Supplementary Information

Section 1 Grey relational degree (GRD)

A grey system means that a system in which part of information is known and part of information is unknown. The fluorescence properties of WSOC are multifactor triggered results of concentrations, chemical compositions, and even co-existing ions of carbonate species in WSOC and could be seen as a grey system. The principle of grey relational analysis (GRA) is to estimate the similarity and degree of the compactness among factors based on the geometric shape of the different sequences. Grey relational degree (GRD) is calculated in GRA. To calculate GRD, references and comparison sequences should be selected and converted to the dimensionless format. The grey relational coefficients ξ of the series and grey relational degree are calculated as follows:

$$\xi_i(k) = \frac{\min_i \min_k |y(k)-x_i(k)| + \rho \max_i \max_k |y(k)-x_i(k)|}{|y(k)-x_i(k)| + \rho \max_i \max_k |y(k)-x_i(k)|} \quad (1)$$

$$GRD_i = \frac{1}{n}\sum_{k=1}^{n} \xi_i(k),\ k = 1,2,\dots,n \quad (2)$$

In which y is the reference sequence and x_i (i=1,2,3...) is the comparison sequences, ρ is the distinguishing coefficient always set as 0.5, ξ is the grey relational coefficients of individual sample of the series, and GRD_i is the grey relational degree calculated by the average of ξ_i (Qiu et al. 2012).

Section 2 Secondary organic carbon (SOC)

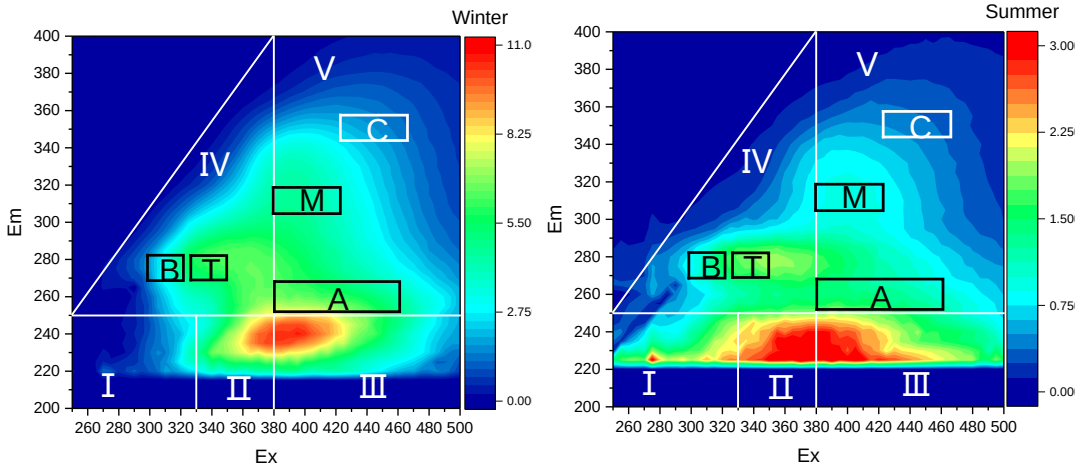
The SOC concentrations were calculated by the method proposed by Castro et al. (1999), as follows:

$$SOC = OC - EC \times (OC/EC)_{min} \quad (3)$$

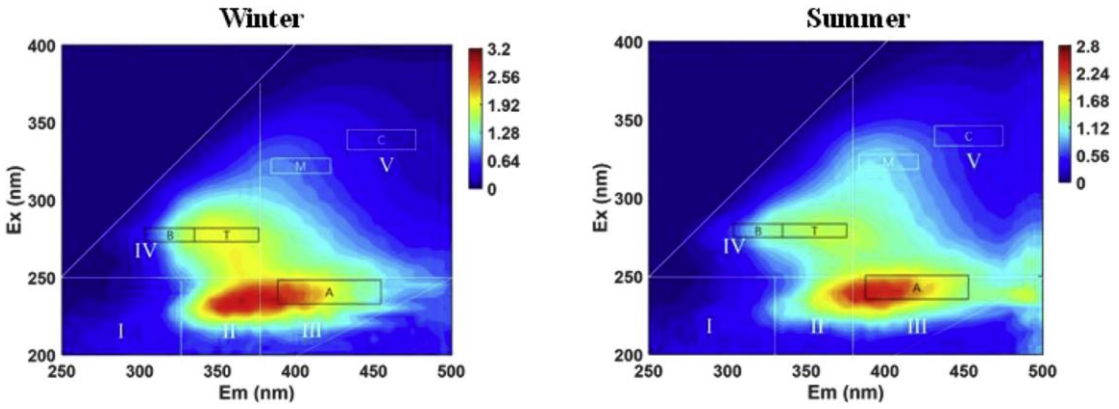
The results were used to examine the connections between grey relational degree and secondary processes.

