General.

We would like to appreciate the editor and reviewers for providing the valuable comments and a better perspective on our work to improve the manuscript. We have revised our manuscript by fully taking the reviewers' comments into account. Responses to specific comments raised by the reviewers are described below. All the changes made and appeared in the revised text are shown in red. All detailed answers to comments are displayed in blue.

Comments of Referee #2 and our responses to them

Comments:

The present study employed a systematic approach to characterize organosulfates in $PM_{2.5}$ samples from both southern and northern Chinese cities during the winter months, complemented by the analysis of smoke particle samples obtained from simulated combustion experiments. The analysis indicated that biomass burning, in contradistinction to the combustion of gasoline, diesel, and coal, exerted a significant influence on the increased levels of particulate isoprene-derived organosulfates observed in northern urban areas. The authors pointed out that stronger biomass and fossil fuel combustion activities in the northern cities resulted in the formation of a greater number of anthropogenic organosulfates. In general, this work offers a compelling example and novel insights into understanding organosulfate pollution in Chinese cities. The manuscript is well organized and its topic is very interesting. Thus, I think it can be accepted after a minor revision.

Response: We sincerely appreciate your professional and constructive review of our manuscript. Your valuable feedback has greatly improved the clarity and quality of our work.

Detailed comments:

1) *Lines 72-74: It is recommended that the author rephrase the sentence to enhance clarity. For example: This complicates our understanding of how aerosol OS pollution is formed and what limits it in a complex polluted atmosphere across different cities in China.*

Response: Thank you for your suggestion. We have rephrased the sentence.

Lines 70-71: …This complicates our understanding of how aerosol OS pollution is formed and what limits it in a complex polluted atmosphere across different cities in China…

2) *Line 102-107: it seems to me that about ten samples were collected in each city, so at least 40 samples were studied by this study, why here stated " a total of four $PM_{2.5}$ samples were collected and stored at a.....? please clarify.*

Response: Thank you very much for your careful review. We apologize for the confusion caused by this. A total of 12 samples were collected from each city. Thus, we collected a total of 48 samples in four cities. The revision has been made in the revised manuscript.

Line 104: …A total of 48 ambient samples…

3) *Line 146: Please change 'a optimized solution' to 'an optimized solution'.*

Response: Thank you for your comment. The sentence has been rephrased in the revised manuscript.

Line 142-144: …we also acknowledge that the developed hydrophilic interaction liquid chromatography method may provide another solution for the measurement of low-MW OSs…

4) *Line149-150: the authors mentioned that the two references (Brüggemann et al. 2020a; Kristensen et al. 2016) emphasize the impact of the sampling process on the quantitative results of OSs. However, Lines 156-157: the authors also mentioned that the possible consequences of sampling without denuding SO_2 for the quantification of OSs were not taken into account in our studies (Brüggemann et al. 2020a; Kristensen et al. 2016). It is strange to quote the same reference in sentences with different meanings. Please clarify.*

Response: We apologize for the incorrect citation. We have clarified the issue and corrected the references accordingly.

Lines 152-154: …Consequently, the possible consequences of sampling without denuding SO_2 for the quantification of OSs were not taken into account in our studies (Yang et al. 2023; Yang et al. 2024)…

5) *Line 158: What are the surrogate standards? How were they obtained? What are the recoveries of the surrogated standards?*

Response: We appreciate your valuable comments on our work. To address the comments, the Supporting Information has been updated with additional content.

Supporting Information

S2. Quantification of OSs

It is evident that OSs with similar carbon backbone structures typically exhibit analogous MS responses (Wang et al. 2021). Consequently, the selection of a surrogate standard for a specific OS was predominantly contingent on the similarity between the carbon chain structures of the targeted OS species and the OS standard (Hettiyadura et al. 2017). Furthermore, the sulfur-containing fragment ions observed in the MS/MS spectra of the standard and targeted OS species have been taken into

consideration (Hettiyadura et al. 2019; Bryant et al. 2021). The recoveries of the aforementioned surrogate standards were, in order, 88%, 84%, 94%, 89%, 88%, 87%, and 84%. Additional details on the identification of OS compounds, their classification and quantifacation, and data quality control are available in our recent publications (Yang et al. 2023; Yang et al. 2024).

6) *Line 159-164：here I suggest to give a brief description on how OS_m and OS_i were defined, which is helpful for readers to quickly understand what the author have done in this study, although more details can be found in **SI**.*

Response: Thank you for the suggestion. The terms "OS_m" and "OS_i" refer to organosulfates generated from monoterpenes and isoprene, respectively. These compounds were generally classified as biogenic OSs due to their natural origin (Wang et al. 2021; Wang et al. 2018).

Lines 159-161: The terms "OS_m" and "OS_i" refer to organosulfates generated from monoterpenes and isoprene, respectively. These compounds were generally classified as biogenic OSs due to their natural origin (Wang et al. 2021; Wang et al. 2018).

7) *Line 159-164，Line 167: Please remove any extra spaces between K^+ and Mg^{2+}.*

Response: We appreciate your attention to detail. The revision has been made.

