Reply to Anonymous Referee #1

We thank Anonymous Referee #1 for the valuable comments on our manuscript. Here we provide point-to-point responses to the Referees' comments. For clarity, the Referees' comments are marked in black, authors' responses are marked in **blue**, and changes in the manuscript are marked in **red**.

This manuscript presents a comprehensive investigation into the chemical composition and sources of aerosols over the Bohai Sea (BS) and Yellow Sea (YS) during summer. The study effectively combines field observations, advanced analytical techniques (including high-resolution mass spectrometry and stable carbon isotope analysis), and receptor modeling to demonstrate the dominant influence of coastal terrestrial emissions, particularly biomass burning, on the aerosol properties of these marginal seas, even under conditions of increased marine air mass influence. The topic is relevant and the conclusions are well-supported by the data. The manuscript is generally well-structured, and the methods are appropriately described. The findings contribute valuable insights to the understanding of land-sea interactions in polluted coastal environments. I recommend publication after addressing the following minor revisions to enhance clarity and impact.

Specific Comments:

1. Line 16: The authors wrote "The characteristics of carbon component ratios in aerosols are similar to those in coastal cities", it is better to provide the exact values.

Author reply:

We have added the necessary OC/EC and WSOC/OC ratios in the Abstract. Moreover, the carbon component ratios of coastal cities reported in the literature are presented in Table S2 of the Supplement.

This was updated in the revised manuscript at Page 1, Line 16–18:

The characteristics of carbon component ratios (mean: 5.58–12.11 for OC/EC, 0.48–0.58 for WSOC/OC) in aerosols are similar to those in coastal cities, and the proportion

of non–sea–salt ions (> 80%) is significantly higher than that of sea salt ions.

2. In Figure 1, Panel A the running time of the backward trajectories should provided. Panel B full name of the acronyms should be given in the caption, the X-axis title should be added. Panel D is confusing and misleading; the four components should not be placed together.

Author reply:

In order to solve the confusion and ambiguity observed in Figure 1, we have added the full name of acronyms and corresponding axis titles in Panel B, redrawn Panel D, and added the running time of the backward trajectory to the figure caption.

The modified Figure 1 is as follows:

