Supporting information for

Co-photolysis of Mixed Chromophores Affects Atmospheric Lifetimes of Brown Carbon

Yalin Wang[a], Tian Qiu[a], Cong Zhang[a], Tianwei Hao[a], Brix Raphael Go[b], Ruifeng Zhang[b], Masao Gen[c], Man Nin Chan[d], Dan Dan Huang[e], Xinlei Ge[f], Junfeng Wang[f], Lin Du[g], Ru-Jin Huang[h], Qi Chen[i], Ka In Hoi[a], Kai Meng Mok[a], Chak K. Chan[b,j], Yong Jie Li[a,*]

[a]Department of Civil and Environmental Engineering, Department of Ocean Science and Technology, and Centre for Regional Oceans, Faculty of Science and Technology, University of Macau, Macau 999078, China
[b]School of Energy and Environment, City University of Hong Kong, Hong Kong 999077, China
[c]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Sendai, Miyagi 980-8577, Japan
[d]Earth System Science Programme, Faculty of Science, and the Institute of Environment, Energy, and Sustainability, The Chinese University of Hong Kong, Hong Kong 999077, China
[e]Shanghai Academy of Environmental Sciences, Shanghai 200233, China
[f]Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China
[g]Environment Research Institute, Shandong University, Shanda South Road 27, Shandong 250100, China
[h]State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China
[i]State Key Joint Laboratory of Environmental Simulation and Pollution Control, BIC-ESAT and IJRC, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China
[j]Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Kingdom of Saudi Arabi

*Correspondence should be addressed to:

Yong Jie Li: yongjieli@um.edu.mo

Summary: 14 pages, 7 figures, 4 tables, 1 scheme

Section S1. Determining the fraction of light absorption

For co-photolysis of two BrC chromophores, the effective quantum yields were calculated via:

$$\Phi_{e,1} = \frac{k_1 c_1}{\sum I_0(\lambda) \times (1 - 10^{-[\varepsilon_1(\lambda)c_1 + \varepsilon_2(\lambda)c_2] \times l}) \times f_1(\lambda) \times \Delta\lambda}, \quad f_1(\lambda) = \frac{\varepsilon_1(\lambda)c_1}{\varepsilon_1(\lambda)c_1 + \varepsilon_2(\lambda)c_2} \quad \text{(S1)}$$

$$\Phi_{e,2} = \frac{k_2 c_2}{\sum I_0(\lambda) \times (1 - 10^{-[\varepsilon_1(\lambda)c_1 + \varepsilon_2(\lambda)c_2] \times l}) \times f_2(\lambda) \times \Delta\lambda}, \quad f_2(\lambda) = \frac{\varepsilon_2(\lambda)c_2}{\varepsilon_1(\lambda)c_1 + \varepsilon_2(\lambda)c_2} \quad \text{(S2)}$$

where k is photolysis rate constants (s^{-1}); ε_1 and ε_1 are molar absorption coefficients (M^{-1} cm^{-1}) of BrC 1 and 2, respectively; l is the optical path (cm); $I(\lambda)$ is light intensity (Einstein L^{-1} s^{-1} nm^{-1}); and c_1 and c_2 (M) are concentrations of BrC 1 and 2, respectively.

Section S2. Correction factor for quantum yield

The photolysis rate of 2-nitrobenzaldehyde (2NB), a chemical actinometer [1], was measured in photolysis experiments under the same conditions with BrC (co-) photolysis in this study. The photolysis rate constant, k_{2NB}, was calculated by fitting the $\ln\left(\frac{[2NB_t]}{[2NB_0]}\right)$ vs. illumination time (t) as the following equation:

$$\ln\left(\frac{[2NB_t]}{[2NB_0]}\right) = -k_{2NB}t \quad \text{(S3)}$$

where $[2NB_t]$ and $[2NB_0]$ are the concentrations of 2NB measured at time t and 0 min, respectively.

The quantum yield of 2NB photolysis in our experiments was calculated by the following equation [2]:

$$\Phi_{2NB} = \frac{k_{2NB}\, c}{\sum I(\lambda)\,(1 - 10^{-\varepsilon(\lambda) \times c \times l})\Delta\lambda} \quad \text{(S4)}$$

where c is the concentration (M) of 2NB (0.02 mM); $I(\lambda)$ is volume-normalized light intensity (Einstein L^{-1} s^{-1} nm^{-1}) of the lamp; $\varepsilon(\lambda)$ is the molar absorption coefficient (M^{-1} cm^{-1}); and l is the optical path (2.2 cm in this study).

