) the pseudo-first order rate constant of FFA,  $k_{FFA, 1O_2}$  is the second-order rate constant between  $^{1}\text{O}_2$  and FFA (1.0 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>),[1]  $k_{^{1}O_2}$  presents the physical quenching of  $^{1}\text{O}_2$  by water (2.5 × 10<sup>5</sup>

s<sup>-1</sup>). Linear plots to determine *k*<sub>FFA</sub> are presented in Figure S2,b.

The formation rate of •OH (R•OH, M s<sup>-1</sup>) were quantified by the addition of TPA (1 mM, non-fluorescent) and the detection of 2-hydroxyterephthalate (HTPA, fluorescent), which is the single hydroxylation product of TPA. This reaction has been shown to proceed with a yield of 35%. The generation of HTPA was linear with time (Figure S2,c). R•OH were calculated using the following equation [1]:

$$\frac{d[HTPA]}{dt} = 0.35 \times k_{.OH,TPA} \times [TPA] [\cdot OH]_{ss} = 0.35 \times R_{.OH}$$
(S3)

where  $k \cdot OH, TPA$  is the second-order rate constant between OH and TPA (3.3 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>).

The quantum yields of <sup>3</sup>DOM\*, <sup>1</sup>O<sub>2</sub>, and <sup>•</sup>OH were calculated using Equation 4 [1].

$$\phi_i = \frac{R_i}{I_0 \sum_{\lambda} F_{\lambda} (1 - 10^{\varepsilon_{\lambda} b c})}$$
(S4)

where  $R_i$  is the formation rate of <sup>3</sup>DOM<sup>\*</sup>, <sup>1</sup>O<sub>2</sub>, and <sup>•</sup>OH in the HA fraction solutions, respectively,  $I_0$  (Es L<sup>-1</sup> s<sup>-1</sup>) is the incident light intensity obtained by the *p*-nitroanisole/pyridine actinometer,  $F_{\lambda}$  is the spectral distribution of the light emitted by the lamp,  $\varepsilon_{\lambda}$  (L mg<sup>-1</sup> cm<sup>-1</sup>) is the absorption coefficient of DOM at a specific wavelength, *b* (cm) is the path lengthinside the reactor, and c (mg L<sup>-1</sup>) is the concentration of DOM.

The solution screening factor (S<sub> $\lambda$ </sub>) is determined from solution absorbance ( $\alpha_{\lambda}$ , cm<sup>-1</sup>) and the light path length (*l*, cm) [3], as in Equation S5.

$$S_{\lambda} = \frac{1 - 10^{-\ell \times \alpha_{\lambda}}}{2.303 \times \ell \times \alpha_{\lambda}} \tag{S5}$$

Solution rates of light absorbance ( $R_{abs}$ ) were determined from the photon flux ( $I_{\lambda}$ , Es cm<sup>-2</sup> s<sup>-1</sup>), measured solution absorbance ( $\alpha_{\lambda}$ , cm<sup>-1</sup>), and the screening factor ( $S_{\lambda}$ ) [4], as in Equation S6.

$$R_{\rm abs} = 2.303 \sum_{\lambda} I_{\lambda} \alpha_{\lambda} S_{\lambda} \tag{S6}$$

The photon flux ( $I_{\lambda}$ , Es cm<sup>-2</sup> s<sup>-1</sup>) is determined by PNA-pyridine actinometry.  $I_{\lambda}$  is determined as a function of  $R_{a,PNA}$ ,  $S_{\lambda}$ , the molar absorptivity of PNA ( $\varepsilon_{\lambda}$ ,  $M^{-1}$  cm<sup>-1</sup>), and *l* as in Equation S7 [3]:

$$I_{\lambda} = R_{a,PNA} \sum_{\lambda} \frac{1}{2.303 \times S_{\lambda} \times \varepsilon_{\lambda} \times \ell}$$
(S7)

 $R_{a,PNA}$  of an actinometer solution is determined from the pseudo-first-order loss rate of PNA ( $k_{obs,PNA}$ ,  $s^{-1}$ ), the initial concentration of PNA ([PNA]t=0, M), and the quantum yield of reaction between PNA and pyridine ( $\Phi_{PNA}$ ) [3], as in Equation S8:

$$R_{a,PNA} = \frac{k_{obs,PNA} [PNA]_{t=0}}{\phi_{PNA}}$$
(S8)

### Text S2

#### Analysis of Bromophenol Products, TMP, FFA, HTPA and PNA

A sample solution (20 mL) after irradiation was spiked with 1  $\mu$ L 2-hydroxy-5-chlorobiphenyl (100  $\mu$ g/L) as the internal standard, and then was acidified to pH ~2 using 2.5 M H<sub>2</sub>SO<sub>4</sub>, followed by extraction with dichloromethane (10 mL, 2x). After dehydration using an anhydrous sodium sulfate column, the extract was concentrated to 200  $\mu$ L for direct analysis by GC–MS. Analysis was performed using an Agilent 7890 GC and 5975C MSD with an EI source operating in SIM mode, using ions at mass/charge ratios (m/z) 172 and 174 for bromophenols determination and 204 and 206 for 2-hydroxy-5-chlorobiphenyl determination. The GC was operated with helium as the carrier gas in the splitless mode with a DB-5ms capillary column (30 m × 0.25 mm × 0.25  $\mu$ m). The following conditions were used for the analysis: a 1- $\mu$ L injection, a source temperature of 230°C and an inlet temperature of 270°C. The column temperature ramp was as follows: 80°C for 2.0 min, 80–270°C at 15°C/min and 270°C hold for 10 min.

The concentrations of TMP, FFA and PNA were measured using a high-performance liquid chromatography (HPLC) system (Waters 717 plus) with a C18 column (5  $\mu$ m, 250 × 4.6 mm, Agilent). The mobile phases were 70% acetonitrile/30% water with 10 mM phosphate buffer for TMP, 30% methyl alcohol/70% water for FFA, and 60% acetonitrile/40% water for PNA. The detection wavelengths were 280, 220 and 315 nm for TMP, FFA, and PNA, respectively. The concentration of HTPA was detected using a fluorescence spectrophotometer ( $\lambda_{ex}$  = 315 nm and  $\lambda_{em}$  = 425 nm).





**Figure** S1 EEM fluorescence spectrum of  $F_A(\mathbf{a})$ ,  $F_B(\mathbf{b})$ , and  $F_C(\mathbf{c})$ .



**Figure S2** The curve of each probe molecule and PNA over time under simulated sunlight: (**a**) TMP, [TMP]<sub>0</sub>=1mM; (**b**) FFA, [FFA]<sub>0</sub>=50μM; (**c**) HTPA, [TPA]<sub>0</sub>=1mM; (**d**) PNA, [PNA]<sub>0</sub>=10μM.

### References

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