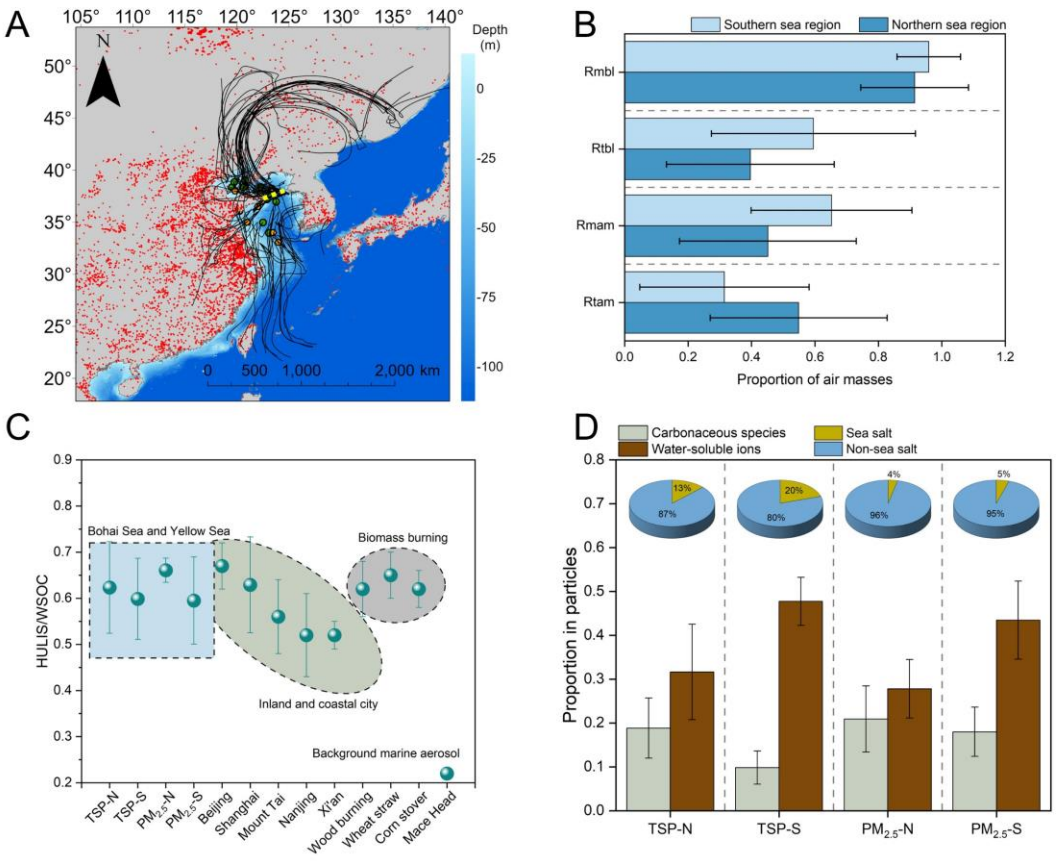

Figure 1. (A) Trajectories of air masses arriving at the Yellow Sea and Bohai Sea during the sampling period. The simulated air mass transport time is 72 hours. Green, yellow and red points represent TSP, $PM_{2.5}$ samples and fire points, respectively. Fire point information comes from https://firms.modaps.eosdis.nasa.gov/map. The yellow dashed line represents the boundary between the northern and southern sea regions. (B) Retention ratio of air masses over land and

ocean, as well as the retention ratio of boundary layer air masses. Rmbl stands for Retention ratio of marine boundary layer air masses, Rtbl stands for Retention ratio of terrestrial boundary layer air masses, Rmam stands for Retention ratio of marine air masses and Rtam stands for Retention ratio of terrestrial air masses. (C) Differences in HULIS/WSOC ratio at different sampling points. (D) Proportion of carbonaceous species and water–soluble ions in particles. The pie charts represent the proportion of sea salt ions and non–sea salt ions in the total ions of each sea region. N and S indicate the northern and southern sea regions, respectively.

3. In Figure 2, The gray circle should change to "The gray circular surface in Panel A".

Author reply:

We have modified the description of the assumed boundary layer in the caption of Figure 2.

The gray circular surface in Panel A (at an altitude of 1000 m), and brighter trajectory colors indicate the transport of air masses above the boundary layer.

4. In Figure 3, the meaning of C1, C2 and C3 should given in the caption. Besides, what is the X-axis of Panel A.

Author reply:

We have modified Figure 3 and added corresponding X-axis of Panel A and the meaning of C1, C2 andC3 to Figure 3. The revised Figure is shown below:

