

## Response to Reviewer 1:

*L. Wen and co-authors present a succinct analysis of recent PM<sub>2.5</sub> observations and trends at urban, rural, and remote sites in the densely populated North China Plain. Their observations suggest aerosol phase nitrate is becoming an increasingly important component of regional PM<sub>2.5</sub> and use an observationally informed box model to assess its primary formation pathways during the day and at night. Observations of particulate nitrate, sulfate, and total mass first show that the fraction of nitrate has statistically significantly increased while sulfate has simultaneously decreased. Diurnal patterns are presented to show regional differences in nitrate formation processes. Calculated excess particle-phase ammonium suggests that aerosol nitrate is likely limited by the oxidation of NO<sub>x</sub>, not emissions of NH<sub>3</sub>. Box model simulations of select day and nighttime nitrate formation events show that daytime formation is largely due to nitric acid partitioning to the particle phase while nocturnal formation is largely the result of aerosol uptake by N<sub>2</sub>O<sub>5</sub>. Lastly, a large number of simulations were conducted, initialized with varying levels of NO<sub>2</sub>, O<sub>3</sub>, and NH<sub>3</sub> to test the sensitivity of daytime and nighttime particle nitrate formation to these species. Results suggest that reductions in nitrogen oxide emissions may be the most effective method to reduce nitrate aerosol in Northern China.*

*The analysis presented here is important to the collective understanding of processes impacting summertime particulate nitrate formation. There are certain areas in this manuscript, however, that require further clarification before publication. The main issue is that further details are required about the box model mechanism and its applicability to daytime processes. Specifically, further details are required to explain how the model treats VOC oxidation by OH and NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> uptake and reaction product partitioning, as well as the partitioning of HNO<sub>3</sub> and reaction with NH<sub>3</sub>. In addition, consideration of the VOC sensitivity to model results in Section 3.4 should be included. Lastly, additional references should be included throughout the manuscript to provide a stronger context for these results. These and additional comments are provided by page and line number (pg:line) below.*

**Response:** we thank the reviewer for the thoughtful review and constructive comments. All of these comments and suggestions are very helpful for improving our manuscript. We have carefully considered and tried to address all of these comments, and significantly revised the manuscript. Briefly, more details about the model mechanism, validation and sensitivity tests have been provided. More references that are relevant to this study have been acknowledged. More discussions of the observational and modelling results have been added. Below we reply in details to the individual comments. For clarity, the reviewer's comments are listed in black italics, while our responses and changes in the manuscript are highlighted in blue and red, respectively.

### **Major Comments**

*3:2-3 – The only direct evidence of pH-dependent N<sub>2</sub>O<sub>5</sub> uptake has been from laboratory studies. With large discrepancies between uptake trends observed in the field and from laboratory studies, the authors do not have enough evidence to make the claim that increasing acidity can lead to an increase in N<sub>2</sub>O<sub>5</sub> uptake. If anything, increasing acidity*

should lead to a decrease in particle phase nitrate as more nitrate partitions to gas-phase  $\text{HNO}_3$ .

**Response:** we agree with the referee that we don't have enough evidence for the dependence of  $\text{N}_2\text{O}_5$  uptake to the aerosol acidity, given the large discrepancy between field studies and laboratory efforts. The original statement has been removed from the revised manuscript.

3:3-5 – *The authors should include additional references to previous studies that have both examined the  $\text{NO}_x$ ,  $\text{O}_3$ ,  $\text{NH}_3$  contributions to particle phase nitrate and quantified the reaction pathways of the  $\text{NO}_3$  radical. This might be a good place to also discuss any expected differences between the extent of nitrate aerosol formation during the summer and winter seasons. Much of the relevant work prior to 2012 is reviewed in Brown and Stutz, 2012. A more recent study by Baasandorj, et al., 2017 and references therein also examine this chemistry during winter. The information included up until this point in the introduction is useful, but more context is required to understand remaining questions surrounding nitrate aerosol formation.*

Brown, S. S., & Stutz, J. (2012). Nighttime radical observations and chemistry. *Chem Soc Rev*, 41(19), 6405-6447. doi:10.1039/c2cs35181a

Baasandorj, M., Hoch, S. W., Bares, R., Lin, J. C., Brown, S. S., Millet, D. B., Martin, R., Kelly, K., Zarzana, K. J., Whiteman, C. D., Dube, W. P., Tonnesen, G., Jaramillo, I. C., & Sohl, J. (2017). Coupling between Chemical and Meteorological Processes under Persistent Cold-Air Pool Conditions: Evolution of Wintertime  $\text{PM}_{2.5}$  Pollution Events and  $\text{N}_2\text{O}_5$  Observations in Utah's Salt Lake Valley. *Environ Sci Technol*, 51(11), 5941-5950. doi:10.1021/acs.est.6b06603

**Response:** thanks for the suggestion. Indeed, there are some remaining questions surrounding the nitrate formation mechanisms, such as the highly variable uptake coefficient of  $\text{N}_2\text{O}_5$  on particles ( $\gamma_{\text{N}_2\text{O}_5}$ ), the reaction pathways of the  $\text{NO}_3$  radical and its competition with the  $\text{N}_2\text{O}_5$  hydrolysis, the seasonal dependence of the  $\text{N}_2\text{O}_5$  hydrolysis reactions, and the vertical mixing of air aloft in the residual layer, etc. We have added the following discussion about this in the revised manuscript.

“To date the detailed relationship between nitrate formation and the chemical mix of  $\text{NO}_x$ ,  $\text{O}_3$  and  $\text{NH}_3$  is still poorly understood. Field measurement studies have shown that the uptake coefficient of  $\text{N}_2\text{O}_5$  onto particles ( $\gamma_{\text{N}_2\text{O}_5}$ ) is highly variable and disagrees with the laboratory-derived parameterizations (Brown and Stutz, 2012; and references therein). The contribution of  $\text{N}_2\text{O}_5$  hydrolysis pathway tends to show a seasonal dependence with the largest influence in the winter season (Brown and Stutz, 2012; Baasandorj et al., 2017). Vertical mixing of air aloft in the residual layer may also contribute to the surface nitrate particles (Baasandorj et al., 2017). Consequently, there are still some remaining questions for better understanding the nitrate formation mechanisms.”

