Dear Editor and Reviewers,

Thank you very much for your great efforts for evaluating our submission!

The review comments are very helpful for improving the original manuscript. We have carefully considered and tried to address all of these comments, and the manuscript has been significantly revised. Below are the detailed point-by-point responses to the review comments. For clarity, the changes we made in the manuscript and supplement are highlighted in red color.

We look forward to receiving further evaluation of our work!

Best regards,
Likun Xue and co-authors

Response to the Editor's Comments:

As discussed by the two referees, this paper presents a useful analysis of particulate nitrate pollution in the North China Plain. I concur in their judgment. In addition to the comments of those referees, I suggest that two additional points be discussed:

Response: we thank the editor for handling and evaluating our submission. These comments are very helpful and we have revised the manuscript according to these comments. Below are the responses to the specific comments, with the changes in the manuscript highlighted in red color.

1) In the Abstract the authors note: "The nitrate/$PM_{2.5}$ and nitrate/sulfate ratios have significantly increased in Ji'nan (2005-2015) and at Mt. Tai (from 2007 to 2014), indicating the worsening situation of regional nitrate pollution." And likewise "This study provides observational evidence of rising trend of nitrate aerosol ..." These statements are necessarily correct only if the absolute concentrations of $PM_{2.5}$ and sulfate have remained constant (or increased). If these two species in the denominator of the two ratios have decreased more rapidly than the ratios themselves, then the regional nitrate pollution may be improving in an absolute (but not relative) sense. A short discussion and clarification of this issue should be included.

Response: we explored the trends in the absolute concentrations of $PM_{2.5}$, sulfate and nitrate in Ji'nan and at Mt. Tai. The figures are shown below. Indeed, the ambient levels of $PM_{2.5}$ and sulfate have rapidly decreased in the NCP region over the past decade, largely owing to the stringent control of SO_2 emissions and primary particles. In comparison, the absolute concentrations of nitrate in $PM_{2.5}$ showed an increasing trend from 2005 (or 2007) to 2015 (0.29 and 0.39 μg/m^3/yr). This confirms the increasing trend of nitrate aerosol pollution in this region. Nevertheless, the available observations since 2011 also showed a decrease in the absolute levels of nitrate aerosol in Ji'nan. This trend may be true given the strict NOx emission control by the central government of China since 2011, but it may be also interfered by the higher aerosol pollution observed during the campaign of 2011 that should be due to the unfavorable meteorological conditions. Anyway, more measurement studies are required to further examine the recent trend of nitrate aerosol since 2011 and assess the impact of the NOx control implemented by the government. The following figures and discussion have been added to clarify this issue in the revised manuscript.

"We also examined the trends in the absolute concentrations of $PM_{2.5}$, nitrate and sulfate in urban Ji'nan and at Mt. Tai (see Fig. S2). As expected, the ambient concentrations of $PM_{2.5}$ (6.3 and 1.4 μg m^{-3} yr^{-1}) and SO_4^{2-} (2.1 and 1.2 μg m^{-3} yr^{-1}) have rapidly decreased at both locations during the past decade, which should be largely attributed to the stringent control of SO_2 emissions and primary particles. In comparison, the absolute concentrations of NO_3^- showed an increasing trend with average rates of change of 0.39 and 0.29 μg m^{-3} yr^{-1}. This confirms the increase of nitrate aerosol pollution in the NCP region. Nevertheless, the available observations since 2011 also showed a decrease in the absolute levels of nitrate aerosol in Ji'nan. This trend may be true considering the strict NOx emission control of China since 2011, but it may be also partly interfered by the higher aerosol pollution observed during the campaign of 2011 with unfavorable meteorological conditions. More measurement

efforts are urgently needed to further examine the recent trend of nitrate aerosol after 2011 and evaluate the impact of the NOx emission control implemented by the Chinese government."
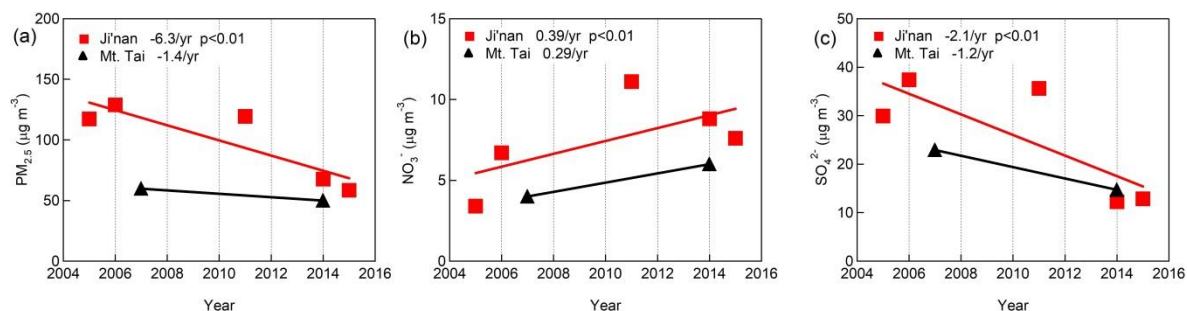

Figure S2. Long-term trends in the absolute concentrations of (a) $PM_{2.5}$, (b) NO_3^-, and (c) SO_4^{2-} in urban Ji'nan and at Mt. Tai in summertime from 2005 to 2015. The fitted lines are derived from the least square linear regression analysis, with the slopes and p values (99% confidence intervals) denoted.

2) In the Conclusions the authors "recommend that further reduction of anthropogenic emissions of NO_X should be the most efficient pathway for the current control of nitrate aerosol ..." The data discussed in the paper were collected in 2014 and earlier years. Satellite data (e.g., Liu et al., 2017) suggest that NO_x over the North China Plain was increasing during the period covered by these data, but has been decreasing rapidly since 2014. The authors should briefly discuss the likely impact of this NO_x reduction.

