General.

We would like to express our sincere appreciation to the editor and reviewers for their valuable feedback and constructive suggestions, which significantly improved the manuscript. We have carefully addressed all the reviewers' concerns and made the revisions. Responses to specific comments raised by the reviewers are described below. All changes made in the revised manuscript are highlighted in red, and our detailed responses to the specific comments are presented below in blue.

Comments of Referee #1 and our responses to them

Comments:

This study investigated the spatial variations of the concentration of different types of organosulfates in cities in southern and northern China. The manuscript further analyzed the factors leading to significant regional differences in organosulfate concentration and composition between the southern and northern cities. Based on principal component analysis, correlation analysis, organosulfate formation mechanism analysis, and field simulation combustion experiments, the authors concluded that the emissions from biomass burning, rather than those from gasoline, diesel, and coal combustion, can play a significant role in the formation of isoprene-derived organosulfates. This is a significant and valuable finding. It thus follows that when attempting to predict winter isoprene emissions in China, it is essential that the influence of biomass combustion emissions is duly taken into account, with due consideration given to the regional differences in question. Overall, the manuscript presents high quality research data based on field observations and simulation experiments. The content presented here will be of interest to the readership of Atmospheric Chemistry and Physics. After the authors address the following minor comments, this manuscript would be suitable for publication.

Response: We are very grateful for your professional and thoughtful review of our manuscript. We have revised the manuscript to address the comments. Our responses to the specific comments and changes made in the manuscript are given below.

Specific comments:

1) *Lines 142-143: I suggest that the authors add specific information about the columns used here or in the supplemental file. It is important to consider this when comparing the analysis method from this study with those from previous or future research.*

Response: Thank you for your suggestion. The T3 column was used in this study, and this information has been incorporated into the manuscript.

Lines 138-140: …The reverse-phase liquid chromatography (RPLC) method was performed on an Acquity UPLC HSS T3 column (2.1mm × 100 mm, 1.8 μm particle size; Waters, USA) in this study.…

2) *Lines 157-158: Why did the authors choose 111 of the OSs for further quantification? I have checked your previously published paper showing quantification of 106 OS species. Is there any difference here? Please clarify.*

Response: Thank you for your question. In our previous study, we quantified 106 species OSs species, which represented the species detected in the $PM_{2.5}$ samples at Urumqi. However, in this study, we analyzed samples from four different cities, thereby facilitating the capture of a more extensive array of OSs. Consequently, we were able to detect additional OS species, resulting in a greater number of species being quantified. This explains why we selected 111 OSs for further quantification in this study.

3) *Lines 172-174: How is this insignificance determined or evaluated?*

Response: Thank you for your comment. In our previous study, the different outputs of the pH values between the cases without and with including OSs as additional sulfates were compared to examine the potential influence of OSs on pH calculation (Yang et al. 2024). An insignificant difference was found between these two predictions, suggesting a negligible contribution of OSs to pH value. In addition, the aerosol pH may be overestimated by 0, 3.5, and 9.5 units when the ratios of total organic sulfur to total inorganic sulfur were 0, 0.73, and 4.66, respectively (Riva et al. 2019). The ratio of the total OSs to total sulfates in Guangzhou, Kunming, Taiyuan, and Xi'an was 0.019, 0.022, 0.017 and 0.021, respectively, further indicating that the effect of OSs on acidity prediction was neglected in this study.

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).

4) *Line 196: Please remove any possible extra spaces between 'sulfate' and 'atmospheric oxidation capacity'.*

Response: Thank you for your comment. We have deleted extra spaces between 'sulfate' and 'atmospheric oxidation capacity'.

Line 195: …"acidity, sulfate, atmospheric oxidation capacity"…

5) *Line 217: Please change 'an' to 'the'.*

Response: The revision has been made (Line 216).

Line 216: …"showed the opposite spatial variation pattern"…

6) *Lines 224-225: Was the correlation analysis presented in Figure S3 using all the data from this study? In addition, I suggest adding 'further' before 'given'.*

Response: Thank you for your insightful comment. The correlation analysis presented in **Figure S3** used all the data in this study. In addition, we have added 'further' before 'given' in Line 230.

