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Reply on RC3

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-AC3, 2022

General Comments

This study quantified the contributions of local emissions and transport from other regions both directly and indirectly to the particulate and total nitrate formation by comparing the results of CMAQ simulation with different emission scenarios. The study also suggests the contributions of chemical formation pathways, aerosol processes, physical transports, and dry deposition to the total and particulate nitrate formation using the CMAQ process analysis tool (Integrated Process Rate (IPR) and Integrated Reaction Rate (IRR)). Since the proportion of nitrate in $PM_{2.5}$ has been increasing in recent years, understanding the mechanisms of particulate and total nitrate formation is important. In this respect, this study suggests interesting and meaningful scientific information. Considerable indirect transport effects on nitrate formation are of particular interest.

Nonetheless, this reviewer suggests minor revisions to the manuscript and raises a few questions or concerns that would hopefully be addressed in the revised manuscript to improve readers' understanding.

Major Comments

- The authors used IPR and IRR to quantify the contributions of various processes to the formation of particulate nitrate, gaseous HNO3, and total nitrate, and these are one of the main results of this study. However, insufficient information on IPR and IRR can make readers confused who are not familiar with CMAQ models. IRR includes chemical reactions in the aerosol phase (which is included in AERO), correct?

Responses: In the manuscript, the Integrated Process Rate (IPR) was applied to investigate the cumulative effect of chemical and physical processes to NO_3^- formation within the PBL. In Figure 5(a, c, e, g), AERO processes (including condensation, coagulation, and aerosol growth) are the dominant contributors of NO_3^- formation. 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. 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. Conceptually, AERO processes is different from chemical reaction pathways.

Minor Comments

- Line 87: dinitrogen à dinitrogen pentoxide?

Responses: We have corrected the manuscript, as following in Line 87: "the heterogeneous hydrolysis of dinitrogen à dinitrogen pentoxide (HET N_2O_5) on the wet particles' surface".

- Line 163 – 164: "Detailed configurations of the WRF model provided in the studies of Hu et al. (2016) and Wang et al. (2021), shown in Table S1,." --> not easy to understand.

Responses: We have corrected the manuscript, see Lines 164-165: "The detailed configurations of the WRF model shown in Table S1, consistent with Hu et al. (2016) and Wang et al. (2021)".

- Line 199: Unlike F_{Local}, F_{Direct}, $F_{Background}$, $F_{Indirect}$ is not easily understood. Suggest adding a brief explanation for this term.

Responses: Thanks for the advice. For the YRD as the target region, indirect transport contribution ($F_{indirect}$) represents that NO_3^- generated from chemical reactions between outside-transported and local-emitted precursors, as suggested by (Qu et al., 2021). F_{Region}, F_{Direct}, and $F_{Indirect}$ were defined in Eq. (2-4), respectively, in which (C_{base} - $C_{outside\text{-}zero}$) represents is the sum concentrations of indirect and direct transport (the total regional transport), and ($C_{YRD\text{-}zero}$ - $C_{all\text{-}zero}$) quantifies the direct transport concentrations. Regional transport (F_{Region}) represents the sum of direct and indirect transport contribution from outside regions.

We have added above explanation and in the revised manuscript in Lines 193-202.

- Line 273: "The results in this study show a better model performance" à Quantitatively, how much the model performance in this study is better than previous studies? What are the most significant differences between this and previous models that affected the model performance?

Responses: It should be emphasized that the description of "Compared to past studies" is unaccurate. As shown in Table 2 and Figure S1, the daily time series of prediction and observation PM2.5, NO2, and O3 concentrations were well-captured in the four seasons of 2017 in selected cities. One possible reason is that the WRF performance is better than our previous works. Other reasons could be associated with using the local anthropogenic emission inventory (SAES, with high-resolution and based on local measure data) to simulate the 2017 YRD region. Hence, the seasonal results of statistical metrics show a better model performance than our previous works. We have checked the description of this sentence. The manuscript has been revised as following in Lines 274-276:

"When compared to our previous studies (Hu et al., 2016;Wang et al., 2021;Ma et al., 2021;Sulaymon et al., 2021;Li et al., 2021), the statistical results in this study show a better model performance."

- Line 274–276 and 283–286: In Fig. S1, predicted PM_5 appears to agree quite well with the observed time series but predicted nitrate in Fig. 2 was underestimated, particularly in April and October. Isn't nitrate an important species for those periods? or overestimation of other species compensated for these underestimations? Or underestimates of RH can explain this?

Responses: 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). We have added above explanation and in the revised manuscript in Lines 472-474.

- Line 299: year respectively à year, respectively.

Responses: We have revised the manuscript, as following in Lines 304-305: "The NO_3^- decreased by 12.0, 6.9, 0.9, 4.8 and 6.1 μg m^{-3} in winter, spring, summer, autumn, and a year, respectively,".

- Line 360: Vertical mixing would be acceptable. However, the development of the PBL starts after sunrise, but the authors discuss the nighttime process.

Responses: Corrected. The description of "through the vertical mixing and development of the PBL" is unaccurate. During midnight (the lowest height of PBL), the nocturnal stable PBL weakens the vertical transport and accelerates the pollutant accumulation near the surface. We have checked the description of this sentence. The manuscript has been revised as following in Lines 364-366:

"TRAN processes constitute the dominant source during midnight (1:00–6:00 am), owing to the stable PBL weakening the contribution of vertical transport and accelerating the accumulation of NO_3^- concentrations at the surface."

- Line 380: To avoid confusion, "opposite with the first-peak time of NO3- production".

Responses: Thanks for the kind advice. We have carefully revised the manuscript and corrected this sentences (see Lines 385-386): "However, in the winter, the peak times of HNO_3 production are opposite with the first-peak time of NO_3^- production, but consistent with the second-peak time".

- Line 404: Incorrect use of "respectively."

Responses: We have corrected the manuscript, as following in Lines 411-413: "The averaged TNO_3 production rates are 0.31 ± 0.14, 0.65 ± 0.37, 1.09 ± 0.68, and 0.28 ± 0.22 ppb h^{-1} in the winter, spring, summer, and autumn, respectively (Table S6).".

- Line 450–451 and 454–456: TRAN (vertical and horizontal transport) processes were the largest SINK in particulate nitrate formation. In Line 450–451, regional transport (although only direct transport is considered) accounts for about 15%. How does "sink" contribute to nitration formation? Is TRAN different from regional transport conceptually?

Responses: This study investigated the contributions of local emission and regional transport to NO_3^- concentrations in the YRD, as well as the dominant processes and chemical pathways to NO_3^- production in Shanghai. Local emissions dominate NO_3^- concentrations in the YRD (50–62%), while regional transport contributes 38–50% to NO_3^- concentrations. TRAN processes act as the main negitive contributor to NO_3^- production within the PBL in Shanghai. Conceptually, TRAN processes is different from regional transport.

References:

Qu, K., Wang, X. S., Xiao, T., Shen, J., Lin, T., Chen, D., He, L.-Y., Huang, X.-F., Zeng, L., Lu, K., Ou, Y., and Zhang, Y.: Cross-regional transport of PM2.5 nitrate in the Pearl River Delta, China: Contributions and mechanisms, Sci. Total Environ., 753, 142439, https://doi.org/10.1016/j.scitotenv.2020.142439, 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.