Response: indeed, some very recent studies have indicated the decrease in the anthropogenic emissions and ambient abundances of NOx over eastern China in the past five years. It is definitely expected that such reduction of NOx would contribute to a decrease in the fine nitrate aerosol in this region. Nevertheless, this still needs to be further confirmed by the long-term observations in the near future. The following discussion has been added in the revised manuscript.

"Some recent studies have reported the rapid decrease in the NOx abundances over eastern China since 2011 (Liu et al., 2017). It can be expected that such reduction of NOx would help to alleviate the nitrate particulate pollution in China. More observational studies are needed to further examine the trend in the nitrate aerosol and assess the contributions of the strict NOx control of China."

Reference:

Liu, F., Beirle, S., Zhang, Q., van der A, R. J., Zheng, B., Tong, D., & He, K. (2017). NO_x emission trends over Chinese cities estimated from OMI observations during 2005 to 2015. Atmospheric Chemistry and Physics, 17, 9261–9275.

Response to Reviewer 1:

L. Wen and co-authors present a succinct analysis of recent PM$_{2.5}$ 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$_{2.5}$ 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$_x$, not emissions of NH$_3$. 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$_2$O$_5$. Lastly, a large number of simulations were conducted, initialized with varying levels of NO$_2$, O$_3$, and NH$_3$ 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$_3$, N$_2$O$_5$ uptake and reaction product partitioning, as well as the partitioning of HNO$_3$ and reaction with NH$_3$. 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$_2$O$_5$ 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$_2$O$_5$ uptake. If anything, increasing acidity

should lead to a decrease in particle phase nitrate as more nitrate partitions to gas-phase HNO₃.

Response: we agree with the referee that we don't have enough evidence for the dependence of N_2O_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 NO_x, O_3, NH_3 contributions to particle phase nitrate and quantified the reaction pathways of the 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 Bassandorj, 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 $PM_{2.5}$ Pollution Events and N_2O_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 N_2O_5 on particles (γN_2O_5), the reaction pathways of the NO_3 radical and its competition with the N_2O_5 hydrolysis, the seasonal dependence of the N_2O_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 NO_x, O_3 and NH_3 is still poorly understood. Field measurement studies have shown that the uptake coefficient of N_2O_5 onto particles (γN_2O_5) is highly variable and disagrees with the laboratory-derived parameterizations (Brown and Stutz, 2012; and references therein). The contribution of N_2O_5 hydrolysis pathway tends to show a seasonal dependence with the largest influence in the winter season (Brown and Stutz, 2012; Baasanforj et al., 2017). Vertical mixing of air aloft in the residual layer may also contribute to the surface nitrate particles (Baasanforj 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 NH_3 and HNO_3 partitioning are related to each other in this model. Since the model does not include the reaction of $HNO_3 + NH_3$,
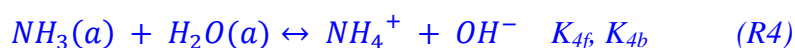
but rather HNO₃ partitioning based on particle acidity, it should be briefly mentioned how NH₃ impacts this reactions. In addition, include rate constant information in Table S1. To that point, further details need to be provided about the $N_2O_5 \rightarrow NO_3^- + NO_2^+$ reaction, which represents the uptake of N_2O_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 HNO_3 and $ClNO_2$. The formation of $ClNO_2$ could significantly reduce the absolute amount of aerosol nitrate formed by N_2O_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 N_2O_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 HNO₃ and NH₃ reactions:

Indeed, the model does not include the reaction of $HNO_3+NH_3=NH_4NO_3$. It describes the gas-to-aqueous phase partitioning and the aqueous phase reactions of HNO_3 and NH_3 by the following reactions.

$$HNO_3(g) \leftrightarrow HNO_3(a) \quad K_{1f}, K_{1b} \qquad\qquad (R1)$$

$$HNO_3(a) \leftrightarrow H^+ + NO_3^- \quad K_{2f}, K_{2b} \qquad\qquad (R2)$$

$$NH_3(g) \leftrightarrow NH_3(a) \quad K_{3f}, K_{3b} \qquad\qquad (R3)$$

$$NH_3(a) + H_2O(a) \leftrightarrow NH_4^+ + OH^- \quad K_{4f}, K_{4b} \qquad (R4)$$

$$H^+ + OH^- \leftrightarrow H_2O(a) \quad K_{5f}, K_{5b} \qquad\qquad (R5)$$

Reactions (R1) and (R3) describe the partitioning of HNO_3 and 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 HNO_3 and NH_3. Reactions (R2) and (R4) represent the reversible ionization equilibrium of HNO_3 and NH_3 in the aqueous phase. Reaction (R5) links the partitioning of HNO_3 and NH_3 with each other. Briefly, increasing NH_3 would decrease the aerosol acidity (by providing more OH⁻), which
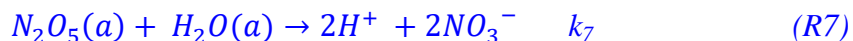
would then enhance the partitioning of HNO$_3$ to the aqueous phase as well as formation of NO$_3^-$.

In the revised manuscript, Table S1 has been revised to include the above detailed description of the HNO$_3$ and NH$_3$ 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$_3$ to the aerosol phase, hydrolysis reactions of N$_2$O$_5$, and aqueous phase reactions of NO$_3$ radicals. The HNO$_3$ partitioning is largely affected by the availability of NH$_3$, since the partitioning of NH$_3$ would decrease the aerosol acidity and hence enhance the partitioning of HNO$_3$ to the aerosol phase (see Table S1)."