The correction factor for the quantum yield of BrC photolysis is calculated as:

$$f_{2NB,corr} = \frac{\Phi}{\Phi_{2NB}} = \frac{0.41}{\phi_{2NB}} \quad \text{(S5)}$$

where Φ is the intrinsic quantum yield of 2NB (0.41) reported in a previous study.[1]

Section S3. Estimation of atmospheric lifetime for particles containing BrC

Generally, the atmospheric lifetimes (τ, s) (Eq. S6) for the BrC chromophores are obtained by taking the reciprocal of photolysis rate constants (j, s^{-1}), which are calculated by Eq. S7 (Eq.3 in the main text, Method 1) [3].

$$\tau = \frac{1}{j} \quad \text{(S6)}$$

$$j_1 = 3.82 \times 10^{-21} \phi \sum F(\lambda)\varepsilon(\lambda)\Delta\lambda \quad \text{(S7)}$$

where Φ is the intrinsic quantum yield (dimensionless); $F(\lambda)$ is wavelength-dependent solar flux (photon cm^{-2} s^{-1} nm^{-1}), shown in Figure S2 (yellow line) [3]; and $\varepsilon(\lambda)$ is the wavelength-dependent molar absorption coefficient (M^{-1} cm^{-1}).

However, for the concentrated particles containing BrC chromophores, there might be light depletion, especially for the larger particles which have longer light paths. Therefore, another equation, as below (Eq.4 in the main text, Method 2),[2] can be used to take concentration and droplet size into account.

$$j_2 = \frac{\sum \Phi_e I(\lambda)(1 - 10^{-\varepsilon(\lambda) \times c \times l})\Delta\lambda}{c} \quad \text{(S8)}$$

where $I(\lambda)$ is the volume-normalized solar intensity (Einstein L^{-1} s^{-1} nm^{-1}), which is converted from solar flux $F(\lambda)$ with particle size considered; c is the concentration (M); and Φ_e is the effective quantum yield, equivalent to the Φ in Eq. S7 if determined from dilute solutions.

Using the data obtained in the 0.05 mM and 500 mM of VL in IPA solutions, we estimated the atmospheric lifetimes of VL with particle radius from 100 nm to 10 μm, as shown in Figure S7, and the details of processing are shown as follows.

S3.1 VL at 0.05 mM (dilute)

We calculated the average light-absorbing fractions (f_{abs}) of the sunlight for particles with 0.05-mM VL and a radius of 100 nm, 1000 nm or 10 μm by Eq. S9 (Eq.2 in the main text) below.

$$f_{abs} = \frac{\sum_{300}^{380}(1 - 10^{-\varepsilon(\lambda) \times c \times l})}{380 - 300} \quad \text{(S9)}$$

where $\varepsilon(\lambda)$ is the wavelength-dependent molar absorption coefficient (M^{-1} cm^{-1}) for VL within 300–380 nm, as shown in Figure S2 (blue line); c is the concentration (M) of VL; and l is the optical path (cm), being 10^{-5}, 10^{-4}, 10^{-3} cm, respectively, for the three particle sizes simulated.

The f_{abs} values for 0.05-mM VL particles of 100 nm, 1000 nm and 10 μm (radius, same hereinafter unless stated otherwise) are much lower than 0.01, which indicates that there is little shadowing effect for the 0.05-mM scenario for particles containing VL. Therefore, the Φ_e values for these particles are very close to the that obtained in dilute bulk solution (0.05 mM), with a value of 0.002 ± 0.0004. Since there is no difference between Method 1 (j_1) and Method 2 (j_2) at low concentrations (< 5 mM) (Figure S5A), we used the simplified equation Eq. S7 (Method 1) to calculate the j values. The j values for particles of 100 nm, 1000 nm and 10 μm were similar, at about (1.28 ± 0.29) × 10^{-4} s^{-1}. The inferred atmospheric lifetime for these cases is 2.17 ± 0.49 h, independent of particle size.

S3.2 VL at 500 mM (concentrated)

For particles containing VL of 500 mM, the f_{abs} value for 100-nm particles is 0.04 as calculated by Eq. S9 and thus there is little shadowing effect, similar to the "dilute" scenario in Section S3.1 above. Therefore, the Φ_e value is close to that derived from experiments in dilute bulk solutions (0.05 mM), being 0.002 ± 0.0004. Using Eq. S7 (Method 1), the j value for 500-mM VL in 100-nm particles (radius) was calculated to be (1.24 ± 0.25) × 10^{-4} s^{-1}, and the inferred atmospheric lifetime was estimated to be 2.24 ± 0.44 h, similar to that in the 0.05-mM scenario.

