Supplement of

Measurement report: Seasonal dynamics and driving factors of aqueous-phase photooxidants in atmospheric particles: Implications for wintertime SOA formation

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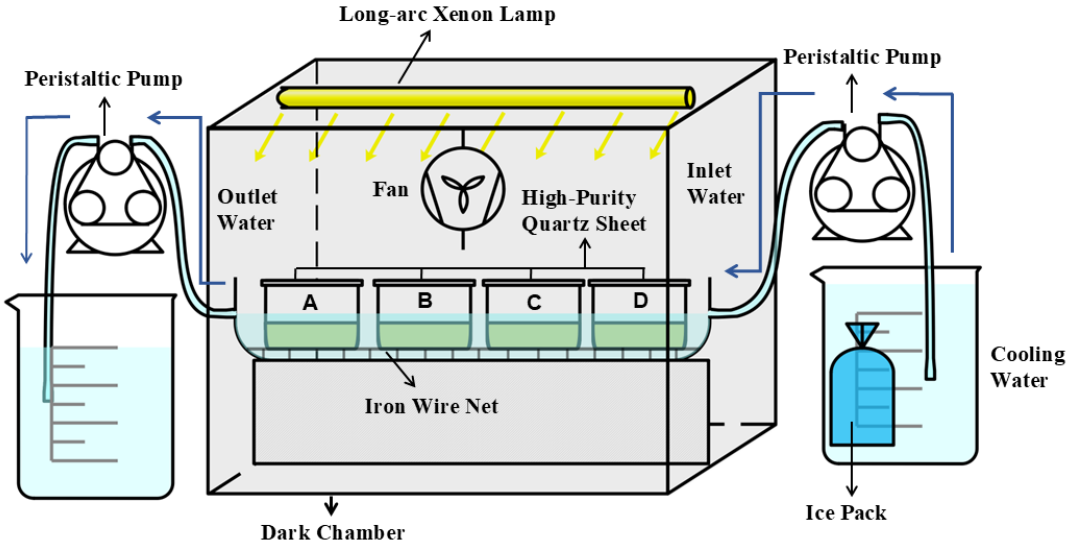
Section S1. Photochemical reaction system

As illustrated in Fig. S1, the aqueous-phase photochemical experiments were conducted in a custom-built reaction system. The entire apparatus was housed in a light-tight enclosure to eliminate interference from ambient light. A 500 W long-arc xenon lamp was horizontally mounted in a lamp housing at the top of the enclosure to simulate tropospheric solar radiation. Given the substantial heat generated during xenon lamp operation, a combined air- and water-cooling system was employed to maintain a relatively constant reaction temperature. Prior to each experiment, a peristaltic pump was used to circulate 4 °C cooling water through the sample tray. Under the combined thermal influence of the xenon lamp and cooling water, the temperature of the water bath remained relatively stable at 25 ± 3 °C.

$PM_{2.5}$ extracts were placed in custom-made cylindrical glass vessels positioned directly beneath and parallel to the xenon lamp tube. The height of the reaction solution in each vessel was maintained below the water level of the cooling bath to ensure effective heat dissipation. A wire mesh was placed at the bottom of the sample tray to maximize contact between the reaction vessel base and the cooling water. High-purity quartz plates were placed atop the vessels to prevent water evaporation and consequent changes in reactant concentrations during irradiation.



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44 **Figure S1.** Schematic plot of the photochemical reactor.