Section 3 Figures

(a)



(b)



(c)

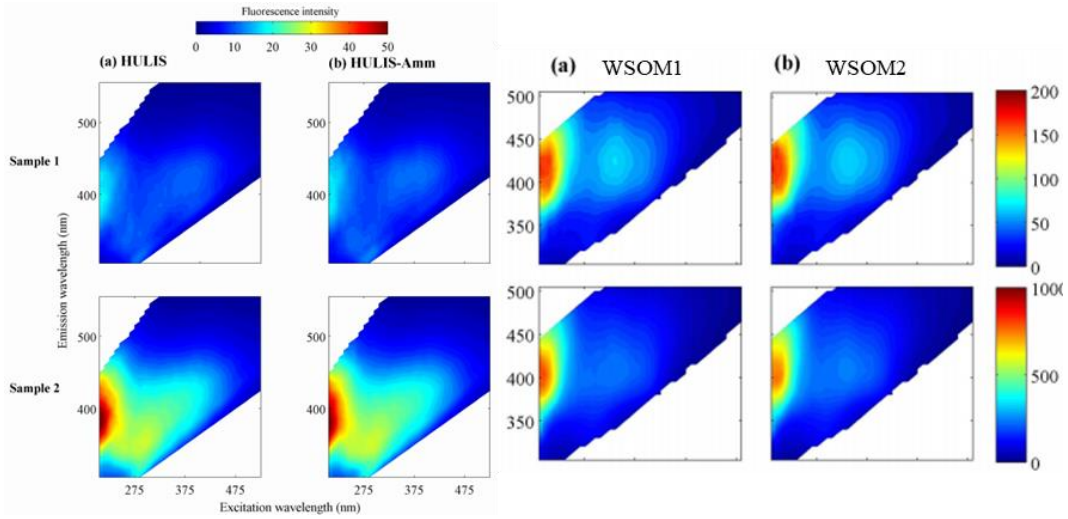


Figure S1 EEM spectra of present research and other studies. (a) The integrated EEM spectra of six-stage particles for winter and summer. (b) and (c) were the fluorophores in Chen et al.(2016) and Qin et al. (2018).

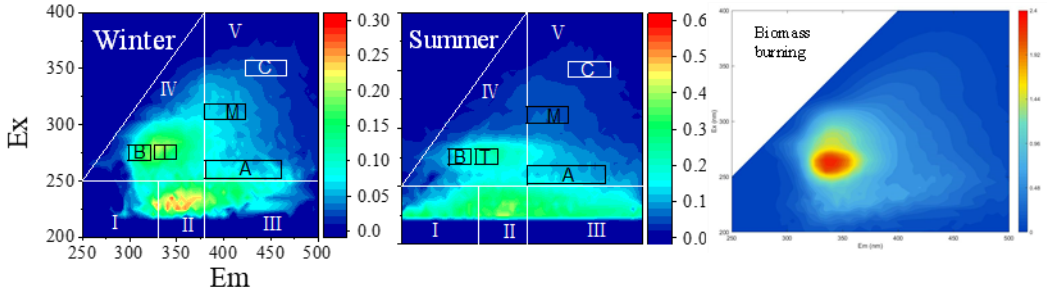


Figure S2 The EEM spectra of coarse mode particles in region IV were accordant with the fluorescence regions of biogenic sources.

