Light Absorption Properties and Composition of Brown carbon in North China Plain: Implication for an Enhancing Role of Nitrogenous Organic Compounds

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Text S1 Positive Matrix Factorization (PMF) source apportionment

PMF, as a receptor model, decomposes the sample matrix into two matrices (factor contributions and factor profiles), and has been widely used in source apportionment of atmospheric pollutants (Wu et al., 2024; Li et al., 2023). Details regarding the PMF model are available on the EPA website (https://www.epa.gov/air-research/epa-positive-matrix-factorization-50-fundamentals-and-user-guide, last access: 16 May 2025). Herein, the EPA PMF 5.0 was employed to conduct source apportionment of organic matter (OM), with input parameters including the mass concentrations of major species (OM, EC, WSOC, NO_3^-, NH_4^+, Mg^{2+}, Ca^{2+}, WSOC, NACs), and organic markers (benzo(b)fluoranthene (BbF), benzo(e)pyrene (BeP),indeno(1,2,3-c,d)pyene (IP), levoglucosan). The samples from all the sampling sites were added together as one data matrix, and the model was run numerous times with 3–7 factors to obtain the optimal solution. Base on the Q value (Q true:14982 and Q robust:14478) and interpretability, three factors were obtained as the optimal solution, which are indicative of a strong correlation between input species and simulated ones (R^2>0.83).

Text S2 Estimation of secondary WSON

To quantify the relative contributions of the primary emission and secondary formation to the particulate WSON, a tracer method analogous to the EC-based approach commonly used for secondary organic carbon was employed here. The equation is as follow:

$$\mathrm{WSONsec}=\mathrm{WSON}-\left[\frac{\mathrm{WSON}}{\mathrm{EC}}\right]_{\mathrm{pri}}\times\mathrm{EC} \qquad \text{S1}$$

Here, WSON, WSONsec and EC denote the mass concentrations of the particle-phase WSON, secondary WSON and EC, respectively. Herein, EC serves as the tracer of the combustion source. $[\frac{WSON}{EC}]_{pri}$ is estimated by fitting the lowest 15% of $[\frac{WSON}{EC}]$ data points. Above method was further extended to estimate the secondary NACs in the present study.

Text S3 Theoretical estimation of chemical forms of SNA

To reveal the major SNA forms during the sampling period, the theoretical ammonium concentration was calculated according to thermodynamic equilibrium with the atmospheric sulfate and nitrate levels. The theoretical ammonium levels were calculated as follows:

$$NH_4^+{}_{calculate}=(\frac{[SO_4^{2-}]}{48}+\frac{[NO_3^-]}{62})\times 18 \quad S2$$

$$NH_4^+{}_{calculate}=(\frac{[SO_4^{2-}]}{96}+\frac{[NO_3^-]}{62})\times 18 \quad S3$$

where $[SO_4^{2-}]$ and $[NO_3^-]$ refer to atmospheric concentrations measured in μg/m^3. The $NH_4^+{}_{calculate}$ is achievable through Equation (5) if $(NH_4)_2SO_4$ and NH_4NO_3 serve as the dominant species. Conversely, equation (6) demonstrates that NH_4HSO_4 and NH_4NO_3 are abundantly present in the analyzed aerosols.

Text S4 Aerosol liquid water content (ALWC), in-situ pH and gas-to-particle-phase partitioning coefficient of ammonia

A robust thermodynamic model (ISORROPIA-II) was employed to theoretically estimate the aerosol liquid water content (ALWC) and in-situ pH in $PM_{2.5}$, which has been widely used in previous studies (Song et al., 2018; Pye et al., 2020). By combining the actual temperature (T) and relative humidity (RH) in the atmosphere and the water-soluble ions composition, the ALWC and H^+ loads can be simulated by running the model under the metastable mode. And the in-situ pH can be calculated by Eq. S2.

$$pH=\frac{[H^+]\times 1000}{ALWC} \quad S4$$

Where the units for H^+ and ALWC are the μg m^{-3}. Gaseous ammonia was not detected in this study, thus, which may lead to overestimation of aerosol acidity. Furthermore, the gas-to-particle-phase partitioning coefficient of ammonia (ε_{NH4+}) was theoretically calculated following the method reported by Nah et al. (2018) and Guo et al. (2017):

$$\varepsilon\left(NH_4^+\right)\cong\frac{\frac{\gamma_{H^+}10^{-pH}}{\gamma_{NH_4^+}}H^*_{NH_3}ALWC\times R\times T\times 0.987\times 10^{-14}}{1+\frac{\gamma_{H^+}10^{-pH}}{\gamma_{NH_4^+}}H^*_{NH_3}ALWC\times R\times T\times 0.987\times 10^{-14}} \quad \text{S5}$$

$$\ln\left(H^*_{NH_3}\right)=25.393-10373.6\left(\frac{1}{T_r}-\frac{1}{T}\right)+4.131\left(\frac{T_r}{T}-\left(1+\ln\left(\frac{T_r}{T}\right)\right)\right) \quad \text{S6}$$

