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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Heterogeneous Formation of Particulate Nitrate under Ammonium-rich Regime during the high $PM_{2.5}$ events in Nanjing, China" *by* Yu-Chi Lin et al.

Anonymous Referee #1

Received and published: 8 October 2019

The comment was uploaded in the form of a supplement:
https://www.atmos-chem-phys-discuss.net/acp-2019-752/acp-2019-752-RC1-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-752, 2019.

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Discussion paper

SO_2 has been significantly reduced in recent years; therefore, the nitrate aerosols become more and more important in China. This study presented a long-time measurement (2016-2017) of water-soluble ions of $PM_{2.5}$ in Yangtze River Delta (Nanjing), China. They found that the nitrate was a major faction of the $PM_{2.5}$ mass. From their study, they found the nitrate was mostly produced by the N_2O_5 heterogeneous uptake under the NH_4^+-rich condition. This study suggests the studied region is located in HNO_3-limit regime and thus the reduction of NO_x may be more helpful to mitigate the PM pollution. The results could help the understanding of the heterogeneous formation of NO_3- aerosol in East China. This paper is well written, the method is sound, and the results could be important for aerosol chemistry community. I recommend this paper may be published after the following comments be addressed.

Line 48: reference is missing here.

Lines 130-136: QA/QC (ion balance) should be provided.

Line 209: should provide more evidence

Lines254-282: the criterion value should be explained in the very beginning.

Lines 328-333: are there any difference between day and night samples?

Lines 360-378: I suggest comparing NO3 increase rate with those reported in other studies

Lines 388-390： I think the authors should present more details about the Eq2. How to get this equation?

Response to Reviewer's comments

(Manuscript No. ACP-2019-752)

Reviewer #1

SO2 has been significantly reduced in recent years; therefore, the nitrate aerosols become more and more important in China. This study presented a long-time measurement (2016-2017) of water-soluble ions of PM2.5 in Yangtze River Delta (Nanjing), China. They found that the nitrate was a major faction of the PM2.5 mass. From their study, they found the nitrate was mostly produced by the N2O5 heterogeneous uptake under the NH4+-rich condition. This study suggests the studied region is located in HNO3-limit regime and thus the reduction of NOx may be more helpful to mitigate the PM pollution. The results could help the understanding of the heterogeneous formation of NO3- aerosol in East China. This paper is well written, the method is sound, and the results could be important for aerosol chemistry community. I recommend this paper may be published after the following comments be addressed.

1st comment

Line 48: reference is missing here.

Author's response:

As suggested, we have added a reference here (Huang et al., 2018) in the revised manuscript. (line 49 on page 2)

2nd comment

Lines 130-136: QA/QC (ion balance) should be provided.

Author's response:

The results of ion balance has been written in lines 205-211 and shown in Figure S2. Good correlations were found between cations and anions during the various sampling periods. The ratio of cation-to-anion was very close to 1.0 during each season, reflecting

good quality of our data in this study.

3rd comment

Line 209: should provide more evidence

Author's response:

Thanks for the reviewer's comment. Previous studies showed that the build-up of nitrate concentrations at the urban site in the early morning was due to enhanced nitrate formation in the residual layer in the mixing troposphere (Baasandorj et al., 2017, ES&T; Prabhakar et al., 2017, ACP). To explain this point, chemical model simulations are needed. However, in this work, we mainly focused on explaining the particulate nitrate behaviors based on observations and we cannot provide more evidence to support the argument as mentioned above. Thus, we have removed the sentence of "The higher nitrate……in the mixing troposphere (Baasandorj et al., 2017; Prabhakar et al., 2017)." in the revised manuscript.

4th comment

Lines254-282: the criterion value should be explained in the very beginning.

Author's response:

Thanks for the reviewer's comment. The criterion value can be calculated as the absolute value of intercept dividing by the slope in each linear regression model. (lines 309-310 on page 12)

5th comment

Lines 328-333: are there any difference between day and night samples?

