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. In particular, we are very grateful to the editor and reviewers for giving us the opportunity to make revision. 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 #1 and our responses to them

Comments:

This manuscript quantified 130 organosulfate species (OSs) in Shanghai in Summer 2021, importantly stratifying aerosol composition in daytime and nighttime, as well as cleaner versus more polluted days in both urban and suburban locations. This study uniquely classifies observed OSs and systematically identifies correlations with factors such as atmospheric oxidation capacity, sulfate pollution, NOx concentrations, aerosol liquid water content, and aerosol pH. Although methods of quantitation and classification of OS species are somewhat oversimplified, this paper still presents important evidence for the driving factors of sulfate chemistry using valuable field data, and thus is likely of interest to the readership of Atmospheric Chemistry and Physics. I recommend this paper for publication after addressing the following minor revisions:

Response: We appreciate the reviewer's valuable comments on our work. The methods of quantitation and classification of OS species were further elaborated in the revised manuscript. In addition, our responses to the specific comments and changes made in

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Specific comments:

1) *Line 76-81: Consider adding more thorough citations of relevant studies (here and/or throughout manuscript, including the following):*

   O'Brien, R. E.; Laskin, A.; Laskin, J.; Rubitschun, C. L.; Surratt, J. D.; Goldstein, A. H. Molecular Characterization of S- and N- Containing Organic Constituents in Ambient Aerosols by Negative Ion Mode High-Resolution Nanospray Desorption Electrospray Ionization Mass Spectrometry: CalNex 2010 Field Study. J. Geophys. Res. Atmos. 2014, 119, 12706−12720.

   Ding, S., Chen, Y., Devineni, S.R., Pavuluri, C.M. and Li, X.D.,Distribution characteristics of organosulfates (OSs) in PM2. 5 in Tianjin, Northern China: Quantitative analysis of total and three OS species. Science of The Total Environment, 2022 834, 155314.

   Hettiyadura, A.P., Xu, L., Jayarathne, T., Skog, K., Guo, H., Weber, R.J., Nenes, A., Keutsch, F.N., Ng, N.L. and Stone, E.A. Source apportionment of organic carbon in Centreville, AL using organosulfates in organic tracer-based positive matrix factorization. Atmospheric Environment, 2018, 186, 74-88.

   Jiang, H., Li, J., Tang, J., Cui, M., Zhao, S., Mo, Y., Tian, C., Zhang, X., Jiang, B., Liao, Y., Chen, Y., and Zhang, G.: Molecular characteristics, sources, and formation pathways of organosulfur compounds in ambient aerosol in Guangzhou, South China, Atmos. Chem. Phys. 2022, 22, 6919–6935.

Hansen, A.M.K., Kristensen, K., Nguyen, Q.T., Zare, A., Cozzi, F., Nøjgaard, J.K., Skov, H., Brandt, J., Christensen, J.H., Ström, J., Tunved, P., Krejci, R. & Glasius, M. Organosulfates and organic acids in Arctic aerosols: speciation, annual variation and concentration levels, Atmospheric Chemistry and Physics, 2014, 14, 15, 7807.

Glasius, M., Bering, M.S., Yee, L.D., de Sá, S.S., Isaacman-VanWertz, G., Wernis, R.A., Barbosa, H.M., Alexander, M.L., Palm, B.B., Hu, W. and Campuzano-Jost, P., Organosulfates in aerosols downwind of an urban region in central Amazon. Environmental Science: Processes & Impacts, 2018, 20, 11,1546-1558.

Stone, E.A., Yang, L., Liya, E.Y. and Rupakheti, M., Characterization of organosulfates in atmospheric aerosols at Four Asian locations. Atmospheric Environment, 2012, 47, 323-329.

Response: We greatly appreciate your suggestion. All references you mentioned above have been added in the revised manuscript.