*Table S1 and Chemical Box Model Description in Main Text –*

*Provide additional information in the text about how  $\text{NH}_3$  and  $\text{HNO}_3$  partitioning are related to each other in this model. Since the model does not include the reaction of  $\text{HNO}_3 + \text{NH}_3$ ,*

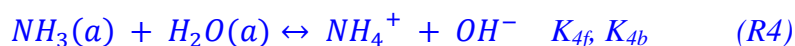
but rather  $\text{HNO}_3$  partitioning based on particle acidity, it should be briefly mentioned how  $\text{NH}_3$  impacts this reactions. In addition, include rate constant information in Table S1. To that point, further details need to be provided about the  $\text{N}_2\text{O}_5 \rightarrow \text{NO}_3^- + \text{NO}_2^+$  reaction, which represents the uptake of  $\text{N}_2\text{O}_5$  onto aerosol. There are many parameterizations that have been used to quantify this process, but there are also large uncertainties and disagreements with field studies (e.g. Chang, et al., 2011). Since this reaction is a major focus of this manuscript, many more details need to be provided for how it was actually treated in the model. In addition, the authors do not include product partitioning between  $\text{HNO}_3$  and  $\text{ClNO}_2$ . The formation of  $\text{ClNO}_2$  could significantly reduce the absolute amount of aerosol nitrate formed by  $\text{N}_2\text{O}_5$  chemistry. Lastly, the authors note that this model has been used previously to simulate nocturnal particle nitrate formation. Has this model been also validated for daytime formation processes?

Chang, W. L., Bhave, P. V., Brown, S. S., Riemer, N., Stutz, J., & Dabdub, D. (2011). Heterogeneous Atmospheric Chemistry, Ambient Measurements, and Model Calculations of  $\text{N}_2\text{O}_5$ : A Review. *Aerosol Science and Technology*, 45(6), 665-695. doi:10.1080/02786826.2010.551672

**Response:** the chemical box model we used in the present study is a little bit different from the commonly used models which usually adopt the experiment-derived parameterizations to represent heterogeneous processes. Our model explicitly describes the gas-phase reactions (by RACM2), aqueous-phase reactions (by CAPRAM2.4), and the gas-aqueous partitioning (phase transfer) processes. We are sorry that the original Table S1 and related descriptions missed some important information about the model configuration. In the revised manuscript, we have elaborated more about the details of representation of some key chemical processes in the model. Below we briefly reply to the specific comments of the reviewer.

### (1) On the representations of the $\text{HNO}_3$ and $\text{NH}_3$ reactions:

Indeed, the model does not include the reaction of  $\text{HNO}_3 + \text{NH}_3 = \text{NH}_4\text{NO}_3$ . It describes the gas-to-aqueous phase partitioning and the aqueous phase reactions of  $\text{HNO}_3$  and  $\text{NH}_3$  by the following reactions.



Reactions (R1) and (R3) describe the partitioning of  $\text{HNO}_3$  and  $\text{NH}_3$  between the gas and aqueous phases, with  $K_{1f}$ ,  $K_{1b}$ ,  $K_{3f}$  and  $K_{3b}$  are functions of the molecular speeds, gas-phase diffusion coefficients, accommodation coefficients, and Henry coefficients of  $\text{HNO}_3$  and  $\text{NH}_3$ . Reactions (R2) and (R4) represent the reversible ionization equilibrium of  $\text{HNO}_3$  and  $\text{NH}_3$  in the aqueous phase. Reaction (R5) links the partitioning of  $\text{HNO}_3$  and  $\text{NH}_3$  with each other. Briefly, increasing  $\text{NH}_3$  would decrease the aerosol acidity (by providing more  $\text{OH}^-$ ), which

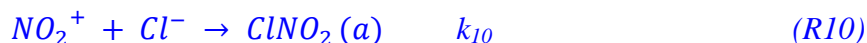
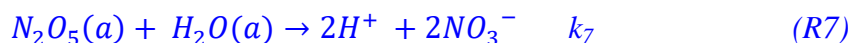
would then enhance the partitioning of HNO<sub>3</sub> to the aqueous phase as well as formation of NO<sub>3</sub><sup>-</sup>.

In the revised manuscript, Table S1 has been revised to include the above detailed description of the HNO<sub>3</sub> and NH<sub>3</sub> partitioning processes. The rate constants for all of the reactions have been provided in Table S1. The following statements have been also added to the revised manuscript to elaborate this reaction pathway.

“This model explicitly describes the gas-to-aqueous phase partitioning of various chemical species, which connects the detailed chemical reactions in both gas and aqueous phases. The chemical reactions representing the nitrate formation in the model are outlined in Table S1. Briefly, these reactions can be categorized into three major formation pathways, namely, partitioning of gaseous HNO<sub>3</sub> to the aerosol phase, hydrolysis reactions of N<sub>2</sub>O<sub>5</sub>, and aqueous phase reactions of NO<sub>3</sub> radicals. The HNO<sub>3</sub> partitioning is largely affected by the availability of NH<sub>3</sub>, since the partitioning of NH<sub>3</sub> would decrease the aerosol acidity and hence enhance the partitioning of HNO<sub>3</sub> to the aerosol phase (see Table S1).”

## (2) On the representation of the N<sub>2</sub>O<sub>5</sub> hydrolysis process

Similar to the HNO<sub>3</sub> partitioning, the model describes explicitly the gas-to-aqueous phase partitioning of N<sub>2</sub>O<sub>5</sub> as well. The uptake coefficient of N<sub>2</sub>O<sub>5</sub> on particles ( $\gamma_{N_2O_5}$ ) was not parameterized within the model. This heterogeneous process is represented by the following chemical reactions in the model.



The reaction (R6) describes the partitioning of N<sub>2</sub>O<sub>5</sub> between the gas and aqueous phases, with K<sub>6f</sub> and K<sub>6b</sub> being functions of the molecular speeds, gas-phase diffusion coefficients, accommodation coefficients, and Henry coefficients of N<sub>2</sub>O<sub>5</sub>. Reactions (R7)-(R9) describe the aqueous-phase reactions of N<sub>2</sub>O<sub>5</sub> with liquid water forming nitrate, with the reaction (R8) being the fastest reaction pathway. Reaction (R10) presents the formation of ClNO<sub>2</sub> from the N<sub>2</sub>O<sub>5</sub> hydrolysis.