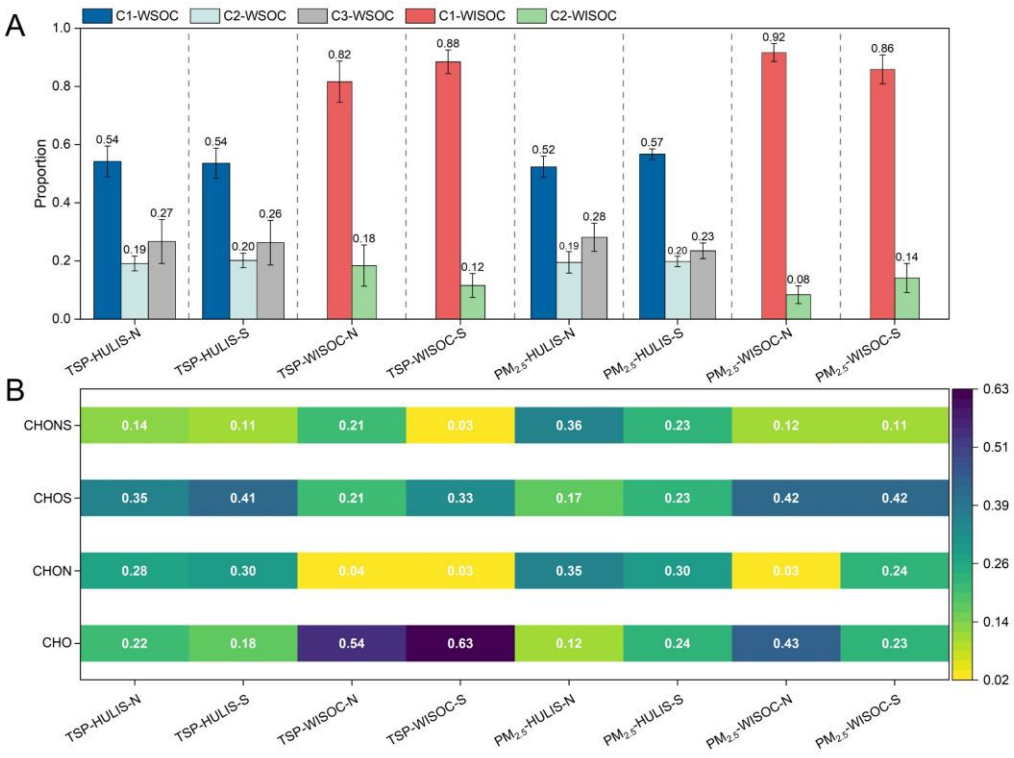

Figure 3. (A) Proportion of fluorescent components in WSOC and WISOC. C1–WSOC and C2–WSOC are two humic–like (HULIS) components in WSOC, C3–WSOC is the protein-like (PRLIS) component in WSOC. C1–WISOC and C2–WISOC are HULIS and PRLIS components in WISOC, respectively. (B) Proportion of four types of potential light–absorbing organic compounds in different types of particles.

5. Line 197-198: Did the author consider all chloride ions to be derived from the sea salts

Author reply:

In the manuscript, we used Na^+ as the sea salt tracer to estimate the proportion of sea salt and non–sea salt ions, rather than Cl^- as a tracer, which is a commonly used method in field observation studies. The reason is that due to the relative stability of Na^+ during the discharge from seawater into the atmosphere, it would neither undergo enrichment nor loss. On the contrary, Cl^- is quite unstable in the atmosphere, as it easily reacts with oxidizing agents (such as OH, NO_3, O_3) and acidic substances (organic and inorganic acids) to form active chlorine species (Su et al., 2022). This process can change the characteristics of Cl^- ratio to other ions in sea salt. Hence, Na^+ is more suitable for

calculating the proportion of sea salt.

In the marginal sea environment, Na^+ may not completely come from sea salt due to strong anthropogenic transport. Hence, we use an anthropogenic Na^+ to total Na^+ ratio range of 50%–80% reported in the literature to estimate the sea salt contribution (as shown in the first paragraph of section 3.2 and in Table S3 in the Supplement) (Wu et al., 2024). No matter how the proportion of Na^+ coming from marine sources changes, the results show that non–sea salt ions contribute significantly more to the total ions than sea salt ions. Briefly, Na^+ is more representative of sea salt than Cl^-, and in this study, changes in the proportion of Na^+ from sea salt did not have a disruptive effect on the results.

Table S3. Proportion of sea salt and non-sea salt ions calculated based on different Na^+ proportions from the ocean.

Proportion of Na^+ from the ocean		Sea salt proportion	Non-Sea salt proportion
100 % Na^+	TSP	0.16±0.14	0.84±0.14
	$PM_{2.5}$	0.04±0.03	0.96±0.03
50 % Na^+	TSP	0.07±0.06	0.93±0.06
	$PM_{2.5}$	0.02±0.02	0.98±0.02
20 % Na^+	TSP	0.04±0.03	0.96±0.03
	$PM_{2.5}$	0.01±0.01	0.99±0.01

6. Line 202-205: the authors mentioned that “aerosols over the northern sea region exhibited higher OC/EC and lower EC concentration (Fig. S2C), indicating a greater influence of atmospheric transformation on aerosols over the northern sea region. Contrary to the OC/EC, the WSOC/OC was higher in the southern sea region. WSOC/OC is often used as an indicator of secondary organic aerosol (SOA) formation, but this ratio is also influenced by biomass burning or environmental factors”. My understanding of this part is that in the norther sea the higher OC/EC ratios indicates secondary organic aerosol formation, the WSOC/OC ratios is higher in the southern sea also indicate secondary organic aerosol formation. If so, why the ratio is contrary between norther and southern sea?

Author reply:

Indeed, secondary organic carbon (SOC) formed from photochemical reactions, homogeneous and heterogeneous phases reactions will enhance the concentration of OC and WSOC (Zhang et al., 2023). Hence, high OC/EC ratios and WSOC/OC ratios were commonly considered as the indicators of secondary organic aerosol (SOA) generation despite the uncertainty associated with their characterization using the above method.

Firstly, the characteristics of OC/EC ratio vary among different emission sources, and combustion sources could directly produce WSOC. For example, the OC/EC ratios from vehicle sources (~1.0) are usually lower than those from biomass burning (7.3) (Ram and Sarin, 2010; Cao et al., 2005). In this study, we also found that WSOC correlates well with nss–K^+ and EC (biomass burning tracer) (Figure R1A and B). Therefore, in addition to secondary formation, OC and WSOC may be affected by the primary combustion source.