Here, γ_{H^+} and $\gamma_{NH_4^+}$ are the activity coefficients of H^+ and NH_4^+, respectively; and both were assumed to be 1 in this study. $H^*_{NH_3}$ is equilibrium constant calculated by Eq S4; R is the gas constant. For the the ε_{NH4+} calculation, the pH value was adjusted slightly, while parameters adopted the average values obtained during the campaign.

Table S1 Information of nitroaromatic compounds detected in this study.

Compounds	Molecular	Formula	CAS number	Abbreviation
4-Nitrophenol	139.11	$C_6H_5NO_3$	100-02-7	4NP
3-Methoxy-4-nitrophenol	153.14	$C_7H_7NO_3$	2581-34-2	3M4NP
2, 4-Dinitrophenol	184.11	$C_6H_4N_2O_5$	51-28-5	2,4DNP
4-Nitroguaiacol	169.14	$C_7H_7NO_4$	3251-56-7	4NGA
5-Nitroguaiacol	169.14	$C_7H_7NO_4$	636-93-1	5NGA
4-Nitrocatechol	155.11	$C_6H_5NO_4$	59030-13-6	4NC
4-Methyl-5-nitrocatechol	169.13	$C_7H_7NO_4$	68906-21-8	4M5NC
3-Nitrosalicylic acid	183.12	$C_7H_5NO_5$	85038-1	3NSA
5-Nitrosalicylic acid	183.12	$C_7H_5NO_5$	96-97-9	5NSA

Table S2 Statistical metrics for evaluation of RF model performance

Statistical metrics	
R^2	0.94
MSE	0.024
RMSE	0.16
MAE	0.1

Note: MSE: mean square error; RMSE: root-mean-square error; MAE: mean absolute error.

Table S3 The abs_{365} and MAE_{365} of water-soluble BrC in $PM_{2.5}$ among different cities in the world.

Location	Year	abs_{365} (Mm^{-1})	MAE ($m^2\ g^{-1}$)	Reference
Beijing	2011	10.2±6.9	1.22±0.11	Cheng et al. (2016)
	2013	14±5.2	1.54±0.16	Yan et al. (2015)
	2018	12.5	1.2	Li et al. (2020b)
	2021	3.5±3.4	1.1±0.4	You et al. (2024)
	2023	2.3±1.9	0.7±0.5	This study
Tianjin	2018	7.9±5	1.04±0.3	Chen et al. (2024)
	2020	7.5±5	1.27±0.3	
	2023	5.7±3.8	1.12±0.05	This study
Handan	2018	16.8±2.7	1.22±0.3	Chen et al. (2024)
	2020	11.1±2.3	1.1±0.27	
	2023	8.2±5.0	1.05±0.02	This study

Jinnan	2014	10.3±6.5	0.88±0.4	Shi et al. (2023)
	2018	5.42	0.65	Zhang et al. (2022)
	2023	6.9±3	1.4±0.02	This study
Nanjing	2018	9.47±5.83	1.27±0.34	Bao et al. (2022)
	2020	3.12±2.41	0.58±0.26	Feng et al. (2023)
	2021	4.73±1.97	1.23±0.26	Cui et al. (2025)
	2023	3.73±2.46	0.62±0.18	Zhou et al. (2025)
Xi'an	2012	22.6±12.3	1.31±0.4	Lei et al. (2023)
	2016	28±16	1.2±0.06	Wu et al. (2020)
	2018	17.8±9.6	2.0±0.6	Li et al. (2020a)
	2021	6.7±1.4	0.83±0.22	Wang et al. (2025)
Guangzhou	2012	3.57±1.34	0.81±0.16	Liu et al. (2018)
	2016	5.8	0.98	He et al. (2023)
	2018	2.5±2	1±0.21	Zou et al. (2023)
	2019	4.3	0.34	Wang et al. (2022)
Seoul, Korea	2012	7.31	1.02	Kim et al. (2016)
Leipzig, Germany	2014	3.91±2.5		Teich et al. (2017)
Milan, Italy	2016	3.0±1.3		Gilardoni et al. (2020)
Pasadena, USA*	2010	0.88±0.71	0.77	Zhang et al. (2011)
Atlanta, USA*	2010	0.61±0.38	1.15	
Southeastern US*	2013	0.42±0.43	0.84±0.37	Xie et al. (2019)