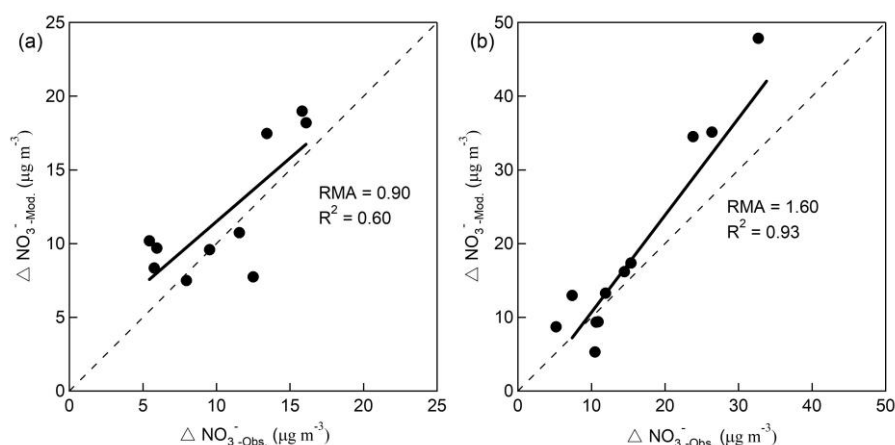
In the revised manuscript, we have clearly elaborated about the treatment of N<sub>2</sub>O<sub>5</sub> hydrolysis process by providing the above detailed chemical reactions in Table S1 and also adding the following statements in the main text.

“For the N<sub>2</sub>O<sub>5</sub> hydrolysis process, the uptake coefficient of N<sub>2</sub>O<sub>5</sub> on particle surfaces ( $\gamma_{N_2O_5}$ ) is the parameter with large uncertainty in modeling studies. Recent studies have shown that  $\gamma_{N_2O_5}$  tends to be largely variable and significant discrepancy exists between field-derived laboratory-derived parameterizations (Chang et al., 2011). The RACM/CAPRAM model used in this study doesn't take  $\gamma_{N_2O_5}$  into account but describes explicitly the N<sub>2</sub>O<sub>5</sub> gas-to-aqueous

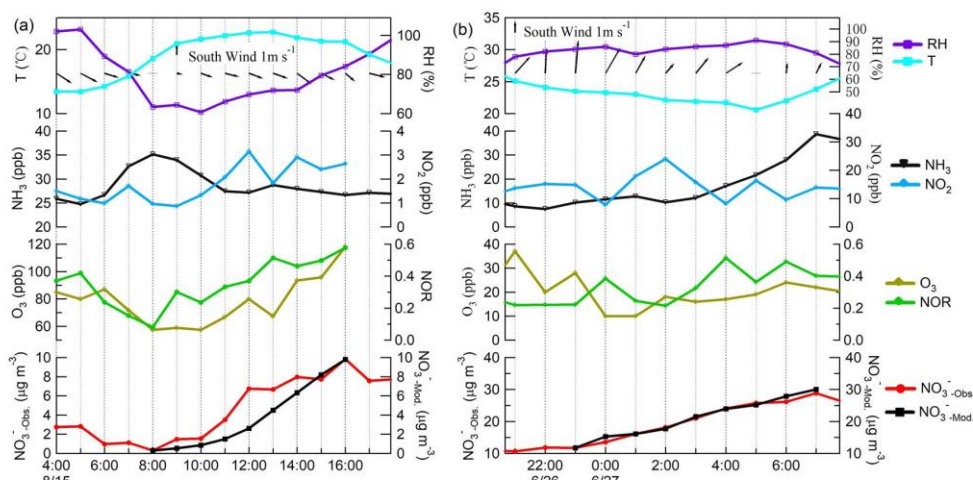
phase partitioning as well as its subsequent aqueous phase reactions. See Table S1 for the detailed treatment of the  $N_2O_5$  hydrolysis processes in the model.”

### (3) On the applicability of the model to simulation of daytime nitrate formation

To our knowledge, this multi-phase chemical box model has not been applied to simulate the daytime nitrate formation in previous studies. However, the model worked quite well for reproducing the observed nitrate increase for the selected cases at three study sites in the present study. Figures 4 and 5 clearly show the comparison between modeled and observed nitrate increase for the selected 21 daytime and nighttime cases, and the scatter plots of the modeled versus observed nitrate increments for the daytime and nighttime cases are shown in Figure R1. Besides, we also compared the modelling results against observations for the individual cases. Figure R2 shows the time series of observed vs. modeled nitrate and related species for two typical cases at daytime and nighttime, respectively. Overall, these figures clearly show the applicability of the box model to the simulation of daytime (and nighttime) nitrate formation. These figures have been provided in the revised supplementary materials.



**Figure R1.** Scatter plots of the modeled versus observed increase of particulate nitrate for the selected daytime (a) and nighttime (b) cases



**Figure R2.** Comparison of modeled versus observed nitrate concentrations as well as related species for two typical cases at (a) daytime and (b) nighttime

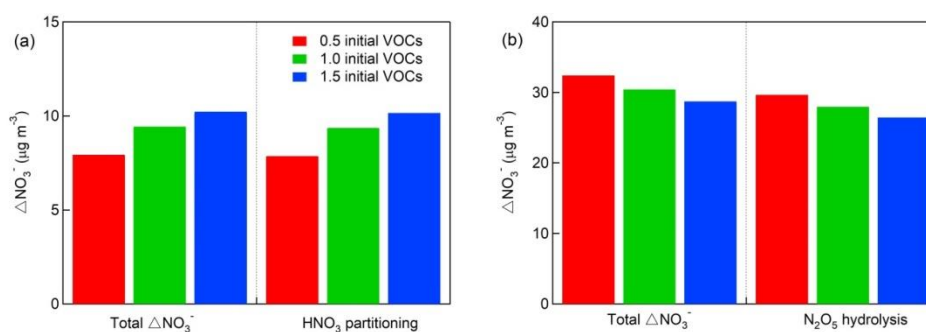
7:8-12 – Provide further information about the number of VOCs that were included as inputs to this model. Also quantify how ‘insensitive’ the model was to input VOC concentrations and how these sensitivity studies were conducted. During previous summertime studies, nocturnal  $\text{NO}_3$  and biogenic VOC concentrations have led to a relatively large  $\text{NO}_3$  reactivity relative to  $\text{N}_2\text{O}_5$  hydrolysis, which makes the model insensitivity here surprising. The authors need to spend more time evaluating this aspect of the model and discussing how this is similar/different to previous studies.