(2) On the representation of the N$_2$O$_5$ hydrolysis process

Similar to the HNO$_3$ partitioning, the model describes explicitly the gas-to-aqueous phase partitioning of N$_2$O$_5$ as well. The uptake coefficient of N$_2$O$_5$ on particles (γN$_2$O$_5$) was not parameterized within the model. This heterogeneous process is represented by the following chemical reactions in the model.

$$N_2O_5\,(g) \leftrightarrow N_2O_5\,(a) \qquad K_{6f},\,K_{6b} \qquad\qquad (R6)$$

$$N_2O_5(a) + H_2O(a) \rightarrow 2H^+ + 2NO_3^- \qquad k_7 \qquad\qquad (R7)$$

$$N_2O_5(a) \rightarrow NO_2^+ + NO_3^- \qquad k_8 \qquad\qquad (R8)$$

$$NO_2^+ + H_2O(a) \rightarrow 2H^+ + NO_3^- \qquad k_9 \qquad\qquad (R9)$$

$$NO_2^+ + Cl^- \rightarrow ClNO_2\,(a) \qquad k_{10} \qquad\qquad (R10)$$

The reaction (R6) describes the partitioning of N$_2$O$_5$ between the gas and aqueous phases, with K$_{6f}$ and K$_{6b}$ being functions of the molecular speeds, gas-phase diffusion coefficients, accommodation coefficients, and Henry coefficients of N$_2$O$_5$. Reactions (R7)-(R9) describe the aqueous-phase reactions of N$_2$O$_5$ with liquid water forming nitrate, with the reaction (R8) being the fastest reaction pathway. Reaction (R10) presents the formation of ClNO$_2$ from the N$_2$O$_5$ hydrolysis.

In the revised manuscript, we have clearly elaborated about the treatment of N$_2$O$_5$ 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$_2$O$_5$ hydrolysis process, the uptake coefficient of N$_2$O$_5$ on particle surfaces (γN$_2$O$_5$) is the parameter with large uncertainty in modeling studies. Recent studies have shown that γN$_2$O$_5$ 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 γN$_2$O$_5$ into account but describes explicitly the N$_2$O$_5$ 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.
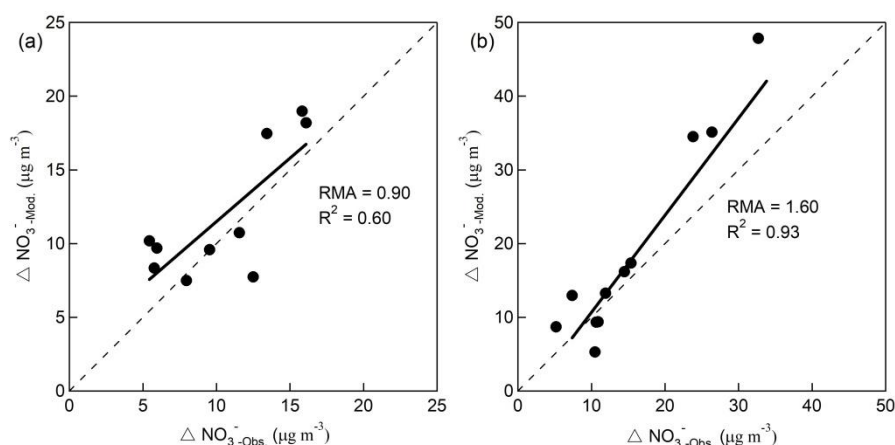

Figure R1. Scatter plots of the modeled versus observed increase of particulate nitrate for the selected daytime (a) and nighttime (b) cases
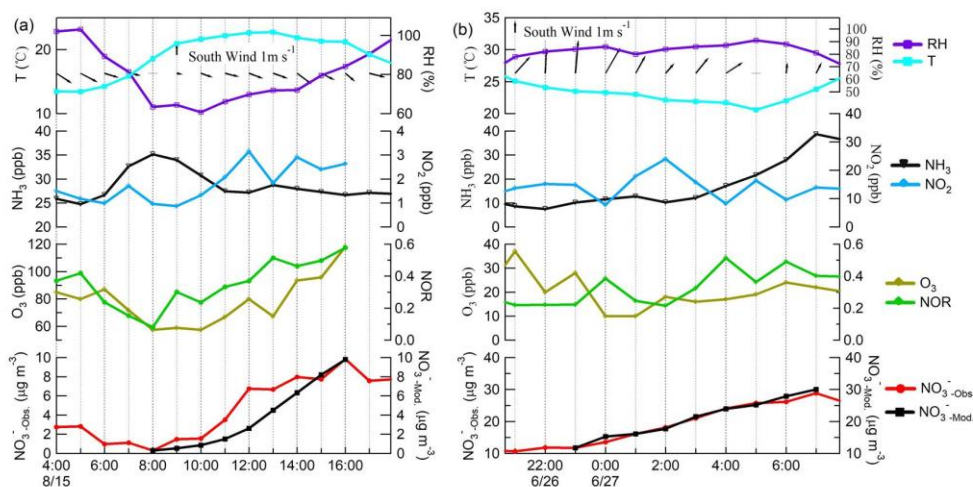

Figure R2. Comparison of modeled versus observed nitrate concentrations as well as related species for two typical cases at (a) daytime and (b) nighttime

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 NO₃ and biogenic VOC concentrations have led to a relatively large NO₃ reactivity relative to N₂O₅ 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 NO_3 with BVOCs may only account for a small fraction of the total N_2O_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."
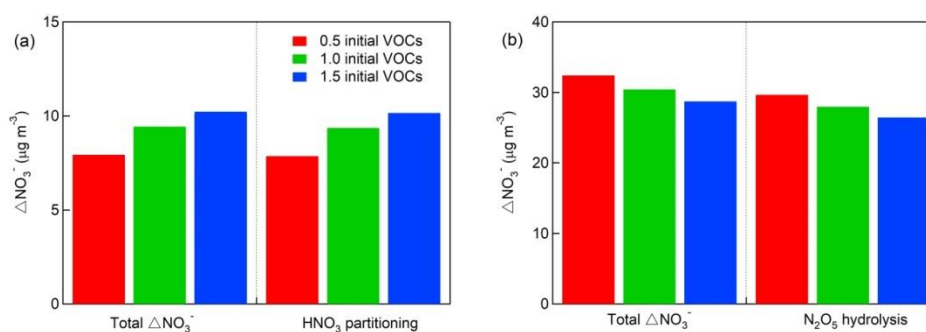