Line 223: …"Further given the significant"…

SI Figure S3: …(using data from four cities)…

7) *Line 248: Please remove any possible extra spaces before 'considering'.*

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

Line 248: …"Considering the lower levels"…

8) *Line 261: Please change ' precisely' to 'further'.*

Response: The revision has been made.

Line 261: …"This further explained the changes"...

9) *Line 269: I suggest the author delete 'fully' or replace it with a more appropriate word.*

Response: The revision has been made.

Line 269: "However, this cannot account for the observed spatial variation of OS_i"

10) *I know that those isoprene-derived organosulfates were detected in the samples*

from the simulated combustion experiments, however, I would like to know how you think about their formation. This could be a critical question for future research in this area, although it does not affect the results of this study.

Response: Thank you for your valuable comment. In this study, the formation of OS_i can be attributed to the oxidation of isoprene in smoke plumes. Previous experimental studies have shown that these OS_i compounds typically form through the heterogeneous and multiphase reactions of isoprene and its oxidation intermediates with sulfate or sulfur dioxide (Surratt et al. 2008; Surratt et al. 2007; Darer et al. 2011). Since our combustion experiments have excluded the direct contribution of ambient aerosol particles to OS_i in smoke particles, it can be expected that these detected OS_i compounds were mainly generated within smoke plumes through the isoprene oxidation pathway mentioned above. It has been demonstrated that directly emitted organic aerosols or VOCs can undergo a chemical reaction within smoke plumes, forming secondary organic compounds within a matter of hours (Wang et al. 2017; Song et al. 2018; Mason et al. 2001). Despite the fact that a few of the mechanisms by which OSs are formed have been verified through field studies, the formation of CHOS and CHONS compounds has been observed to occur in the biomass burning plume (Zhang et al. 2024; Song et al. 2018; Tang et al. 2020). Thus, these previous case studies further support our consideration that OS_i compounds formed in biomass burning-derived smoke particles in this study can be attributed to increasing isoprene emission caused by field biomass burning (Zhu et al. 2016) and favorable aqueous secondary organic aerosols (SOA) formation during the aging process of the biomass burning plume (Gilardoni et al. 2016).

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

11) *I suggest the authors add a space after Ali. in Figure S3. Furthermore, how was the relative intensity calculated in Figure S5? Please clarify it.*

Response: Thank you for your comment. **Figure S3** has been updated. 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**).

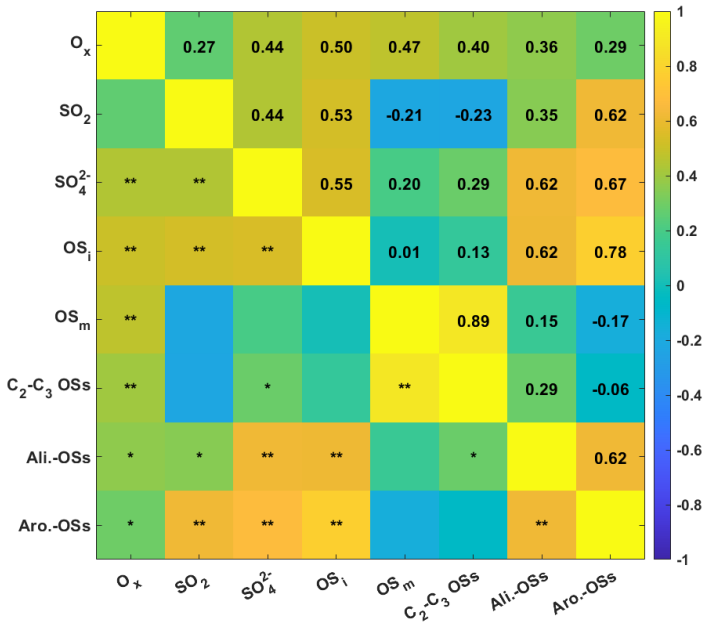

Figure S3. Diagrams presenting Pearson correlations among the concentrations of O_x, SO_2, SO_4^{2-}, and the different OSs (using data from four cities). The numbers in the matrix refer to the correlation coefficients (r). Symbols * and ** indicate $P < 0.05$ and $P < 0.01$, respectively.

Figure S6. 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.

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

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