**Response:** over 40 VOC species were considered in the modeling analyses in the present study. The detailed VOC compounds and their concentrations as the model inputs have been documented in a table in the revised supplement.

We should note that we didn’t have VOC measurements during the present study, and we only took the campaign-average concentrations of VOCs available from previous studies for the same study sites (or study area) as the model inputs. The model was initialized with such average VOC concentrations. Sensitivity studies were conducted by adjusting the initial VOC concentrations to 0.5 or 1.5 times of the base data, and the model-simulated nitrate increases were compared between the sensitivity tests and base runs. As shown from Figure R3, both sensitivity model runs produced comparable daytime and nocturnal nitrate formation to the base runs (the differences were within 12%). This should be mainly due to the low levels of biogenic VOCs (i.e., isoprene and pinenes) at the study sites, and the reactions of  $\text{NO}_3$  with BVOCs may only account for a small fraction of the total  $\text{N}_2\text{O}_5$  loss.

In the revised manuscript, the original statements have been revised as follows to discuss this aspect, with Figure R3 being added in the supplement.

“The VOC measurements were not made during the present study, and we used the campaign average data previously collected in the same areas during summertime for approximation (Zhu et al., 2016 and 2017). The detailed VOC species and their concentrations as the model input are documented in Table S3. We conducted sensitivity tests with 0.5 or 1.5 times of the initial VOC concentrations, and found that the model simulation was somewhat insensitive to the initial VOC data (the differences between sensitivity tests and base run were within 12%; see Figure S1). This should be mainly due to the low levels of biogenic VOCs in the study area. Given the lack of in-situ VOC measurements, however, the treatment of VOC data presents a major uncertainty in the presented modeling analyses.”



**Figure R3.** Sensitivity of the model-simulated (a) daytime and (b) nighttime nitrate formation to the initial VOCs



10:22 – How were day and night defined for the  $\text{NO}_3$  production case studies? In addition, how did the authors separate events that were likely driven by mixing and transport and not chemical production? For example, morning production periods may be a result of vertical mixing, not chemical production.

**Response:** in the present study, the day and night time windows were defined as 7:00-19:00 and 19:00-07:00 local time, respectively. The selected nitrate formation cases should meet the following criteria: 1) the nitrate accumulation process should last for a considerable time period; 2) the observed NOR ( $\text{NOR} = [\text{NO}_3^-] / ([\text{NO}_3^-] + [\text{NO}_x])$ ) was increasing throughout the event; (3) the meteorological conditions were stable with constant small winds or a calm condition, without wet deposition. These criteria ensure that the observed nitrate formation was confined to the same air mass. To avoid the potential influence of vertical mixing in the early morning, the data in 06:00-09:00 local time at the surface sites (Ji'nan and Yucheng) have been excluded from the revised analyses. The following statements have been added in the revised manuscript to elaborate more about this issue, and the relevant discussions have been updated throughout the manuscript.

The selected cases met the following criteria: 1) the nitrate formation (accumulation) process should last for a considerable time period (i.e., at least three hours); 2) the observed NOR ( $\text{NOR} = [\text{NO}_3^-] / ([\text{NO}_3^-] + [\text{NO}_x])$ ) was increasing throughout the event; 3) the meteorological conditions were stable with constant wind direction or a calm condition and without wet deposition; 4) the data in the early morning period (i.e., 06:00-09:00 LT) were excluded from analyses to eliminate the potential influence from downward mixing of air aloft to the surface sites.

10:25-11:11 – Include references to previous studies that have assessed the relative contributions of these different product pathways. This will help place these results in a broader context.

**Response:** this suggestion has been adopted in the revised manuscript. The following discussion has been added to compare our results to the related previous studies.

“These results are in line with the previous studies that have assessed the nitrate formation pathways. For example, Pathak et al. (2011) found that the  $\text{N}_2\text{O}_5$  hydrolysis contributed to 50%-100% of the nocturnal nitrate formation in Beijing and Shanghai. Based on the field measurements of  $\text{N}_2\text{O}_5$  and related parameters, Wang et al. (2017) suggested that the  $\text{N}_2\text{O}_5$  hydrolysis contributed comparably to or even higher than the partitioning of  $\text{HNO}_3$  to nitrate formation in Beijing in a daily basis. Overall, the significant roles of  $\text{HNO}_3$  partitioning and  $\text{N}_2\text{O}_5$  hydrolysis in nitrate formation have been well outlined (Brown and Stutz, 2012).”

Pathak, R. K., Wang, T., and Wu, W. S.: Nighttime enhancement of  $\text{PM}_{2.5}$  nitrate in ammonia-poor atmospheric conditions in Beijing and Shanghai: Plausible contributions of heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$  partitioning, *Atmos. Environ.*, 45, 1183-1191, 2011.

Wang, H., Lu, K., Chen, X., Zhu, Q., Chen, Q., Guo, S., Jiang, M., Li, X., Shang, D., Tan, Z., Wu, Y., Wu, Z., Zou, Q., Zheng, Y., Zeng, L., Zhu, T., Hu, M., and Zhang, Y.: High  $\text{N}_2\text{O}_5$  concentrations observed in urban Beijing: implications of a large nitrate formation pathway,

Environ. Sci. Tech., 4, 416-420, 2017.

