Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., author comment AC2
https://doi.org/10.5194/acp-2022-426-AC2, 2022

Reply on RC2

Jinjin Sun et al.

Author comment on "Seasonal modeling analysis of nitrate formation pathways in Yangtze River Delta region, China" by Jinjin Sun et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-426-AC2, 2022

The study provides a comprehensive overview of the pathways of nitrate formation in the Yangtze River Delta region. The study is of great interest and adds to the knowledge of the chemistry involved in the NO_3^- formation and factors affecting these pathways for an urbanized and heavily populated region. The study is of importance as it provides a seasonal analysis of the NO_3^- formation process which can be highly useful for regulators for planning and mitigation strategies. The paper is well written easy to follow. However, following are a few comments and suggestions which I think will help in improving the overall clarity of the paper.

Major comments:

- The authors should highlight the reason for using SAES emission inventory over the YRD region instead of the MEIC or REAS emission inventory. The authors should also mention the resolution at which the SAES inventory provides emissions.

Responses: Thanks for the comment. In this manuscript, the anthropogenic emissions for the 2017 YRD region were released by the Shanghai Academy of Environmental Sciences (SAES) (An et al., 2021), a high-resolution (4 km × 4 km) air pollutant emission inventory for the entire YRD region. An et al. (2021) revealed that the SAES emission inventory was updated by using emission factors, and $PM_{2.5}$ and NMVOC speciation profiles based on local measure in the YRD region. An et al. (2021) also compared with the MEIC inventory , found that the gases precursors (SO_2 and NO_x) emissions estimated in the SAES emission inventory were lower and more realistic, and particulate matter emissions were higher due to the consideration of dust sources. Moreover, the SAES emission inventory has been thoroughly evaluated in our previous works (Liu et al., 2020;Qin et al., 2021;Li et al., 2021). In those previous studies, the statistical results of predictied $PM_{2.5}$, NO_2, and O_3 concentrations show a better model performance in the YRD region.

Above information about the SAES emission inventory have been added in the revised manuscript (see Lines 166-168): "The anthropogenic emissions for the 2017 YRD region were established by the Shanghai Academy of Environmental Sciences (SAES), a high-resolution (4 km × 4 km) anthropogenic emission inventory across the entire YRD region (An et al., 2021).".

- Line 271-273: The authors may provide a reason for the better performance of the model in predicting the concentrations of PM_5, O_3 and NO_2 when compared to past

studies.

Responses: Table 2 and Figure S1 indicated that the seasonal results of $PM_{2.5}$, O_3 and NO_2 show a better model performance than our previous works. We think the most likely reason is that we used the local anthropogenic emission inventory (SAES, with high-resolution and based on local measure data) to simulate the YRD region. As stated in the manuscript, our meteorological peroformance is comparable to previous studies. But in this study, we used the local emission inputs. As explained in our first response, modeling results using the finer resolution YRD local emissions showed a better model performance in the YRD region when compared to using the MEIC emission inventory.

- The authors may highlight key mitigation strategies for NO_3^-, based on the pathways identified as major contributors to NO_3^- in the YRD region.

Responses: Thanks for the suggestion. Our findings illustrate that local emissions dominate NO_3^- formation in the YRD (50–62%), more specifically, locally-emitted NOx reacting with OH and partitioning into particles with NH_3 (mostly from local sources, more than 93.0%), indicating that the coordinated control of precursors (i.e., NOx and NH_3) and reduction of the oxidative capacity of the atmosphere is crucial for NO_3^- reduction.

Furthermore, regional transport contributes 38–50% to NO_3^- formation in the YRD region. Indirect transport contributes 24–37% through transported O_3 reacting with local NOx at night, indicating that the simultaneous controlling of O_3 and NO_3^- in the larger scale region is also important for NO_3^- reduction in the YRD.

Above discussion have been added in the revised manuscript in lines 460-468.

- The authors should add a section highlighting the limitations of the current study.

Responses: Limitations of the current study have been added in the revised manuscript in Lines 469-484.

