Response to Review Comments by Editor on "Bayesian Inference-Based Estimation of Hourly Primary and Secondary Organic Carbon at Suburban Hong Kong: Multi-temporal Scale Variations and Evolution Characteristics during $PM_{2.5}$ episodes" by S. Wang et al.

We thank the editor for the detailed comments. Below is our point-by-point response to each comment, marked in blue. The revised text in the main manuscript is also marked in blue.

1. I suggest to delete the statement of "with sulfate identified as the most suitable SOC tracer" in Line 20 to avoid misleading of introducing sulfate as a "recommended" tracer.

Response: Suggestion taken. The statement has been deleted in the revised manuscript.

2. In Line 250-251: It is better to provide more specific discussion about where and when SOC formation pathways could be different from sulfate from our current understanding. For example, southeastern US, NCP in China, and the Amazon forest are all interested area where the SOA formation and sulfate origin are distinct.

Response: We thank the reviewer for this suggestion and made the following changes.

Lines 248-258:

> Considering the similarities in formation pathways, the BI-SO_4^{2-} model would yield more accurate estimations when regional transport has a stronger influence compared to local formation processes. Conversely, when SOC formation pathways are significantly disconnected in time and in space from those of sulfate, the performance of the BI-SO_4^{2-} model would be less satisfactory. For example, in clean regions like the southeast US and Amazon where SOA were dominated by fast local oxidation chemistry of biogenic VOCs (Xu et al., 2015; Riemer et al., 1998; Langford et al., 2022), sulfate may not serve as a good tracer to track SOA in the BI-SO_4^{2-} model. In urban areas where daytime photochemical processing may play a significant role in SOA formation, e.g., summertime Beijing (Duan et al., 2020), sulfate may also fail as a proper tracer. Thus, an integrative evaluation of available PM composition, along with related air pollutant and meteorological conditions, is recommended to aid identification of a suitable SOC tracer in implementing the BI method, as well as assessing the interpretability of the BI method derived POC and SOC data.

References:

Duan, J., Huang, R.-J., Li, Y., Chen, Q., Zheng, Y., Chen, Y., Lin, C., Ni, H., Wang, M., Ovadnevaite, J., Ceburnis, D., Chen, C., Worsnop, D. R., Hoffmann, T., O'Dowd, C., and Cao, J.: Summertime and wintertime atmospheric processes of secondary aerosol in Beijing, Atmos. Chem. Phys., 20, 3793-3807, http://doi.org/10.5194/acp-20-3793-2020, 2020.

Langford, B., House, E., Valach, A., Hewitt, C. N., Artaxo, P., Barkley, M. P., Brito, J., Carnell, E., Davison, B., MacKenzie, A. R., Marais, E. A., Newland, M. J., Rickard, A. R., Shaw, M. D., Yáñez-Serrano, A. M., and Nemitz, E.: Seasonality of isoprene emissions and oxidation products above the remote Amazon, Environmental Science: Atmospheres, 2, 230-240, http://doi.org/10.1039/d1ea00057h, 2022.

Riemer, D., Pos, W., Milne, P., Farmer, C., Zika, R., Apel, E., Olszyna, K., Kliendienst, T., Lonneman, W., Bertman, S., Shepson, P., and Starn, T.: Observations of nonmethane hydrocarbons and oxygenated volatile organic compounds at a rural site in the southeastern United States, J. Geophys. Res.-Atmos., 103, 28111-28128, http://doi.org/10.1029/98jd02677, 1998.

Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S. H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proc Natl Acad Sci U S A, 112, 37-42, http://doi.org/10.1073/pnas.1417609112, 2015.

3. The authors highlight the potential nighttime aqueous-phase reactions for SOC. Please clarify whether this analysis would be affected by the choice of sulfate as the SOC tracer?

Response: Previous field measurements and chamber studies have observed significant SOA (or SOC) enhancement with increasing water uptake and acidification, highlighting the important role of aqueous phase reactions in facilitating secondary organic aerosol formation (Huang et al., 2018; Mcneill et al., 2012; Guo et al., 2012). Recent studies pointed out that abundant aerosol water content and acidic conditions may also notably promote secondary sulfate formations in ambient environment (Huang et al., 2023; Wang et al., 2019). Furthermore, it has been reported that SOA could be directly mediated by the abundance of sulfate (Xu et al., 2015).

