Response to comments of anonymous referees # 2

General comments

This study presented observation results and theoretical calculations, and thereby proposed the so-called “mutual promotion effect between aerosol particle liquid water and nitrate formation”. This study focused on an interesting topic, and is presented in a relatively clear way. However, the major problem I see is the confusion between “equilibrium” and “formation”. I would recommend this manuscript for publication in ACP only if the following concerns can be nicely addressed.

As described above, this study kind of mixed up the concept of “equilibrium” and “formation”. Now let’s assume a system without N_2O_5. If the aerosols are already deliquencent, as the RH increase, the liquid water content (LWC) will increase, and the gas-particle partitioning of both NH_3 and HNO_3 will be influenced. Indeed, the final result might be that more HNO_3 partitioned on the pariticle phase and increasing the LWC, until a new equilibrium is reached that with more LWC and higher particle-phase NO_3^- fraction. However, this process should be viewed as a new “equilibrium” driven by the elevated RH, and not “formation” of HNO_3. In this sense, there’s no so-called “mutual promotion formation” concept. A lot of factors could influence this equilibrim, including aerosol acidity, activity and phase partitioning, but in any sense, there’s no

"formation" in terms of total HNO_3 in the system.

Moreover, the authors seems to argue that that although gas-phase NH_3 and HNO_3 are also “supersaturated” under dry conditioned (in comparison with the equilibrium dissociation constant of NH_4NO_3 (Kp) under dry conditions), their condensation loss is “limited by its uptake rate”. Once the aerosols get deliquescent, the update rate would be accelerated and more NO_3^- will be present onto the particle phase. I agree this process may happen during the initial dry-wet transition periods, but what’s the timescale? I would say that the system would transfer from the “rate-limited regime” under dry conditions to “equilibrium-controlled regime” soon after this transition, on the scale of hours. Afterwards, as I described above, the apparent increase in NO_3 is only a result of equilibrium moving due to RH variations, if there’re no influences from other factors. In this sense, I don’t get the where the “mutual promotion” lies in – if it’s referring merely to those several hours, I won’t consider it as an important process in the haze development.

Many thanks to the reviewer for the valuable comments and suggestions. I agree with the reviewer that it is essential to interpret clearly about the “equilibrium” or “formation”, “uptake rate limited” or “equilibrium-controlled regime”, and discuss the relative contributions of HNO_3 partitioning and N_2O_5 hydrolysis to particulate nitrate. We therefore have re-written the Sec. 3.2. 1) We found out that the aerosol particles were not reaching equilibrium during 29th Feb-4th Mar., 2019 as shown in Figure 3 below, which means the gaseous NH_3 and HNO_3 was supersaturated in the atmosphere throughout this haze event. In this case, the mutual promotion of aerosol liquid water and particulate nitrate enhancement happened throughout the haze development, and the increasing RH accelerated this process. I do apologize that I didn’t clearly describe the “formation”, is in terms of particulate nitrate, sometimes I described as nitrate (can refer to total nitrate in the system as well) which might mislead the audience. I have revised the terminology as suggested to avoid the unnecessary confusion, details shown below. 2) We agree with the reviewer that the “rate-limited regime” could be just in the time scale of hours after particles get deliquescent and system would transfer to “equilibrium-controlled regime” soon with the presence of aerosol liquid water. The corresponding discussion of “limited by its uptake rate” has been removed.

We have revised the Sec. 3.2 of the manuscript, as shown below.

“To illustrate the facilitation of particulate nitrate enhancement from HNO_3 in the presence of liquid water, we performed the theoretical calculation of equilibrium

between particulate NH_4NO_3 and gaseous NH_3 and HNO_3 under dry and ambient conditions, respectively. The dissociation constant of NH_4NO_3 (Kp) in dry condition was calculated using Eq. [5] without considering the influence of the liquid water. As shown in Figure 3, the equilibrium Kp in the dry condition ranged from 0.06 (275.3 K) to 4.61 (291.5 K) ppb^2 during the 'haze period'. Taking account of the aerosol liquid water, the equilibrium vapor pressure of HNO_3 and NH_3 over particles was calculated by E-AIM Model II (www.aim.env.uea.ac.uk). Note that this calculation assumes negligible interaction between dissolved organic components and the activity of NO_3^-. In the presence of aerosol associated water, the product of equilibrium vapor pressure of NH_3 and HNO_3 calculated from E-AIM was 10~60% lower than the equilibrium Kp in the dry condition during the marked 'haze period'. This means, the presence of aerosol liquid water changed the equilibrium and would favor the particulate nitrate enhancement. However, the aerosol particles didn't reach the equilibrium between particulate NH_4NO_3 and the gases (NH_3 + HNO_3) during the investigated period, as the measured product of the NH_3 and HNO_3 partial pressure (2.55~9.63 ppb^2) was supersaturated compared to the equilibrium values in both dry and deliquescent particles. In this case, the partitioning of gaseous NH_3 and HNO_3 in the atmosphere into the particle phase could be accelerated and leaded particulate nitrate enhancement as increasing of ambient RH. Owing to the nature of highly hydrophilic, the increased ammonium nitrate mass fraction leads to further water uptake. Such a mutual promotion of particulate nitrate and aerosol liquid water enhancement becomes more pronounced with the increasing pollution throughout the haze event owing to the simultaneously increasing ambient RH. Consistently, a significant co-increase of particulate nitrate and aerosol liquid water was observed during haze development as shown in Figure 4. At first, a steep increase of particulate nitrate in total nitrate mass ratio (from ~12% to ~98%) was observed as the aerosol liquid water enhanced up to ~20 $\mu g/m^3$. And then, the particulate nitrate mass kept increasing with further increase of aerosol liquid water. We observed that, ~98% of nitrate was present as particle phase when aerosol liquid water was higher than ~20 $\mu g/m^3$. It is worth noting that N_2O_5 hydrolysis during nighttime can contribute extra HNO_3 in the wet denuding method *within GAC-IC system. This effect might cause uncertainty on the molar ratio of particulate nitrate in the total nitrate as a function of aerosol liquid water during nighttime. However, the consistency of this function between daytime and the nighttime (Figure 4) suggests a negligible influence of N_2O_5 interference on our analysis during the investigated period."*