Secondly, organic compounds that cannot be extracted by water may also come from secondary formation. Recent studies have shown that water–soluble organic aerosols (WSOA) account for nearly 59% of organic aerosols (OA) (Zhang et al., 2022b). For example, in this study, we found that some relatively saturated aliphatic compounds were dominated by molecules with O/N ≥ 3, likely suggesting secondary products from reactions of hydrocarbons with NO_x (see last paragraph of Section 3.3), despite their low water solubility. Besides, the SOC calculated using the minimum R^2 method has moderate correlation with WSOC and a slope lower than 1 (Figure R1C), further indicating that partial SOC may be water insoluble. Therefore, high OC/EC ratios may not necessarily correspond directly to high WSOC/OC ratios.

Thirdly, OC from non–combustible sources (such as soil or dust) that cannot be extracted by water or organic solvent may also lead to a higher OC/EC ratio. For example, incomplete combustion of biomass can produce plant fibers rich in hydrocarbons, and soil or dust also contribute to carbonaceous species (Gao et al., 2022b; Arun et al., 2021). We found that OC have a strong correlation with nss–Ca^{2+} (dust tracer).

In order to further elucidate that high OC/EC ratios may not correspond to high

WSOC/OC ratios, we summarized the ratio characteristics reported in the literature, and they are shown in Figure R1C below.

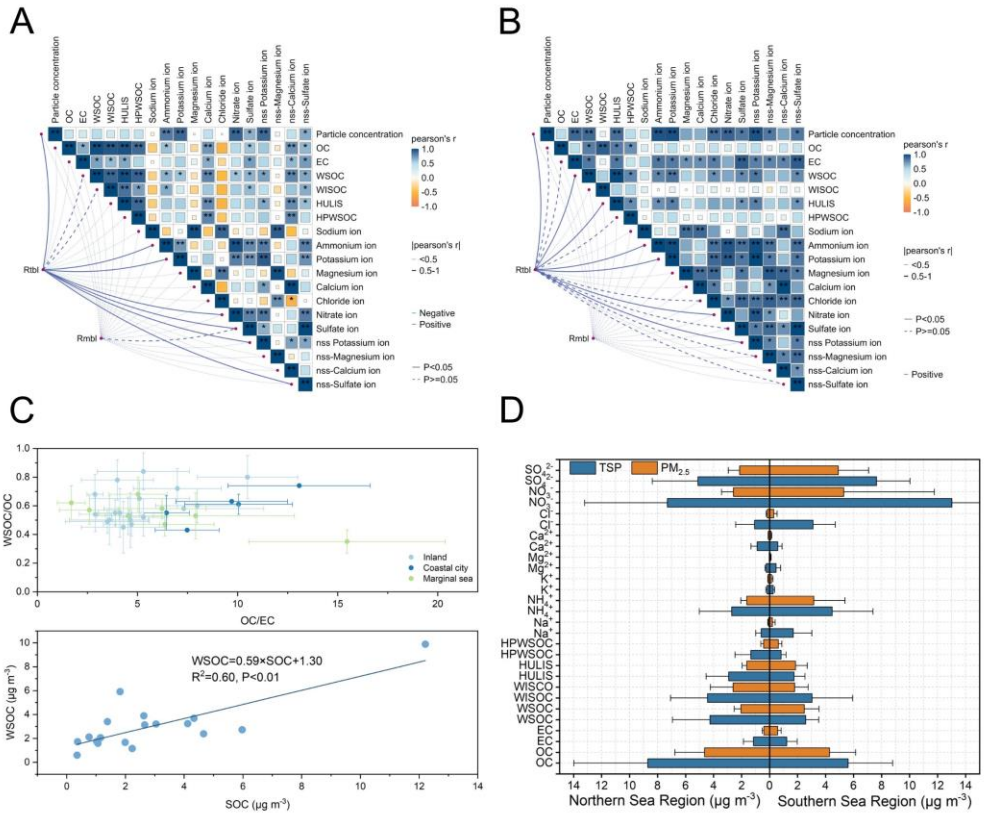

Figure R1. Correlation map of major components in (A) TSP and (B) $PM_{2.5}$. (C) OC/EC and WSOC/OC ratios reported in field studies and the correlation between WSOC and SOC. (D) Concentration comparison of chemical composition in different sea regions.