Figure R3. Sensitivity of the model-simulated (a) daytime and (b) nighttime nitrate formation to the initial VOCs

10:22 – How were day and night defined for the NO₃ 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 (NOR=$[NO_3^-]/([NO_3^-]+[NO_x])$) 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 (NOR=$[NO_3^-]/([NO_3^-]+[NO_x])$) 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 N_2O_5 hydrolysis contributed to 50%-100% of the nocturnal nitrate formation in Beijing and Shanghai. Based on the field measurements of N_2O_5 and related parameters, Wang et al. (2017) suggested that the N_2O_5 hydrolysis contributed comparably to or even higher than the partitioning of HNO_3 to nitrate formation in Beijing in a daily basis. Overall, the significant roles of HNO_3 partitioning and N_2O_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 $PM_{2.5}$ nitrate in ammonia-poor atmospheric conditions in Beijing and Shanghai: Plausible contributions of heterogeneous hydrolysis of N_2O_5 and 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 N_2O_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 no 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)."
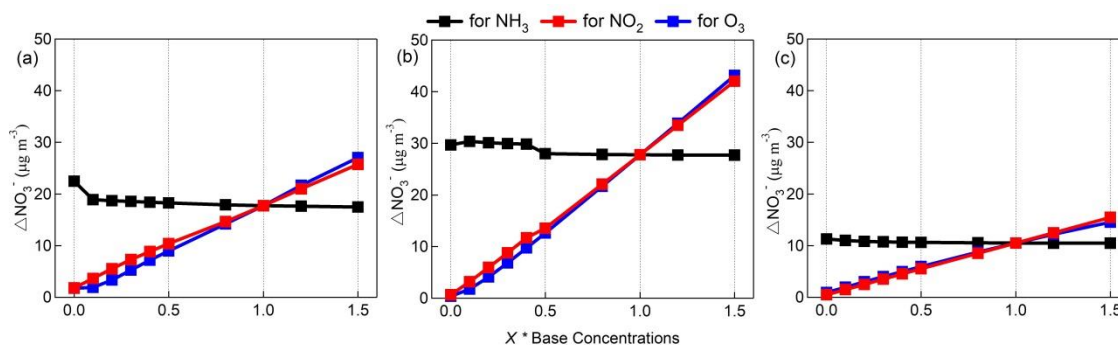
Revised Figure 7. Model-simulated nighttime average NO_3^- enhancements as a function of the X times of the base concentrations of NH_3, NO_2 and O_3 in (a) urban Ji'nan, (b) rural Yucheng and (c) Mt. Tai.
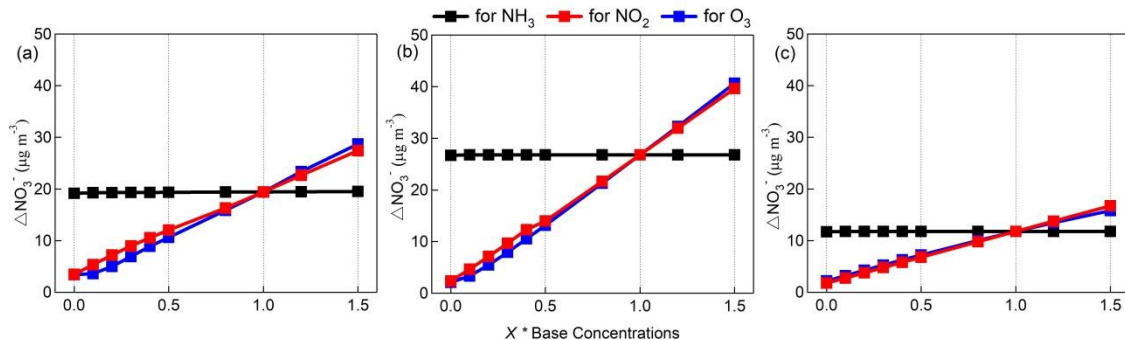
Figure R4. The same as above but without the inputs of Cl⁻ data in the model.

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 NO_x, NH_3, and O_3, the daytime abundance of OH would also change as well as the contribution from nocturnal NO_3+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 N_2O_5 heterogeneous chemistry. More particle nitrate has been shown to reduce N_2O_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 NO_3 (and N_2O_5). Thus VOCs can affect the formation of HNO_3 during the day and the N_2O_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 NOx, O_3, 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 NOx, O_3 and 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 NO_2, O_3 and NH_3). During the day, both NO_2 and VOCs affect the formation of HNO_3, and NO_2 may be more important because it is the direct precursor of HNO_3. NH_3 does not affect the HNO_3 formation but enhances its partitioning to the aerosol phase. Thus VOCs should not alter the relationship of nitrate with NO_2 and NH_3 as described in Fig. 8, as NO_2 and NH_3 actually contribute to nitrate formation in different manners. For the nocturnal formation, both NO_2 and O_3 are direct precursors of N_2O_5, while VOCs only affect nitrate formation indirectly by altering the budget of N_2O_5 loss via the BVOCs+NO_3 reactions. Hence VOCs should also not qualitatively change the relationship of nitrate with NO_2 and 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 N_2O_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 NOx, O_3 and NH_3, there are also some other factors that influence the nitrate formation. For example, VOCs are principal O_3 precursors, and regulate the abundances of OH and losses of NO_3 (and N_2O_5). Thus VOCs can affect the daytime HNO_3 formation and nocturnal N_2O_5 hydrolysis, which in turn affect the nitrate formation. In addition, the increasing nitrate aerosol may reduce the N_2O_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 NOx, O_3, 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 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 (NO_3^-) is a principle component...'