For 1000-nm particles, however, the f_{abs} value was calculated to be 0.28 using Eq. S9. Therefore, there is only partial shadowing (light absorbed partly but not depleted) and the Φ_e value is still similar to that in dilute bulk solution (0.002 ± 0.0004). Considering the longer light path for 1000-nm particles, the j value was calculated by Eq. S8 (Method 2), where the volume-normalized solar intensity (I (λ), Einstein L^{-1} s^{-1} nm^{-1}) is converted from solar flux (F(λ), photon cm^{-2} s^{-1} nm^{-1}) with particle size considered. The j value for 1000-nm particles with 500-mM VL was calculated to be (9.72 ± 1.94) × 10^{-5} s^{-1}. The atmospheric lifetime was thus estimated to be 2.86 ± 0.57 h, 32% longer than that for the scenario with 0.05 mM VL and 1000-nm particles, which is mainly caused by the shadowing effect due to a lower volume-normalized photon flux.

For 10-μm VL particles, the f_{abs} value is 0.65 as calculated by Eq. S9. The shadowing effect is significant as the light is almost depleted, and thus the Φ_e value should be similar to that derived from experiments using 500-mM bulk solutions (1.48 ± 0.6). The j value for 10-μm particles with

500-mM VL was calculated by Eq. S8 (Method 2) to be $(2.66 \pm 1.08) \times 10^{-2}$ s^{-1}. The atmospheric lifetime was estimated to be 0.01 ± 0.004 h, two orders of magnitude less than that for 10-μm particles with 0.05 mM VL, which is mainly caused by the significant sensitizing effect under the light depletion condition. Note that although the sensitizing effect might play a major role in the accelerated degradation of VL, shadowing might also contribute indirectly because a high f_{abs} value will leaves a great portion of VL molecules in the ground state and react with photosensitization-generated reactive intermediates.

Tables

Table S1 Experimental conditions of aqueous-phase BrC photolysis.

BrC	Concentration (mM)	Standalone	+ VA (mM)		+ VL (mM)		+ 4NC (mM)		+ 4NP (mM)	
			0.05	0.5	0.05	0.5	0.05	0.5	0.05	0.5
VA	0.02	+								
	0.05	+			+	+	+	+		
	0.5	+			+	+	+	+		
	2	+								
	5	+								
VL	0.02	+								
	0.05	+	+	+			+	+		
	0.5	+	+	+			+	+		
	2	+								
	5	+								
4NC	0.02	+								
	0.05	+	+	+	+	+			+	+
	0.5	+	+	+	+	+			+	+
	2	+								
	5	+								
4NP	0.02	+								
	0.05	+			+	+	+	+		
	0.5	+			+	+	+	+		
	2	+								
	5	+								

Note: Each "+" represents an experiment conducted under air-saturated condition.

Table S2 Experimental conditions of BrC photolysis in isopropanol (IPA) solutions.

BrC	Concentration (mM)	Standalone	+ VL (mM)		+ 4NC (mM)	
			0.05	5	0.05	0.5
VL	0.05	+			+	+
	5	+				+
	500	+				
4NC	0.05	+	+			
	0.5	+	+	+		
	5	+				

Note: Each "+" represents an experiment conducted under air-saturated condition.

Table S3 Experimental conditions of aqueous-phase BrC photolysis under N_2-saturated conditions.