Lines 165-166: …The concentrations of SO_4^{2-}, Ca^{2+}, NO_3^-, Na^+, K^+, Mg^{2+}, Cl^-, and NH_4^+…

8) *Line 172-174: here should give a reference to support this conclusion.*

Response: Thank you for your comment. We have added some references to support this.

Lines 171-174: The influence of OSs on ALW and pH was not taken into account in the present study due to their negligible contribution to the prediction outcomes, as indicated by Riva et al. (2019) and Yang et al. (2024).

9) *Line 233: Does the spatial variation of OS_i concentration have temperature dependence?*

Response: Thank you for your comment. A new Figure (as **Figure S4**) has been added to demonstrate that the spatial variation of OS_i was not temperature-dependent.

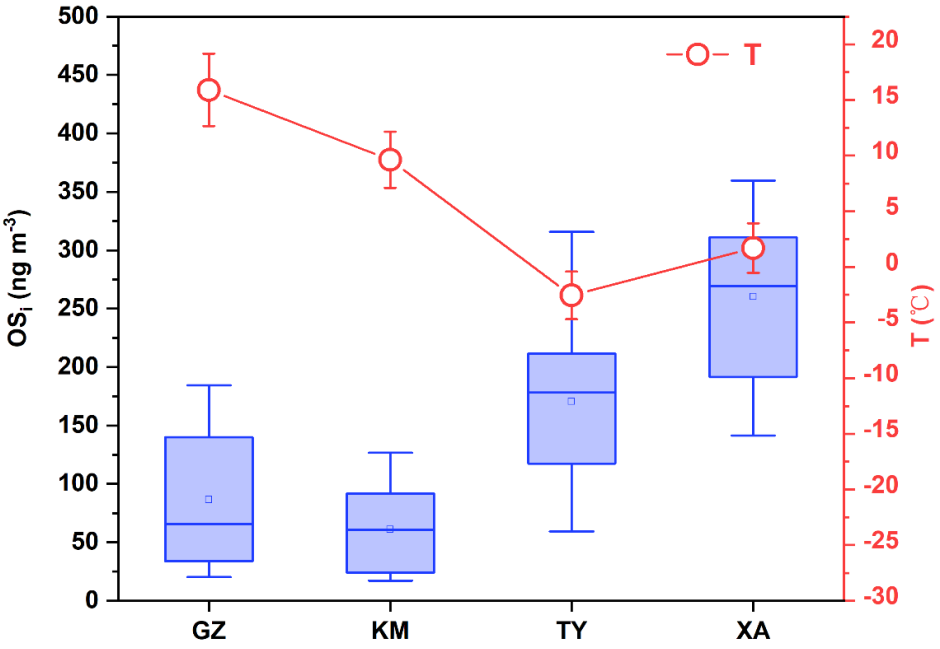

Figure S4 Spatial variation of OS_i concentration and temperature (T).

Lines 269-270: However, this cannot account for the observed spatial variation of OS_i (**Figure 2c** and **Figure S4**).

10) *Line 239: For the statement 'indicator ($C_L \times C_T$) of biogenic VOC emission rate',*

please add some references to support it.

Response: The references have been added in the revised manuscript.

Lines 237-239: …Furthermore, the indicator ($C_L \times C_T$) of biogenic VOC emission rate (Ding et al. 2016; Guenther et al. 1993) was also higher in southern cities than in northern cities (**Figure 2b**)…

11) *Line 281: what are the "N-base compounds" ? please give more explanation.*

Response: Thank you for your valuable comment. N-base compounds are CHN species that contain exclusively C, H, and N atoms, and have been demonstrated to exhibit high sensitivity as molecular indicators in identifying biomass burning (Wang et al. 2017).

Lines 281-283: …N-base compounds are CHN species that contain exclusively C, H, and N atoms, and have been demonstrated to exhibit high sensitivity as molecular indicators in identifying biomass burning (Wang et al. 2017).…

12) *Section 3.3: Are the OS_i species detected in smoke particles directly emitted or are they produced secondarily?*

Response: Thank you for your valuable comment. The OS_i species detected in smoke particles may not be directly emitted but are produced secondarily. The formation of these compounds is predominantly initiated by the oxidation of isoprene, followed by complex reactions within the smoke plume (Wang et al. 2017; Song et al. 2018; Mason et al. 2001).

More discussions are presented in Lines 321–352 in the revised manuscript.

13) *Figure 5: Based on my understanding, OS_i-BB can not only come from biomass combustion, but also from atmospheric transformation of isoprene derived from biological sources. Therefore, although these OS species were indeed detected in the particulate matter released from biomass burning, in order to avoid misleading readers into thinking that these OS species were all from biomass burning release, I recommend the author to add relevant explanations in the caption.*

Response: Thank you for your valuable feedback. To ensure that readers are not misled into thinking that these OS species are solely from biomass burning emissions, the relevant explanation has been added in the figure caption.

Lines 455-457: It is noteworthy that OS_i-BB can originate not only from biomass combustion, but also from the secondary formation of isoprene emitted from biogenic sources.

At last, we deeply appreciate the time and effort you've spent in reviewing our manuscript.

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