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 Reviewer #2 and our responses to them

Comments:

This study by Yang and colleagues focused on quantification of organosulfates species in the ambient PM2.5 samples collected in urban and suburban Shanghai in summer 2021. The manuscript compared the diurnal variations of particulate OSs between an urban site and suburban site. The manuscript further investigated the correlation between OSs and other factors such as [UV], [O$_3$], [SO$_4^{2-}$], [NOx], meteorological conditions, and aerosol pH and liquid water content. Based on those analyses, the manuscript concludes that the daytime photochemistry and elevated anthropogenic sulfate are the main drivers of OS formation in summertime Shanghai. Overall, the manuscript conveys a quality presentation of valuable field data and will appeal to the readership of Atmospheric Chemistry and Physics. The following are the detailed comments that I suggest the authors address before the manuscript can be accepted for publication.

Response: We appreciate the reviewer's valuable comments on our work. Our responses to the specific comments and changes made in the manuscript are given below.

Major Comments:

1) My main concern with the manuscript is the lack of adequate account of the quantification method and assessment of the uncertainty associated with using surrogate standards. This is important when comparing the results from this work to other studies in the literature (Line 197-213) and for future reference.

Response: We appreciate the reviewer's valuable comments. This is a very critical issue. More descriptions and 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. 2021); moreover, 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 (Wang et al. 2019; Tao et al. 2014; Kundu et al. 2013; Meade et al. 2016; Wang et al. 2018). Detailed quantification method and assessment of the uncertainty have also been shown in our previous study (Wang et al. 2021).

The added descriptions in the revised manuscript were shown below (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). 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). We found that most of OSs without identified structural information in previous studies and this study had significantly lower peak intensity compared to those listed in Table 1, implying that these OS compounds have weak impact on total OS abundance in ambient aerosols. 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)...

2) Line 123 mentions camphorsulfonic acid was used as an internal standard. It is a relatively strong acid and may catalyze secondary processes during sample preparation.

For example, oxidized organic vapors that are precursors to OSs deposited on the filter, dissolved in the extracts, and reacted with sulfate to form OSs (Fleming et al., 2019, 10.1021/acsearthspacechem.9b00036). OSs can also undergo acid-catalyzed hydrolysis. Please discuss the extent to which camphorsulfonic acid may lead to artifacts and bias the quantification results.

Response: The internal standard we used was sodium camphor sulfonate instead of camphor sulfonic acid. We are very sorry for this writing error. However, we believe that this is a very noteworthy issue. Thus, we added experiments to explore the impact of camphor sulfonic acid as an internal standard on the measurement results. As shown in Figure 1, there was no significant difference in ion signals between sample extracts with adding sodium camphor sulfonate and camphor sulfonic acid as internal standards.
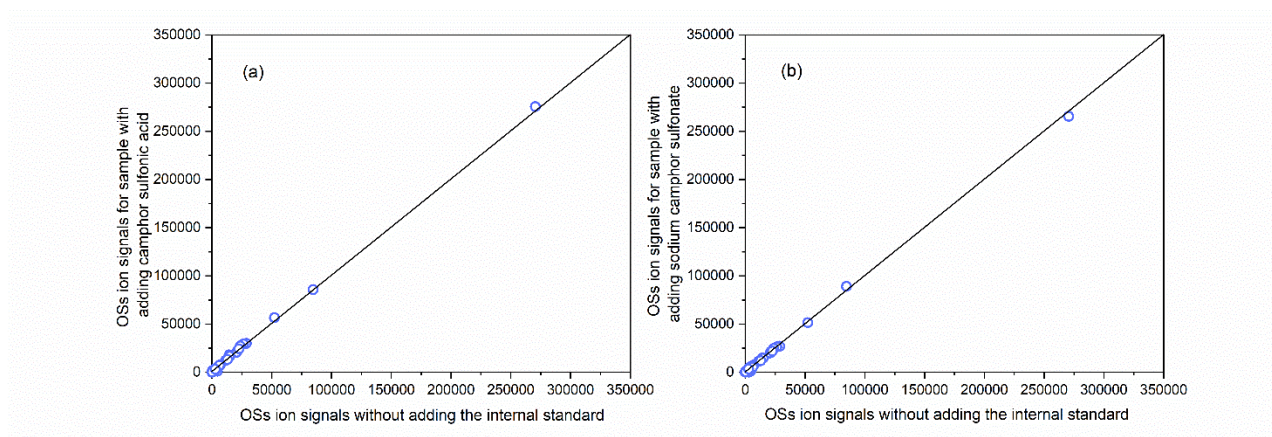
Figure 1. A comparison of ion signals of the 130 semi-quantified OSs in sample extracts with adding (a) camphor sulfonic acid or (b) sodium camphor sulfonate as internal standards and without adding the internal standard.