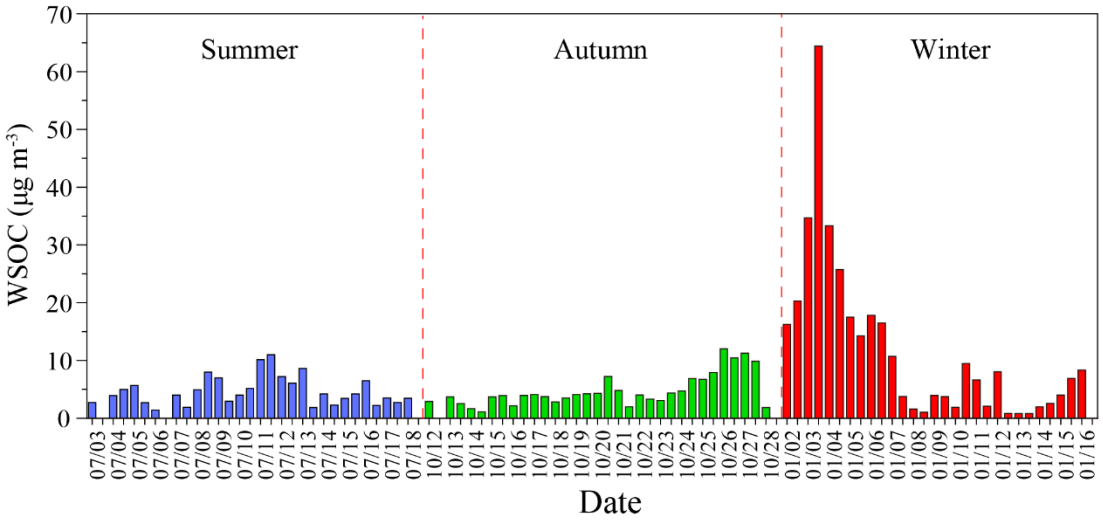
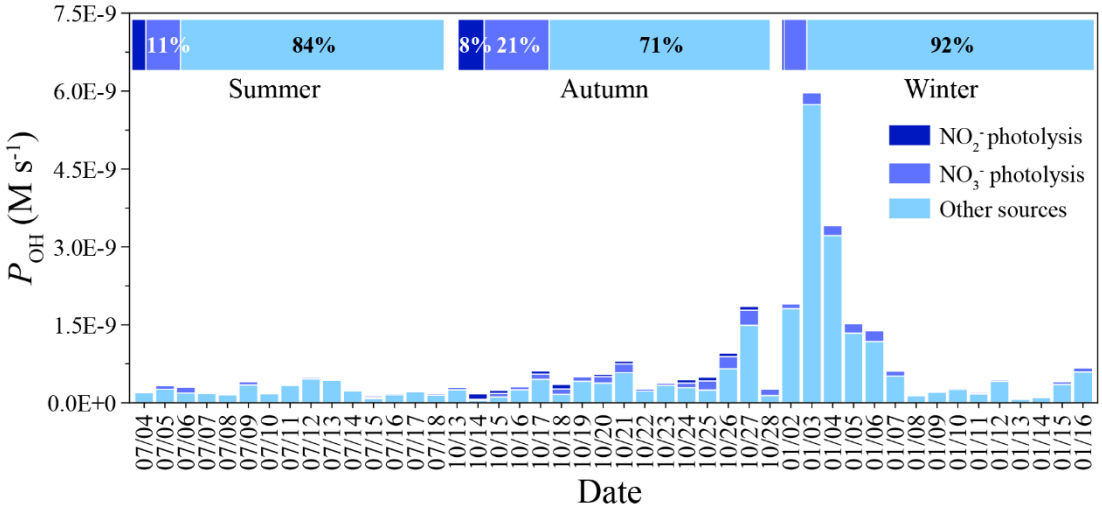


Figure S2. Seasonal concentration variations of water-soluble organic compounds (WSOC) in $PM_{2.5}$.



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49 **Figure S3.** Contributions of NO_2^- and NO_3^- photolysis to ·OH photoproduction rate

50 (P_{OH}, M·s^{-1}) in $PM_{2.5}$ extract in different seasons.

Table S1. Pseudo-first-order rate constants (*k'*) for the consumption of 2,6-dimethoxyphenol (SYR) and methyl jasmonate (MeJA) in photochemical oxidation experiments.

Probe	*k'*	Summer	Autumn	Winter
SYR	k'_{SYR} (s^{-1}) [a]	(1.00±0.35)×10^{-4}	(1.40±0.80)×10^{-4}	(4.42±4.87)×10^{-4}
	$k'_{SYR,\ OH}$ (s^{-1}) [b]	(4.29±1.15)×10^{-5}	(5.03±2.36)×10^{-5}	(4.86±3.03)×10^{-5}
	$k'_{SYR,\ 1O2*}$ (s^{-1}) [c]	(4.49±1.85)×10^{-6}	(1.49±0.45)×10^{-5}	(1.10±0.78)×10^{-4}
	$k'_{SYR,\ 3C*}$ (s^{-1}) [d]	(4.85±3.21)×10^{-5}	(7.09±8.15)×10^{-5}	(2.79±4.10)×10^{-4}
	$k'_{SYR,\ 3C*}$ /WSOC ($M^{-1}\cdot s^{-1}$)	0.073±0.041	0.098±0.090	0.269±0.332
MeJA	k'_{MeJA} (s^{-1}) [a]	(1.11±0.53)×10^{-5}	(1.97±0.88)×10^{-5}	(3.38±2.90)×10^{-5}
	$k'_{MeJA,\ OH}$ (s^{-1}) [b]	(1.11±0.30)×10^{-5}	(1.30±0.61)×10^{-5}	(1.25±0.78)×10^{-5}
	$k'_{MeJA,\ 1O2*}$ (s^{-1}) [c]	(7.49±0.31)×10^{-8}	(2.49±0.75)×10^{-7}	(1.84±1.30)×10^{-6}
	$k'_{MeJA,\ 3C*}$ (s^{-1}) [d]	- [e]	(6.25±6.48)×10^{-6}	(1.92±2.12)×10^{-5}
	$k'_{MeJA,\ 3C*}$ /WSOC ($M^{-1}\cdot s^{-1}$)	- [e]	0.0084±0.0063	0.0125±0.0050

[a] The experimentally measured pseudo-first-order rate constants for SYR and MeJA decay in photochemical oxidation experiments.