We found that the majority of OC/EC and WSOC/OC ratios in field studies are between 5–10 and 0.4–0.7, respectively (Nayak et al., 2022; Arun et al., 2021; Wu et al., 2019; Zhang et al., 2022a; Chen et al., 2020; Chen et al., 2023; Luo et al., 2020; Rajeev et al., 2022; Zhao et al., 2023), in consistency with our results. In addition, there are no similar changes in the trend of OC/EC and WSOC/OC ratios, which means that the generation of SOA may not lead to a simultaneous increase in OC/EC ratios and WSOC/OC ratios. Finally, we believe that the opposite ratio characteristics of OC/EC and WSOC/OC between two sea regions may indicate differences in the contributions from different sources, or different atmospheric transformation characteristics in the two sea regions. Therefore, the sole consideration of the impact of the SOA generation on their ratios

would not be appropriate.

Related to this, we have made revisions in the second paragraph of Section 3.2 as follows (Page 9, Line 217–232):

Regionally, aerosols over the northern sea region exhibited high OC/EC (see Table S2). Contrary to OC/EC, the WSOC/OC ratio was high in the southern sea region. Although higher OC/EC and WSOC/OC may indicate the influence of secondary organic aerosol (SOA), the contrary ratio characteristics in different sea regions indicate that SOA formation is not enough to explain this phenomenon. For example, we found that OC exhibit strong correlations with nss–Ca^{2+} and EC, while WSOC exhibits not only a moderate correlation with secondary inorganic ions (NH_4^+, NO_3^- and nss–SO_4^{2-}), but also a positive correlation with nss–K^+ and EC (Fig. S3A and B). This indicates that in addition to secondary transformation, primary combustion and non–combustion sources contribute to OC and WSOC (Cai et al., 2020). Besides, the SOC calculated using the minimum R^2 method exhibits a moderate correlation with WSOC, with a slope lower than 1 (Fig. S3C). This indicates that SOC may partially be water insoluble (Zhang et al., 2022b). The majority of OC/EC and WSOC/OC ratios in field studies fall between 5–10 and 0.4–0.7, respectively (Nayak et al., 2022; Arun et al., 2021; Wu et al., 2019; Zhang et al., 2022a; Chen et al., 2020; Chen et al., 2023; Luo et al., 2020; Rajeev et al., 2022; Zhao et al., 2023) (see Fig. S3C), consistent with the results of this study. In addition, no similar changes were observed between the trends of OC/EC ratios and WSOC/OC ratios, indicating that the generation of SOA may not lead to a simultaneous increase in OC/EC ratios and WSOC/OC ratios. Therefore, combustion sources, non–combustion sources, and atmospheric transformation may be potential reasons for the difference of ratios between the two sea regions. But the EC concentration in the southern sea region is high, indicating that the impact of the primary combustion source seems to be greater (Fig. S3D).

7. Line 205-210: the authors said that "WSOC originates not only from primary biomass burning emissions but also from SOA formation", the authors need to provide more direct evidence. The authors provide WSOC showed significant correlations with

EC and nss–K^+, and the spatial distribution of the WSOC/OC aligned with that of EC, nss–K^+ and K^+ concentration which only indicates the primary sources.

Author reply:

We thank the Referee for pointing out this. Indeed, WSOC exhibit a moderate correlation with secondary inorganic ions and SOC as shown in Figure. S3 in Supplement. Necessary revisions have been made in the second paragraph of Section 3.2 in the manuscript.

Page 9, Line 220–223:

For example, we found that OC exhibits strong correlations with nss–Ca^{2+} and EC, while WSOC exhibits not only a moderate correlation with secondary inorganic ions (NH_4^+, NO_3^- and nss–SO_4^{2-}), but also a positive correlation with nss–K^+ and EC (Fig. S3A and B). This indicates that in addition to secondary transformation, primary combustion and non–combustion sources contribute to OC and WSOC (Cai et al., 2020).