This manuscript investigated the seasonal variations in the NO_3^- formation mechanisms, including local emission and regional transport contributions, as well as dominant processes and major chemical pathways in the YRD region. However, there are still some limitations in this manuscript, such as the insufficient heterogeneous chemistry on the dust particles' surface and uncertainties in precursors emissions in the CMAQ model affect the model performance of NO_3^- during the spring and autumn (Xie et al., 2022). Furthermore, the Integrated Reaction Rate (IRR) analysis was employed to quantify the rates of TNO_3 (sum of NO_3^- and HNO_3) chemical reactions pathways, which potentially lead to differences in chemical pathways rates and contributions between NO_3^- and TNO_3. Figure 6(b) illustrates that TNO_3 chemical production is dominated by the $OH+NO_2$ pathway on the daily timescale, accounting for 69.3–86.9 % in Shanghai. Notably, due to the higher temperature during the daytime, the potential production for NO_3^- is not as high as that of the nocturnal chemical pathway (mainly the HET N_2O_5 pathway at night), which potentially lead to underestimate in the nocturnal pathway contribution to NO_3^-.

Minor Comments:

- Line 90 and 132-133: Check grammar.

Responses: Corrected. We have carefully revised the manuscript and corrected the grammatical sentences in Lines 88-91 and 132-135.

- Line 102-104 and 133-134: Rephrase the sentence to improve clarity.

Responses: Corrected. We have rephrased the sentences, as following in Lines 102-104: "Prabhakar et al. (2017) revealed that the active nocturnal NO_3^- formation from the upper PBL contributed 80 % to daytime surface NO_3^- concentrations in winter of 2013 in California.", and lines 133-135: "Most previous studies have focused on only a few short period of NO_3^- pollution episodes, and lacked the seasonal analysis for the full year.".

- Fig S4, S8, S10 and Table S7 have not been referred to in the main manuscript.

Responses: Corrected. Table S7 and Figs S4, S8, S10 have been removed in the Supplementary material. The manuscript has been revised accordingly.

References:

An, J., Huang, Y., Huang, C., Wang, X., Yan, R., Wang, Q., Wang, H., Jing, S., Zhang, Y., Liu, Y., Chen, Y., Xu, C., Qiao, L., Zhou, M., Zhu, S., Hu, Q., Lu, J., and Chen, C.: Emission inventory of air pollutants and chemical speciation for specific anthropogenic sources based on local measurements in the Yangtze River Delta region, China, Atmos. Chem. Phys., 21, 2003-2025, 10.5194/acp-21-2003-2021, 2021.

Li, L., Xie, F., Li, J., Gong, K., Xie, X., Qin, Y., Qin, M., and Hu, J.: Diagnostic analysis of regional ozone pollution in Yangtze River Delta, China: A case study in summer 2020, Sci. Total Environ., 151511, https://doi.org/10.1016/j.scitotenv.2021.151511, 2021.

Liu, T., Wang, X. Y., Hu, J. L., Wang, Q., An, J., Gong, K., Sun, J., Li, L., Qin, M., Li, J., Tian, J., Huang, Y., Liao, H., Zhou, M., Hu, Q., Yan, R., Wang, H., and Huang, C.: Driving Forces of Changes in Air Quality during the COVID-19 Lockdown Period in the Yangtze River Delta Region, China, Environ. Sci. Technol. Lett., 7, 779-786, 10.1021/acs.estlett.0c00511, 2020.

Qin, M., Hu, A., Mao, J., Li, X., Sheng, L., Sun, J., Li, J., Wang, X., Zhang, Y., and Hu, J.: PM2.5 and O3 relationships affected by the atmospheric oxidizing capacity in the Yangtze River Delta, China, Sci. Total Environ., 152268, https://doi.org/10.1016/j.scitotenv.2021.152268, 2021.

Xie, X., Hu, J., Qin, M., Guo, S., Hu, M., Wang, H., Lou, S., Li, J., Sun, J., Li, X., Sheng, L., Zhu, J., Chen, G., Yin, J., Fu, W., Huang, C., and Zhang, Y.: Modeling particulate nitrate in China: current findings and future directions, Environ. Int., 107369, https://doi.org/10.1016/j.envint.2022.107369, 2022.