In this study, we observed positive correlations between BI-SO_4^{2-} SOC and AWC and acidity during nighttime episodic hours, suggesting potential nocturnal aqueous-phase reactions for SOC formation. We further explore the relationships of SOC with AWC and acidity by using NH_4^+ as SOC tracer. As shown in Figure R1, the relationships are less significant compared with those using SO_4^{2-}. These results are reasonable since the BI-NH_4^+ SOC have higher uncertainties with less satisfied model performance (indicating by BIC) compared with BI-SO_4^{2-} SOC. Due to the challenge in directly measuring AWC and acidity, we use ISOPPIRA II model to compute the AWC and acidity, in which sulfate is an important model input. Therefore, the effects of sulfate on influencing the AWC and acidity simulation, and SOC results could not be ruled out. Sulfate, as an abundant secondary constituent of $PM_{2.5}$, is a key player in multiple formation pathways of SOA. There are chemical and physical basis for our conclusion of the importance of potential nighttime aqueous-phase reactions for SOC. We do not think it is an "artifact" of selecting sulfate as the SOC tracer in our BI-method.

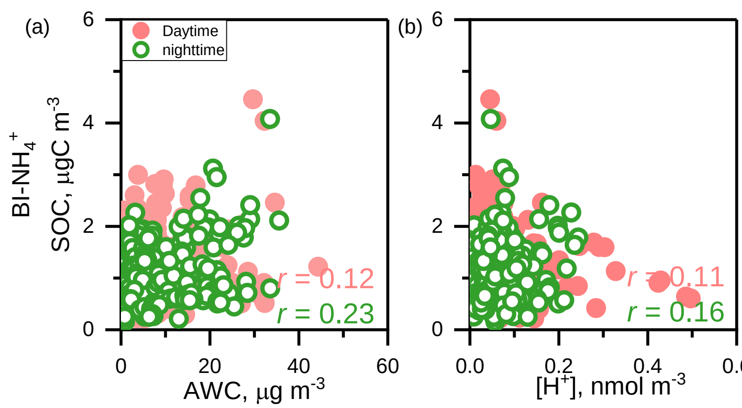

Figure R1. Scatter plot of SOC with (a) aerosol water contents (AWC) and (b) [H^+] during the winter haze episodes. The solid red circle represents daytime hours, blank green circle represents nighttime hours.

References:

Guo, S., Hu, M., Guo, Q., Zhang, X., Zheng, M., Zheng, J., Chang, C. C., Schauer, J. J., and Zhang, R.: Primary sources and secondary formation of organic aerosols in Beijing, China, Environ. Sci. Technol., 46, 9846-9853, http://doi.org/10.1021/es2042564, 2012.

Huang, D. D., Zhang, Q., Cheung, H. H. Y., Yu, L., Zhou, S., Anastasio, C., Smith, J. D., and Chan, C. K.: Formation and Evolution of aqSOA from Aqueous-Phase Reactions of Phenolic Carbonyls: Comparison between Ammonium Sulfate and Ammonium Nitrate Solutions, Environ Sci Technol, 52, 9215-9224, http://doi.org/10.1021/acs.est.8b03441, 2018.

Huang, X., Liu, Z., Ge, Y., Li, Q., Wang, X., Fu, H., Zhu, J., Zhou, B., Wang, L., George, C., Wang, Y., Wang, X., Su, J., Xue, L., Yu, S., Mellouki, A., and Chen, J.: Aerosol high water contents favor sulfate and secondary organic aerosol formation from fossil fuel combustion emissions, Npj Clim Atmos Sci, 6, http://doi.org/10.1038/s41612-023-00504-1, 2023.

McNeill, V. F., Woo, J. L., Kim, D. D., Schwier, A. N., Wannell, N. J., Sumner, A. J., and Barakat, J. M.: Aqueous-phase secondary organic aerosol and organosulfate formation in atmospheric aerosols: a modeling study, Environ Sci Technol, 46, 8075-8081, http://doi.org/10.1021/es3002986, 2012.

Wang, H., Ding, J., Xu, J., Wen, J., Han, J., Wang, K., Shi, G., Feng, Y., Ivey, C. E., Wang, Y., Nenes, A., Zhao, Q., and Russell, A. G.: Aerosols in an arid environment: The role of aerosol water content, particulate acidity, precursors, and relative humidity on secondary inorganic aerosols, Sci Total Environ, 646, 564-572, http://doi.org/10.1016/j.scitotenv.2018.07.321, 2019.

Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S. H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proc Natl Acad Sci U S A, 112, 37-42, http://doi.org/10.1073/pnas.1417609112, 2015.

4. Please provide clear descriptions for figures.

Figure 1a and 2a: The error bars are not explained.

Response: Suggestion taken.