Note: * indicates the samples collected in summer

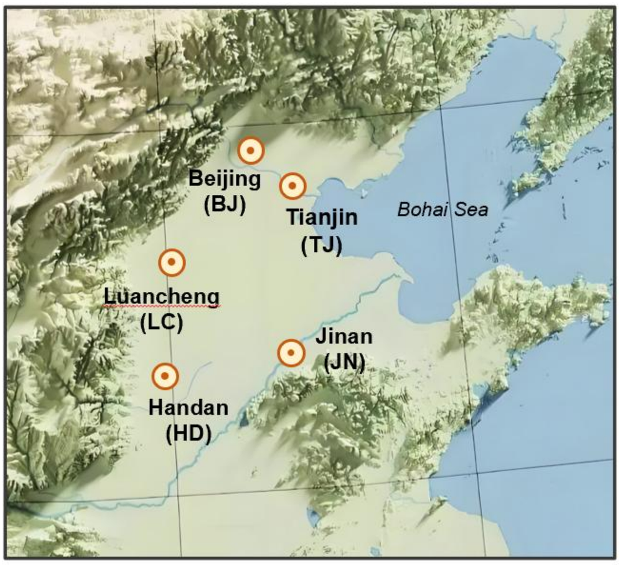

Figure S1 Topographic distribution the sampling sites in the NCP. (The maps are the reproductions from ©Baidu (https://image.baidu.com/, last access: 16 July 2025))

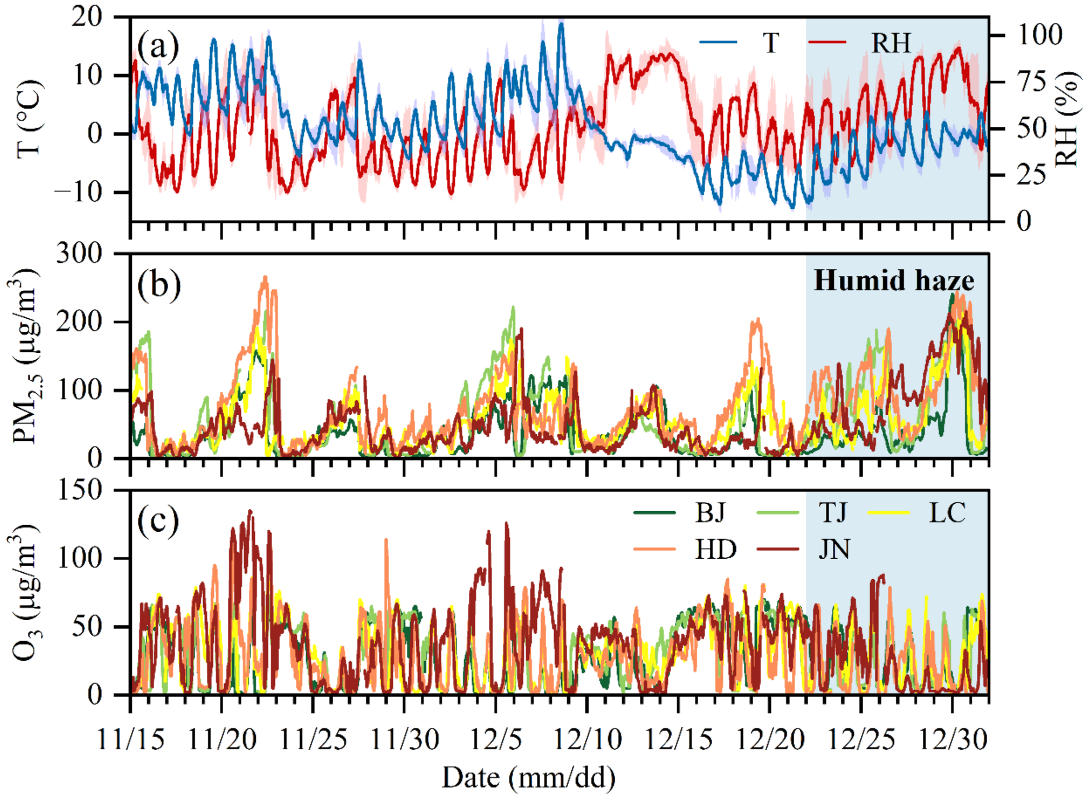

Figure S2 Temporal variations of meteorological factors, $PM_{2.5}$ and O_3 at five sampling sites. (The shade indicates the humid haze event.)