Line 53: …(Tolocka andTurpin 2012; Stone et al. 2012; Surratt et al. 2008; Hettiyadura et al. 2018)…

Lines 78-80: …(Kristensen andGlasius 2011; Hettiyadura et al. 2017; Hawkins et al. 2010; Stone et al. 2012; Hettiyadura et al. 2018; Hansen et al. 2014; Glasius et al. 2018)…

Lines 82-83: …(Wang et al. 2021; Ding et al. 2022; Jiang et al. 2022; Nozière et al. 2010; O'brien et al. 2014) …

2) *Line 135: Clarify here in the main text that surrogate standards were used for quantitation, with the caveat that this practice can introduce error due to differences in ionization efficiency with ESI.*

Response: We totally agree with your point of view. This is an issue that deserves special attention. Thus, more descriptions have been added in the revised manuscript (Lines 139−169).

Lines 139−169: ..It is worth noting that most of identified OSs were semi-quantified using surrogate standards because of the lack of authentic standards (Staudt et al. 2014; Hettiyadura et al. 2015). The surrogate OS standards included potassium phenyl sulfate (98%, Tokyo Chemical Industry), methyl sulfate (99%, Macklin), sodium octyl sulfate (95%, Sigma-Aldrich), glycolic acid sulfate (artificial synthesis), lactic acid sulfate (artificial synthesis), limonaketone sulfate (artificial synthesis), and α-pinene sulfate (artificial synthesis) (Olson et al. 2011; Wang et al. 2017; Hettiyadura et al. 2019; Hettiyadura et al. 2017; Wang et al. 2018), as detailed by our previous study (Wang et al. 2021)…

…In general, the differential ionization efficiencies and fragmentation patterns in the OS measurement may introduce biases (Hettiyadura et al. 2017). Consequently, the OS species shown in Table 1 and Table S1 should not be regarded as an accurate measure of OS compounds, but a best solution in the absence of authentic OS standards (Hettiyadura et al. 2015; Hettiyadura et al. 2017; Hettiyadura et al. 2019; Wang et al. 2021)…

3) *Line 135: What was the criteria for choosing specific surrogate compounds for quantitation of observed species?*

Response: Considering that OSs with similar structures of carbon backbone typically have similar MS responses (Wang et al. 2017; Wang et al. 2021), the selection of surrogate standard for a given OS was primarily based on the similarities in the carbon chain structure of the standard and targeted OS species (Hettiyadura et al. 2017). Furthermore, the similarities of the sulfur-containing fragment ions in the MS/MS spectra of the standard and targeted OS species have also been adopted (Wang et al. 2021; Hettiyadura et al. 2019).

Lines 147−160: …Considering that OSs with similar structures of carbon backbone typically have similar MS responses (Wang et al. 2021; Wang et al. 2017), the selection of surrogate standard for a given OS was primarily based on the similarities in the carbon chain structure of the standard and targeted OS species (Hettiyadura et al. 2017). Furthermore, the similarities of the sulfur-containing fragment ions in the MS/MS spectra of the standard and targeted OS species have also been adopted (Wang et al. 2021; Hettiyadura et al. 2019). For OSs that have been reported in previous studies, MS/MS can further support their structural identifications (Table 1). However, most of OSs without identified structural information were classified and semi-quantified according to their molecular formulas and correlation analysis with known OSs and unidentified OSs (Sect. S1) (Bryant et al. 2021; Hettiyadura et al. 2019). Details about the standards used for quantitative OS species as well as about the classification or identification of OSs were shown in Table 1, Table S1, and Supplementary Information (Sect. S1)…

4) Line 137/ Table S2,S3: Are the reported concentrations corrected for recoveries?

Response: In this study, we did not use recoveries to correct the results. The recoveries of OS standards ranged from 84% to 94% (87% ± 4%) in this study. In addition, (Hettiyadura et al. 2015) has been demonstrated to efficiently recover 83%–121 % of organosulfates with aliphatic, aromatic, carbonyl, hydroxyl, and carboxyl acid groups. Thus, we assumed that there is a high extraction efficiency for major OS species in this study, as indicated by previous studies (Hettiyadura et al. 2019; Hettiyadura et al. 2017; Bryant et al. 2021; Wang et al. 2018; Wang et al. 2021).