Sincerely, we are very grateful to the reviewers for this excellent comment.

2) *Line 474-476: Can authors elaborate "The dilution and deposition effects from the daytime to the nighttime…"? The dilution effect decreases from daytime to the nighttime. The diurnal pattern of VC (Figure S4) also suggests that dilution and diffusion happen more frequently during daytime. Therefore, the quoted statement seems contradictory and doesn't explain the significantly lower concentration of C_2-C_3 OS and OS_a species during nighttime as stated in the previous sentence. The same contradiction occurs in Line 403-406.*

Response: We apologize for these confusing expressions. Our original intention was to explain that the OSs observed in the nighttime may partially come from the OSs generated during the daytime. This is because the enhanced diffusion effect during the daytime can result in a decrease in the amount of OS produced during the daytime to deposit into the nighttime.

More revisions have been made in the manuscript, as shown below (Lines 445–453).

Lines 446–454: …Another possible explanation for the decreased OS concentration in the nighttime is that these OSs were mainly formed during the daytime, but had a lower abundance in the nighttime due to deposition and weak nighttime formation. Namely, considering the strong diffusion effect during the daytime and the weak diffusion effect at the nighttime (**Figure S4**), the nighttime OSs may be partially derived from OSs formed via photochemical processes during the daytime. This is because the enhanced diffusion effect during the daytime can result in a decrease in the amount of OS produced during the daytime to deposit into the nighttime.

3) *Can the authors comment on the potential bias in acidity prediction as OSs were not*

considered in the thermodynamic model? The bias is expected to increase when organic sulfate contribution to total sulfates increases (Riva et al., 2019, 10.1021/acs.est.9b01019).

Response: We investigated different outputs of the pH values calculated by ISORROPIA-II between the cases with and without considering OSs as additional sulfates. The pH values predicted from these two cases (2.55 ± 0.93 vs 2.65 ± 0.94 at the urban site and 2.17 ± 0.68 vs 2.23 ± 0.74 at the suburban site) have an insignificant difference. This calculation result should be reasonable because the average ratio of the total OSs to total inorganic sulfates in the urban and suburban sites was 0.048 ± 0.03 and 0.046 ± 0.03, respectively. In addition, the average ratio of the total OSs to total inorganic sulfates was much lower than the observations at the Southeastern United States (0.73) and the Amazon (4.66) (Riva et al. 2019). Thus, OSs were expected to have an insignificant impact on pH prediction.

The added descriptions in the revised manuscript were shown below (Lines 185–191). Lines 185–191: …In particular, we compared different outputs of the pH values calculated by ISORROPIA-II between the cases with and without considering OSs as additional sulfates to investigate potential impact of OSs on pH prediction (Riva et al. 2019). The pH values predicted from these two cases (2.55 ± 0.93 vs 2.65 ± 0.94 at the urban site and 2.17 ± 0.68 vs 2.23 ± 0.74 at the suburban site) have an insignificant difference. Thus, OSs were expected to have a considerably small contribution to pH prediction in this study…

4) *Line 197-213 and Table S4: Please give a more thorough account of studies that*

measured ambient OSs. Examples are but not limited to as follows:

Ma, Y.; Xu, X.; Song, W.; Geng, F.; Wang, L. Seasonal and Diurnal Variations of Particulate Organosulfates in Urban Shanghai, China. Atmos. Environ. 2014, 85, 152–160. https://doi.org/10.1016/j.atmosenv.2013.12.017.

Meade, L. E.; Riva, M.; Blomberg, M. Z.; Brock, A. K.; Qualters, E. M.; Siejack, R. A.; Ramakrishnan, K.; Surratt, J. D.; Kautzman, K. E. Seasonal Variations of Fine Particulate Organosulfates Derived from Biogenic and Anthropogenic Hydrocarbons in the Mid-Atlantic United States. Atmos. Environ. 2016, 145, 405–414. https://doi.org/10.1016/j.atmosenv.2016.09.028.

Rattanavaraha, W.; Chu, K.; Budisulistiorini, S. H.; Riva, M.; Lin, Y.-H.; Edgerton, E. S.; Baumann, K.; Shaw, S. L.; Guo, H.; King, L.; Weber, R. J.; Neff, M. E.; Stone, E. A.; Offenberg, J. H.; Zhang, Z.; Gold, A.; Surratt, J. D. Assessing the Impact of Anthropogenic Pollution on Isoprene-Derived Secondary Organic Aerosol Formation in PM2.5 Collected from the Birmingham, Alabama, Ground Site during the 2013 Southern Oxidant and Aerosol Study. Atmos Chem Phys 2017, 16 (8), 4897–4914. https://doi.org/10.5194/acp-16-4897-2016.