Author's response:

Thanks for the reviewer's comment. As suggested, we made correlation analysis of Fn

vs. Ox and Fn vs. ALWC during the high $PM_{2.5}$ events for daytime and nighttime aerosol samples. The results showed that weak correlations between Fn and Ox were found in both daytime and nighttime. In contrast, Fn correlated very well with ALWC in both daytime and nighttime aerosol samples. This suggested that heterogeneous process played an important role in forming nitrate aerosols during both daytime and nighttime in the high $PM_{2.5}$ episodes. (line 388 on page 15, lines 389-394 on page 16 and Figure 7)

(a)

(b)

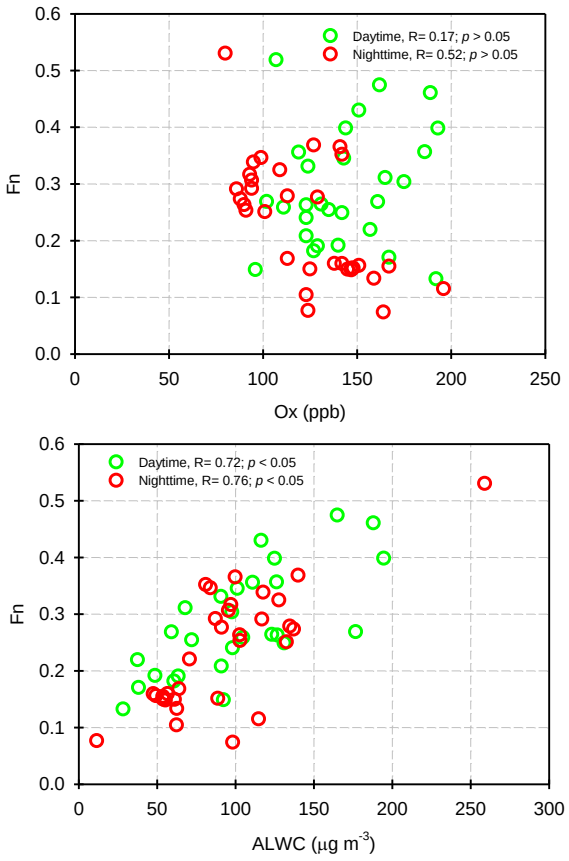

Figure 7 Scatter plots of (a) Fn against Ox and (b) Fn against ALWC in daytime and nighttime aerosol samples during the high hourly $PM_{2.5}$ concentration conditions (hourly $PM_{2.5} \geqq 150$ μg m^{-3}).

6th comment

Lines 360-378: I suggest comparing NO3 increase rate with those reported in other studies.

Author's response:

As suggested, we have compared the production rate of NO_3^- between this work and the previous studies. In this work, the average NO_3^- production rate due to heterogeneous process was 12.6 ± 7.3 % h^{-1} (4.1 ± 3.6 μg m^{-3} h^{-1}). Previous studies showed that heterogeneous process of nitrate formation exhibited rates of 14.4 % h^{-1} (file measurement) and 14.3 % h^{-1} (lab. work). Our value was in accordance with those of the literatures (Calvert and Stockwell, 1983, ES&T; Pathak et al., 2011, ACP). On the contrary, the average growth rate of NO_3^- by gas-oxidation process was 2.5 ± 0.1 % h^{-1} (0.8 ± 0.3 μg m^{-3} h^{-1}). This value was in line with that (2.4 % h^{-1}) in the subtropical polluted urban site where nitrate aerosols were mainly produced by gas-oxidation reaction (Lin et al., 2007). Moreover, we also found some cases in which the elevated NO_3^- might have been from both gas-phase and heterogeneous reactions, and the corresponding growth rate of $NO_3^-$was approximately 7.5 ± 3.0 % h^{-1} (2.5 ± 0.2 μg m^{-3} h^{-1}).(lines 432-440 on page 17 and lines 441-445 on page 18)

7th comment

Lines 388-390： I think the authors should present more details about the Eq2. How to get this equation?