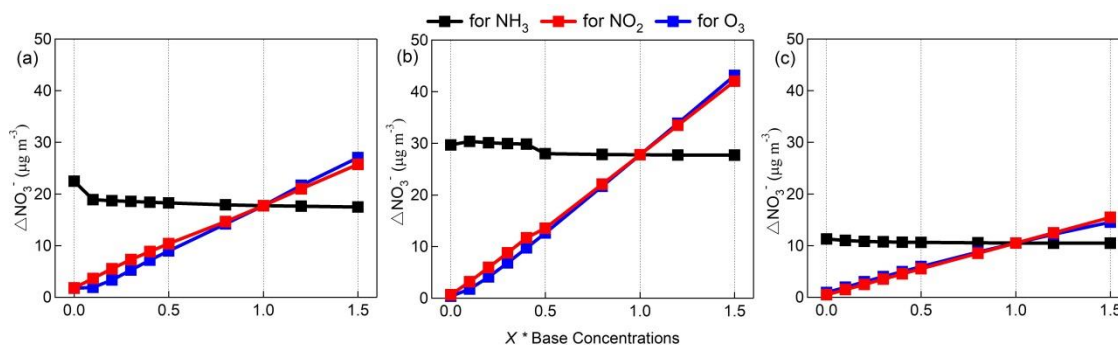
Brown, S. S. and Stutz, J.: Nighttime radical observations and chemistry, Chem. Soc. Rev., 41, 6405-6447. doi: 10.1039/c2cs35181a, 2012.

12:21-22 –See comment on uptake pH dependence above. Without additional information about the model parameterization of  $N_2O_5$  uptake (see previous comment), it is also difficult to see the relationship between acidity,  $N_2O_5$  uptake, and particle nitrate. If anything, a decrease in particle nitrate is expected with increasing acidity, as nitrate partitions to the gas phase. Further discussion about this particular model result is required.

**Response:** the model representation of the  $N_2O_5$  hydrolysis process has been described above and provided in the revised manuscript. We agree with the reviewer that there is not enough evidence for the dependence of  $N_2O_5$  uptake to aerosol acidity. As shown from the revised Fig. 7 (see below), the model-simulated nocturnal nitrate formation is quite insensitive to the abundance of  $NH_3$ , although large reductions of  $NH_3$  resulted in slight increases of nitrate at Ji'nan and Yucheng. We have checked for this result by examining all of the reaction rates related to nitrate formation, and found that it may be due to the change in the partitioning of formations of nitrate and  $ClNO_2$  from the  $N_2O_5$  hydrolysis. Increasing the aerosol acidity would restrict the reaction of  $NO_2^+$  with  $Cl^-$  producing  $ClNO_2$  (since  $Cl^-$  reacts with  $H^+$  more quickly), and thus would enhance the formation of nitrate aerosol through reaction (R9). We conducted sensitivity tests without the inputs of  $Cl^-$ , and the results showed that the nighttime nitrate formation is insensitive to  $NH_3$  (see Fig. R4).

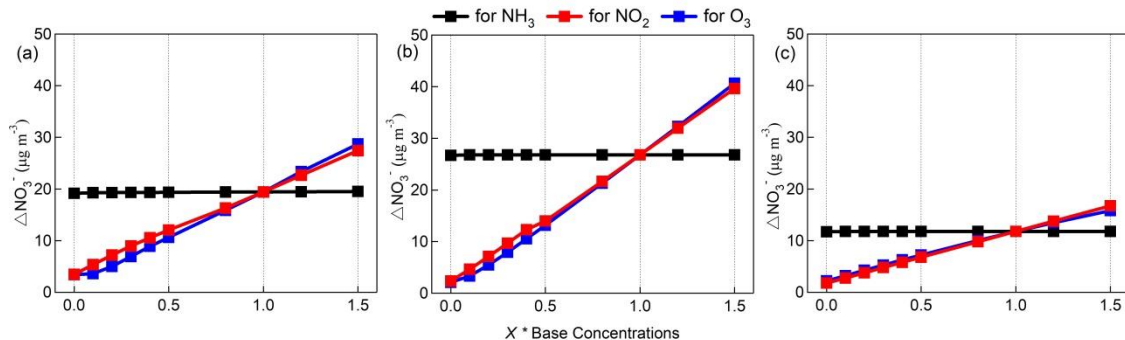
In the revised manuscript, the original statements have been revised as follows.

“In comparison, nitrate formation was not sensitive to  $NH_3$  at all three sites. Interestingly, large reductions of  $NH_3$  (c.a. >60% at Yucheng and >90% in Ji'nan) would result in a slight increase of the  $NO_3^-$  aerosol formation. This should be due to the increase of aerosol acidity by reducing the  $NH_3$  levels, which could change the partitioning of the formations of both nitrate and  $ClNO_2$  from the  $N_2O_5$  hydrolysis. Increasing the aerosol acidity would restrict the reaction of  $NO_2^+$  with  $Cl^-$  yielding  $ClNO_2$ , and hence enhance the formation of nitrate aerosol. We conducted sensitivity tests without the inputs of  $Cl^-$ , and the results didn't show any increase in nitrate formation with reduction of  $NH_3$  (figures not shown).”



**Revised Figure 7.** Model-simulated nighttime average  $NO_3^-$  enhancements as a function of the X times of the base concentrations of  $NH_3$ ,  $NO_2$  and  $O_3$  in (a) urban Ji'nan, (b) rural Yucheng and (c) Mt. Tai.





**Figure R4.** The same as above but without the inputs of  $\text{Cl}^-$  data in the model.

12:29-13:4 – Similar to previous comments, the authors need to include additional evidence of the applicability of this box model to daytime conditions. For example, the authors should include at least one figure showing that the model is able to reproduce the absolute amount of particle nitrate that was observed.

**Response:** as discussed above, the RACM2/CRPRAM2.4 multi-phase model overall worked well for the simulation of nitrate formation during the day. The model reasonably reproduced the observed nitrate formation for the selected cases in the present study. Some evidence including the scatter plots of modeled versus observed nitrate increase as well as time series for typical cases have been provided in the revised supplement. See the response to the above comment for the details (including Figures R1 and R2).

Section 3.4 – The authors need to mention the role of VOCs in both the daytime and nighttime sensitivity studies. The results presented in this section are only valid for constant VOC speciation and absolute values. If either of these changes with simultaneous reductions in  $\text{NO}_x$ ,  $\text{NH}_3$ , and  $\text{O}_3$ , the daytime abundance of OH would also change as well as the contribution from nocturnal  $\text{NO}_3 + \text{VOC}$  chemistry. These would alter the results presented in Figures 8 and 9. The authors should address this additional sensitivity by testing a few additional cases with changes in initial VOC concentrations. In addition, there is no discussion about how the changing aerosol composition (i.e. increasing nitrate) is expected to change the contribution from  $\text{N}_2\text{O}_5$  heterogeneous chemistry. More particle nitrate has been shown to reduce  $\text{N}_2\text{O}_5$  uptake and it is unclear how or if this sensitivity is included in the model.