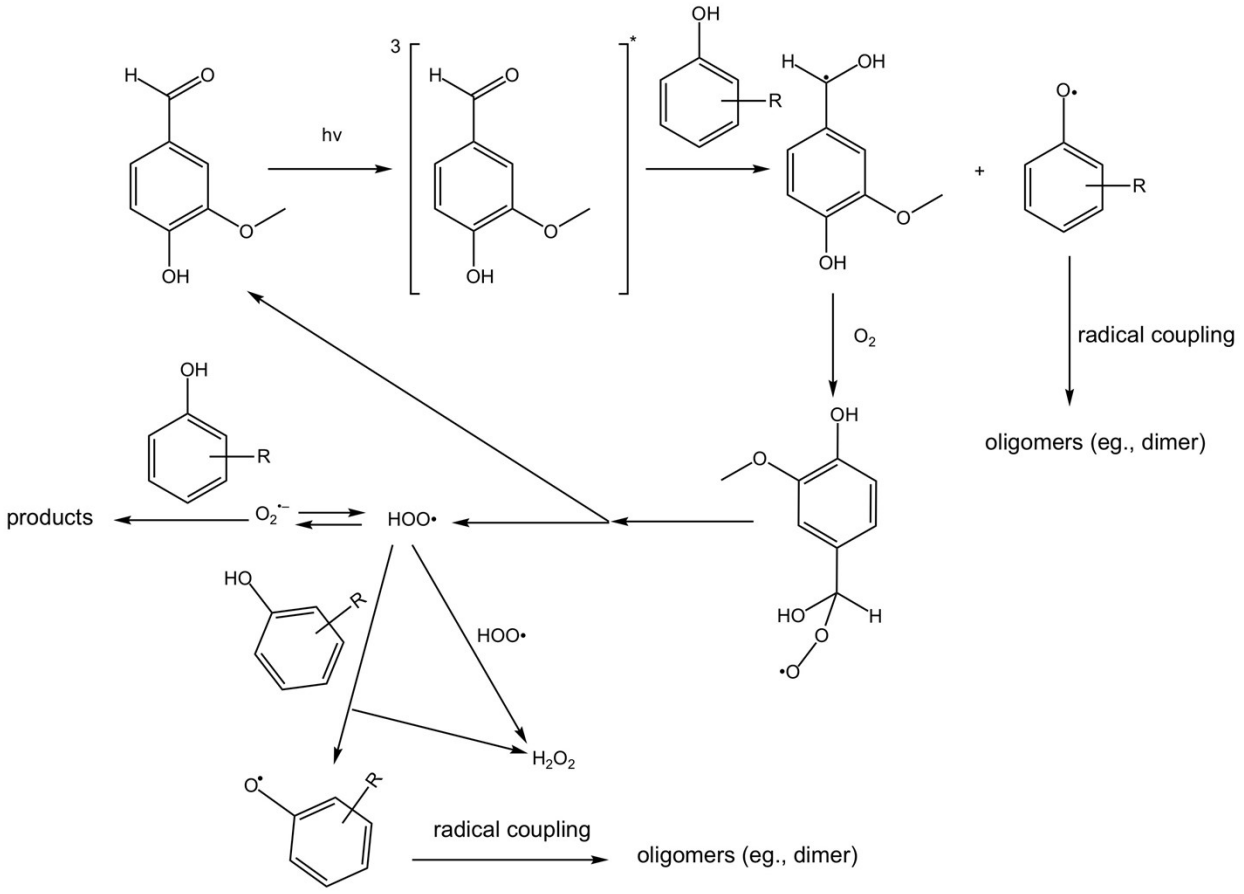
BrC	Concentration (mM)	Standalone	+ VL (mM)		+ 4NC (mM)	
			0.05	0.5	0.05	0.5
VA	0.05	+				
	0.5	+				
	5	+				
VL	0.05	+			+	+
	0.5	+			+	+
	5	+				
4NC	0.05	+	+	+		
	0.5	+	+	+		
	5	+				
4NP	0.05	+				
	0.5	+				
	5	+				

Note: Each "+" represents an experiment conducted under N_2-saturated condition.

Table S4 Main products of VL photolysis alone or co-photolysis with 4NC.

VL photolysis	Formula	Pathway	Ion peak	m/z calculated	m/z measured	Δ (mDa)
Alone or mixed	$C_8H_8O_4$	Hydroxylation	$C_8H_7O_4^-$	167.0344	167.0348	0.4
Alone or mixed	$C_{16}H_{14}O_6$	Dimerization	$C_{16}H_{13}O_6^-$	301.0712	301.0713	0.1
Mixed	$C_{14}H_{11}NO_7$	Cross-reaction	$C_{14}H_{10}NO_7^-$	304.0457	304.0462	0.5

Scheme



Scheme S1 Possible mechanisms in the photosensitization reactions by vanillin (VL) with phenols, including itself, and other phenols such as vanillic acid (VA), 4-nitrocatechol (4NC), 4-nitrophenol (4NP) used in this study, which are all denoted with an unspecific "-R" group on the phenolic ring.

Figures

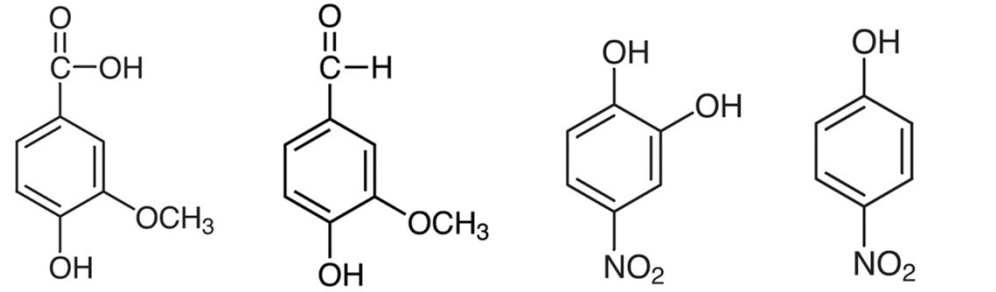


Fig. S1 Structures of the BrC model compounds used in this work.

