Supporting Information

Photochemistry of Dissolved Black Carbon Released from Biochar: Reactive Oxygen Species Generation and Phototransformation

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Calculation of the steady-state concentration and apparent quantum yield of singlet oxygen

The degradation rate of furfuryl alcohol (FFA) can be expressed as:

$$-\frac{d[FFA]}{dt} - k_{FFA}[\,{}^1O_2\,]\;\;[FFA] \qquad (1)$$

$$-\frac{d[FFA]}{dt} = k_{FFA}[\,{}^1O_2\,]_{ss}[FFA] = k_{ex}[FFA] \qquad (2)$$

where k_{ex} is the experimentally determined pseudo-first order rate constant of FFA degradation.

Steady state ${}^1O_2$ concentration can be determined as:

$$[\,{}^1O_2\,]_{ss} = \frac{k_{ex}}{k_{FFA}} \qquad (3)$$

Where k_{FFA}=1.2 × 10^8 $M^{-1}s^{-1}$.[1]

The ${}^1O_2$ production rate (R_p) can be determined as:

$$R_p = [\,{}^1O_2\,]_{ss} \times k_d \qquad (4)$$

Where k_d = 2.4 × $10^7 s^{-1}$ which repents the quenching of ${}^1O_2$ by water.[2]

The rate of light absorption, R_a, can be determined as:

$$R_a = \sum_\lambda \left(E^0_{p,\lambda}\left(1 - 10^{-\frac{A_\lambda}{l}z}\right)/z \right) \qquad (5)$$

Where $E^0_{p,\lambda}$ is the spectra photon irradiance (meinsteins cm^{-2} s^{-1}) at the solution surface as determined by a spectrometer USB2000+ (Ocean Optics, FL, USA), λ is the wavelength (nm), z is the depth of the solution (cm), A_λ is the absorbance of solution measured by the UV-vis spectrometer. And l(cm) is the optical path length of the cuvette used in the UV-vis measurement. R_a was intergated from 290 to 400 nm.[2] The apparent quantum yield of $^1O_2$ can be determined as:

$$\Phi_{\text{singlet oxygen}} = R_p/R_a \qquad (6)$$

Comparison of k_{ex} among altered dissolved BC.

The UV-vis absorption spectra of altered dissolved BC such as demineralized and photobleached dissolved BC were different from the original sample, leading to different photon absorption during photoreactions. In order to take account of changes in photon absorption, their pseudo-first-order FFA degradation rate constants were normalized by the photon absorption ratio, $R_a/R_{a,\text{ original dissolved BC}}$. R_a was calculated using equation 5. The normalized pseudo-first-order FFA degradation rate constants were used in the comparison of photoactivity which isolated the role of changes in chemistry, rather than changes in light absorption.