Author's response:

Thanks for the reviewer's comment. In the revised manuscript, we have re-organized the section of "3.7 NH_3/HNO_3 limitation of nitrate aerosol formation". We used the ISORROPIA II model to evaluate whether control of NH_3 or HNO_3 (NO_x) is a better way to reduce particulate NO_3^- concentrations in Nanjing. ISORROPIA II is a

thermodynamic equilibrium model which is built based on the Na^+ - Cl^- - Ca^{2+} - K^+ - Mg^{2+} - SO_4^{2-} - NH_4^+ - NO_3^- - H_2O aerosol system (lines 140-143 on page 6). The input of this model includes the concentrations of total ammonium (NH_3 + NH_4^+), total chloride (HCl + Cl^-), SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} along with ambient T and RH. In addition to ALWC and pH, ISORROPIA II model can also fit the observed SIA species very well (lines 462-466 on page 18 and Figure S7). Thus, we used this model to predict the concentrations of particulate nitrate under different total nitrate and ammonium conditions (lines 469-491 on page 19) and we deleted Eq. 2 in the revised manuscript.

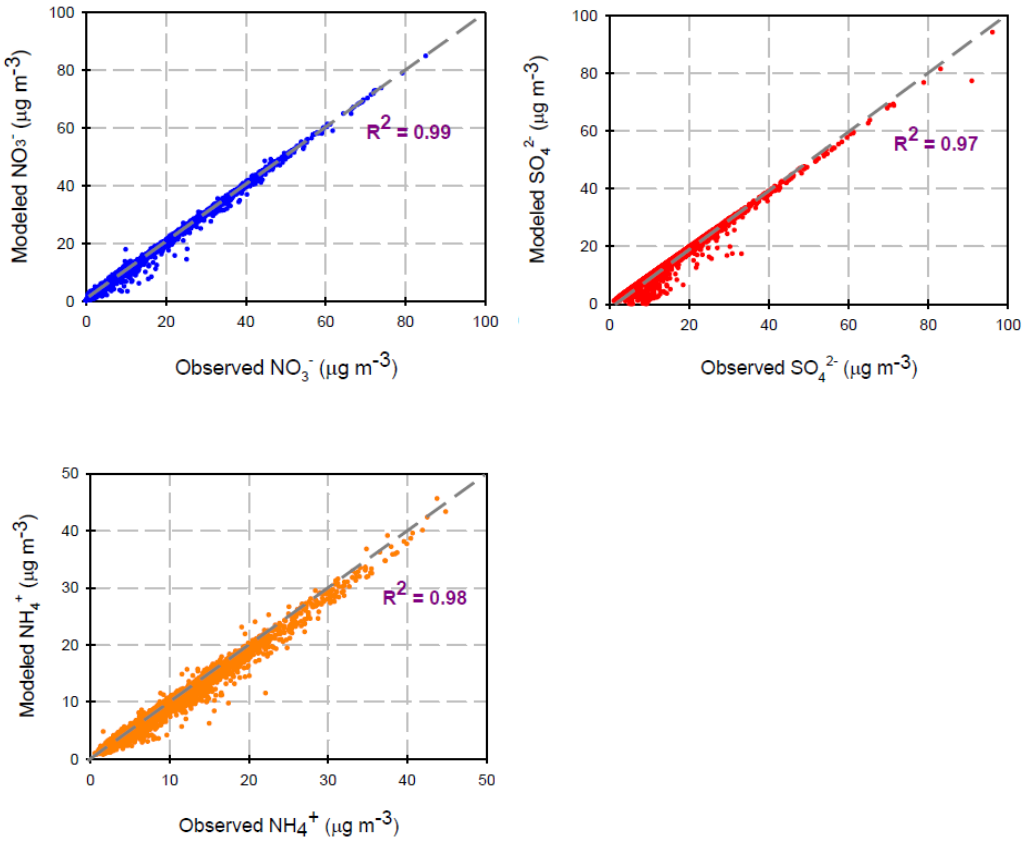

Figure S7 Scatter plots of modeled results vs. observations of NO_3^-, SO_4^{2-} and NH_4^+ in $PM_{2.5}$ in Nanjing during the sampling periods.