Dear editor,

Thanks for all your kindly editing work and two anonymous reviewers' and Dr Gavin Philips valuable comments. We have revised the manuscript and drafted point-by-point response to the reviewers on the behalf of all co-authors. This file includes: 1) Response to Gavin Philips, 2) Response to comments of anonymous referees # 1, 3) Response to comments of anonymous referees # 2, 4) tracked manuscript version. Please find the details at below.

Thanks, and best regards,

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Response to Gavin Philips:

The subject of the paper is the uptake of dinitrogen pentoxide onto PM including the hydrolytic uptake on aqueous aerosol. The process is very likely to occur in GAC instruments and the resulting nitrate measured by the IC will very likely contain a substantial contribution from the hydrolysis of nitrogen pentoxide within the GAC sampling system, where two nitrate ion result from the sampling of one dinitrogen pentoxide molecule. In situations where the chemistry of the N2O5/nitric acid/PM system is being studied, I would think that a consideration of this issue would be important at the very least in estimating the uncertainties of the experimental approach.

A description of the effect as observed in the Applikon MARGA was published in Phillips, G. J., Makkonen, U., Schuster, G., Sobanski, N., Hakola, H., and Crowley, J. N.: The detection of nocturnal N2O5 as HNO3 by alkali- and aqueous-denuder techniques, Atmos. Meas. Tech., 6, 231–237, https://doi.org/10.5194/amt-6-231-2013, 2013. All instruments using the same or similar means of determining nitric acid will very likely suffer from this effect.

Have the authors considered this effect? What uncertainty does it introduce into the data analysis?

Thanks for your valuable comments about this interference of N_2O_5 *on* HNO_3 *detection of GAC-IC. We have tested the potential interference of* N_2O_5 *in the studied period, and added the corresponding discussion into the revised manuscript.*

To test the potential N_2O_5 *interference within investigated period, we re-grouped the measured dataset into the daytime (7:00 ~ 18:00 LT) and nighttime (18:00 ~* $07{:}00^{+1}$ *LT) periods. As the rapid photolysis* *of NO_3 radical and limited N_2O_5 concentration during daytime, N_2O_5 and its interference on GAC measurement are negligible during daytime. As shown in the revised Figure 4 below, we found a consistent pattern of molar ratio of particulate nitrate in the total nitrate ($m_{NH_4NO_3}/(m_{NH_4NO_3}+m_{HNO_3})$) as a function of aerosol liquid water during the nighttime (green solid triangle) and daytime periods (red solid triangle). During the nighttime, the interference of N_2O_5 contributes higher HNO_3 in GAC measurement. That means, an underestimation of the $m_{NH_4NO_3}/(m_{NH_4NO_3}+m_{HNO_3})$ during nighttime was expected. This is consistent with the slightly underestimation (about 4%~8%) of the $m_{NH_4NO_3}/(m_{NH_4NO_3}+m_{HNO_3})$ during the nighttime when aerosol particle liquid water is less than 10 μg/m^3, as shown in revised Figure 4.*

As discussed above, the interference of N_2O_5 on HNO_3 observations is not expected to change the conclusions of our study during the investigated period in Beijing. We have added the discussion of this N_2O_5 interference in the revised manuscript (line 312-317, revised clean version manuscript) as shown below:

"The function between the particulate nitrate fraction and aerosol liquid water is given in Figure 4. 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 explain the slightly underestimation of the particulate nitrate fraction in the total nitrate during nighttime when aerosol liquid water is less than 10 μg/m^3(Figure 4). However, the general 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."