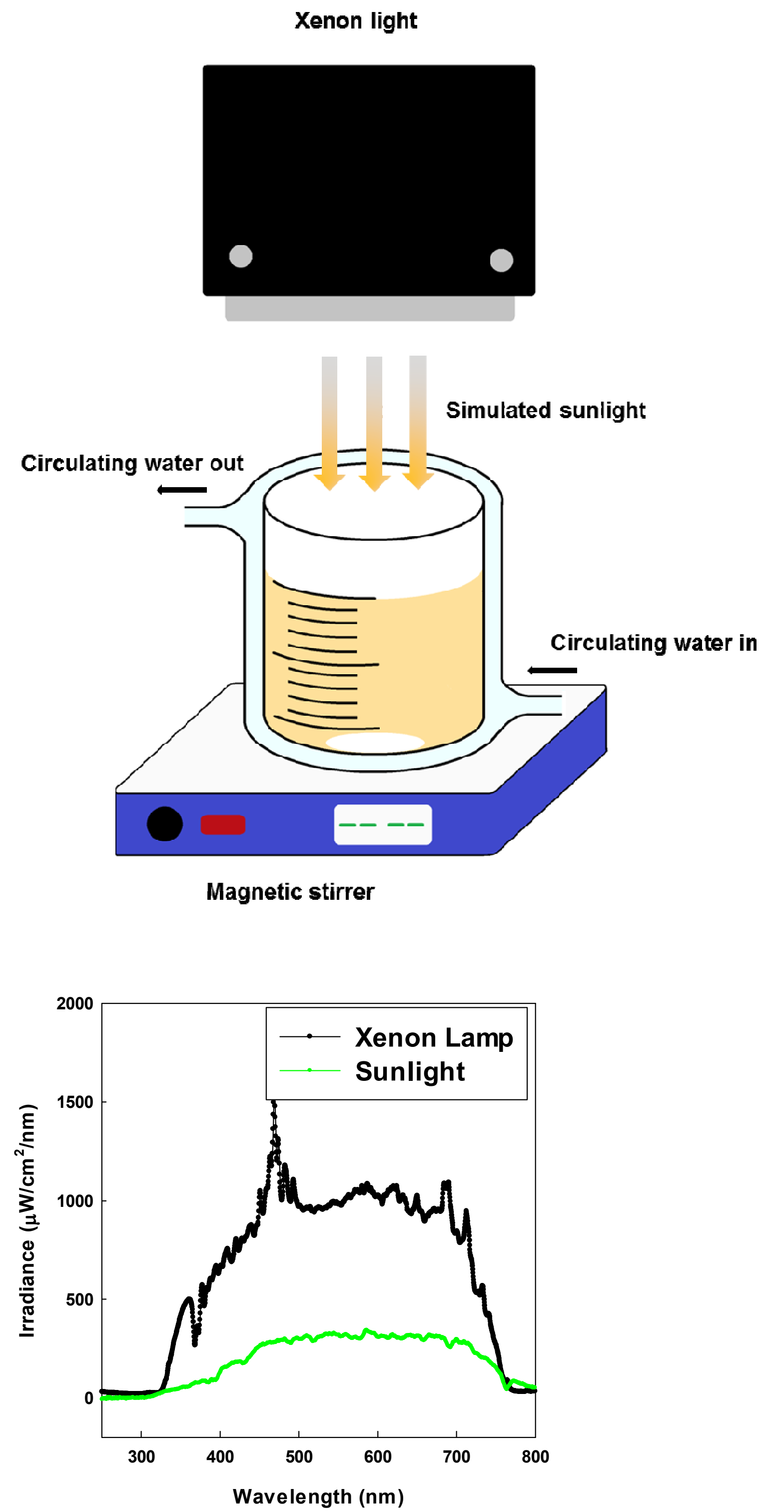


Figure S1. (a) Experimental setup for the irradiation experiments, and (b) the spectra of the xenon lamp and sunlight (on the campus of Nanjing University, 3 pm, 11/27/2015) measured using a spectrometer USB2000+.

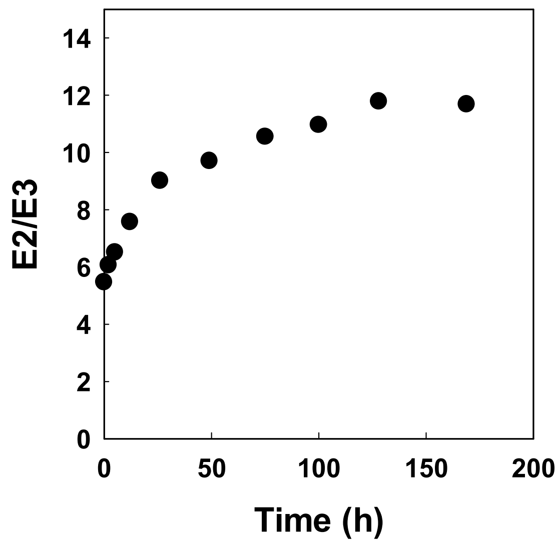


Figure S2. E2/E3 ratio (i.e., the absorbance at 254 nm divided by that at 365 nm) of dissolved BC as a function of irradiation time.

