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 #3 and our responses to them

Comments:

The primary objective of this study is to elucidate the role of non-biogenic emissions (e.g., rice straw, pine branch, gasoline, diesel, and coal combustion) in the formation of isoprene-derived organosulfates in aerosols in China during winter. The authors synthesized data from large-scale observational studies (comparing northern and southern Chinese cities) with data from simulated combustion experiments. They demonstrate that biomass burning emissions are a significant contributor to aerosol organosulfates in northern cities, rather than fossil fuel combustion emissions. The overall results provide valuable insights into the formation of aerosol organosulfates associated with biomass burning, making this a noteworthy and meaningful finding. Generally, the manuscript is well-structured and presents a robust experimental approach with clear results. I recommend that this paper be published in Atmospheric Chemistry and Physics once the authors address the following comments.

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. We have carefully revised the manuscript to address the comments.

Major comments:

1) The identification of over 100 organosulfates is impressive. While the use of *surrogate standards is not ideal, it is currently the best solution in the absence of authentic standards. Therefore, please provide a detailed explanation of the criteria used for selecting surrogate standards for quantifying organosulfate species in this section or supplementary information. Additionally, the recoveries of individual organosulfate surrogate standards should be included in the manuscript or supplementary information, as this is crucial for ensuring data quality.*

Response: We are grateful for the insightful comments provided by the reviewer. More discussions have been added in the revised manuscript. Briefly, we further emphasized that the differential ionization efficiencies and fragmentation patterns in the OS measurement may introduce biases (Wang et al. 2017; Wang et al. 2021b). Detailed quantification method and data quality control have also been shown in our previous studies (Wang et al. 2021b; Yang et al. 2023; Yang et al. 2024).

Supporting Information:

S2. Quantification of OSs

…It is evident that OSs with similar carbon backbone structures typically exhibit analogous MS responses (Wang et al. 2021a). 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)…

Additional Comments:

1) *Keywords: I recommend adding "biomass burning" to the list of keywords.*

Response: Thank you for your comment. The revision has been made.

Line 42: …Spatial variation, Influencing factors, Biomass burning…

2) *Line 140: The rationale for centrifuging is unclear, especially since a syringe filter was used earlier. It would be helpful to clarify whether the centrifuge was employed later due to solid precipitate formation in the extracts after adding water.*

Response: Indeed, centrifugation does not cause any precipitation. However, the instrument administrator requires us to centrifuge to minimize the risk of instrument blockage.

3) *Table S5 and Figure S5: Please describe the methodology used to calculate the relative intensity.*

Response: Thank you for your comment. The relative signal intensity refers to the percentage of the target OS signal intensity in the total signal intensity of the OS group to which the target OS belongs.

SI: **Table S5**: Relative signal intensity of identified OS_a in different smoke particle samples. The relative signal intensity refers to the percentage of the target OS signal intensity in the total signal intensity of the OS group to which the target OS belongs.

Figure S6. Mean relative signal intensities of typical aromatic OSs (i.e., $C_6H_5O_4S^-$, $C_7H_7O_4S^-$, $C_8H_7O_4S^-$, and $C_9H_9O_4S^-$) in different smoke particle samples. The relative signal intensity refers to the percentage of the target OS signal intensity in the total signal intensity of the OS group to which the target OS belongs.

4) *Line 392: In the caption of Figure S6, please clarify what panels a and b represent.*

Also, indicate which data were used for the correlation analysis in Figure S8.

Response: Thank you for your comment. In the caption of Figure S6, we have clarified that panels (a) and (b) represent the Pearson correlation diagrams for the cases in southern cities and northern cities, respectively. Additionally, we have indicated that data from four cities were used for the correlation analysis in Figure S8.

Supporting Information:

Figure S6. Diagrams presenting Pearson correlations among different OSs and important parameters for the cases in (a) southern cities and (b) northern cities…

Figure S8. Diagrams presenting Pearson correlations among the different OSs and important parameters (using data from four cities) ...

5) *It would be beneficial to determine whether the authors can provide a quantitative estimation of the contribution of biomass combustion emissions to aerosol isoprene-derived organosulfates, even though this may be a challenging task.*

Response: We appreciate the valuable comment. On average, biomass burning-related OS_i (OS_i-BB) accounted for 58% – 64% and 86% – 87% of the total OS_i concentration in southern and northern cities, respectively. It is imperative to acknowledge that OS_i-BB can originate not only from biomass combustion but also from the secondary formation of isoprene emitted from biogenic sources. At least in this study, the higher proportion of the OS_i in northern cities can support our consideration that non-biogenic OS_i was an important contributor to OS_i in northern cities. However, given the potential for both biomass burning and biogenic isoprene to contribute to OS_i formation, separating their respective contributions remains challenging, particularly when relying solely on OS_i concentrations. To disentangle the contribution of biomass combustion emissions to OS_i, further detailed studies are necessary.