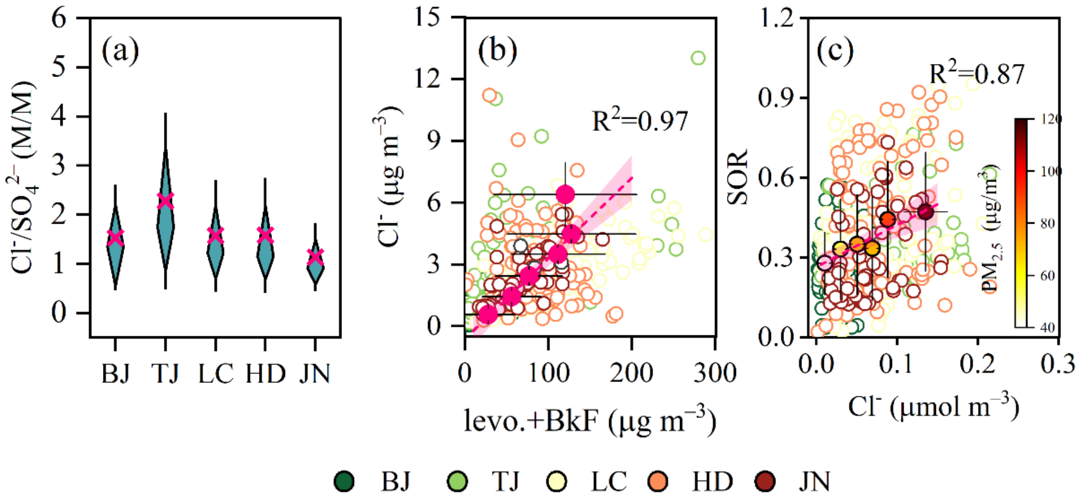

Figure S3 The source of the abundant chloride across the NCP and its effect on sulfate formation. **(a)** Molar ratio of Cl^- and SO_4^{2-}; Linear fit regression for Cl^- with BbF+ levoglucosan (b) and SOR **(c)**.

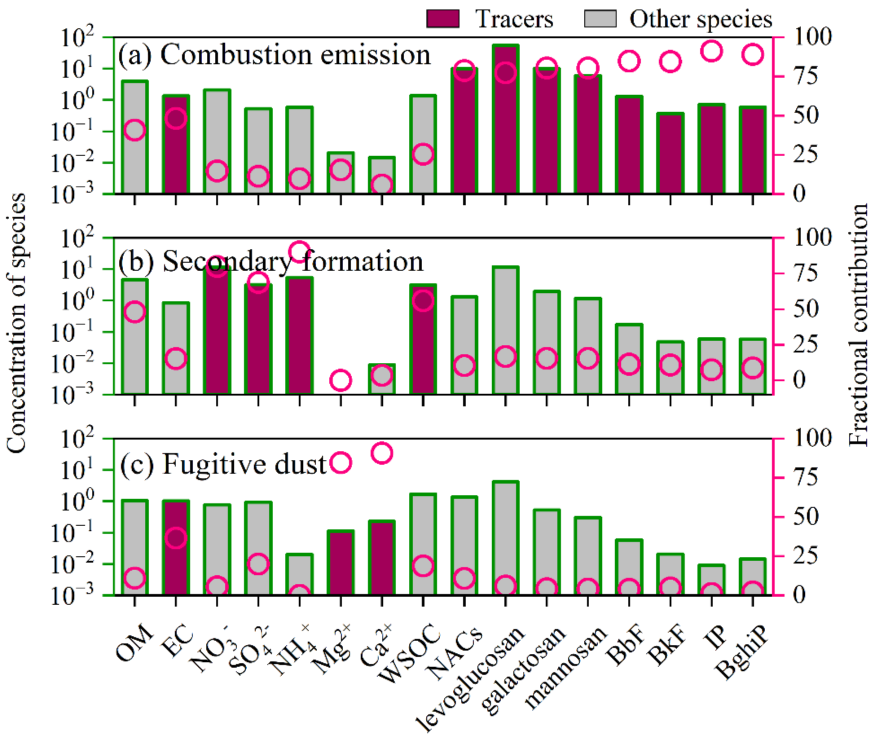

Figure S4 Source apportionment for OM at five sampling sites during the campaign.