The added descriptions in the revised manuscript were shown below (Lines 169–171). Lines 169–171: …The recoveries of OS standards ranged from 84% to 94% (87% ± 4%). Thus, we assumed that there is a high extraction efficiency for major OS species in this study, as indicated by previous studies (Wang et al. 2021; Hettiyadura et al. 2015).

5) Line 222-224: Add citation to support statement.

Response: More references have been added in the revised manuscript (Line 266).

6) Table S1: In the version of Table S1 at the end of the main text, a footnote states "Compounds have been confirmed through structural identification using MS/MS." True structural confirmation can only be achieved using authentic standards, and thus this statement is not necessarily correct. Consider rewording to say that MS/MS data supports tentative structural identification based on the listed references. If associated references have confirmed structures using authentic standards, an additional column

on the table with the structure names would be helpful (beyond just the chemical formula).

Response: We are very sorry for this confusing expression. We have changed the original inappropriate sentence to "MS/MS data supports tentative structural identification based on the listed references". In addition, the additional column about the structure information has been added in the Table 1 (Lines 906–907).

7) *Lines 402-403: If both 2MGA-OS and 2MT-OS are products of isoprene oxidation, why do you suspect this is the case?*

Response: During isoprene oxidation by •OH, 2-MT-OS and 2-MGA-OS are produced under low (i.e., IEPOX pathway) and high (i.e., HMML or methacrylic acid epoxide (MAE) pathways) NO_x conditions, respectively (Hettiyadura et al. 2017; Surratt et al. 2010; Nguyen et al. 2015). The 2-MT-OS/2-MGA-OS mean ratio in the daytime was 9.7–12.1, indicating that IEPOX pathway was dominated. In theory, the IEPOX pathway mainly occurs in the daytime. However, the 2-MT-OS/2-MGA-OS mean ratio in the nighttime was 13.1–15.0, which was significantly higher than that in the daytime. Thus, a plausible explanation for this is that the IEPOX pathway may be a potential mechanism to generate OS_i in the nighttime.

8) *Line 490: How was aerosol pH measured?*

Response: A thermodynamic model (ISORROPIA-II) was used to predict the value of pH (Guo et al. 2015; Hennigan et al. 2015). The model was operated with particle-

phase concentrations of Na^+, SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, Ca^{2+}, K^+, and Mg^{2+}, as well as ambient temperature and relative humidity as the inputs. Moreover, the forward mode with the thermodynamically metastable state was selected (Wang et al. 2021; Xu et al. 2020), which was shown to give a more accurate representation of aerosol pH than results obtained from the reverse-mode calculations (Guo et al. 2015; Hennigan et al. 2015). Although the uncertainties will exist during pH prediction, this simplified calculation can largely represent the actual value of pH (Guo et al. 2015; He et al. 2018) (Lines 179–191).

Technical Corrections:

1) *Table S1: There are two versions of Table S1, one in the supplement and one at the end of the main text- these should be labeled differently because they are two separate tables.*

Response: We greatly appreciate your meticulous review. The "Table S1" has been changed to "Table 1" in the revised manuscript (Lines 906-907).

2) *Line 207: Typo "rang" should be corrected to "range"*

Response: We greatly appreciate your meticulous review. The revision has been made (Line 245).

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

Reference:

Bryant, D. J., Elzein, A., Newland, M., White, E., Swift, S., Watkins, A., Deng, W., Song, W., Wang, S., Zhang, Y., Wang, X., Rickard, A. R., and Hamilton, J. F.: Importance of Oxidants and Temperature in the Formation of Biogenic Organosulfates and Nitrooxy Organosulfates, ACS Earth Space Chem., 5, 2291-2306, 10.1021/acsearthspacechem.1c00204, 2021.

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