

## Responses to the Reviewer #1' Comments

“Measurement report: Size distributions of urban aerosols down to 1 nm from long-term measurements” by Deng et al.

We appreciate valuable comments from the reviewer, which helped to improve this manuscript. We have addressed them in the following paragraphs (the text in italics is the comments, followed by our response). Additionally, all changes made are highlighted in the revised manuscript.

*This manuscript reports the characteristics of atmospheric aerosol size distributions from ~1 nm to 10  $\mu\text{m}$  with an emphasis on sub-3nm particles from four-year measurements in urban Beijing. On the basis of cluster analysis, three typical types of number size distributions (i.e., daytime NPF type, daytime non-NPF type, and nighttime type) were identified. Based on the modified Whitby model, the simplification of aerosol size distributions in sub-3 nm sizes, i.e., the power function, was introduced. From the source identification of sub-3nm particles in urban Beijing, except for NPF, vehicle emission is another important source. Besides, the concentrations and diel patterns of  $\text{H}_2\text{SO}_4$  monomer and dimer were also reported to better explain the formation mechanisms of NPF.*

*This is a unique dataset for which publication is worthwhile. This manuscript is well structured and written. Hence, I would ask one minor revision and recommend the publication of this article in Atmospheric Chemistry & Physics.*

*Minor comments:*

*Compared to lognormal distributions of larger particles, please add more discussion on why the power function was suitable to depict aerosol size distributions in sub-3 nm sizes.*

**Response:** Thanks for the suggestion. We have added some discussions on the reasons why the power function was chosen to depict aerosol size distribution in the sub-3 nm size range (lines 134-137 in the revised manuscript and Fig. S4 in the Supplementary Information (SI)):

“Note that the power law function was chosen to fit in the sub-3 nm size range because it can well capture the monotonic decrease from  $\text{H}_2\text{SO}_4$  monomer to dimer and then to the sizes representative of aerosol particles. The log-normal distribution function is not a good fit in the sub-3 nm size range (Fig. S4), and especially a “mode” with a peak diameter of ~0.4 nm resulting from such a fit seems not to be reasonable.”

*Figure 2, were  $\text{H}_2\text{SO}_4$  monomer and dimer concentration converted into  $dN/d\log D_p$  according to their mass diameters?*

**Response:** In Fig. 2 (and also Figs. 3, S3, S6, S7, and S9), we converted the  $\text{H}_2\text{SO}_4$  monomer and dimer concentration into  $dN/d\log d_p$  according to their mass diameters using the the method by Jiang et al. (2011). We added some descriptions of the conversion in the revised manuscript (lines 128-130):

“It should be also noted that, in Figs. 2, 3, S3, S6, S7 and S9, the concentration of  $\text{H}_2\text{SO}_4$  monomers and dimers was converted into  $dN/d\log d_p$  using the method by Jiang et al. (2011).”

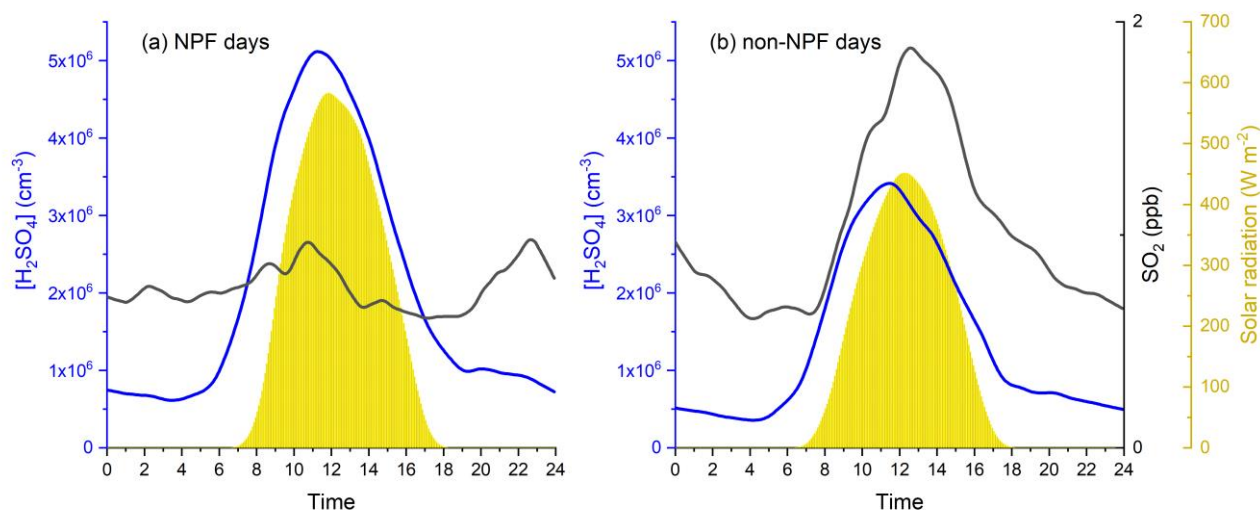
*Figure 3, the label of Y-axis “ $dNd\log D_p$ ” should be “ $dN/d\log D_p$ ”. Please check other figures in the*