Glasius, M.; Hansen, A. M. K.; Claeys, M.; Henzing, J. S.; Jedynska, A. D.; Kasper-Giebl, A.; Kistler, M.; Kristensen, K.; Martinsson, J.; Maenhaut, W.; Nøjgaard, J. K.; Spindler, G.; Stenström, K. E.; Swietlicki, E.; Szidat, S.; Simpson, D.; Yttri, K. E. Composition and Sources of Carbonaceous Aerosols in Northern Europe during Winter. Atmos. Environ. 2018, 173, 127–141. https://doi.org/10.1016/j.atmosenv.2017.11.005.

Riva, M.; Chen, Y.; Zhang, Y.; Lei, Z.; Olson, N. E.; Boyer, H. C.; Narayan, S.; Yee, L. D.; Green, H. S.; Cui, T.; Zhang, Z.; Baumann, K.; Fort, M.; Edgerton, E.; Budisulistiorini, S. H.; Rose, C. A.; Ribeiro, I. O.; Oliveira, R. L. e; Santos, E. O. dos; Machado, C. M. D.; Szopa, S.; Zhao, Y.; Alves, E. G.; Sá, S. S. de; Hu, W.; Knipping, E.

M.; Shaw, S. L.; Junior, S. D.; Souza, R. A. F. de; Palm, B. B.; Jimenez, J.-L.; Glasius, M.; Goldstein, A. H.; Pye, H. O. T.; Gold, A.; Turpin, B. J.; Vizuete, W.; Martin, S. T.; Thornton, J. A.; Dutcher, C. S.; Ault, A. P.; Surratt, J. D. Increasing Isoprene Epoxydiol-to-Inorganic Sulfate Aerosol Ratio Results in Extensive Conversion of Inorganic Sulfate to Organosulfur Forms: Implications for Aerosol Physicochemical Properties. Environ Sci Technol 2019, 53 (15), 8682–8694. https://doi.org/10.1021/acs.est.9b01019.

Chen, Y.; Dombek, T.; Hand, J.; Zhang, Z.; Gold, A.; Ault, A. P.; Levine, K. E.; Surratt, J. D. Seasonal Contribution of Isoprene-Derived Organosulfates to Total Water-Soluble Fine Particulate Organic Sulfur in the United States. Acs Earth Space Chem 2021. https://doi.org/10.1021/acsearthspacechem.1c00102.

I also encouraged authors to check out more references in Brüggemann, M.; Xu, R.; Tilgner, A.; Kwong, K. C.; Mutzel, A.; Poon, H. Y.; Otto, T.; Schaefer, T.; Poulain, L.; Chan, M. N.; Herrmann, H. Organosulfates in Ambient Aerosol: State of Knowledge and Future Research Directions on Formation, Abundance, Fate, and Importance. Environ Sci Technol 2020, 54 (7), 3767–3782. https://doi.org/10.1021/acs.est.9b06751.

Response: We appreciate the reviewer's kind and valuable comments. All references you mentioned have been added in the **Table S4**.

Technical Correction

1) *Line 66: "hydroxymethel-methyl-α-lactone" should be hydroxymethyl-methyl-α-lactone*

Response: The revision has been made in the revised manuscript (Lines 66–67).

2) *Line 130: "Quodropole" should be "Quadrupole"?*

Response: The revision has been made in the revised manuscript (Line 132).

3) *Line 254: The concentrations are shown in Figure 1(b) and 1(c) instead of 1(e) and 1(f)?*

Response: The revision has been made in the revised manuscript (Line 297).

4) *Figure 1: What do the dashed dividing lines in (a), (b), and (c) represent? Please clarify in the figure caption.*

Response: The revision has been made in the revised manuscript (Lines 919–922).

Lines 919–922 :…The areas divided by dashed lines in Figures a-c indicate $C_5H_{11}O_7S^-$, $OS_{i\text{-other}}$, NOS_i, and NOS_m in sequence, as illustrated in Figure b. The areas divided by dashed lines in Figures d-f indicate aromatic and aliphatic OSs in sequence, as illustrated in Figure d.

5) *Figure 2: Does OS_i include $C_5H_{11}O_7S^-$ in the figure? The scale of OS/OM looks off. Is it percentage number?*

Response: We are very sorry for the confusion caused by our figure. $C_5H_{11}O_7S^-$ was included in the OS_i. In addition, the scale of OS/OM was shown on the far right side of the panels (a-b).

Line 930 :…$C_5H_{11}O_7S^-$ (major OS_i species), NOS_i, and OS/OM (%);…

6) *Authors mislabeled the table in the main text "Table S1".*

   Response: The revision has been made in the revised manuscript (Line 905).

7) *Table S4: Hettiyadura et al. 2017 (Centreville, AL) appears twice. One is categorized as "Suburban" and the other "Forest". The concentrations are also different.*

   Response: The sampling site at Centreville, AL was described as a rural and forested area (Hettiyadura et al. 2017). In the updated Table S4, Centreville, AL has been classified into a rural site.