Lines 445–447: …Given the potential for both biomass burning and biogenic isoprene to contribute to OS_i formation, separating their respective contributions remains challenging…

Figure 5 …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…

Technical Corrections:

1) *Line 146: Change "an optimized solution" to "the optimized solution."*

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

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

2) *Lines 149 and 153: Please correct the two spelling errors present.*

Response: Thank you for your careful review. The revision has been made.

Line 146: …In addition, it has been indicated in previous studies…

Line 150: …Moreover, there is currently no study evaluating the relative…

3) *Line 364: Amend "... be also supported…" to "...also be supported…"*

Response: The revision has been made.

Line 366: …This can also be supported by previous principal component analysis…

4) *S2. Quantification of OSs. Line 116: Ensure the correct citation format: (Hettiya… Ding et al. 2022a).*

Response: We have updated the citation.

Supporting information

…Consequently, the majority of the identified OSs were quantified using surrogate standards (Hettiyadura et al. 2019; Bryant et al. 2021; Wang et al. 2018; Ding et al. 2022)…

5) *Figures S3 and S5: I suggest removing the hyphen in "Ali.-OSs" and "Aro.-OSs."*

Response: Thank you for your kind suggestion to improve the clarity of the figures. Although the hyphen was retained, we re-output the figure to make the display of each parameter clearer.

Supporting information

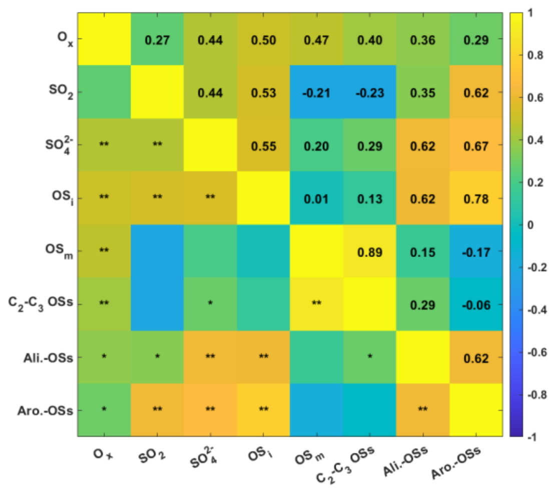

Figure S3. Diagrams presenting Pearson correlations among the concentrations of O_x, SO_2, SO_4^{2-}, and the different OSs (using data from four cities). The numbers in the matrix refer to the correlation coefficients (*r*). Symbols * and ** indicate $P < 0.05$ and $P < 0.01$, respectively.

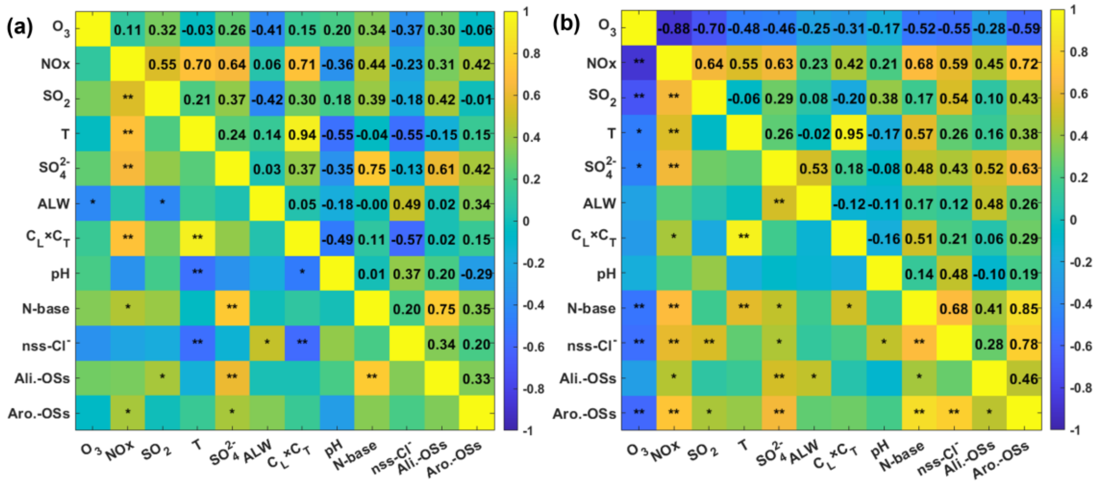

Figure S6. Diagrams presenting Pearson correlations among different OSs and important parameters for the cases in (a) southern cities and (b) northern cities. The numbers in the matrix refer to the correlation coefficients (*r*). Symbols * and ** indicate $P < 0.05$ and $P < 0.01$, respectively.

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

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