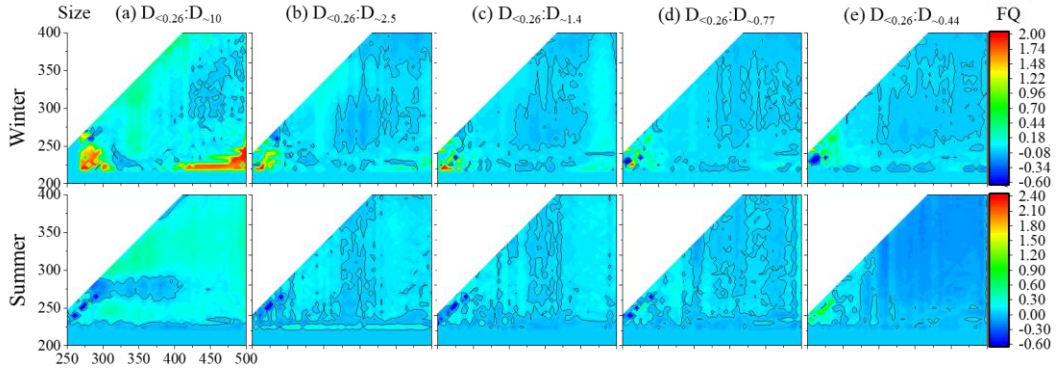


Figure S3 The fluorescence quotient among EEM of particle size < 0.26 μm and the particles larger than it. (a) $D_{<0.26}$:$D_{\sim0.44}$ (b) $D_{\sim0.44}$:$D_{\sim0.77}$ (c) $D_{\sim0.77}$:$D_{\sim1.4}$ (d) $D_{\sim1.4}$:$D_{\sim2.5}$ (e) $D_{\sim2.5}$:$D_{\sim10}$

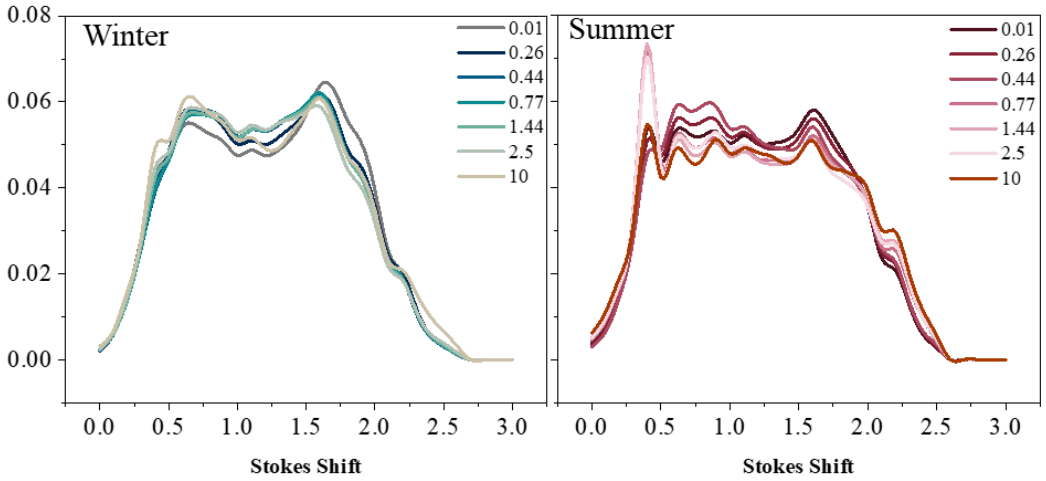


Figure S4 Stokes shift of fluorescent WSOC in different particle sizes. Hydrophobic fractions tend to have higher intensity in stokes shifts >1.2, possibly as a result of the larger scale of the π conjugated system or higher π-electron density. In contrast, hydrophilic contents (such as polysaccharides) usually have lower aromaticity and, hence, smaller π-conjugated systems.

