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Reply on RC1

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.,
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RC1, Reviewer #1:

Nitrate has been the dominant chemical component of PM_{2.5} in China during winter haze days in recent years. This manuscript used the CMAQ air quality model to investigate the impact of local emission and regional transport on nitrate formation as well as its major formation pathways in the Yangtze River Delta (YRD) region during the four seasons of 2017. Overall, the results are interesting and meaningful for future emission control strategy design. The manuscript is well written and easy to follow. I recommend accepting this manuscript after some minor revisions.

Comments:

- Lines 277-282: From Figure 2, the model performance in Hefei is better than the other three sites. Why do the authors only focus on the results in Shanghai, Hangzhou, and Changzhou?

Responses: The statistics in Figure 2b show that Hefei has the best performance on nitrate modeling throughout the year. However, the measurement of nitrate in Hefei is not available in January, when nitrate shows the highest concentration and is of most concern. As the simulation of nitrate has been evaluated in winter in Shanghai, Hangzhou, and Changzhou, we performed the analysis for the three cities. We clarified in the manuscript in Lines 279-285:

"The daily concentrations of NO₃⁻ are efficiently predicted in four supersites, all within the benchmark (NMB ≤ ±0.60, NME ≤ 0.75, and R > 0.6). But in Hefei (Fig. 2b), the wintertime NO₃⁻ measurement data is not available, when NO₃⁻ shows the highest concentrations and is of most concern. Good agreement between predicted and observed values is demonstrated on daily timescales, especially in Shanghai (NMB = -0.49, R = 0.70), Hangzhou (NMB = 0.11, MB = 0.64) and Changzhou (NMB = 0.36, R = 0.56).".

- Lines 283-284: Underestimation of NO₃⁻ can also be found in spring, and the bias may even be larger than that in summer and autumn. It's better to provide the model performance in each season.

Responses: Thanks for the suggestion. We have evaluated nitrate simulation in each season and added Figure S2 in the Supplementary material (SI). We mentioned this in

Lines 287-289: "Fig. S2 shows the hourly predicted and observed NO_3^- concentrations in each season. NO_3^- concentrations are generally underestimated during the summer and autumn."

- Lines 313-314: Local emission only contributes negatively in winter and autumn, shouldn't be "in the four seasons".

Responses: We have corrected the manuscript, see Lines 320-321: "For O_3 , the local emissions have negative contribution in winter (-46%) and autumn (-12%)."

- Lines 315-317: The indirect transport doesn't seem to contribute as large as -7% in autumn according to Figure 3b. Please check the numbers.

Responses: We have carefully checked the numbers in Figure 3b, where -7% represents the mean contributions of the four seasons. The sentences have been rephrased in the manuscript, see Lines 321-323: "The negative contributions of the indirect transport are -6, -8, -8, and -4 % in winter, spring, summer, and autumn, respectively."

- Line 317: Avoid such expressions as "-12%--42%".

Responses: Corrected. We have revised the manuscript, as following in Lines 323-324: "In Fig. 3d, the indirect transport contributes from -42% to -12% of OH concentrations in the four seasons. "

- Line 70: Please check the format of this paragraph.

Responses: Thanks for the suggestion. We have checked the format of this paragraph. The manuscript has been revised as following in Lines 69-73:

"Owing to the stringent emission control strategies since 2013, primary $\text{PM}_{2.5}$, the major precursors (i.e., sulfur dioxide (SO_2) and nitrogen oxides (NO_x = nitric oxide (NO) + nitrogen dioxide (NO_2)) emissions have decreased substantially in China, which led to significant decreases in total $\text{PM}_{2.5}$ and sulfate (SO_4^{2-}) mass concentrations."

- Lines 373, 376, and 381: " HNO_3^- " should be " HNO_3 ".

Responses: Corrected. The manuscript has been carefully revised the manuscript in Lines 379, 382, and 387.

- Line 415: Providing TNO_3 production rates from different pathways at different model layers would be more helpful.

Responses: Thanks for the advice. We added a figure in the SI (Fig.S8) with a few lines of discussion regarding TNO_3 production rates at different model layers in the manuscript (see Lines 432 to 440):

"As shown in the revised Figure S8, the seasonal TNO_3 production rates (ppb/h) and contributions (%) of the major pathways have been compared between vertical layers and PBL. The OH+ NO_2 pathway dominated TNO_3 production at all layers, accounting for more than 58%, 78%, 80%, and 83% in winter, spring, summer, and autumn, respectively. The OH+ NO_2 pathway rate decreases with altitude at vertically layers, where its contribution decreases from 87% to 58%, from 91% to 78%, from 93% to 80%, and from 95% to 83% in the four seasons, respectively. The HET N_2O_5 pathway becomes more important for the TNO_3 production within layers 4~8 (250 to 580 m) in winter, accounting for 37% (Fig. S8b)."

- Figure 7: The text in the figure is too small. Please make it larger.

Responses: Corrected. Figure 7 (a-b) has been disassembled into Figures 7 and 8 in the revised manuscript, and the manuscript has been revised accordingly in Lines 441-459.

- Lines 440-445: The indirect transport of nitrate can also be formed from the transported HNO₃ from outside YRD region reacting with the locally-emitted NH₃. As can be seen from Figure 3, direct transport contributes considerably to HNO₃. The authors should clarify this in the revision.

Responses: In Lines 195-201, the indirect transport contribution (F_{indirect}) represents that NO₃⁻ generated from chemical reactions between outside-transported and local-emitted precursors, as calculated in Eq. (4). Hence, F_{indirect} is mainly formed via two chemical pathways (the OH+NO₂ and HET N₂O₅ pathway), not including formed via by transported HNO₃ and local-emitted NH₃. Figures 7 and 8 suggest that the transported O₃ from outside YRD region react with the locally-emitted NO₂, supporting TNO₃ production via the HET N₂O₅ chemical pathway at nighttime. We have added definition about F_{indirect} in the manuscript (see Lines 195 to 197):

“indirect transport (NO₃⁻ contributed by transported and local-emitted precursors via the OH+NO₂ and HET N₂O₅ chemical pathway)”.

- Line 772: Table 3 is not for “model performance”.

Responses: Corrected. Table 3 has been modified in the manuscript in Line 821.

- Line 106: Actually, atmospheric oxidant doesn't include N₂O₅.

Responses: Corrected.