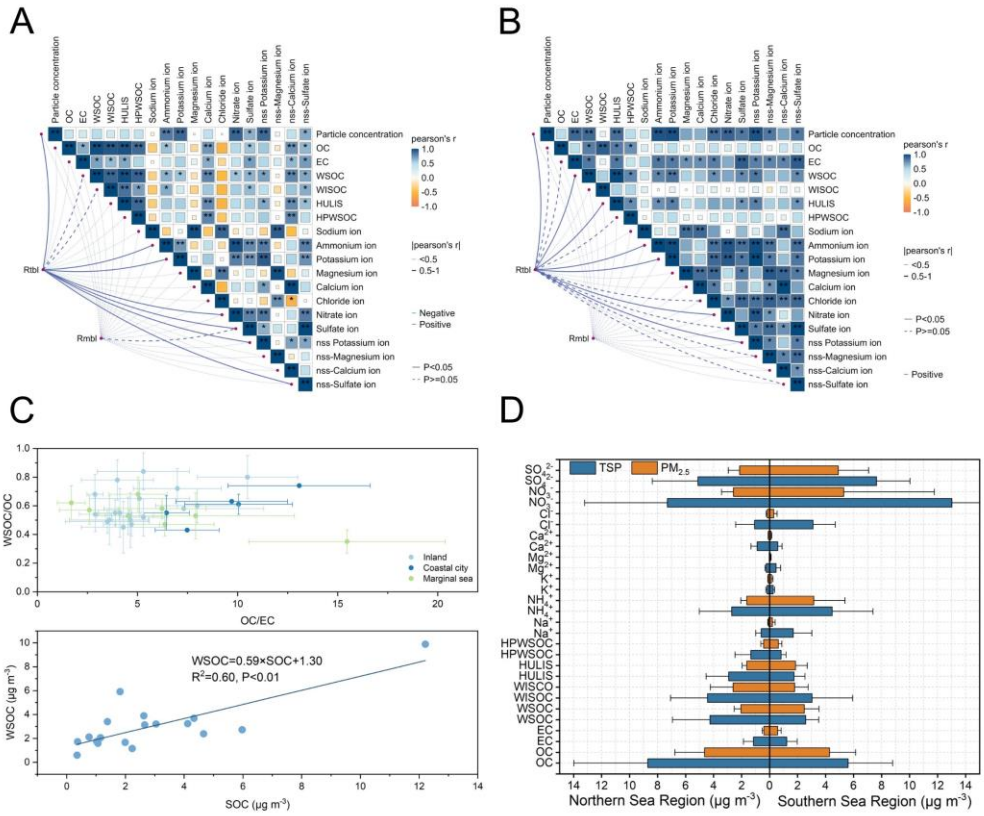

Figure S3. Correlation map of major components in (A) TSP and (B) $PM_{2.5}$. (C) OC/EC and WSOC/OC ratios reported in field studies and the correlation between WSOC and SOC. (D) Concentration comparison of the chemical composition in different sea regions.

References

Arun, B. S., Gogoi, M. M., Hegde, P., Borgohain, A., Boreddy, S. K. R., Kundu, S. S., and Babu, S. S.: Carbonaceous Aerosols over Lachung in the Eastern Himalayas: Primary Sources and Secondary Formation of Organic Aerosols in a Remote High-Altitude Environment, ACS Earth Space Chem., 5, 2493–2506, https://doi.org/10.1021/acsearthspacechem.1c00190, 2021.

Cao, J., Wu, F., Chow, J., Lee, S., Li, Y., Chen, S., An, Z., Fung, K., Watson, J., Zhu, C. J. A. C., and Physics: Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China, Atmos. Chem. Phys., 5, 3127–3137, https://doi.org/10.5194/acp-5-3127-2005, 2005.

Chen, H., Yan, C., Fu, Q., Wang, X., Tang, J., Jiang, B., Sun, H., Luan, T., Yang, Q., Zhao, Q., Li, J., Zhang, G., Zheng, M., Zhou, X., Chen, B., Du, L., Zhou, R., Zhou, T., and Xue, L.: Optical properties and molecular composition of wintertime atmospheric water-soluble organic carbon in different coastal cities of eastern China, Sci. Total Environ., 892, 164702, https://doi.org/10.1016/j.scitotenv.2023.164702, 2023.

Chen, P., Kang, S., Tripathee, L., Ram, K., Rupakheti, M., Panday, A. K., Zhang, Q., Guo, J., Wang, X., Pu, T., and Li, C.: Light absorption properties of elemental carbon (EC) and water-soluble brown carbon (WS-BrC) in the Kathmandu Valley, Nepal: A 5-year study, Environ. Pollut., 261, 114239, https://doi.org/10.1016/j.envpol.2020.114239, 2020.