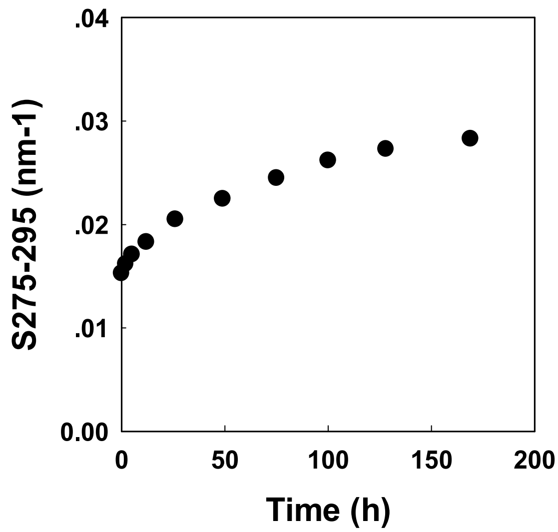


Figure S3. Spectral slopes calculated for the range of 275-295 nm of dissolved BC as a function of irradiation time.

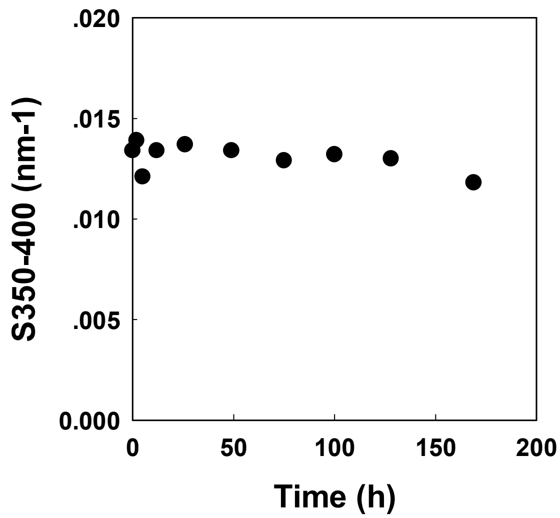


Figure S4. Spectral slopes calculated for the range of 350-400 nm of dissolved BC as a function of irradiation time.

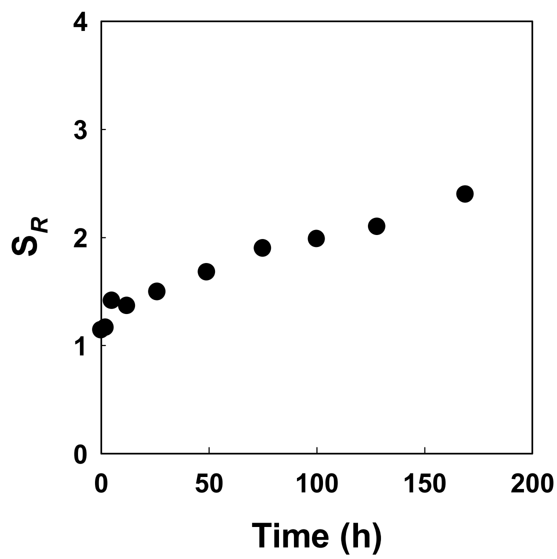


Figure S5. Slope ratio (S_R) of 100 mg/L dissolved BC as a function of irradiation time.

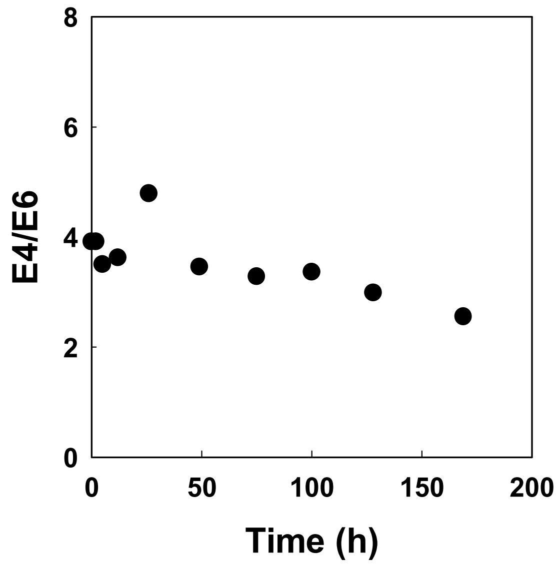


Figure S6. E4/E6 ratio (i.e., the absorbance at 465 nm divided by that at 665 nm) of dissolved BC as a function of irradiation time.