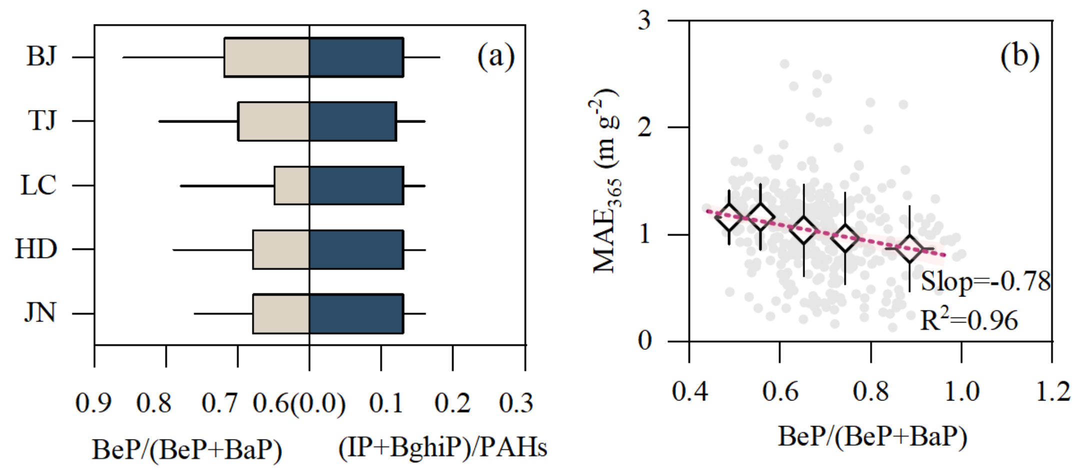

Figure S5 BeP/(Bep+Bap) and (IP+BghiP)/PAHs ratios at all the sampling sites **(a)**; Dependence of MAE_{365} on BeP/(Bep+Bap) across the NCP **(b)**.

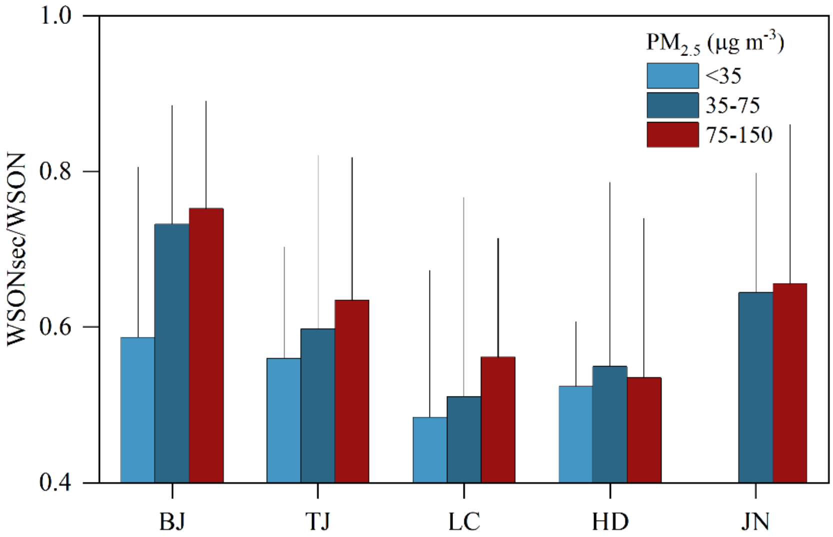

Figure S6 Comparison of the percentage of WSONsec in the total under different $PM_{2.5}$ loads.

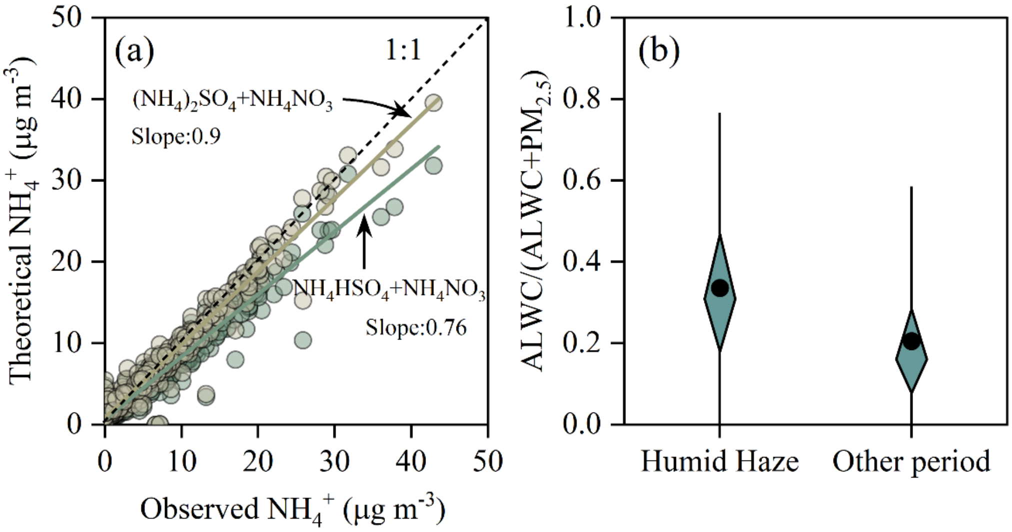

Figure S7 Comparison of the calculated and observed NH_4^+concentrations across the NCP **(a)**; The ALWC/(ALWC+$PM_{2.5}$) ratio at different periods **(b)**.