[b] The pseudo-first-order rate constants for probe reactions with ·OH radical. These values were calculated as the product of the second-order rate constants (k_{SYR+OH} and $k_{MeJA+OH}$) and the steady-state concentration of ·OH determined in Sect. 3.1.1.

[c] The pseudo-first-order rate constants for probe reactions with $^1O_2$*. These values were calculated as the product of the second-order rate constants ($k_{SYR+1O2}$ and $k_{MeJA+1O2*}$) and the steady-state concentration of $^1O_2$* determined in Sect. 3.1.2.

[d] The pseudo-first-order rate constants for SYR and MeJA reactions with ^{3}C*. Neglecting contributions from other oxidants, these were calculated as: $k'_{SYR,\ 3C*} = k'_{SYR} - k'_{SYR,\ OH} - k'_{SYR,\ 1O2*} - j_{SYR}$; $k'_{MeJA,\ 3C*} = k'_{MeJA} - k'_{MeJA,\ OH} - k'_{MeJA,\ 1O2*} - j_{MeJA}$.

[e] For summer samples, the calculated values of $k'_{MeJA,\ 3C*}$ were frequently negative; therefore, the contribution of ^{3}C* to MeJA consumption in summer samples was considered negligible.

Table S2. Correlation coefficients of air temperature (T), relative humidity (RH), and ozone (O_3) concentration with various components in $PM_{2.5}$.

r	**T**	**RH**	**O_3**
NO_3^-	-0.31	0.44*	-0.59***
WS-Fe	0.37*	0.39*	-0.075
WSOC	-0.052	-0.11	-0.28
levoglucosan	-0.63***	-0.060	-0.74***
cholesterol	-0.088	-0.044	-0.38*
phthalic acid	-0.091	0.25	-0.19
methylnitrocatechol	-0.78***	-0.19	-0.88***
cis-pinonic acid	0.76***	0.33	0.53***
2-methylerythritol	0.87***	0.43*	0.69***
3-hydroxyglutaric acid	0.86***	0.45*	0.67***

*$p \leq 0.05$，**$p \leq 0.01$，***$p \leq 0.001$

Table S3. Second-order rate constants (k) for reactions of typical anthropogenic and biogenic precursors with ·OH, $^1O_2$*, and ^{3}C*.

Precursors	k_{OH} ($M^{-1}\cdot s^{-1}$)		k_{1O2*} ($M^{-1}\cdot s^{-1}$)		k_{3C*} ($M^{-1}\cdot s^{-1}$)	
	Values	**References**	**Values**	**References**	**Values**	**References**
Anthropogenic organic precursors						
Phenol	1.6×10^{10}	(Kroflič et al., 2020)	2.9×10^{8}	(Li et al., 2023)	3.0×10^{8}	(Smith et al., 2015)
Resorcinol	5.8×10^{9}	(Smith et al., 2015)	2.0×10^{7}		7.1×10^{8}	
Hydroquinone	1.1×10^{10}		2.5×10^{7}		1.5×10^{9}	
Eugenol	2.6×10^{10}	(Sun et al., 2021)	3.6×10^{7}	(Tratnyek and Holgne, 1991)	3.6×10^{9}	(Kaur et al., 2019)
Vanillin	4.0×10^{8}	(Li et al., 2014)	3.5×10^{5}	(Machado et al., 1997)	1.9×10^{9}	(Ma et al., 2021)
Biogenic organic precursors						
Methyl jasmonate	6.7×10^{9}	(Richards-Henderson et al., 2014a)	6.0×10^{6}	(Richards-Henderson et al., 2014b)	2.5×10^{8}	(Richards-Henderson et al., 2014b)
Methyl salicylate	8.4×10^{9}		$<1.0\times10^{5}$		9.8×10^{8}	
Foliate acetate	8.6×10^{9}		3.9×10^{6}		1.1×10^{9}	
Cis-3-hexen-1-ol	5.3×10^{9}		2.5×10^{6}		6.7×10^{7}	
2-methyl-3-buten-2-ol	8.0×10^{9}		8.0×10^{5}		4.0×10^{7}	