Response: changed as suggested.

2:21-24 – Formation of NO_3 and N_2O_5 does not only occur at night. Add a sentence clarifying that this process also occurs during the day, but rapid photolysis of NO_3 and thermal decomposition of N_2O_5 minimize this pathway relative to oxidation of NO_2 by the OH radical. Also suggest changing to 'the reaction of NO_2 and O_3 produce the nitrate radical (NO_3), which forms an equilibrium with N_2O_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 NO_2 and O_3 produces the nitrate radical (NO_3), which forms an equilibrium with N_2O_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 NO_3 and thermal decomposition of N_2O_5 during the day."

2:25 – Change 'nitrogen oxides' to '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 NO_3 VOC oxidation, which can lead

to nitrate containing SOA or direct NO_3 uptake onto aerosol.

Response: its means the uptake of NO_3 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_3 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^-) 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 ± the standard deviation. Also specify the different years for the Ji'nan results. Since the measurements we 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 $PM_{2.5}$ levels were recorded at the receptor rural site (Yucheng; with campaign average ± SD of 97.9 ± 53.0 µg m^{-3}), followed by the urban (Ji'nan; 68.4 ± 41.7 and 59.3 ± 31.8 µg m^{-3} in 2014 and 2015, respectively) and mountain sites (Mt. Tai; 50.2 ± 31.7 µg m^{-3}). Nitrate shows a similar gradient with average concentrations ranging from 6.0 ± 4.6 µg m^{-3} at Mt. Tai to 13.6 ± 10.3 µg 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 NO₃ destruction with fresh 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 $PM_{2.5}$ between eastern Chinese cities and a western Chinese city (Xi'an). A recent study reported an average fraction of 7% for $NO_3^-/PM_{2.5}$ 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 $NO_3^-/PM_{2.5}$ 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 NH₄? The authors could also look at the molar ratio of total NH₃ (g) +NH₄ (p) to total NO₃ (p) + HNO₃ (g) to assess the extent of excess ammonium.

Response: we didn't consider chloride in the calculation of excess 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 NH_4^+ ($18*([NH_4^+]-1.5*[SO_4^{2-}]-[NO_3^-]-[Cl^-])$) were in the range of 0.9-4.3 μg m^{-3}, which were slightly smaller than the estimation without Cl^- (1.4-5.2 μg m^{-3}). We also checked the molar ratios of $([NH_3]+[NH_4^+])/([HNO_3]+[NO_3^-])$, which were in high levels of 9-44 due to high concentrations of SO_2, SO_4^{2-} and NH_3 (and/or the measurement uncertainties of MARGA for NH_3 and HNO_3). We have revised the analysis by considering chloride into the excess NH_4^+ calculation in the revised manuscript.

"Finally, NH_4^+ was generally in excess in $PM_{2.5}$. The average excess NH_4^+ (excess NH_4^+ =$18*([NH_4^+]-1.5*[SO_4^{2-}]-[NO_3^-]-[Cl^-])$)) were calculated in the range of 0.9-4.3 μg 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 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_3 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 mitigations 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_{10} and $PM_{2.5}$ concentrations have significantly declined in recent several years. However, the entire PM pollution problem has not been thoroughly mitigated. The $PM_{2.5}$ concentrations are still at relatively high levels in some developed regions owning 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 $PM_{2.5}$ 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/kqzlzkbgyb2092938.jhml). 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_3 reactions are referring to VOC oxidation and condensation or direct NO_3 uptake and reaction.

Response: as discussed above, it refers to the direct NO_3 uptake and reaction (see Table S1). The original statement has been revised as follow.

"Hydrolysis of N_2O_5 contributed to the remaining (4-6%), and the direct uptake and aqueous-phase reactions of 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).

Response to Reviewer 2:

The manuscript "Summertime fine particulate nitrate pollution in the North China Plain: Increasing trends, formation mechanisms, and implications for control policy" by Liang Wen and Co-Authors presents the results from measurements conducted in three sites in the North China Plane (urban, rural and remote), in the summertime of 2014 and 2015. Mass and composition of inorganic soluble ions of $PM_{2.5}$ were measured, together with aerosol size distributions, NO, NO_2, O_3, CO, SO_2 concentrations and meteorological parameters. The measurements were compared to previous studies to infer temporal trends of the aerosol nitrate. Additionally, the measurements were compared to the output of the RACM2/CAPRAM2.4 model. The model results were also used to infer the dominant nitrate formation mechanism during the day and at night. Ultimately, the authors performed a sensitivity analysis, modifying the concentrations of precursor gases (NO_x or NH_3) in their model to probe which scenario would be the most effective in order to reduce $PM_{2.5}$ pollution in the area.

The Referee thinks that the paper addresses relevant scientific questions within the scope of ACP, presenting data of interest to the scientific community. However, 1) the abstract should be rephrased and made clearer; 2) Additional references should be included to give proper credit to related work; 3) some of the methods and assumptions used in the paper should be better outlined and clarified; and 4) some of the figures should be improved for a more straightforward interpretation. The Referee recommends publication in ACP after the comments below are properly addressed.

Response: we thank the referee for the positive comments and helpful suggestions. We have addressed all of the referee's comments in the revised manuscript, as detailed below in the responses to the specific comments. For clarity, the referees' comments are listed below in black italics, while our responses and changes in the manuscript are shown in blue and red, respectively.