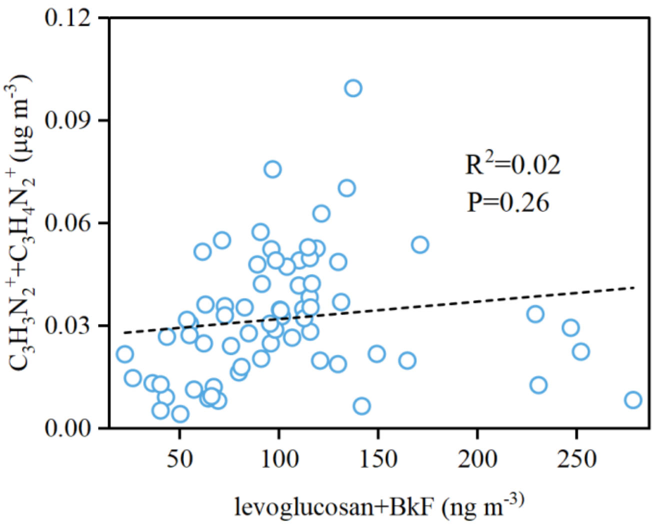

Figure S8 Scattering plot of Ims-related fragments versus levoglucosan+BkF

Reference

Bao, M. Y., Zhang, Y. L., Cao, F., Lin, Y. C., Hong, Y. H., Fan, M. Y., Zhang, Y. X., Yang, X. Y., and Xie, F.: Light absorption and source apportionment of water soluble humic-like substances (HULIS) in PM2.5 at Nanjing, China, Environmental Research, 206, 10.1016/j.envres.2021.112554, 2022.

Chen, H. B., Zhou, R. Z., Fang, L., Sun, H. L., Yang, Q. Y., Niu, H. Y., Liu, J. W., Tian, Y. Z., Cui, M., and Yan, C. Q.: Variations in optical properties of water- and methanol-soluble organic carbon in PM 2.5 in Tianjin and Handan over the Wintertime of 2018-2020, Atmospheric Research, 303, 10.1016/j.atmosres.2024.107332, 2024.

Cheng, Y., He, K. B., Du, Z. Y., Engling, G., Liu, J. M., Ma, Y. L., Zheng, M., and Weber, R. J.: The characteristics of brown carbon aerosol during winter in Beijing, Atmospheric Environment, 127, 355-364, 10.1016/j.atmosenv.2015.12.035, 2016.

Cui, W. N., Wang, Z. S., Feng, W., Qin, C., Liao, H., Wang, Y. H., and Xie, M. J.: Evaluating coarse PM composition and sources based on bulk and molecular speciation of PM2.5 and PM10 in Nanjing, East China, Journal of Environmental Sciences, 152, 155-166, 10.1016/j.jes.2024.04.038, 2025.

Feng, W., Wang, X. Y., Shao, Z. J., Liao, H., Wang, Y. H., and Xie, M. J.: Time-Resolved Measurements of PM2.5 Chemical Composition and Brown Carbon Absorption in Nanjing, East China: Diurnal Variations and Organic Tracer-Based PMF Analysis, Journal of Geophysical Research-Atmospheres, 128, 10.1029/2023jd039092, 2023.

Gilardoni, S., Massoli, P., Marinoni, A., Mazzoleni, C., Freedman, A., Lonati, G., De Iuliis, S., and Gianelle, V.: Spatial and Temporal Variability of Carbonaceous Aerosol Absorption in the Po Valley, Aerosol and Air Quality Research, 20, 2624-2639, 10.4209/aaqr.2020.03.0085, 2020.