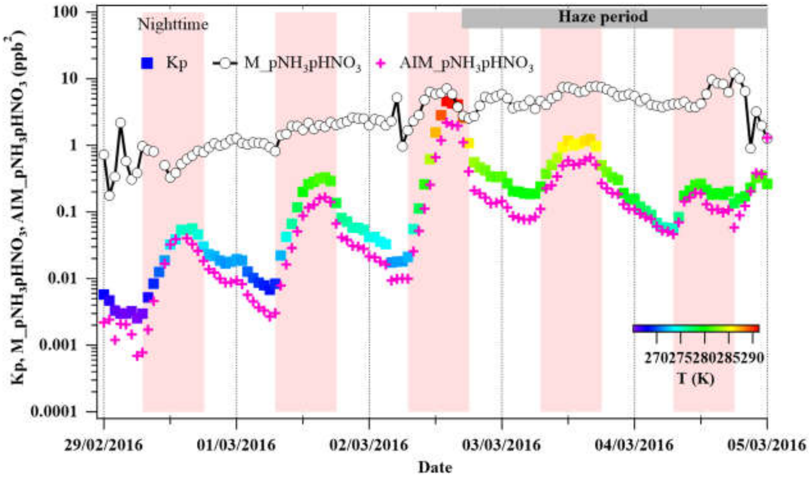

Figure 3 in the old version. The comparison of the calculated temperature-dependent dissociation constant of NH_4NO_3 (Kp) (Seinfeld. and Pandis., 2006) in the absence of liquid water, the product of equilibrium vapor pressure of gaseous NH_3 and HNO_3 from E-AIM, and the product of mixing ratios of gaseous NH_3 and HNO_3 measured by GAC-IC (M_pNH_3pHNO_3). Here, Kp is colored by the ambient temperature ranging 265~293K during February 29 to March 5, 2016.

The only way that I would agree the concept of "mutural promotion formation" is that, the uptake by N_2O_5 under high RH is so important that it contributed signicantly to the total HNO_3. This is not shown in this study. I would suggest to distinguish the relative contribution of HNO_3 partitioning and N_2O_5 uptake on the final enhancement of particle-phase NO_3^-.

3) A previous study, as part of this BEST-ONE campaign, has distinguished the relative contribution of HNO_3 (75~99%) and N_2O_5 (1~25%) to the particulate nitrate (Lu et al., 2019), as shown in Fig. R1.

The relative contribution of particulate nitrate from N_2O_5 and HNO_3 has been added to the beginning of the Sec. 3.2 Mutual promotion between liquid water and particulate nitrate enhancement as shown below.

"Lu et al. (2019) conducted a box model to calculate the potential particulate nitrate formation during the same investigated period of the BEST-ONE project. They found out that HNO_3 from daytime photooxidation of NO_2 was the major source of the particulate nitrate (>75%), whereas the contribution of N_2O_5 pathway was lower than 25% (Lu et al., 2019)."

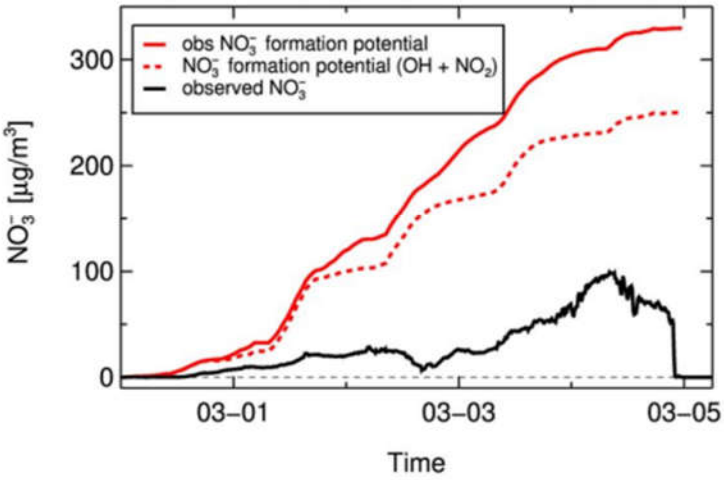

Fig. R1. Calculated contributions from HNO_3 $(\cdot OH+NO_2)$ shown as dashed red line and total particulate nitrate formation potential (solid red line) by box model during the same observational period. The difference between these two was the N_2O_5 contribution. This figure is sourced from the Figure S13 of Lu et al. (2019).

Lu, K., Fuchs, H., Hofzumahaus, A., Tan, Z., Wang, H., Zhang, L., Schmitt, S. H., Rohrer, F., Bohn, B., Broch, S., Dong, H., Gkatzelis, G. I., Hohaus, T., Holland, F., Li, X., Liu, Y., Liu, Y., Ma, X., Novelli, A., Schlag, P., Shao, M., Wu, Y., Wu, Z., Zeng, L., Hu, M., Kiendler-Scharr, A., Wahner, A., and Zhang, Y.: Fast Photochemistry in Wintertime Haze: Consequences for Pollution Mitigation Strategies, Environmental Science & Technology, 53, 10676-10684, 10.1021/acs.est.9b02422, 2019.

Seinfeld., J. H., and Pandis., S. N.: Atmospheric Chemistry and Physics: from air pollution to climate change, John wiley & Sons, INC, 2006.