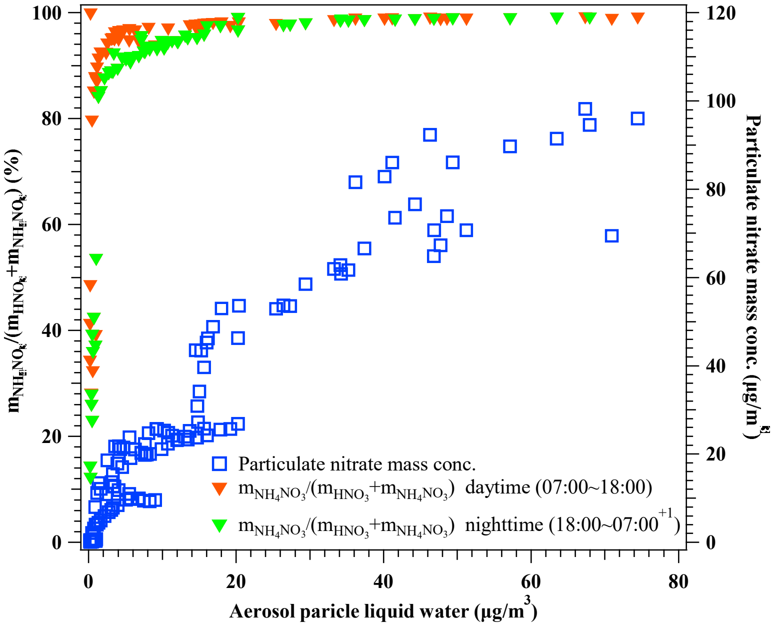


Figure 4: The relationship between aerosol particle liquid water and the molar ratio of particulate nitrate in the total nitrate, $m_{NH_4NO_3}/(m_{HNO_3}+m_{NH_4NO_3})$ (left axis) during the nighttime 18:00~07:00+1 (green solid triangle) and the daytime at 07:00 ~ 18:00 (red solid triangle), and mass concentration of particulate nitrate as a function of aerosol liquid water (right axis) during the period of during February 29 to March 5, 2016. Here, particulate nitrate was measured by HR-ToF-AMS and the HNO_3 in the gas phase was measured by GAC-IC. Aerosol liquid water was calculated by H-TDMA-derived method.

Response to comments of anonymous referees # 1

General comments

Wang et al. reported their field observation of chemical composition in particulate matter (PM) in Beijing. Based on the data together with measured meteorological parameters, they estimated condensational loss rate of nitrate precursor gases for nitrate formation and aerosol liquid water. In addition, they discussed the interplay between increased particulate nitrate and aerosol particle liquid water, suggesting that particulate nitrate increased the aerosol liquid water and the aerosol liquid water promoted condensational loss of nitrate precursor gases (N_2O_5 and HNO_3), i.e., increasing particulate nitrate. This study has highlighted an increasing importance of particulate nitrate during a polluted episode in wintertime in Beijing, and would be an important contribution to the understanding of recent change in chemical composition of PM. I would recommend this manuscript for publication in ACP after addressing the following issues.

Many thanks to the reviewer for the comments and suggestions. We have improved the manuscript accordingly. Please find a point-by-point response below.

Specific comments:

Q1. Lines 85-86: The statement on "via well chemical pathways" is a bit misleading for the oxidation of SO_2 because sulfate production mechanisms from the SO_2 oxidation during haze episodes in Beijing are still ongoing debate (Cheng et al., 2016; Gen et al., 2019).

Cheng et al., Science Advances 2.12 (2016): e1601530.

Gen et al., Environmental Science & technology, (2019): 53, 8757-8766.

Thanks for the useful suggestion. The reviewer is right that the particulate sulphate formation is still ongoing debate, not well-established yet.

The original sentence has been revised as shown below.

"In atmospheric environments influenced by anthropogenic activities, particulate secondary inorganic compounds are often dominated by particulate sulfate and nitrate (Heintzenberg, 1989), which originate from the oxidation of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) via multiple chemical pathways (Calvert et al., 1985;Cheng et al., 2016;Wang et al., 2016;Gen et al., 2019a, b)."

Q2. I can understand that nitrate mass fraction in secondary inorganic components has increased. However, I am not sure why the absolute mass concentration of nitrate can increase despite the reduction of NO_x over North China. More discussion on this point deserves to appear in the introduction.

Thanks for your helpful comment. The description of increasing nitrate mass concentration by 7% in the manuscript between 2006 and 2015 was from model simulation with the input for NO_x emissions of 20.8 Tg (2006) and assumed value of 24.26 Tg (2015) (Wang et al., 2013). However, NO_x emissions showed a declining trend during the period of 2010~2017 (Liu et al., 2017;Vu et al., 2019;de Foy et al., 2016). The mass concentration of particulate nitrate showed a declining trend as well as sulfate during 2013~2017 (Wang et al., 2019).

