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

L. Wen and co-authors 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_2O_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_2O_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.

Major Comments

3:2-3 – The only direct evidence of pH-dependent N_2O_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_2O_5 uptake. If anything, increasing acidity should lead to a decrease in particle phase nitrate as more nitrate partitions to gas-phase HNO_3.

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 PM2.5 Pollution Events and N2O5 Observations in Utah's Salt Lake Valley. *Environ Sci Technol, 51*(11), 5941-5950. doi:10.1021/acs.est.6b06603

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 HNO_3 partitioning based on particle acidity, it should be briefly mentioned how 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 N_2O_5 -> 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 N2O5: A Review. *Aerosol Science and Technology, 45*(6), 665-695. doi:10.1080/02786826.2010.551672

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 NO_3 and biogenic VOC concentrations have led to a relatively large NO_3 reactivity relative to N_2O_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.

10:22 – How were day and night defined for the 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.

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.

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.

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.

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 change 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.

Typographical and Minor Comments:

1:14 – Change 'include the downtown' to 'include locations downtown'

1:18 – Change 'have significantly increased' to 'have statistically significantly increased'

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.)

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.

2:2 – Change to 'evidence of a rising trend'

2:9 – Remove 'the' before 'climate change'

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

2:15 – Clarify particle phase nitrate vs. gas-phase nitrate radical. i.e. change to 'Particle-phase nitrate (NO_3^-) is a principle component…'

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.

2:25 – Change 'nitrogen oxides' to 'NO_x'

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.

3:12 – Change 'depositions' to ' deposition'

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'

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.

3:26 – Change 'mountainous' to 'remote' for consistency

3:29 – Change to 'statistically significant'

4:4 – Change to 'increasing trend of nitrate aerosol in Northern China,…'

4:17 – Change 'last' to 'worst'

4:28 – Remove ' due to the closer distance'

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

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.

7:2-3 – Change to 'observed in-situ' and 'available data'

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

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.

8:6 – Clarify what the authors mean by 'different extent of chemical processing'. For example, are the authors referring to NO_3 destruction with fresh NO emissions or air transport allowing more processing time?

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.

8:22 – What about the role of ammonium chloride in the calculation of excess NH_4? The authors could also look at the molar ratio of total NH_3 (g) +NH_4 (p) to total NO_3 (p) + HNO_3 (g) to assess the extent of excess ammonium.

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?

9:3 – Change to 'The absolute nighttime NO_3 levels'

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.

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

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

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

10:21 – Change to 'deposition'

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

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.

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