**Response:** we agree with the reviewer that VOCs indeed play an important role in the nitrate formation. VOCs are principal ozone precursors, and regulate the daytime abundances of OH and nocturnal loss of  $\text{NO}_3$  (and  $\text{N}_2\text{O}_5$ ). Thus VOCs can affect the formation of  $\text{HNO}_3$  during the day and the  $\text{N}_2\text{O}_5$  reactivity at night, both of which in turn affect the nitrate formation.

There are many factors that can influence the nitrate formation, such as  $\text{NO}_x$ ,  $\text{O}_3$ ,  $\text{NH}_3$ , VOC speciation and abundances, and aerosol compositions. The detailed dependence of nitrate formation to all of these factors is very complex. In this study, we chose to only examine the dependence of nitrate formation to  $\text{NO}_x$ ,  $\text{O}_3$  and  $\text{NH}_3$ , with constant VOC levels and speciation. The average VOC concentrations previously collected at Mt. Tai were used to initialize the model to represent the regional average condition for VOCs.

Although we don't investigate the dependence of nitrate formation to VOCs, we think that changing VOCs should not **qualitatively** change the results presented in Figs. 8 and 9 (the relationship of nitrate with  $\text{NO}_2$ ,  $\text{O}_3$  and  $\text{NH}_3$ ). During the day, both  $\text{NO}_2$  and VOCs affect the formation of  $\text{HNO}_3$ , and  $\text{NO}_2$  may be more important because it is the direct precursor of  $\text{HNO}_3$ .  $\text{NH}_3$  does not affect the  $\text{HNO}_3$  formation but enhances its partitioning to the aerosol phase. Thus VOCs should not alter the relationship of nitrate with  $\text{NO}_2$  and  $\text{NH}_3$  as described in Fig. 8, as  $\text{NO}_2$  and  $\text{NH}_3$  actually contribute to nitrate formation in different manners. For the nocturnal formation, both  $\text{NO}_2$  and  $\text{O}_3$  are direct precursors of  $\text{N}_2\text{O}_5$ , while VOCs only affect nitrate formation indirectly by altering the budget of  $\text{N}_2\text{O}_5$  loss via the  $\text{BVOCs}+\text{NO}_3$  reactions. Hence VOCs should also not qualitatively change the relationship of nitrate with  $\text{NO}_2$  and  $\text{O}_3$  as shown in Fig. 9.

Furthermore, we have conducted sensitivity studies with varying levels of VOCs and found the modeled nitrate formation was rather insensitive to the absolute VOC concentrations (Fig. R3). The VOC speciation, especially the fraction of BVOCs, may have an important effect on the nocturnal nitrate formation. At least, the modeling results obtained in the present study should be applicable to the polluted urban atmospheres with little VOC emission in the North China Plain.

We should note that we also didn't consider the impact of the expected changes in the aerosol composition on nitrate formation. We agree with the reviewer that the increasing nitrate may reduce the  $\text{N}_2\text{O}_5$  uptake and to some extent restrict the nocturnal nitrate formation. This issue was not tested in this study.

In the revised manuscript, we have clearly elucidated the limitation of the present modeling analyses, by the following statements.

“It is worth noting that in addition to  $\text{NO}_x$ ,  $\text{O}_3$  and  $\text{NH}_3$ , there are also some other factors that influence the nitrate formation. For example, VOCs are principal  $\text{O}_3$  precursors, and regulate the abundances of OH and losses of  $\text{NO}_3$  (and  $\text{N}_2\text{O}_5$ ). Thus VOCs can affect the daytime  $\text{HNO}_3$  formation and nocturnal  $\text{N}_2\text{O}_5$  hydrolysis, which in turn affect the nitrate formation. In addition, the increasing nitrate aerosol may reduce the  $\text{N}_2\text{O}_5$  uptake and restrict the nocturnal nitrate formation. These aspects were not quantified in this study. Our modeling analyses were performed with constant VOC level and chemical speciation. Further studies are needed to explore the detailed dependence of nitrate formation to the variety of factors including  $\text{NO}_x$ ,  $\text{O}_3$ ,  $\text{NH}_3$ , VOCs, aerosol composition and meteorological conditions.”

***Typographical and Minor Comments:***

1:14 – Change ‘include the downtown’ to ‘include locations downtown’

**Response:** the original sentence has been revised as follows.

“The measurement sites include an urban site in downtown Ji’nan – the capital city of Shandong Province, a rural site downwind of Ji’nan city, and a remote mountain site at Mt. Tai (1534 m a.s.l.)”

1:18 – Change ‘have significantly increased’ to ‘have statistically significantly increased’

**Response:** changed.

1:22 – Change ‘at daytime’ to ‘during the day’. Make this change throughout the entire manuscript (e.g. 2:14, 2:29, 9:14, 12:3, etc.)

**Response:** this has been changed throughout the entire manuscript.

1:24 – Reword sentence. Suggest changing to, ‘The presence of  $\text{NH}_3$  contributes to the formation of nitrate aerosol during the day, while decreasing formation at night.

**Response:** changed as suggested.

2:2 – Change to ‘evidence of a rising trend’

**Response:** changed.

2:9 – Remove ‘the’ before ‘climate change’

**Response:** removed.

2:14 – Point out that policy mitigation strategies will also depend on understanding aerosol composition and sources.

**Response:** this sentence has been revised as follows.

“Understanding the chemical composition and sources of atmospheric particles is crucial for quantifying their environmental consequences and formulating science-based mitigation strategies.”

2:15 – Clarify particle phase nitrate vs. gas-phase nitrate radical. i.e. change to ‘Particle-phase nitrate ( $\text{NO}_3^-$ ) is a principle component...’