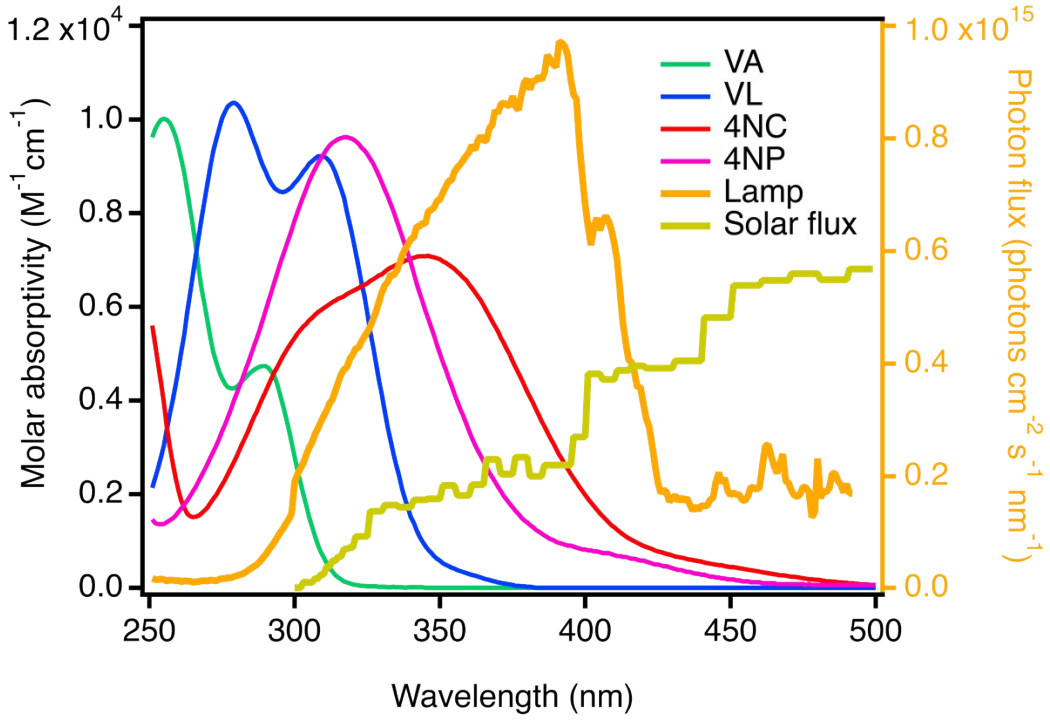


Fig. S2 Molar absorptivity of vanillic acid (VA), vanillin (VL), 4-nitrocatechol (4NC), and 4-nitrophenol (4NP) and the photon flux of our lamp (orange line) and solar flux[3] (yellow line).