Note: The second-order rate constants for reactions of each precursor with triplet excited organic matter were calculated as $k_{3C*}=\chi_{3C1*}\times k_{3C1*}+\chi_{3C2*}\times k_{3C2*}$. Given that the reactivity of ^{3}C* in the atmospheric $PM_{2.5}$ extracts in this study was equivalent to that of a mixture of 44% ^{3}DMB* and 56% ^{3}3MAP* (i.e., χ_{3C1}=44%, χ_{3C2}=56%), k_{3C1*} and k_{3C2*} represent the rate constants for reactions of each precursor with ^{3}DMB* and ^{3}3MAP*, respectively. For precursors lacking literature-reported rate constants with ^{3}3MAP*, the values were approximated using the rate constants with ^{3}DMB*.

References:

Kaur, R., Labins, J. R., Helbock, S. S., Jiang, W., Bein, K. J., Zhang, Q., and Anastasio, C.: Photooxidants from brown carbon and other chromophores in illuminated particle extracts, Atmos. Chem. Phys., 19, 6579-6594, https://doi.org/10.5194/acp-19-6579-2019, 2019.

Kroflič, A., Schaefer, T., Huš, M., Phuoc Le, H., Otto, T., and Herrmann, H.: OH radicals reactivity towards phenol-related pollutants in water: temperature dependence of the rate constants and novel insights into the [OH–phenol]˙ adduct formation, Phys. Chem. Chem. Phys., 22, 1324-1332, https://doi.org/10.1039/c9cp05533a, 2020.

Li, F., Zhou, S., Du, L., Zhao, J., Hang, J., and Wang, X.: Aqueous-phase chemistry of atmospheric phenolic compounds: A critical review of laboratory studies, Sci. Total Environ., 856, https://doi.org/10.1016/j.scitotenv.2022.158895, 2023.

Li, Y. J., Huang, D. D., Cheung, H. Y., Lee, A. K. Y., and Chan, C. K.: Aqueous-phase photochemical oxidation and direct photolysis of vanillin – a model compound of methoxy phenols from biomass burning, Atmos. Chem. Phys., 14, 2871-2885, https://doi.org/10.5194/acp-14-2871-2014, 2014.

Ma, L., Guzman, C., Niedek, C., Tran, T., Zhang, Q., and Anastasio, C.: Kinetics and Mass Yields of Aqueous Secondary Organic Aerosol from Highly Substituted Phenols Reacting with a Triplet Excited State, Environ. Sci. Technol., 55, 5772-5781, https://doi.org/10.1021/acs.est.1c00575, 2021.

Machado, Gomes, Campos, Terrones, Perez, Ruggiero, and Castellan.: Photoreactivity of lignin model compounds in the photobleaching of chemical pulps .2. Study of the

degradation of 4-hydroxy-3-methoxy-benzaldehyde and two lignin fragments induced by singlet oxygen, Journal of Photochemislry and photobiology, A: Chemistry, 99-106, https://doi.org/10.1016/s1010-6030(97)00161-5, 1997.

Richards-Henderson, N. K., Hansel, A. K., Valsaraj, K. T., and Anastasio, C.: Aqueous oxidation of green leaf volatiles by hydroxyl radical as a source of SOA: Kinetics and SOA yields, Atmos. Environ., 95, 105-112, https://doi.org/10.1016/j.atmosenv.2014.06.026, 2014a.

Richards-Henderson, N. K., Pham, A. T., Kirk, B. B., and Anastasio, C.: Secondary Organic Aerosol from Aqueous Reactions of Green Leaf Volatiles with Organic Triplet Excited States and Singlet Molecular Oxygen, Environ. Sci. Technol., 49, 268-276, https://doi.org/10.1021/es503656m, 2014b.

Smith, J. D., Kinney, H., and Anastasio, C.: Aqueous benzene-diols react with an organic triplet excited state and hydroxyl radical to form secondary organic aerosol, Phys. Chem. Chem. Phys., 17, 10227-10237, https://doi.org/10.1039/c4cp06095d, 2015.

Sun, Y., Chen, X., Liu, L., Xu, F., and Zhang, X.: Mechanisms and kinetics studies of the atmospheric oxidation of eugenol by hydroxyl radicals and ozone molecules, Sci. Total Environ., 770, https://doi.org/10.1016/j.scitotenv.2021.145203, 2021.

Tratnyek and Holgne: Oxidation of substituted phenols in the environment A QSAR analysis of rate constants for reaction with singlet oxygen, Applied & Environmental Microbiology, 3360–3367, 1991.