**Response:** changed as suggested.

2:21-24 – Formation of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  does not only occur at night. Add a sentence clarifying that this process also occurs during the day, but rapid photolysis of  $\text{NO}_3$  and thermal decomposition of  $\text{N}_2\text{O}_5$  minimize this pathway relative to oxidation of  $\text{NO}_2$  by the OH radical. Also suggest changing to ‘the reaction of  $\text{NO}_2$  and  $\text{O}_3$  produce the nitrate radical ( $\text{NO}_3$ ), which forms an equilibrium with  $\text{N}_2\text{O}_5$  that can be subsequently taken up onto aerosol to enhance nitrate aerosol.

**Response:** the original statement has been changed as follows.

“In dark conditions, the reaction of  $\text{NO}_2$  and  $\text{O}_3$  produces the nitrate radical ( $\text{NO}_3$ ), which forms an equilibrium with  $\text{N}_2\text{O}_5$  that can be subsequently taken up onto particles to enhance nitrate aerosol. The contribution from this pathway is minimized by the rapid photolysis of  $\text{NO}_3$  and thermal decomposition of  $\text{N}_2\text{O}_5$  during the day.”

2:25 – Change ‘nitrogen oxides’ to ‘ $\text{NO}_x$ ’

**Response:** changed.

2:25-26 – Unclear what the authors mean by ‘aqueous transformations of the nitrate radical’. The authors should clarify whether they are referring to  $\text{NO}_3$  VOC oxidation, which can lead

*to nitrate containing SOA or direct NO<sub>3</sub> uptake onto aerosol.*

**Response:** its means the uptake of NO<sub>3</sub> radical onto aerosol and the subsequent aqueous phase reactions with some water-soluble ions and species (see Table S1 for these reactions). For clarity, the original statement has been revised as follows in the revised manuscript.

“There are also some other formation routes of fine nitrate, such as the uptake of NO<sub>3</sub> radicals onto aerosols and its subsequent aqueous reactions with some water-soluble species (Hallquist et al., 1999; see also Table S1).”

3:12 – Change ‘depositions’ to ‘deposition’

**Response:** changed.

3:15-17 – Rephrase sentence. Suggest changing to ‘In comparison, several recent observational studies have indicated an increasingly important role of aerosol nitrate, which may even dominate summertime haze formation in the NCP’

**Response:** changed as suggested.

3:20-23 – Change to ‘To the best of our knowledge, there are no previous observational reports of increasing nitrate aerosol over northern China. Long-term measurements are necessary to confirm and quantify this trend, and better understand nitrate formation mechanisms in China.

**Response:** changed as suggested, thanks.

3:26 – Change ‘mountainous’ to ‘remote’ for consistency

**Response:** changed.

3:29 – Change to ‘statistically significant’

**Response:** changed.

4:4 – Change to ‘increasing trend of nitrate aerosol in Northern China, ...’

**Response:** changed.

4:17 – Change ‘last’ to ‘worst’

**Response:** changed.

4:28 – Remove ‘due to the closer distance’

**Response:** removed.

5:19 – Specify, was particle phase chloride or HCl measured during this study?

**Response:** both particle phase chloride (Cl<sup>-</sup>) and gaseous HCl were measured by the MARGA system during this study. This has been specified in the revised manuscript.

6:16 – Provide the number of chemical reactions in the mechanism to provide the reader with a sense for how explicit daytime VOC degradation is treated.

**Response:** the model couples the gas-phase RACM2 and aqueous-phase CAPRAM2.4, both of which are connected by a phase transfer module. The RACM2 is a lumped mechanism that consists of 363 chemical reactions to describe the degradation of the variety of VOCs, and the CAPRAM2.4 contains 438 chemical reactions to represent the aqueous reactions of various inorganic and organic compounds. The number of chemical reactions in these mechanisms has been provided in the revised manuscript.

7:2-3 – *Change to ‘observed in-situ’ and ‘available data’*

**Response:** changed.

7:4-5 – *Was a hygroscopic growth factor applied to the aerosol measurements? If so, how was the growth factor curve determined?*

**Response:** The influence of hygroscopic growth was not considered in the previous analysis. In the revised analysis, a hygroscopic growth factor was adopted from Lewis (2008) and Achtert et al. (2009) to take into account the effect of hygroscopic growth on the particle size and surface. All of the modeling analyses were re-performed with the updated particle radius and surface, and the original major conclusions were unchanged. In the revised manuscript, all of the relevant descriptions and results have been updated.

Lewis, E. R.: An examination of Köhler theory resulting in an accurate expression for the equilibrium radius ratio of a hygroscopic aerosol particle valid up to and including relative humidity 100%, *J. Geophys. Res.*, 113, doi: 10.1029/2007jd008590, 2008.

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, 2009.

7:25-8:5 - *Clarify that the reported values are the campaign average  $\pm$  the standard deviation. Also specify the different years for the Ji’nan results. Since the measurements were not conducted simultaneously, the authors should also discuss expected differences in the reported averages based on the time of year. Lastly, discuss the potential role of atmospheric mixing and transport and how these processes could affect the results at each site.*

**Response:** the original discussion has been revised according to the referee’s suggestions. See below for the revised discussion.

“The highest PM<sub>2.5</sub> levels were recorded at the receptor rural site (Yucheng; with campaign average  $\pm$ SD of 97.9 $\pm$ 53.0  $\mu\text{g m}^{-3}$ ), followed by the urban (Ji’nan; 68.4 $\pm$ 41.7 and 59.3 $\pm$ 31.8  $\mu\text{g m}^{-3}$  in 2014 and 2015, respectively) and mountain sites (Mt. Tai; 50.2 $\pm$ 31.7  $\mu\text{g m}^{-3}$ ). Nitrate shows a similar gradient with average concentrations ranging from 6.0 $\pm$ 4.6  $\mu\text{g m}^{-3}$  at Mt. Tai to 13.6 $\pm$ 10.3  $\mu\text{g m}^{-3}$  at Yucheng.”

“It should be noted that these measurements were not conducted simultaneously, and thus difference in the reported data at three study sites can be expected in view of the potential difference in the meteorological conditions which affect atmospheric mixing and transport processes. However, the spatial distributions of emissions, and atmospheric chemical and physical processes are still believed to be the major factor shaping the observed regional

pattern of aerosol pollution.”

8:6 – Clarify what the authors mean by ‘different extent of chemical processing’. For example, are the authors referring to  $\text{NO}_3$  destruction with fresh  $\text{NO}$  emissions or air transport allowing more processing time?