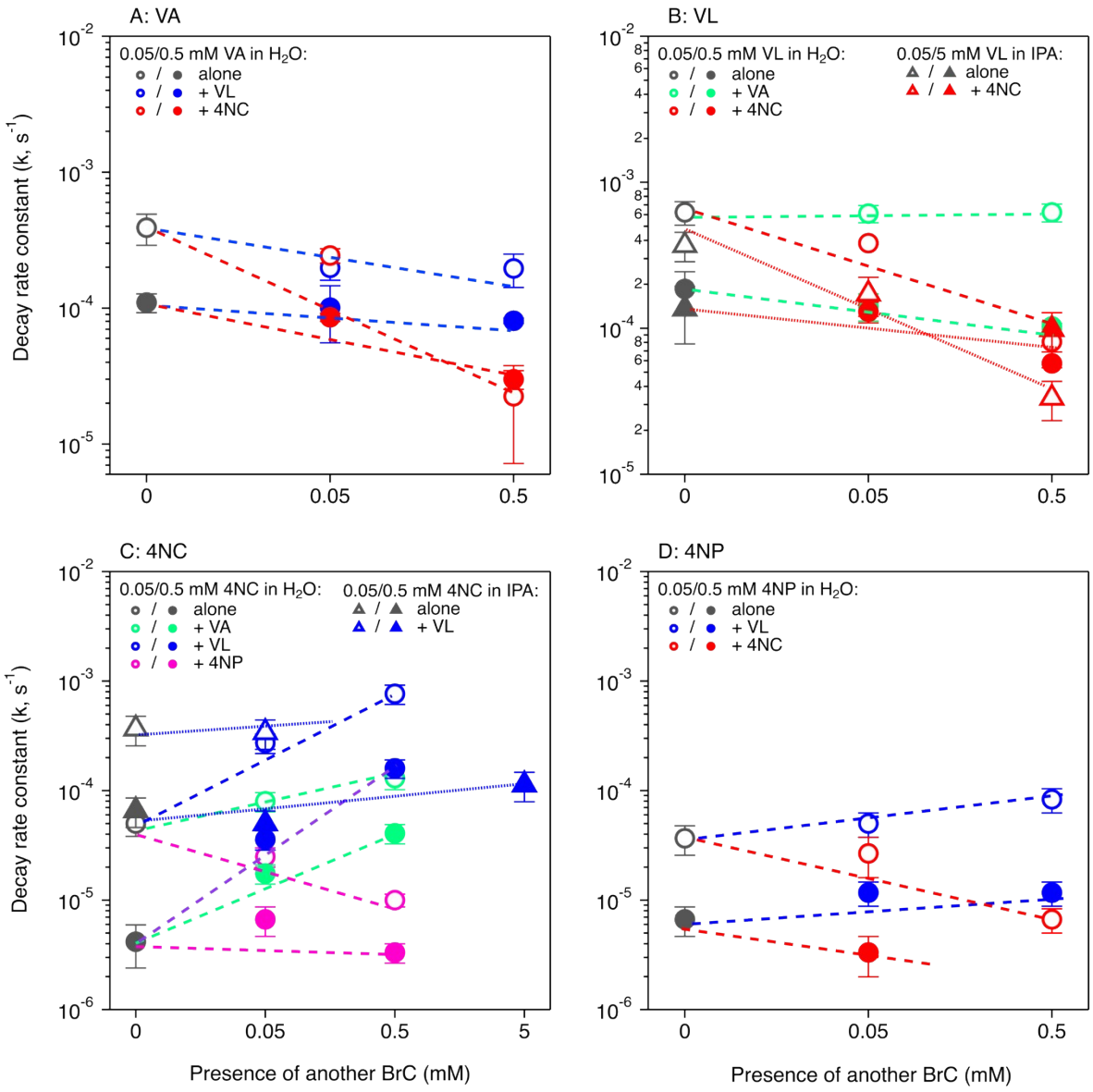


Fig. S3 Decay rate constant (k, s^{-1}) of (A) vanillic acid (VA), (B) vanillin (VL), (C) 4-nitrocatechol (4NC), and (D) 4-nitrophenol (4NP) under three mixing conditions: MP + MP, NP+ NP, and MP + NP. The circles are data from experiments in aqueous solutions, while triangles are data from experiments in isopropanol (IPA) solutions. The hollow and solid symbols represent the data for lower concentration (0.05 mM) and higher concentration (0.5 or 5 mM), respectively. The dashed and dotted lines are not fitting results and are merely to guide the eyes. The error bars represent the standard deviations from the results of triplicate experiments.

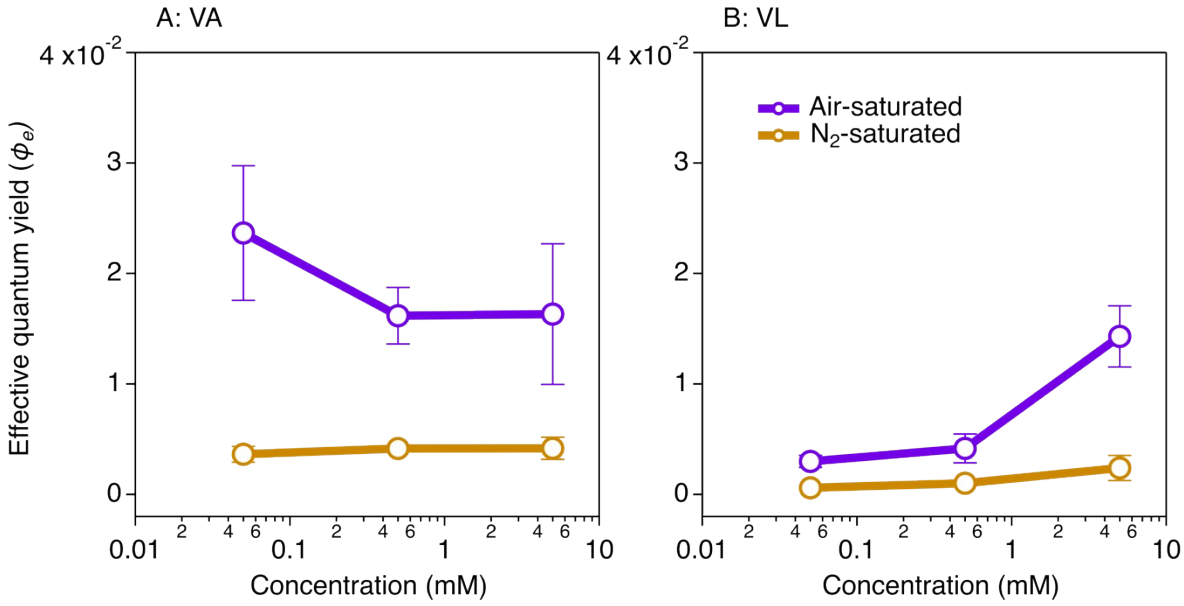


Fig. S4 Effective quantum yield (Φ_e) of (A) vanillic acid (VA) and (B) vanillin (VL) as a function of concentration under air- or N_2-saturated conditions.