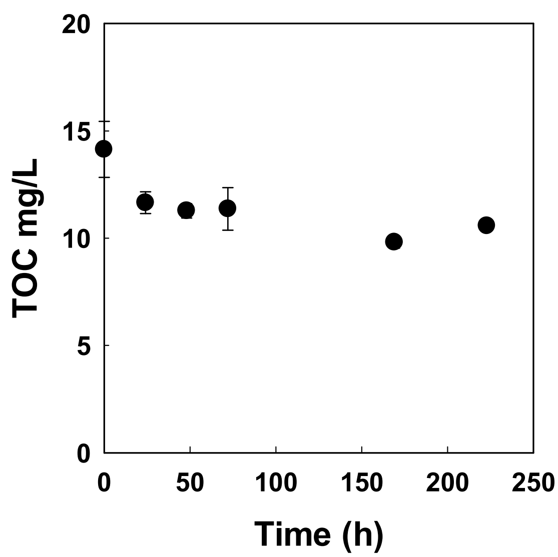


Figure S7. Photo-mineralization of dissolved BC under simulated sunlight as measured by TOC. Error bars represent ± one standard deviation from the average of triplicates.

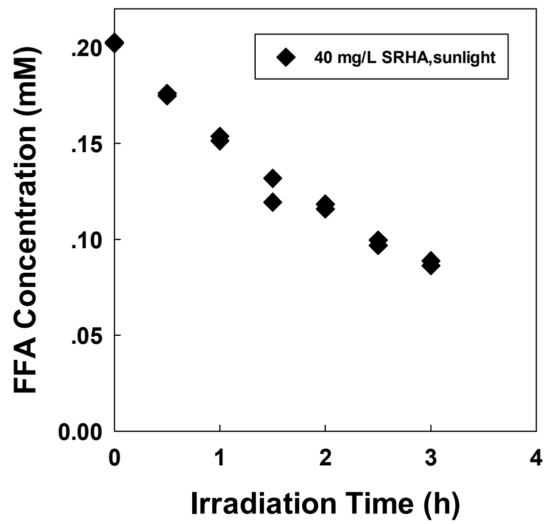


Figure S8. FFA loss, representing $^1O_2$ generation as a function of irradiation time with 40 mg/L (20.8 mg C/L) Suwannee River humic acid (SRHA).

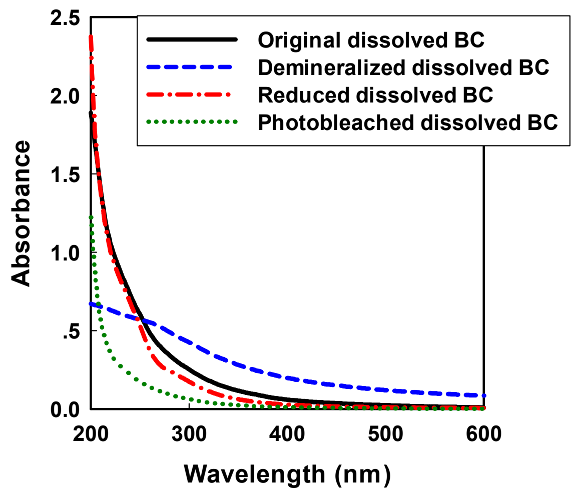


Figure S9. UV-vis absorbance spectra of 100 mg/L original dissolved BC, $NaBH_4$-treated dissolved BC (reduced dissolved BC), and 24h-photobleached dissolved BC; and the UV-vis absorbance spectrum of 30 mg/L demineralized dissolved BC. Spectra was measured in a 1 cm path length quartz cell.