Guo, H. Y., Liu, J. M., Froyd, K. D., Roberts, J. M., Veres, P. R., Hayes, P. L., Jimenez, J. L., Nenes, A., and Weber, R. J.: Fine particle pH and gas-particle phase

partitioning of inorganic species in Pasadena, California, during the 2010 CalNex campaign, Atmospheric Chemistry and Physics, 17, 5703-5719, 10.5194/acp-17-5703-2017, 2017.
He, T., Wu, Y., Wang, D., Cai, J., Song, J. Z., Yu, Z. Q., Zeng, X. Y., and Peng, P.: Molecular compositions and optical properties of water-soluble brown carbon during the autumn and winter in Guangzhou, China, Atmospheric Environment, 296, 10.1016/j.atmosenv.2022.119573, 2023.
Kim, H., Kim, J. Y., Jin, H. C., Lee, J. Y., and Lee, S. P.: Seasonal variations in the light-absorbing properties of water-soluble and insoluble organic aerosols in Seoul, Korea, Atmospheric Environment, 129, 234-242, 10.1016/j.atmosenv.2016.01.042, 2016.
Lei, Y. L., Zhang, K., Lu, Y. Y., Qin, Y. M., Li, L. J., Li, J. J., Liu, X. D., Wu, C., Zhang, S., Chen, Y. B., Zhang, J. K., Zhang, F., and Wang, G. H.: Characterization of water-soluble brown carbon in atmospheric fine particles over Xi'an, China: Implication of aqueous brown carbon formation from biomass burning, Science of the Total Environment, 881, 10.1016/j.scitotenv.2023.163442, 2023.
Li, D. P., Wu, C., Zhang, S., Lei, Y. L., Lv, S. J., Du, W., Liu, S. J., Zhang, F., Liu, X. D., Liu, L., Meng, J. J., Wang, Y. S., Gao, J., and Wang, G. H.: Significant coal combustion contribution to water-soluble brown carbon during winter in Xingtai, China: Optical properties and sources, Journal of Environmental Sciences, 124, 892-900, 10.1016/j.jes.2022.02.026, 2023.
Li, J. W., Chen, Q. C., Hua, X. Y., Chang, T., and Wang, Y. Q.: Occurrence and sources of chromophoric organic carbon in fine particulate matter over Xi'an, China, Science of the Total Environment, 725, 10.1016/j.scitotenv.2020.138290, 2020a.
Li, X. R., Yang, Y., Liu, S. Q., Zhao, Q., Wang, G. H., and Wang, Y. S.: Light absorption properties of brown carbon (BrC) in autumn and winter in Beijing: Composition, formation and contribution of nitrated aromatic compounds, Atmospheric Environment, 223, 10.1016/j.atmosenv.2020.117289, 2020b.
Liu, J. W., Mo, Y. Z., Ding, P., Li, J., Shen, C. D., and Zhang, G.: Dual carbon isotopes (14C and 13C) and optical properties of WSOC and HULIS-C during winter in Guangzhou, China, Science of the Total Environment, 633, 1571-1578, 10.1016/j.scitotenv.2018.03.293, 2018.
Nah, T., Guo, H. Y., Sullivan, A. P., Chen, Y. L., Tanner, D. J., Nenes, A., Russell, A., Ng, N. L., Huey, L. G., and Weber, R. J.: Characterization of aerosol composition, aerosol acidity, and organic acid partitioning at an agriculturally intensive rural southeastern US site, Atmospheric Chemistry and Physics, 18, 11471-11491, 10.5194/acp-18-11471-2018, 2018.
Pye, H. O. T., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett, J. L., Fahey, K. M., Hennigan, C. J., Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I. T., McNeill, V. F., Riemer, N., Schaefer, T., Shi, G. L., Tilgner, A., Walker, J. T., Wang, T., Weber, R., Xing, J., Zaveri, R. A., and Zuend, A.: The acidity of atmospheric particles and clouds, Atmospheric Chemistry and Physics, 20, 4809-4888, 10.5194/acp-20-4809-2020, 2020.
Shi, X. Y., Zhang, J. Z., Zhou, X. H., Cao, Z. Y., Luo, Y. Y., and Wang, W. X.:

Wintertime characteristics of water-soluble organic carbon in PM2.5 during haze and non-haze days in Jinan in the North China Plain, Atmospheric Environment, 310, 10.1016/j.atmosenv.2023.119985, 2023.

Song, S. J., Gao, M., Xu, W. Q., Shao, J. Y., Shi, G. L., Wang, S. X., Wang, Y. X., Sun, Y. L., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmospheric Chemistry and Physics, 18, 7423-7438, 10.5194/acp-18-7423-2018, 2018.

Teich, M., van Pinxteren, D., Wang, M., Kecorius, S., Wang, Z. B., Müller, T., Mocnik, G., and Herrmann, H.: Contributions of nitrated aromatic compounds to the light absorption of water-soluble and particulate brown carbon in different atmospheric environments in Germany and China, Atmospheric Chemistry and Physics, 17, 1653-1672, 10.5194/acp-17-1653-2017, 2017.