The caption has been revised as "Figure 1. (a) Box plot of $\overline{\mathbf{K_1}}$ and $\overline{\mathbf{K_2}}$ values across different seasons (the squares and horizontal lines in the box denote the average and median, the lower and upper boundaries of the boxes represent the 25th and 75th percentile values, and whisker are 10th and 90th percentile). (b) The diurnal variations of $\overline{\mathbf{K_1}}$ and $\overline{\mathbf{K_2}}$ in individual seasons (solid lines represent the average values, area indicate one standard deviation of the results)."

The caption has been revised as "Figure 2. (a) Time series of meteorological parameters (wind speed, wind direction, temperature, and RH), gaseous pollutants (O_3, and NO_x), $PM_{2.5}$ (the red dash line marks the WHO AQG IT-4 value), OC and EC, as well as POC and SOC (the *y*-axis error bars represent uncertainties derived from BI method) and (b) Seasonal variations (the circle and horizontal lines in the box denote the average and median, the lower and upper boundaries of the boxes represent the 25th and 75th percentile values, and whisker are 10th and 90th percentile) during the observation period (16 July 2020–31 December 2021) at the HKUST supersite."

Figure 2b: Box-whistler information is missing.

Response: Suggestion taken. The box-whisker has been defined in the caption.

Figures 4 and 5: Aren't the box bottom and top 25th and 75th, respectively? What are exactly the whistlers?

Response: The box-whisker information has been included in the caption.

"Figure 4. Concentrations of SOC as a function of (a) temperature bins and (b) RH bins under different $PM_{2.5}$ groups in individual seasons during the entire measurement period (the circles and horizontal lines in the box denote the average and median, the lower and upper boundaries of the boxes represent the 25th and 75th percentile values, and whisker are 10th and 90th percentile).

"Figure 5. Concentrations of SOC as a function of (a) O_x bins (b) NO_x bins under different $PM_{2.5}$ groups in individual seasons during the entire measurement period (the circles and horizontal lines in the box denote the average and median, the lower and upper boundaries of the boxes represent the 25th and 75th percentile values, and whisker are 10th and 90th percentile).

Figure 6a: What are the error bars?

Response: The error bars have been defined in the revised manuscript. They are copied here for easy reference:

“Figure 6. Comparison of select pollutant levels during episodes and non-episodes for individual episodes. The comparison parameters include concentrations of (a) O_3, (b) NO_x, (c) $PM_{2.5}$, (d) POC, and (e) SOC, (f) POC and SOC percentage contributions, and mass increment ratios of (g) O_3 and NO_x, (h) $PM_{2.5}$, and (i) POC and SOC. In panels (a)-(e), the filled squares represent the average values during-episode concentrations while the empty circles represent the average of all non-episode hours throughout the individual season, the error bars represent one standard deviation of the results. In panels (g)-(i), the light-yellow shaded zone marks the mass increment ratio (calculated as mass concentration during the episode divided by that during the non-episode hours in the same season) values of less than 1.

Figure 7b and 8b are too small. The box and whistler information is missing. The stars are not explained.

Response: Suggestion taken. Figure 7b and 8b have been modified to be clearer.

The caption has been revised as

“Figure 7. SOC variation characteristics during typhoon episodes in summer 2021. (a) Time series of meteorological parameters (wind speed and direction), gaseous pollutants (O_3 and NO_x), $PM_{2.5}$ mass concentrations, POC and SOC levels and their relative percentage contributions, with the yellow shadow area marking individual episode periods of EP45-51. (b) Concentrations of SOC as a function of temperature, RH, O_x (O_3+NO_2) and NO_x bins, with daytime and nighttime episode hours plotted separately (the squares and horizontal lines in the box denote the average and median, the lower and upper boundaries of the boxes represent the 25th and 75th percentile values, and whisker are 10th and 90th percentile. Significance level (p) by t-test: ****$p < 0.0001$, ***$0.0001 < p < 0.001$, **$0.001 < p < 0.01$, *$0.01 < p < 0.05$).

“Figure 8. SOC variation characteristics during haze episodes in winter 2020 and 2021. (a) Time series of meteorological parameters (wind speed and direction), gaseous pollutants (O_3 and NO_x), $PM_{2.5}$ mass concentrations, POC and SOC levels and their relative percentage contributions, with the yellow shadow area marking individual episodes (EP10-13 and EP62-65). (b) Concentrations of SOC as a function of temperature, RH, O_x (O_3+NO_2) and NO_x bins, with daytime and nighttime episode hours plotted separately (the squares and horizontal lines in the box denote the average and median, the lower and upper boundaries of the boxes represent the 25th and 75th percentile values, and whisker are 10th and 90th percentile. Significance level (p) by t-test: ****$p < 0.0001$, ***$0.0001 < p < 0.001$, **$0.001 < p < 0.01$, *$0.01 < p < 0.05$).