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

Reference:

Hettiyadura, A. P. S., Jayarathne, T., Baumann, K., Goldstein, A. H., de Gouw, J. A., Koss, A., Keutsch, F. N., Skog, K., and Stone, E. A.: Qualitative and quantitative analysis of atmospheric organosulfates in Centreville, Alabama, Atmos. Chem. Phys., 17, 1343-1359, 10.5194/acp-17-1343-2017, 2017.

Kundu, S., Quraishi, T. A., Yu, G., Suarez, C., Keutsch, F. N., and Stone, E. A.: Evidence and quantitation of aromatic organosulfates in ambient aerosols in Lahore, Pakistan, Atmospheric Chemistry and Physics, 13, 4865-4875, 10.5194/acp-13-4865-2013,

2013.

Meade, L. E., Riva, M., Blomberg, M. Z., Brock, A. K., Qualters, E. M., Siejack, R. A., Ramakrishnan, K., Surratt, J. D., and Kautzman, K. E.: Seasonal variations of fine particulate organosulfates derived from biogenic and anthropogenic hydrocarbons in the mid-Atlantic United States, Atmospheric Environment, 145, 405-414, 10.1016/j.atmosenv.2016.09.028, 2016.

Riva, M., Chen, Y., Zhang, Y., Lei, Z., Olson, N. E., Boyer, H. C., Narayan, S., Yee, L. D., Green, H. S., Cui, T., Zhang, Z., Baumann, K., Fort, M., Edgerton, E., Budisulistiorini, S. H., Rose, C. A., Ribeiro, I. O., RL, E. O., Dos Santos, E. O., Machado, C. M. D., Szopa, S., Zhao, Y., Alves, E. G., de Sa, S. S., Hu, W., Knipping, E. M., Shaw, S. L., Duvoisin Junior, S., de Souza, R. A. F., Palm, B. B., Jimenez, J. L., Glasius, M., Goldstein, A. H., Pye, H. O. T., Gold, A., Turpin, B. J., Vizuete, W., Martin, S. T., Thornton, J. A., Dutcher, C. S., Ault, A. P., and Surratt, J. D.: Increasing Isoprene Epoxydiol-to-Inorganic Sulfate Aerosol Ratio Results in Extensive Conversion of Inorganic Sulfate to Organosulfur Forms: Implications for Aerosol Physicochemical Properties, Environ. Sci. Technol., 53, 8682-8694, 10.1021/acs.est.9b01019, 2019.

Tao, S., Lu, X., Levac, N., Bateman, A. P., Nguyen, T. B., Bones, D. L., Nizkorodov, S. A.,

Laskin, J., Laskin, A., and Yang, X.: Molecular characterization of organosulfates in organic aerosols from Shanghai and Los Angeles urban areas by nanospray-desorption electrospray ionization high-resolution mass spectrometry, Environ. Sci. Technol., 48, 10993-11001, 10.1021/es5024674, 2014.

Wang, K., Zhang, Y., Huang, R. J., Wang, M., Ni, H., Kampf, C. J., Cheng, Y., Bilde, M., Glasius, M., and Hoffmann, T.: Molecular Characterization and Source Identification of Atmospheric Particulate Organosulfates Using Ultrahigh Resolution Mass Spectrometry, Environ Sci Technol, 53, 6192-6202, 10.1021/acs.est.9b02628, 2019.

Wang, Y., Ren, J., Huang, X. H. H., Tong, R., and Yu, J. Z.: Synthesis of Four Monoterpene-Derived Organosulfates and Their Quantification in Atmospheric Aerosol Samples, Environ. Sci. Technol., 51, 6791-6801, 10.1021/acs.est.7b01179, 2017.

Wang, Y., Zhao, Y., Wang, Y., Yu, J. Z., Shao, J., Liu, P., Zhu, W., Cheng, Z., Li, Z., Yan, N., and Xiao, H.: Organosulfates in atmospheric aerosols in Shanghai, China: seasonal and interannual variability, origin, and formation mechanisms, Atmos. Chem. Phys., 21, 2959-2980, 10.5194/acp-21-2959-2021, 2021.

Wang, Y., Hu, M., Guo, S., Wang, Y., Zheng, J., Yang, Y., Zhu, W., Tang, R., Li, X., Liu, Y., Le Breton, M., Du, Z., Shang, D., Wu, Y., Wu, Z., Song, Y., Lou, S., Hallquist, M.,

and Yu, J.: The secondary formation of organosulfates under interactions between biogenic emissions and anthropogenic pollutants in summer in Beijing, Atmos. Chem. Phys., 18, 10693-10713, 10.5194/acp-18-10693-2018, 2018.