manuscript and SI.

**Response:** Thanks for catching this. We have corrected it and carefully checked this issue throughout the entire manuscript and the SI.

Figure 4, for panel C, if available, it would be better to add the diurnal patterns of solar radiation and SO<sub>2</sub>. Also, around 5 a.m., the concentration of sulfuric acid started to rise. Did sulfuric acid follow the diel pattern of radiation at around 5 a.m.? If not, please comment on it.

**Response:** We added a figure including the diurnal patterns of H<sub>2</sub>SO<sub>4</sub> concentration, solar radiation, and SO<sub>2</sub> on NPF and non-NPF days during the measurement period in the SI (Fig. S10). As shown in Fig. R1 (Fig. S10 in the revised SI), the concentration of H<sub>2</sub>SO<sub>4</sub> generally follows the diurnal pattern of solar radiation both on NPF and non-NPF days. This is because as the most vital oxidant to transfer SO<sub>2</sub> into H<sub>2</sub>SO<sub>4</sub> by gas-phase oxidation, OH radicals are strongly correlated to solar radiation.



**Figure R1.** The diurnal variations of H<sub>2</sub>SO<sub>4</sub> monomer concentration, SO<sub>2</sub> concentration and solar radiation on (a) NPF days and (b) non-NPF days during the measurement period. Median values were used in this figure.

However, H<sub>2</sub>SO<sub>4</sub> concentration did increase at ~5 a.m. when there was basically no solar radiation both on NPF and non-NPF days. This might be induced by the production of OH radicals from the ozonolysis of alkenes during the nighttime. Previous studies indicate that the ozonolysis of alkenes can form OH radicals in the absence of solar radiation and thus can lead to the increase of H<sub>2</sub>SO<sub>4</sub> concentration before sunrise (Guo et al., 2021). Other pathways forming OH radicals also likely exist for the increase of H<sub>2</sub>SO<sub>4</sub> concentration before sunrise.

Even though there are pathways to produce H<sub>2</sub>SO<sub>4</sub> without involving solar radiation, the photolysis of ozone is the most important source to produce OH radicals to form H<sub>2</sub>SO<sub>4</sub> in our study. Also, the formation of H<sub>2</sub>SO<sub>4</sub> is not the focus of our study, so we did not explain the possible formation pathways of H<sub>2</sub>SO<sub>4</sub> in detail in the manuscript but added some discussions in the SI (lines 125-126):

“The increased H<sub>2</sub>SO<sub>4</sub> concentration at ~5 a.m. might be induced by the production of OH radicals from the ozonolysis of alkenes during the nighttime (Guo et al., 2021).”

**Reference:**

Guo, Y., Yan, C., Li, C., Ma, W., Feng, Z., Zhou, Y., Lin, Z., Dada, L., Stolzenburg, D., Yin, R., Kontkanen, J., Daellenbach, K. R., Kangasluoma, J., Yao, L., Chu, B., Wang, Y., Cai, R., Bianchi, F., Liu, Y., and Kulmala, M.: Formation of nighttime sulfuric acid from the ozonolysis of alkenes in Beijing, *Atmospheric Chemistry and Physics*, 21, 5499-5511, 10.5194/acp-21-5499-2021, 2021.

Jiang, J., Zhao, J., Chen, M., Eisele, F. L., Scheckman, J., Williams, B. J., Kuang, C., and McMurry, P. H.: First Measurements of Neutral Atmospheric Cluster and 1–2 nm Particle Number Size Distributions During Nucleation Events, *Aerosol Science and Technology*, 45, ii-v, 10.1080/02786826.2010.546817, 2011.