Response to Reviewer's Comments

Second Review of "Summertime fine particulate nitrate pollution in the North China Plain: Increasing trends, formation mechanisms, and implications for control policy" by Wen L., et al.

L. Wen and co-authors have appropriately, thoughtfully, and thoroughly addressed comments and concerns raised in the first review. Below are additional comments on the updated manuscript. Many are editorial in nature, but a few minor details listed below should be addressed prior to acceptance.

Response: we thank the reviewer for the further evaluation and helpful comments on our revised manuscript. Below we address all of these comments point by point, and the manuscript has been further revised accordingly. Again, the referees' comments are listed in black italics, while our responses and changes in the manuscript are shown in blue and red, for clarity.

Minor Comments:

Page 7: line 12 – 7:15 – Additional model and chemical reaction information provided by the authors during revision is very helpful. Please also provide an estimate of the N_2O_5 uptake coefficient included in the model and briefly compare to other field-studies. Even though $\gamma(N_2O_5)$ is not explicitly included in the mechanism, I believe this uptake coefficient can be estimated from the $N_2O_5(g) \leftrightarrow N_2O_5(a)$ rate constant, using: $k\ (s^{-1}) = 0.25*\gamma(N_2O_5)*SA*c$, where SA is the aerosol surface area and c is the mean molecular speed. I suggest adding this information as it will put the magnitude of N_2O_5 hydrolysis in this study into context of previous studies.

Response: we thank the reviewer for this very good comment. According to the reviewer's suggestion, we have estimated the $\gamma(N_2O_5)$ values from the $N_2O_5(g) \leftrightarrow N_2O_5(a)$ rate constant and the measured aerosol surface area, and the average $\gamma(N_2O_5)$ (±SD) for our selected cases was 0.018 ± 0.00006. Such $\gamma(N_2O_5)$ values are well within the reported ranges of $\gamma(N_2O_5)$ derived from field observations in other locations worldwide (e.g., 0.001-0.1; Tham et al., 2018 and references therein), and are comparable to or slightly lower than those derived at several sites in northern China, i.e., Mt. Tai (0.021-0.103), Wangdu (0.006-0.034), Beijing (0.012-0.055), and Ji'nan (0.042-0.092). The following information has been added in the revised manuscript.

"We estimated the $\gamma(N_2O_5)$ from the reaction rate for the N_2O_5 gas-to-particle partitioning and the measured aerosol surface area concentrations, and derived an average $\gamma(N_2O_5)$ (±SD) of 0.018 ± 0.00006 for our selected cases. Such levels are well within the reported range of $\gamma(N_2O_5)$ derived from the field observations in other locations worldwide (e.g., 0.001-0.1), including several polluted areas in northern China (Tham et al., 2018; and references therein)."

7:16 – What does the model assume for the deposition of nitrate and HNO_3? Dry deposition likely impacts the ground site observations. How do the assumptions pertaining to deposition impact the model results in later sections?

Response: the model doesn't consider the deposition of nitrate aerosol, but considers the dry deposition of HNO_3. The deposition velocity of HNO_3 was set as 2 cm s^{-1}, and the boundary layer height was set to vary from 200 m to ~1300 m for our cases in the model. We compared the loss rates of HNO_3 from dry deposition and from the HNO_3 gas-to-particle partitioning, and found dry deposition only presented a very minor fraction of the total HNO_3 sink (<1%). Therefore, dry deposition should not affect the subsequent modelling results in this study. In the revised manuscript, the following statements have been added to clarify this issue.

"The dry deposition velocity of HNO_3 was set as 2 cm s^{-1} in the model. With such configuration, dry deposition only presents a minor fraction of the daytime HNO_3 sink (<1%), compared to the HNO_3 gas-to-particle partitioning."

7:29 – What aerosol composition was assumed for the hygroscopic growth calculation?

Response: we just took the parameterization from literature, which was derived from field observations at a rural site of Beijing. Thus it is based on the aerosol composition measured at a rural site in the North China Plain. The original statement has been revised as follows to elaborate this in the revised manuscript.

"A hygroscopic growth factor obtained from the NCP region by Achtert et al. (2009) was adopted to take into account the effect of hygroscopic growth on particle size and surface."

Achtert, P., Birmili, W., Nowak, A., Wehner, B., Wiedensohler, A., Takegawa, N., Kondo, Y., Miyazaki, Y., Hu, M., and Zhu, T.: Hygroscopic growth of tropospheric particle number size distributions over the North China Plain, J. Geophys. Res., 114, doi: 10.1029/2008jd010921, 2009.

8:3-8:6 – What method was used for the VOC measurements?

Response: the VOC measurements at Mt Tai and Yucheng were made off-line based on the canister sampling coupled with analysis by GC+FID/MS. At Ji'nan, the VOC measurements were conducted by an online GC+FID analyzer. We have added this information in Table S3 in the revised manuscript.

12:19 – How was the early morning period of 06-09:00 LT selected? If the concern is boundary layer expansion and entrainment, this process typically continues past 09:00. If $p(NO_3^-)$ is mixed down from aloft in the morning (as previous studies have hypothesized), how would this impact the results in this manuscript?

