

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 #2

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This manuscript “Heterogeneous Formation of Particulate Nitrate under Ammonium-rich Regime during the high PM_{2.5} events in Nanjing, China” by Lin et al. investigates the formation of nitrate under polluted conditions. The conclusion on the importance of the heterogeneous formation of nitrate is drawn from the good linear relationship between the nitrogen conversion ratios (Fn) and aerosol liquid water (ALW), in contrast to the poor correlation between nitrate and Ox. However, good linear relationship does not necessarily correspond to a causal relationship between the two variables. This is particularly true for the semi-volatile nitrate, the partitioning of which between gas and particle-phases is also associated with other factors such as temperature and RH. The morning peak of nitrate as reported in this manuscript (Fig. 4) could be caused

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by the photo-chemical production of nitrate after sun rise and the subsequent condensation on pre-existing particles before the temperature increases and RH decreases afterwards. Also, regional transport should be considered. In particular, the evaporation and re-condensation of nitrate during transport could also result in an increase of nitrate in the morning, coinciding with increase of ALW. Apart from the major issues mentioned above, there are several parts of the manuscript that need better interpretation or clarification as can be seen below.

Specific comments: Line 33-35. What is the absolute production rate? Please provide both $\mu\text{g m}^{-3} \text{h}^{-1}$ and $\% \text{h}^{-1}$.

Line 146-148. It is not clear what are the inputs for the ISORROPIA II model. Why use “forward” instead of “backward” mode? One should acknowledge the uncertainty of this model. Specifically, is organics causing uncertainty in the model?

Line 179-180. Please provide correlation coefficient here.

Line 198-200. It is not clear how the theoretical equilibrium constants were derived? I saw large disagreement between the theoretical and observed values in every season in Fig. S3.

Line 266-268. Negative values of excess NH_4^+ means deficit instead of excess. Please reword here.

Line 257-259. It is not clear how the criteria values were derived from the linear regression model. Is it the intercept or slope?

Line 302-306. Why not correct for background values for the calculation of Fn. Background values could have a big effect on Fn, leading to large uncertainties. Also, the diffusion rate or the distribution of gas and particles are different.

Line 310-312. Please explain why they are comparable, and why higher than other sites rather than just comparison of values.

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Line 318-319. You are saying nitrate was totally formed from gas phase reaction during the day-time. Then, where does nitrate go during the night? It disappears or is transported to downwind sites? If transported, then, the nitrate transported from your upwind site could reach your sampling site in the evening?

Line 329-331. You mentioned that nitrate could be formed through gas-phase processes. Here, you are saying it is not from gas-phase reactions because of poor linear correlation between F_n and O_x .

Line 364-366. It is not clear how to get 70%. What are the absolute values of growth rate here, and in other cases?

Line 384-385. You are assuming HNO_3+NH_4 is the major pathway, but in previous part and in Table S1. Night time $N_2O_5+H_2O$ is the major pathway.

Figure 1. please provide better resolution. Also, the color bar has repeated 102, and Figure 1 is not discussed in the main text. If the goal of Fig. 1 is to show the location of the sampling site, it should be in supplementary.

Figure 2. Please provide year on the x-axis. Also indicate season and the cases you selected in Table S1 and Fig. 8.

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