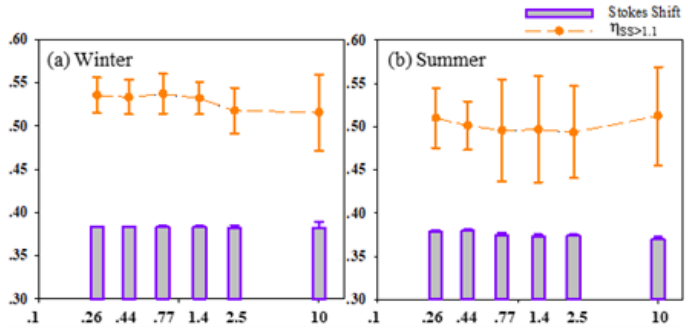


Figure S5 Some fluorescence indices that were not presented in our article. (a) and (b) were the size distribution of average fluorescence intensity of SS (purple bars) and $\eta_{SS>1.1}$ (orange lines) for winter and summer, respectively.

Section 4 Comparison of Pearson correlation analysis and grey relational analysis (GRA) results

In the manuscript file, we performed grey relational analysis to uncover the underlying connections between WSOC and AFI. Since the fluorescence was generated by part of WSOC, it was conjectured that the AFI and WSOC could be present by mathematical method. We tried the

correlation analysis firstly in Table S 1. The WSOC (and AFI) of particles <0.26 μm significantly correlated with that of larger particles both in winter and summer. However, the relations between WSOC and AFI were not significant, especially in winter, which was out of the expectation. A possible explanation was that the miscellaneous WSOC in different particles sizes might lead to fortuitous fluorescence intensities.

GRA could reflect the fellowship of factors to the reference line. The relations between WSOC and AFI (Table S 1 (c) on the right) were strong in both seasons. Besides, the GRD variation patterns of decrease first and then increase for six particle size stages were just in contrast to that of humification factors, $\eta_{WH>320,}$ and other fluorescence indices. GRD was negatively correlated with SOC (p<0.01).

Table S 1 The grey relational degree of WSOC and AFI between six particle sizes.

		Pearson correlation			Grey relational analysis		
	μm	a	b	c	a	b	c
Winter	0.26	1	1	0.129	1.000	1.000	0.950
	0.44	0.947**	0.429	0.020	0.883	0.824	0.871
	0.77	0.787**	0.724**	0.335	0.833	0.879	0.933
	1.4	0.591*	0.399	0.596*	0.766	0.830	0.928
	2.5	0.637*	-0.141	0.875**	0.771	0.779	0.974
	10	0.461	0.567*	0.664*	0.808	0.840	0.982
Summer	0.26	1	1	0.854**	1.000	1.000	0.930
	0.44	0.990**	0.943**	0.975**	0.656	0.700	0.853
	0.77	0.956**	0.920**	0.874**	0.612	0.720	0.929
	1.4	0.946**	0.825*	0.687	0.672	0.720	0.921
	2.5	0.647	0.827*	0.225	0.645	0.750	0.922
	10	0.793*	0.635	0.739*	0.577	0.641	0.948

** Correlation is significant at the 0.01 level.

* Correlation is significant at the 0.05 level.

a. GRA was performed by setting WSOC of 0.26 μm as references and the rest particle sizes as a comparison.

b. GRA was performed by setting AFI of 0.26 μm as references and the rest of particle sizes as a comparison.

c. GRA was performed by setting WSOC of each particle size as references and corresponding AFI as a comparison.

References

Chen, Q C, F Ikemori and M Mochida, 2016. Light Absorption and Excitation-Emission Fluorescence of Urban Organic Aerosol Components and Their Relationship to Chemical Structure. Environ. Sci. Technol. 50: 10859-10868.

Qin, J, L Zhang, X Zhou, et al., 2018. Fluorescence fingerprinting properties for exploring water-soluble organic compounds in PM 2.5 in an industrial city of northwest China. Atmos. Environ. 184: 203-211.

Qiu, B., Wang, F., Li, Y. and Zuo, W.: Research on method of simulation model validation based

on improved grey relational analysis, Phys. Pro., 25, 1118-1125, https://doi.org/10.1016/j.phpro.2012.03.208, 2012.