**Response:** it means that longer air transport allows more time for chemical processing. This has been clarified in the revised manuscript, see below.

“The air masses sampled at Mt. Tai were more aged and longer air transport allowed more time for chemical processing.”

8:14-17 – Nitrate fractions of 7-14% don’t seem to be particularly large and don’t ‘elucidate the significance of nitrate aerosol in the haze pollution over eastern China’. Perhaps this argument would be more convincing if the authors cited aerosol nitrate fractions from other locations to put these results in context.

**Response:** the original statements may be misleading for readers who are not very familiar with China. This argument just compares the fraction of nitrate in  $\text{PM}_{2.5}$  between eastern Chinese cities and a western Chinese city (Xi’an). A recent study reported an average fraction of 7% for  $\text{NO}_3^-/\text{PM}_{2.5}$  in Xi’an, compared to 12-14% in Beijing, Shanghai and Guangzhou, three megacities in eastern China. Our measurements found similar fractions (i.e., 11-14%) of  $\text{NO}_3^-/\text{PM}_{2.5}$  at three sites in the NCP region (also in the east). So we argue that nitrate aerosol may be more important for haze pollution in eastern China compared to western China. For clarity, this argument has been removed from the revised manuscript.

8:22 – What about the role of ammonium chloride in the calculation of excess  $\text{NH}_4$ ? The authors could also look at the molar ratio of total  $\text{NH}_3$  (g) +  $\text{NH}_4$  (p) to total  $\text{NO}_3$  (p) +  $\text{HNO}_3$  (g) to assess the extent of excess ammonium.

**Response:** we didn’t consider chloride in the calculation of excess  $\text{NH}_4^+$  given its much lower levels compared to sulfate and nitrate. In the revised analysis, particulate chloride has been taken into account. The updated excess  $\text{NH}_4^+$  ( $18 \cdot ([\text{NH}_4^+] - 1.5 \cdot [\text{SO}_4^{2-}] - [\text{NO}_3^-] - [\text{Cl}^-])$ ) were in the range of 0.9-4.3  $\mu\text{g m}^{-3}$ , which were slightly smaller than the estimation without  $\text{Cl}^-$  (1.4-5.2  $\mu\text{g m}^{-3}$ ). We also checked the molar ratios of  $([\text{NH}_3] + [\text{NH}_4^+]) / ([\text{HNO}_3] + [\text{NO}_3^-])$ , which were in high levels of 9-44 due to high concentrations of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_3$  (and/or the measurement uncertainties of MARGA for  $\text{NH}_3$  and  $\text{HNO}_3$ ). We have revised the analysis by considering chloride into the excess  $\text{NH}_4^+$  calculation in the revised manuscript.

“Finally,  $\text{NH}_4^+$  was generally in excess in  $\text{PM}_{2.5}$ . The average excess  $\text{NH}_4^+$  (excess  $\text{NH}_4^+ = 18 \cdot ([\text{NH}_4^+] - 1.5 \cdot [\text{SO}_4^{2-}] - [\text{NO}_3^-] - [\text{Cl}^-])$ ) were calculated in the range of 0.9-4.3  $\mu\text{g m}^{-3}$  at our three study sites.”

8:27-9:3 – What are the proposed reasons for different diurnal profiles in the urban and rural locations? Is there any available information about the role of mixing nitrate formed aloft down to the surface in the morning?

**Response:** The main reason might be attributed to the difference in the  $\text{NO}_2$  patterns in urban and rural locations. The downward mixing of nitrate formed aloft may be an important factor



contributing to the early morning peak of nitrate, although we don't have direct evidence for this from the available observations.

9:3 – Change to *'The absolute nighttime NO<sub>3</sub> levels'*

**Response:** changed.

9:25 – Was the significance test done at the 95 or 99% level? I.e. is  $p < 0.05$  or  $0.01$ ? Make sure this is consistent throughout the text and figures.

**Response:** the significance test was done at the 99% level with  $p < 0.01$ . The caption in Figure 3 has been revised.

9:26-27 – Change to *'statistically significant'*

**Response:** changed.

10:3 – Change to *'Our observations provide direct evidence of a statistically significant increase of summertime nitrate aerosol...'*

**Response:** changed.

10:11 – Clarify what mitigation strategies have been implemented. This sentence makes it sound as if the entire pollution problem has already been mitigated.

**Response:** a variety of mitigation strategies have been implemented to cut emissions from industry, transport, biomass burning, road dust, etc., and to optimize the energy structure. As a result, the ambient PM<sub>10</sub> and PM<sub>2.5</sub> concentrations have significantly declined in recent several years. However, the entire PM pollution problem has not been thoroughly mitigated. The PM<sub>2.5</sub> concentrations are still at relatively high levels in some developed regions owing to the abundant secondary components such as nitrate and secondary organic aerosols. The original statements have been revised as follows.

*“In recent years, the strict anti-pollution measures implemented by the central government have led to a significant reduction in the primary PM<sub>2.5</sub> in the NCP, while secondary aerosols such as nitrate are still at high levels and present the major challenge for further mitigation of haze pollution (<http://www.cnemc.cn/kqzlkbgbyb2092938.jhtml>). Nitrate and its precursors should be the next major target for the future control of regional haze pollution in China.”*

10:21 – Change to *'deposition'*

**Response:** changed.

Table S2 – Average is typically abbreviated Avg. not Ave.

**Response:** corrected.

11:3 – See comment above, unclear if *'aqueous'* NO<sub>3</sub> reactions are referring to VOC oxidation and condensation or direct NO<sub>3</sub> uptake and reaction.

**Response:** as discussed above, it refers to the direct NO<sub>3</sub> uptake and reaction (see Table S1). The original statement has been revised as follow.

“Hydrolysis of  $\text{N}_2\text{O}_5$  contributed to the remaining (4-6%), and the direct uptake and aqueous-phase reactions of  $\text{NO}_3$  radicals was negligible.”

*11:25-12:11 – Suggest including an example plot in the supplement of the correlation between observed and modeled nitrate aerosol.*

**Response:** we adopt this suggestion and have added the correlation plots between observed and modeled nitrate aerosols for the daytime and nighttime cases in the supplement (see Fig. R1).