Gao, P., Zhou, C., Lian, C., Wang, X., and Wang, W.: Morphology and Composition of Insoluble Brown Carbon from Biomass Burning, ACS Earth Space Chem., 6, 1574–1580, https://doi.org/10.1021/acsearthspacechem.2c00064, 2022b.

Luo, Y., Zhou, X., Zhang, J., Xue, L., Chen, T., Zheng, P., Sun, J., Yan, X., Han, G., and Wang, W.: Characteristics of airborne water-soluble organic carbon (WSOC) at a background site of the North China Plain, Atmos. Res., 231, 104668, https://doi.org/10.1016/j.atmosres.2019.104668, 2020.

Nayak, G., Kumar, A., Bikkina, S., Tiwari, S., Sheteye, S. S., and Sudheer, A. K.: Carbonaceous aerosols and their light absorption properties over the Bay of Bengal during continental outflow, Environ Sci Process Impacts, 24, 72–88, https://doi.org/10.1039/d1em00347j, 2022.

Rajeev, P., Choudhary, V., Chakraborty, A., Singh, G. K., and Gupta, T.: Light absorption potential of water-soluble organic aerosols in the two polluted urban locations in the central Indo-Gangetic Plain, Environ. Pollut., 314, 120228, https://doi.org/10.1016/j.envpol.2022.120228, 2022.

Ram, K. and Sarin, M. M.: Spatio-temporal variability in atmospheric abundances of EC, OC and WSOC over Northern India, J. Aerosol. Sci., 41, 88–98, https://doi.org/10.1016/j.jaerosci.2009.11.004, 2010.

Su, B., Wang, T., Zhang, G., Liang, Y., Lv, C., Hu, Y., Li, L., Zhou, Z., Wang, X., and Bi, X.: A review of atmospheric aging of sea spray aerosols: Potential factors affecting chloride depletion, Atmos. Environ., 290, 119365, https://doi.org/10.1016/j.atmosenv.2022.119365, 2022.

Wu, G., Ram, K., Fu, P., Wang, W., Zhang, Y., Liu, X., Stone, E. A., Pradhan, B. B., Dangol, P. M., Panday, A. K., Wan, X., Bai, Z., Kang, S., Zhang, Q., and Cong, Z.: Water-Soluble Brown Carbon in Atmospheric Aerosols from Godavari (Nepal), a Regional Representative of South Asia, Environ. Sci. Technol., 53, 3471–3479, https://doi.org/10.1021/acs.est.9b00596, 2019.

Wu, X., Kong, Q., Lan, Y., Sng, J., and Yu, L. E.: Refined Sea Salt Markers for Coastal Cities Facilitating Quantification of Aerosol Aging and $PM_{2.5}$ Apportionment, Environ. Sci. Technol.,

58, 8432–8443, https://doi.org/10.1021/acs.est.3c10142, 2024.

Zhang, J., Qi, A., Wang, Q., Huang, Q., Yao, S., Li, J., Yu, H., and Yang, L.: Characteristics of water-soluble organic carbon (WSOC) in $PM_{2.5}$ in inland and coastal cities, China, Atmos. Pollut. Res., 13, 101447, https://doi.org/10.1016/j.apr.2022.101447, 2022a.

Zhang, X., Zhang, X., Talifu, D., Ding, X., Wang, X., Abulizi, A., Zhao, Q., and Liu, B.: Secondary formation and influencing factors of WSOC in $PM_{2.5}$ over Urumqi, NW China, Atmos. Environ., 293, 119450, https://doi.org/10.1016/j.atmosenv.2022.119450, 2023.

Zhang, Z., Sun, Y., Chen, C., You, B., Du, A., Xu, W., Li, Y., Li, Z., Lei, L., Zhou, W., Sun, J., Qiu, Y., Wei, L., Fu, P., and Wang, Z.: Sources and processes of water-soluble and water-insoluble organic aerosol in cold season in Beijing, China, Atmos. Chem. Phys., 22, 10409–10423, https://doi.org/10.5194/acp-22-10409-2022, 2022b.

Zhao, S., Qi, J., and Ding, X.: Characteristics, seasonal variations, and dry deposition fluxes of carbonaceous and water-soluble organic components in atmospheric aerosols over China's marginal seas, Mar. Pollut. Bull., 191, 114940, https://doi.org/10.1016/j.marpolbul.2023.114940, 2023.