

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, NO₂, O₃, CO, SO₂ 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 NH₃) 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 NO₂, and to a lesser extent by O₃ and NH₃. In comparison, the nighttime formation is controlled by both NO₂ and O₃. The presence of NH₃ 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 N₂O₅ on Tropospheric Aerosols – Impact on the Global Distributions of NO_x, O₃, 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.

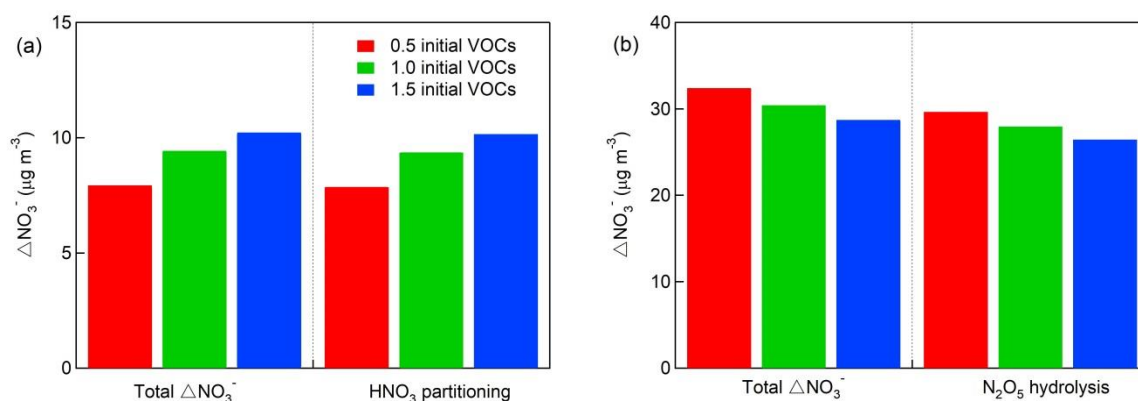


Figure R1. Sensitivity of the model-simulated (a) daytime and (b) nighttime nitrate formation to the initial VOCs

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 (\pm 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 $1.3 \pm 1.7 \mu\text{g m}^{-3}$) and rural Yucheng ($1.2 \pm 1.2 \mu\text{g m}^{-3}$), with a relatively lower level at Mt. Tai ($0.7 \pm 0.5 \mu\text{g m}^{-3}$).”

Page 8-9, Line 29-2: “...nitrate formation process throughout the nighttime with a NO_3^- increase of $16.9 \mu\text{g m}^{-3}$...” 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 $16.9 \mu\text{g m}^{-3}$ 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 $16.9 \mu\text{g m}^{-3}$ 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 $\text{PM}_{2.5}$ 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.