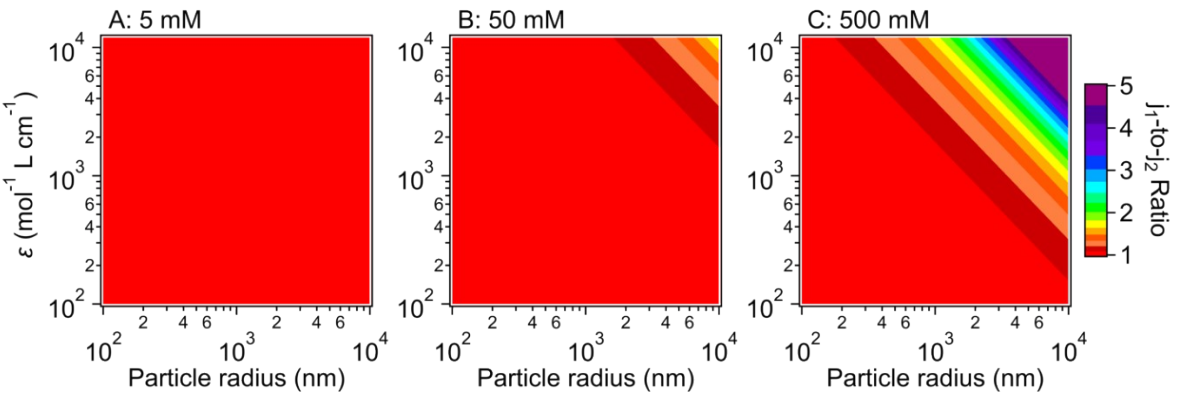


Fig. S5 Ratio of j_1 value to j_2 value for BrC concentrations at (A) 0.05 mM, (B) 50 mM, and (C) 500 mM.

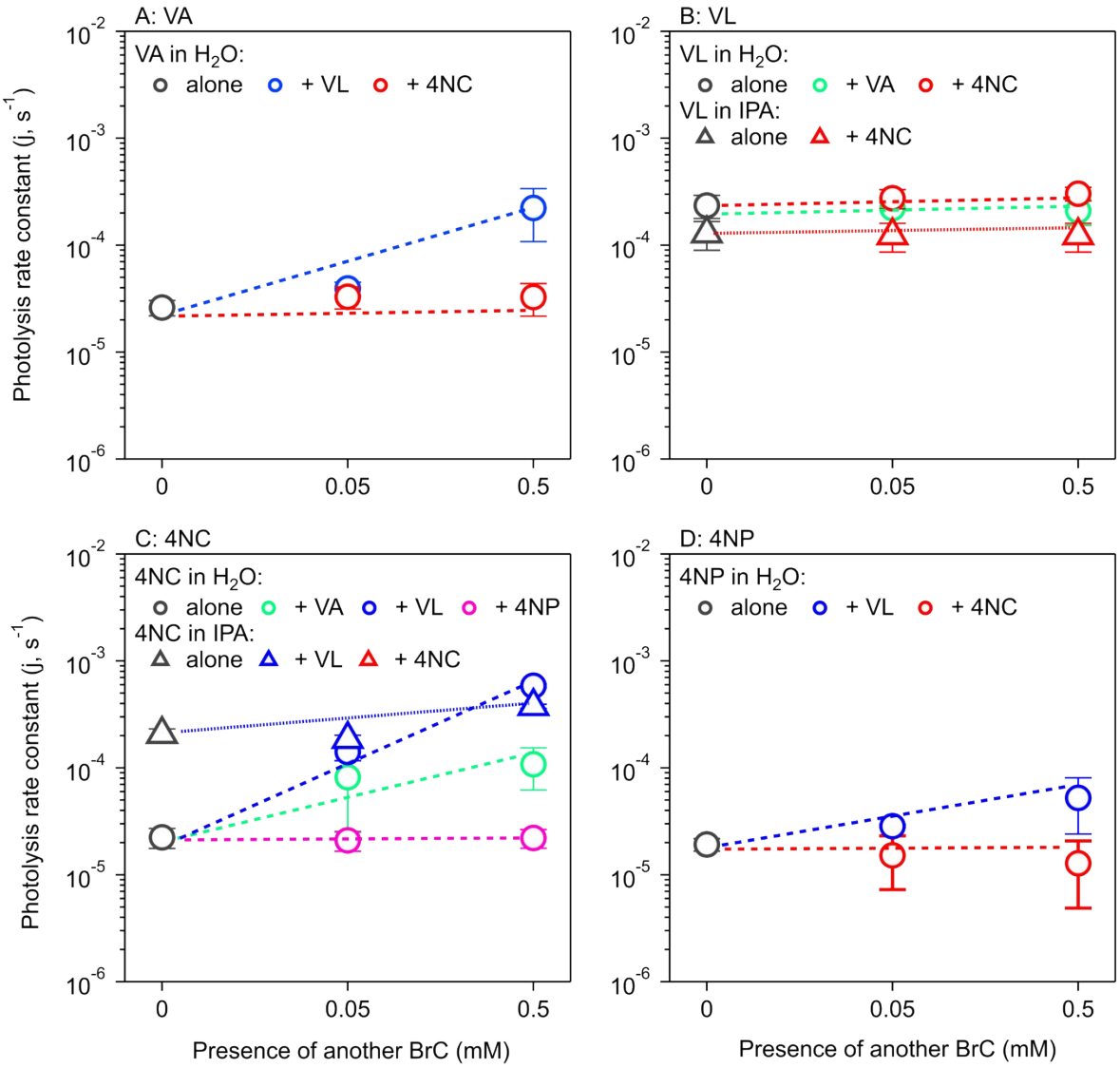
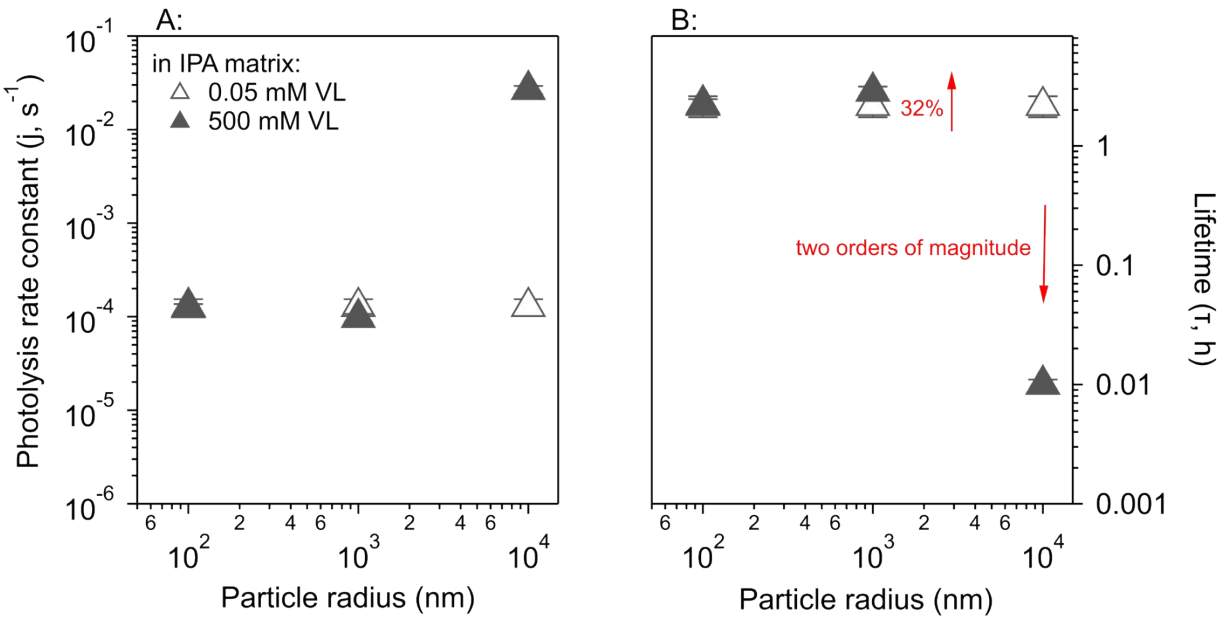