Abstract

The Referee thinks that the abstract should be improved. In the current version, a few long sentences and some confusing passages prevent an efficient understanding of the interesting results of the study. In particular:

Page 1, Line 14: The Referee suggests breaking the sentence in two parts. One sentence telling about the measurements and one describing the NCP.

Response: this long sentence has been separated into two short ones, as follows.

"The North China Plain (NCP) is one of the most industrialized and polluted regions in China. To obtain a holistic understanding of the nitrate pollution and its formation mechanisms over the NCP region, intensive field observations were conducted at three sites during summertime in 2014-2015."

Page 1, Line 14-16: the expression "…downtown and downwind Ji'nan…" can be confusing for the Reader that approaches for the first time the description of the measurements sites. Please reword the sentence to make sure that it is clear that those are two distinct sites and

that the urban site is downtown Ji'nan and the rural site is downwind of Ji'nan.

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.)."

Page 1, Line 24-27: The Referee recommends breaking the sentence. One sentence for the day time results and one for the night time results. Additionally, please reword the expression "... plays a slightly negative role…" The word negative is vague and a possible source of confusion for the Reader. Consider using "contributes to a slight decrease in nitrate" or similar.

Response: this sentence has been rephrased as follows.

"The daytime nitrate production in the NCP region is mainly limited by the availability of NO_2, and to a lesser extent by O_3 and NH_3. In comparison, the nighttime formation is controlled by both NO_2 and O_3. The presence of NH_3 contributes to the formation of nitrate aerosol during the day, while slightly decreasing nitrate formation at night."

Introduction

Page 2, Line 21: The authors should consider adding a reference to Song, C. H. and G. R. Carmichael (2001). "Gas-particle partitioning of nitric acid modulated by alkaline aerosol." Journal of Atmospheric Chemistry 40(1): 1-22.

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

Page 2, Line 24: The authors should consider adding a reference to Brown, S. S. and J. Stutz (2012). "Night-time radical observations and chemistry". Chem. Soc. Rev., 41, 6405-6447. doi: 10.1039/c2cs35181a.

Response: added.

Page 2, Line 25: The authors should consider adding a reference to Dentener, F. J. and P. J. Crutzen (1993). "Reaction of N_2O_5 on Tropospheric Aerosols – Impact on the Global Distributions of NO_x, O_3, and OH." Journal of Geophysical Research- Atmospheres 98(D4): 7149-7163.

Response: added.

Material and methods

Page 7, Line 8-11: The Referee strongly suggests that the Authors indicate the VOC average data used. This is an important information that is omitted in the manuscript and without which it is not possible to reproduce the model results.

Response: the average VOC data used as model inputs in the present study have been provided in the revised supplementary materials (see Table S3).

Page 7, Line 11-12: The Referee strongly suggests that the Authors indicate the range used

for the VOC concentrations in the sensitivity test. Additionally, the statement "...the nitrate formation was insensitive to the input VOC concentrations." should be quantified.

Response: the 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 R1, 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 NO_3 with BVOCs may only account for a small fraction of the total N_2O_5 loss.
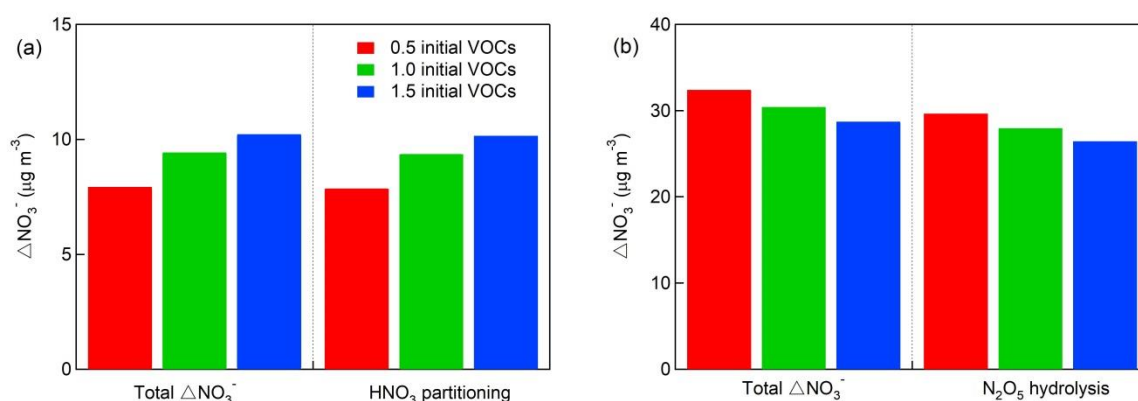

Figure R1. Sensitivity of the model-simulated (a) daytime and (b) nighttime nitrate formation to the initial VOCs

In the revised manuscript, the original statements have been revised as follows to discuss this aspect, with Figure R1 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 present modeling analyses."

Results and discussion

In the manuscript, there is no mention of chloride in the aerosol particles. Is it because there was none? The Referee recommends that the Authors add a sentence on the amount of chloride in the particles measured during the study.

Response: we had concurrent chloride data in the present study. It was not mentioned before because we wanted to focus on nitrate in the original analysis. In the revised manuscript, the measured average levels (± standard deviation) of fine particulate Cl^- have been added in Table 1. The following statement was also added to discuss the amount of chloride measured

at three sites in this study.

"Chloride showed comparable levels in urban Ji'nan (1.3 ± 2.1 and 1.3 ± 1.7 µg m^{-3}) and rural Yucheng (1.2 ± 1.2 µg m^{-3}), with a relatively lower level at Mt. Tai (0.7 ± 0.5 µg m^{-3})."