Response: to be honest, the early morning period of 06:00-09:00 LT was arbitrarily selected

in the analysis. However, we think this should not affect the analysis results in this manuscript, because the observed increase of nitrate aerosol during these selected cases were only used to compare with the model-simulated $p(NO_3^-)$. All of the subsequent analyses were based on the modelling results (including only chemistry). Furthermore, the observed nitrate increments during these selected periods show quite good correlations with the model-simulated $p(NO_3^-)$. In the revised manuscript, the following statement has been modified to clarify this.

"4) the data in the early morning period (i.e., 06:00-09:00 LT) were excluded from analyses to roughly eliminate the potential influence from downward mixing of air aloft to the surface sites."

14:7 – What does it mean when the model still predicts nitrate aerosol formation at night when there is no NH_3 present in the model (shown in Figure 7)?

Response: it means that the nitrate formation from the hydrolysis of N_2O_5 is not sensitive to the availability of NH_3. This has been discussed in the manuscript. Anyway, the model was actually initialized with an amount of NH_4^+ in the aerosol phase.

15:2 – Cite Roberts 2008 for the current theory on how particle acidity impacts the yield of $ClNO_2$.

> *Roberts, J. M., Osthoff, H. D., Brown, S. S., & Ravishankara, A. R. (2008). N_2O_5 oxidizes chloride to Cl_2 in acidic atmospheric aerosol. Science, 321(5892), 1059. https://doi.org/10.1126/science.1158777*

Response: this reference has been cited in the revised manuscript.

16:10 – 16:19 – Thank you to the authors for adding the paragraph on line 17:13. In addition, how sensitive are the results in Figures 7 and 9 to changes in the N_2O_5 gas → particle conversion rate (i.e. uptake coefficient) and $ClNO_2$ formation rate? In theory, if N_2O_5 uptake is inefficient, there will no longer be a linear increase in nitrate with concentrations of O_3 and NO_2 as shown in Figure 7. Have the authors have considered sensitivity tests to these parameters? In addition to the added paragraph, the authors should also note that the results in Figure 9 only hold if the sensitivity of nitrate production to N_2O_5 uptake does not change under different NOx and O_3 conditions. The authors should also clarify that the model simulations are constrained to ground-based observations and the chemistry aloft may show a different sensitivity than in Figures 7 and 9.

Response: we have not considered the sensitivity tests to these parameters. As shown in the response to the reviewer's first comment, existing field studies in the North China Plain have found fast heterogeneous uptake of N_2O_5 onto particles, with field-derived $\gamma(N_2O_5)$ values of 0.042-0.092 in Ji'nan, 0.021-0.103 at Mt. Tai, 0.006-0.034 at Wangdu, and 0.012-0.055 in Beijing. The estimated average $\gamma(N_2O_5)$ value used in our model was 0.018, which was even smaller than these values obtained from field observations. The $ClNO_2$ formation depends on

the measured levels of Cl^- and the explicit aqueous-phase reactions of NO_2^+ with Cl^-. Thus the N_2O_5 uptake should be efficient in the NCP region, and our representation in the model may be a lower estimation of the N_2O_5 uptake process. Besides, the clarifications suggested by the reviewer have been added in the revised manuscript. See below.

"The results in Figure 9 only hold if the sensitivity of nitrate production to N_2O_5 uptake does not change under different NOx and O_3 conditions. Furthermore, the model simulations are constrained to ground-based observations and the chemistry aloft may show a different sensitivity than in Figures 7 and 9. These aspects were not quantified in this study. Further studies are needed to explore the detailed dependence of nitrate formation to the variety of factors including NOx, O_3, NH_3, VOCs, aerosol composition, and meteorological conditions."

Figure 2 – It might be more helpful to use the "Error bars" to plot the standard deviation of each measurement, not the error in the measurement. That way, the variation in the diurnal average profile can be evaluated. I will leave it up to the authors for what they choose to show.

Response: Figure 2 has been modified as suggested, with standard deviations being plotted.

Editorial Comments:
1:18 – change to "Using historical observations, the nitrate/$PM_{2.5}$ and…"

Response: changed.

2:9 – remove "the" before "Earth's"

Response: removed.

2:15 – change to "environmental and health consequences, and…"

Response: changed.

2:26 – Move "during the day" to after "minimized"

Response: done.

3:4-3:10 – Switch the order of the sentences starting on line 3:4, "Field measurements…" and on line 3:7, "The contribution…"

Response: done.

3:6 – Add McDuffie et al., 2018 and Tham et al., 2018 to the Brown and Stutz reference, since both papers provide overviews of the current state of agreement between field-derived uptake coefficients and laboratory-based parameterizations.

McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez-Hilfiker, F., Lee, B. H., Thornton, J. A., et al. (2018). Heterogeneous N_2O_5 uptake during winter: Aircraft measurements during the 2015 WINTER campaign and critical evaluation of current parameterizations. Journal of Geophysical Research: Atmospheres. https://doi.org/10.1002/2018JD028336

Tham, Y. J., Wang, Z., Li, Q., Wang, W., Wang, X., Lu, K., et al. (2018). Heterogeneous N_2O_5 uptake coefficient and production yield of $ClNO_2$ in polluted northern China: Roles of aerosol water content and chemical composition. Atmospheric Chemistry and Physics Discussions, 2018, 1-27. https://doi.org/10.5194/acp-2018-313

Response: these latest references have been added.