Wang, D. W., Shen, Z. X., Zhang, Q., Lei, Y. L., Zhang, T., Huang, S. S., Sun, J., Xu, H. M., and Cao, J. J.: Winter brown carbon over six of China's megacities: light absorption, molecularcharacterization, and improved source apportionment revealed by multilayerperceptron neural network, Atmospheric Chemistry and Physics, 22, 14893-14904, 10.5194/acp-22-14893-2022, 2022.

Wang, D. W., Shen, Z. X., Bai, G. Z., Zhang, L. M., Huang, S. S., Zheng, H. H., Li, C. L., Sun, J., Xu, H. M., and Cao, J. J.: Oxidized Nitrogen-Containing Organic Compounds Formation Enhanced the Light Absorption of PM2.5 Brown Carbon, Journal of Geophysical Research-Atmospheres, 130, 10.1029/2024jd042960, 2025.

Wu, C., Liu, X., Zhang, K., Zhang, S., Cao, C., Li, J., Li, R., Zhang, F., and Wang, G.: Measurement report: Formation of tropospheric brown carbon in a lifting air mass, Atmospheric Chemistry and Physics, 24, 9263-9275, 10.5194/acp-24-9263-2024, 2024.

Wu, C., Wang, G. H., Li, J., Li, J. J., Cao, C., Ge, S. S., Xie, Y. N., Chen, J. M., Li, X. R., Xue, G. Y., Wang, X. P., Zhao, Z. Y., and Cao, F.: The characteristics of atmospheric brown carbon in Xi'an, inland China: sources, size distributions and optical properties, Atmospheric Chemistry and Physics, 20, 2017-2030, 10.5194/acp-20-2017-2020, 2020.

Xie, M. J., Chen, X., Holder, A. L., Hays, M. D., Lewandowski, M., Offenberg, J. H., Kleindienst, T. E., Jaoui, M., and Hannigan, M. P.: Light absorption of organic carbon and its sources at a southeastern US location in summer, Environmental Pollution, 244, 38-46, 10.1016/j.envpol.2018.09.125, 2019.

Yan, C. Q., Zheng, M., Sullivan, A. P., Bosch, C., Desyaterik, Y., Andersson, A., Li, X. Y., Guo, X. S., Zhou, T., Gustafsson, Ö., and Collett, J. L.: Chemical characteristics and light-absorbing property of water-soluble organic carbon in Beijing: Biomass burning contributions, Atmospheric Environment, 121, 4-12, 10.1016/j.atmosenv.2015.05.005, 2015.

You, B., Zhang, Z. Q., Du, A. D., Li, Y., Sun, J. X., Li, Z. J., Chen, C., Zhou, W., Xu, W. Q., Lei, L., Fu, P. Q., Hou, S. J., Li, P., and Sun, Y. L.: Seasonal characterization of chemical and optical properties of water-soluble organic aerosol in Beijing, Science of the Total Environment, 930, 10.1016/j.scitotenv.2024.172508, 2024.

Zhang, J. M., Qi, A. A., Wang, Q. H., Huang, Q., Yao, S., Li, J. X., Yu, H., and Yang, L. X.: Characteristics of water-soluble organic carbon (WSOC) in PM2.5 in inland and coastal cities, China, Atmospheric Pollution Research, 13, 10.1016/j.apr.2022.101447, 2022.

Zhang, X. L., Lin, Y. H., Surratt, J. D., Zotter, P., Prévôt, A. S. H., and Weber, R. J.: Light-absorbing soluble organic aerosol in Los Angeles and Atlanta: A contrast in secondary organic aerosol, Geophysical Research Letters, 38, 10.1029/2011gl049385, 2011.

Zhou, B. H., Huang, Y., Feng, L. Y., Zhang, Z. H., Li, H. W., Wu, Y., Ye, J. H., and Ge, X. L.: Optical Properties and Molecular Composition of Fine Organic Aerosols in Nanjing, China: A Comparison of 2019 and 2023, Toxics, 13, 10.3390/toxics13060443, 2025.

Zou, C. L., Cao, T., Li, M. J., Song, J. Z., Jiang, B., Jia, W. L., Li, J., Ding, X., Yu, Z. Q., Zhang, G., and Peng, P.: Measurement report: Changes in light absorption and molecular composition ofwater-soluble humic-like substances during a winter haze bloom-decay processin Guangzhou, China, Atmospheric Chemistry and Physics, 23, 963-979, 10.5194/acp-23-963-2023, 2023.