Page 8-9, Line 29-2: "…nitrate formation process throughout the nighttime with a NO$_3^-$ increase of 16.9 µg m^{-3}…" it is hard to understand where this number comes from. This is because the nighttime is not clearly defined in the manuscript. The Referee suggests to add a definition of night time (maybe using the solar elevation angle) and to add to figure 2 a visual aid (maybe a shaded area) to visually separate nighttime and daytime.

Response: in the revised manuscript, the nighttime period is defined from 19:00 to 7:00 local time. Figure 2 has been improved as suggested to show the nighttime period with shaded areas. However, the 16.9 µg m^{-3} of nitrate increment was calculated from 16:00 to 8:00, which covers the defined night time window. The original statement has been revised as follows in the revised manuscript.

"At Yucheng, the average diurnal profile displays a continuous nitrate formation process throughout the nighttime with a NO$_3^-$ increase of 16.9 µg m^{-3} from 16:00 to 8:00 LT, followed by a sharp decrease during daytime with a trough in the late afternoon (16:00 LT)."

Page 11, Line 5-11: It is not clear if the RMA slope is from simulated vs observed or vice versa. I guess it is the former case, but it would be advisable to specify if the model over or under predicts the measurements.

Response: yes, it is simulation versus observation. This has been clarified in the revised manuscript.

Page 11, Line 19-24: I suggest moving this sentence to the next paragraph. The Reader is left hanging at the end of this sentence that, I feel, is a preamble to the first sentence of next paragraph.

Response: we have adopted this suggestion to move these sentences to the next paragraph.

Figures and Tables

The Referee recommends adding an additional table with 3 columns: 1) time of the measurements, 2) location name, and 3) description (urban/rural/remote). This would help the reader navigate the paper more easily.

Response: we have added such a table in the revised supplementary materials (see Table S2).

Table 1: The Referee thinks it would interesting for the Reader if the Authors would add mean values and standard deviations for O$_3$, SO$_2$, CO, mean diameter and mean number, as the Authors state that those data were available. Additionally, adding the values for the ratio of the sum or the inorganic species divided PM$_{2.5}$ would be a valuable information that would avoid extra work for the reader.

Response: these information have been added to Table 1 in the revised manuscript.

Figure 2: Please specify if those are averages over all period and add the x-axis label.

Response: these are average diurnal data for the 2014 campaigns. The x-axis label (time of day) has been added.

Figure 3: Please add x-axis label and standard deviation.

Response: the x-axis label has been added. For the historical data, only average values were taken from the previous literatures, and the standard deviations for some years were not available. Thus standard deviations are not provided in this figure.

Figure 4 and 5: Please add uncertainty bars to the histograms in the top panel.

Response: added. The uncertainty was expressed here by the standard error of the differences between simulated and observed increase of nitrate aerosol.

Figure 8 and 9: Please explain in the caption what are the dashed lines.

Response: the dashed lines are only plotted to artificially separate the three zones with distinct sensitivity of nitrate formation to relevant species. This has been explained in figure captions in the revised manuscript.

Page 2, Line 27 and Page 11, Line 12: I suggest removing "Obviously". It is unnecessary and condescending towards the Reader.

Response: removed.

Page 3, Line 28: Please specify that in the notation "nitrate/$PM_{2.5}$" and "nitrate/sulfate" the Authors is referring to ratios.

Response: done.

Page 3, Line 4 and Page 8, Line 10: I suggest removing "relatively". It is unnecessary unless the Authors are able to specify relatively to what.

Response: removed.

Response to Reviewer 3:

Fine particulate nitrate pollution has been found to play more and more important role in haze pollution in China. This paper reports measurement results of nitrate and relevant species at three distinctly different sites in the North China Plain, the most polluted region in eastern China, and interprets the main daytime and nighttime formation mechanisms of nitrate and discusses its implications for air pollution measures in this region. This paper gives very important insights into the formation mechanisms of summertime fine particulate nitrate and into the control policy of haze pollution in China. It was very well organized and written and can be accepted for publication in ACP as the following points are addressed.

Response: we thank the reviewer for the positive comments and helpful suggestions. We have addressed all of the following points and revised the original manuscript accordingly. For clarity, the referees' comments are listed below in black italics, while our responses and changes in the manuscript are shown in blue and red, respectively.

Major points:

1) The difference between the Mt. Tai and ground surface sites as well as its implication need to be highlighted. The Mt. Tai site locates around 1465 m a.s.l., which is almost near the top of planetary boundary layer (PBL) in summer. This site is not only a "remote site" in this region, but also can provide more insights into the different chemical mechanisms inside or above the PBL, or in the nocturnal PBL and the residual layer. These issue need to be sharpen in the data analysis or in the discussions.

Response: this point raised by the referee is important and constructive. The Mt. Tai data can indeed provide insights into the chemical conditions in the top boundary layer (daytime) and residual layer (nighttime). Our observations at Mt. Tai demonstrate the serious nitrate aerosol pollution throughout the planetary boundary layer in the NCP region. The nitrate formation mechanisms, including the major formation routes and the sensitivities to NOx, O_3 and NH_3, were fairly consistent between Mt. Tai and the surface sites. This suggests the regional homogeneity of the in-situ formation of fine nitrate aerosol within the boundary layer in the NCP region. We have added the following discussion about this issue in the revised manuscript.

"It should be noted that the Mt. Tai site is located at around 1465 m a.s.l., which is almost near the top of PBL in summer. Thus the Mt. Tai data can provide insights into the chemical conditions in the top boundary layer at daytime and in the residual layer during the night. Our observations at Mt. Tai demonstrate the serious nitrate aerosol pollution throughout the PBL in the NCP region. Furthermore, the nitrate formation mechanisms, including the major formation routes and sensitivities to NOx, O_3 and NH_3, were fairly consistent between Mt. Tai and the surface sites. This implies the regional homogeneity in the in-situ formation of fine nitrate aerosol within the PBL over the NCP region."