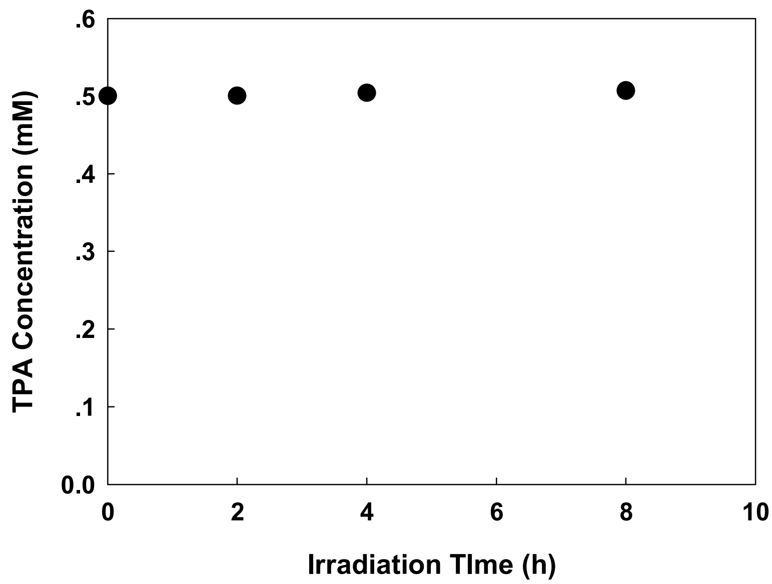
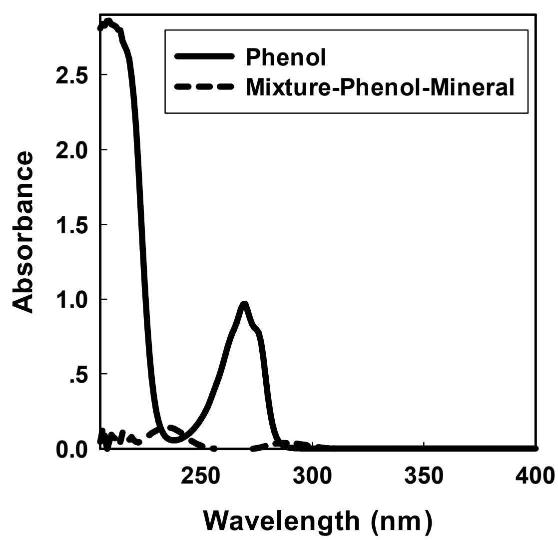


Figure S10. TPA loss, representing •OH generation, as a function of irradiation time with 100 mg/L dissolved BC under simulated sunlight.



Fiugre S11. UV-vis spectrum of 60 mg/L phenol and the spectrum of the mixture of 60 mg/L phenol and 50 mg/L minerals subtracted by the spectra of 60 mg/L phenol and 50 mg/L minerals. Spectra was measured in a 1 cm path length quartz cell.

Table S1. Experimental conditions for photochemical experiments.

Photochemical Experiments		DBC Concentration (mg/L)	ROS Probe/ Scavenger	Probe/ Scavenger Concentration	Solution Volume (mL)
DBC Phototransformation		100	/	/	100
ROS Production	$^1O_2$	100	FFA	0.2 mM	100
	O_2^{-}	100	XTT	0.05 mM	100
	•OH	100	TPA	0.5 mM	100
Effect of DBC Structure on ROS Production	original DBC	100	FFA, XTT	0.2, 0.05 mM	20
	reduced DBC	100	FFA, XTT	0.2, 0.05 mM	100
	photobleached DBC	100	FFA, XTT	0.2, 0.05 mM	20
	demineralized DBC	30	FFA, XTT	0.2, 0.05 mM	20
	minerals	50	FFA, XTT	0.2, 0.05 mM	20
Role of ROS in DBC Phototransformation	control	100	/	/	20
	$^1O_2$	100	NaN_3	10 mM	20
	$^1O_2$	100	D_2O	90 % (v:v)	20
	O_2^{-}	100	SOD	5 mg/L	20

Table S2. Composition of the minerals in dissolved BC as determined by the X-ray fluorescence spectrometer.

Formula	K_2O	SiO_2	SO_3	Cl	Na_2O	CaO	MgO	P_2O_5	Rb_2O
wt%	60.6	20.8	12.5	3.0	1.4	1.1	0.3	0.2	0.1

Reference

(1) Haag, W. R.; Hoigne, J.; Gassman, E.; Braun, A. M., Singlet oxygen in surface waters .1. Furfuryl alcohol as a trapping agent. *Chemosphere* **1984,** *13*, 631-640.

(2) Dalrymple, R. M.; Carfagno, A. K.; Sharpless, C. M., Correlations between dissolved organic matter optical properties and quantum yields of singlet oxygen and hydrogen peroxide. *Environ. Sci. Technol.* **2010,** *44*, 5824-5829.