Fig. S6 Photolysis rate constant (j, s^{-1}) of (A) vanillic acid (VA), (B) VL (vanillin), (C) 4-nitrocatechol (4NC), and (D) 4-nitrophenol (4NP) in aqueous solutions (in hollow black) under three mixing cases: MP + MP, NP+ NP, and MP + NP. The estimation assumes particles of 100-nm radius and concentration of 0.02–0.5mM. The circles are data from experiments in aqueous solutions, while the triangles are data from experiments isopropanol (IPA) solutions. The dashed and dotted lines are not fitting results and are merely to guide the eyes.



187

188 Fig. S7 Estimation of (A) photolysis rate constant (j, s^{-1}) and (B) atmospheric lifetime (τ, h) of VL
189 in IPA matrix with different particle sizes. The error bars represent the standard deviations from
190 the results of triplicate experiments.

191

References

1. Galbavy, E. S.; Ram, K.; Anastasio, C., 2-Nitrobenzaldehyde as a chemical actinometer for solution and ice photochemistry. J. Photoch. Photobio. A 2010, 209, (2), 186-192.
2. Lignell, H.; Epstein, S. A.; Marvin, M. R.; Shemesh, D.; Gerber, B.; Nizkorodov, S., Experimental and Theoretical Study of Aqueous cis-Pinonic Acid Photolysis. J. Phys. Chem. A 2013, 117, (48), 12930-12945.
3. Finlayson-Pitts, B. J.; Pitts, J. N., CHAPTER 3 - Spectroscopy and Photochemistry: Fundamentals. In Chemistry of the Upper and Lower Atmosphere, Finlayson-Pitts, B. J.; Pitts, J. N., Eds. Academic Press: San Diego, 2000; pp 43-85.