3:7-3:9 – After the Baasandorj reference, add ", but will be dependent on the rate of NO_3 formation and reaction, and the N_2O_5 uptake coefficient ($\gamma(N_2O_5)$) and formation yield of $ClNO_2$."

Response: this statement has been added.

3:9 – 3:10 – Add the following references to the Baasandorj reference, which all discuss the vertical transport of nitrate aerosol:

Brown, S. G., Hyslop, N. P., Roberts, P. T., McCarthy, M. C., & Lurmann, F. W. (2006). Wintertime Vertical Variations in Particulate Matter (PM) and Precursor Concentrations in the San Joaquin Valley during the California Regional Coarse PM/Fine PM Air Quality Study. Journal of the Air & Waste Management Association, 56(9), 1267-1277. https://doi.org/10.1080/10473289.2006.10464583

Prabhakar, G., Parworth, C. L., Zhang, X., Kim, H., Young, D. E., Beyersdorf, A. J., et al. (2017). Observational assessment of the role of nocturnal residual-layer chemistry in determining daytime surface particulate nitrate concentrations. Atmospheric Chemistry and Physics, 17(23), 14747-14770. https://doi.org/10.5194/acp-17-14747-2017

Pusede, S. E., Duffey, K. C., Shusterman, A. A., Saleh, A., Laughner, J. L., Wooldridge, P. J., et al. (2016). On the effectiveness of nitrogen oxide reductions as a control over ammonium nitrate aerosol. Atmospheric Chemistry and Physics, 16(4), 2575-2596. https://doi.org/10.5194/acp-16-2575-2016

Watson, J. G., & Chow, J. C. (2002). A wintertime PM2.5 episode at the Fresno, CA, supersite. Atmospheric Environment, 36(3), 465-475. https://doi.org/https://doi.org/10.1016/S1352-2310(01)00309-0

Response: all of these references have been added in the revised manuscript.

3:19 – Change to "about a 75% reduction"

Response: changed.

4:15 – insert "the" before "North China Plain"

Response: done.

5:15 – Insert "the" before "mountain peak"

Response: done.

5:17 – Change to "descriptions"

Response: changed.

6:11 – Change to "quantified in-situ"

Response: changed.

6:20 – Remove "well qualified and"

Response: removed.

6:27 – Remove "the" before "gas-and aqueous…"

Response: removed.

7:12 – Add Tham et al., 2018 and McDuffie et al., 2018 from above to the Chang 2011 reference. These studies provide information on the up-to-date status of field-parameterization differences.

Response: added.

7:15 – Change to "utilized previously to simulate…"

Response: changed.

8:9 – Clarify what "differences" you are referring to

Response: it refers to the difference in the model-simulated nitrate increment (formation) between base and sensitivity simulations. This has been clarified in the revised manuscript.

8:14 – Change to "Simulations were conducted…"

Response: changed.

8:16 – Change to "major aerosol formation…"

Response: changed.

9:14 – Change to "differences"

Response: changed.

9:15 – Change to "differences"

Response: changed.

10:1 – Add "power" before "plant"

Response: added.

10:3 – Change "were" to "was"

Response: changed.

10:14 – Change to" "thermal decomposition of aerosol"

Response: changed.

11:7 – Change to "derived at Mt. Tai from data collected in 2007 and 2014, affirming…" This clarifies that this trend is based on two years of data.

Response: changed.

11:18 – Add at the end of the sentence, "at Ji'nan and Mt. Tai, respectively".

Response: added.

11:21 and 11:25 – Subscript NOx

Response: done.

12:5 – Change "a more and more" to "an increasingly"

Response: changed.

13:10 – Change "over" to "out"

Response: changed.

16:4 – Remove "to be"

Response: removed.

17:7 – Change "that" to "the"

Response: changed.

17:17 – Add appropriate references for that statement that increasing aerosol nitrate may reduce the N_2O_5 uptake coefficient.

Response: the reference of Chang et al. 2011 has been added in the revised manuscript.

Chang, W. L., Bhave, P. V., Brown, S. S., Riemer, N., Stutz, J., and Dabdub, D.: Heterogeneous Atmospheric Chemistry, Ambient Measurements, and Model Calculations of N_2O_5: A Review, Aerosol Sci. Tech, 45, 665-695, 10.1080/02786826.2010.551672, 2011.

18:18 – Change "series" to "serious"

Response: changed.

Table S1 – Are the units in cm^3 $molecules^{-1}$ s^{-1}? If so, change "mol" to "molec.". If not, disregard this comment.

Response: the units are cm^3 $mole^{-1}$ s^{-1} for the aqueous phase reactions, not the cm^3 $molecule^{s-1}$ s^{-1}.

Figures 8 & 9 – label the three sensitivity regimes on the contour plots.

Response: done.