2) For the MCM modeling of episodes, the model was run at observational-based mode (OBM). Available measurement data, including nitrate, were used as the model inputs. This method of course could help identify the ongoing chemical processes in the air masses, but it is difficult to trace back to the historical contribution of chemical processes. For example, the

observed NH_4NO_3, already existed as initial condition, could be converted into HNO_3 *through thermodynamics and further cause an "artificial" mechanism from HNO_3 *partitioning. Is that possible to do some sensitivity test by removing or reduction the observed* *nitrate concentration in the MCM OBM? Otherwise, the authors should mention the* *weakness or uncertainty of the observational-base modelling when they interpret the* *modeling results.*

Response: we are sorry that the original description of the model setup may be not clear. The RACM-CAPRAM model was only constrained by the hourly measurement data of trace gases and meteorological parameters. The measured aerosol ions data such as nitrate, sulfate and ammonium were only used as initial conditions of the model simulation. The model was initialized with the measured nitrate concentration at the beginning of the episodes, and then simulated the formation of nitrate with constraints of other relevant species. Thus, there should be no artificial mechanism from HNO_3 partitioning with such model setup. We have clarified the detailed model setup by the following statements in the revised manuscript.

"The measured aerosol ions data such as nitrate, sulfate and ammonium were only used as initial conditions of the model simulation. The model was initialized with the measured nitrate concentration at the beginning of the episodes, and then simulated the formation of nitrate with constraints of other relevant species."

Minor points:

1) Please use same scale in Y-axis for the comparison of results from different sites, such as *Figure 2, Figure 6 and Figure 7. I understand that the authors would like to highlight some* *peaks in each panel. However, it is more important to make a comparison between different* *sites.*

Response: these figures have been modified as suggested in the revised manuscript.

2) About the trends of nitrate/$PM_{2.5}$ and nitrate/sulfate in Figure 3, can we also show the *trends of nitrate, NO_2 and O_3 concentration if the data are also available?*

Response: we don't have measurement data for NO_2 and O_3 before 2010 in Ji'nan. For Mt. Tai, the measured summertime O_3 levels in 2014 (75±21 ppbv) were comparable to those in 2007 (72±19 ppbv), but the NO_2 measurements were not available in 2007. The nitrate data were available at both sites, and we have plotted the trends of nitrate concentrations in the figure below. This figure has been provided in the revised supplementary materials.
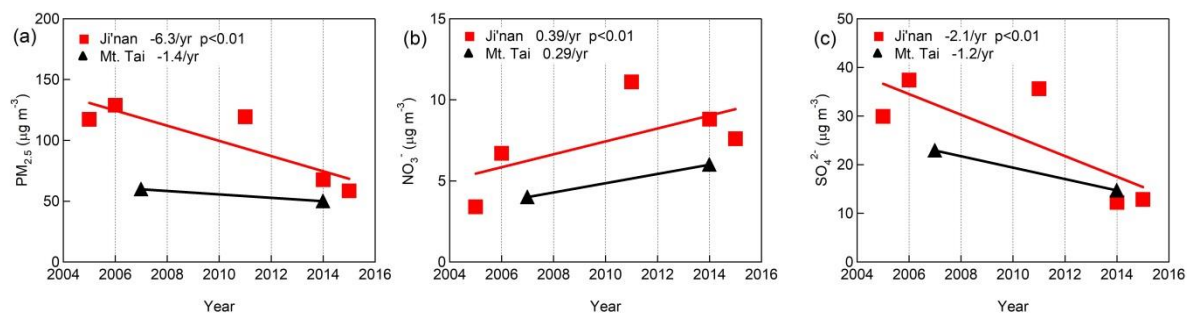

Figure S2. Long-term trends in the absolute concentrations of (a) $PM_{2.5}$, (b) NO_3^-, and (c)

SO_4^{2-} in urban Ji'nan and at Mt. Tai in summertime from 2005 to 2015. The fitted lines are derived from the least square linear regression analysis, with the slopes and p values (99% confidence intervals) denoted.

3) References of MARGA measurement: Please add some references of measurements based on this instrument, especially those done in the high aerosol loading environment in China.

Response: two references regarding the deployment of MARGA instrument in the polluted environments of China (Wen et al., 2015; Xie et al., 2015) have been cited in the revised manuscript.

Wen, L., Chen, J., Yang, L., Wang, X., Xu, C., Sui, X., Yao, L., Zhu, Y., Zhang, J., Zhu, T., and Wang, W.: Enhanced formation of fine particulate nitrate at a rural site on the North China Plain in summer: The important roles of ammonia and ozone, Atmos. Environ., 101, 294-302, 2015.

Xie, Y., Ding, A., Nie, W., Mao, H., Qi, X., Huang, X., Xu, Z., Kerminen, V.-M., Petäjä, T., Chi, X., Virkkula, A., Boy, M., Xue, L., Guo, J., Sun, J., Yang, X., Kulmala, M., and Fu, C.: Enhanced sulfate formation by nitrogen dioxide: Implications from in situ observations at the SORPES station, J. Geophys. Res., 120, 12679–12694, 10.1002/2015JD02360, 2015.

4) Page 7, Line 1 and Line 12-14. "Mixing layer height" and "boundary layer height", please use consistent words. In addition, the boundary layer height not only "affects dry deposition", the boundary layer height (or mixing layer height) determines the dispersion capacity of air pollutants emitted from ground surface.

Response: "boundary layer height" has been used in the revised manuscript. We agree that the boundary layer height determines the dispersion capacity of surface air pollutants, but we should note that dispersion was not considered in our box model. The model assumes that the air pollutants are well mixed within the box.

5) Page 9, line 4-5. The uplifted PBL: the developed PBL or uplifted PBL height.

Response: "the developed PBL" was used as suggested.