The discussion on nitrate mass concentration trend was added in the Introduction and the corresponding context is rephrased, as shown below.

"In the recent years, China has also managed to reduce SO_2 emissions by 75% during 2007~2015 (Li et al., 2017) and declined by ~15.1% per year during 2013~2017 (Vu et al., 2019), whereas NO_x emissions declined only by ~10% between 2011 and 2015 (de Foy et al., 2016) and by ~ 4.3% per year during 2013~2017 (Vu et al., 2019). The strict emission control reduced the $PM_{2.5}$ mass concentration and the corresponding chemical components in China significantly (Vu et al., 2019). The annual mean $PM_{2.5}$ mass loading decreased by 39.6% during 2013~2017 in Beijing-Tianjin-Hebei region, and the SO_4^{2-} and NO_3^- mass concentrations in the $PM_{2.5}$ declined by 40% and 34% respectively during 2015~2017 in Beijing (Vu et al., 2019). However, NH_3 emissions have been observed by satellites to increase by ~30% from 2008 to 2016 over the North China Plain (NCP) (Liu et al., 2018). The faster reduction rate of SO_2 than NO_x emissions in conjunction with elevated NH_3 level, made it reasonable of switching dominant inorganic component in fine aerosol particles from sulfate to nitrate in the recent years similar like European countries (Sun et al., 2015;Hu et al., 2017;Hu et al., 2016;Wu et al.,

2018;Guo et al., 2014;Huang et al., 2014;Huang et al., 2010;Ge et al., 2017;Xu et al., 2019;Xie et al., 2019;Li et al., 2018). Field measurements in Beijing show that annually averaged NO_3^-/SO_4^{2-} molar ratio of NR-PM_1 (non-refractory PM_1) in 2012 (1.3~1.8) (Sun et al., 2015) has significantly increased compared to that in 2008 (0.9~1.5) (Zhang et al., 2013). Comparably, the NO_3^-/SO_4^{2-} molar ratio of $PM_{2.5}$ in Beijing increased substantially, from 1.5 before 2013 to 3.33 in 2017 (Xu et al., 2019).”

Q3. The authors need to explain how they estimate the uptake coefficient of N_2O_5 because they discussed factors affecting the coefficients.

We had briefly described how to estimate the uptake coefficient of N_2O_5 in the Method section. In the revised version, we have improved this description, provided a clearer summary of the method and refer more details to the corresponding references, as shown below.

“The uptake coefficient of N_2O_5 was estimated following the method proposed in Chen et al. (2018) and Chang et al. (2016) and references therein. The influences of RH, temperature, multiple inorganic particle compositions, secondary organic aerosol (SOA) and primary organic aerosol are considered. The uptake suppression effect of N_2O_5 due to the presence of SOA was considered following the method in Anttila et al. (2006). Based on our source apportionment using Positive matrix factorization (SoFi tool, ME2, Francesco Canonaco, PSI), two oxygenated organic aerosol factors (OOA), usually interpreted as SOA, and three primary organic aerosol factors (POA) were determined. The fraction of SOA in the total organic aerosol (OA) was 60%~90% during the observed period, which is quite consistent with the results of a previous study in Beijing (Huang et al., 2014). Hence, 75% was used as

the ratio of SOA/OA in our model to estimate the suppression effect of SOA on the uptake of N_2O_5 following the work of Anttila et al. (2006). The reaction of chloride with N_2O_5 was not considered in this study due to its limited mass concentration (on average 5% of the PM_1 mass concentration during the marked haze period), which could cause minor uncertainty in the k_N_2O_5 calculation. The detailed information regarding the estimation γ_{N2O5} is given in Chen et al. (2018), and influence of different chemical components on γ_{N2O5} is summarized in the Table 1 of Chen et al. (2018).”

Q4. Lines 268-270: I think that this depends on RH. Need to verify it.

Good point. To verify this, I used the online thermodynamic model UManSysProp (http://umansysprop.seaes.manchester.ac.uk/) to calculate the hygroscopic growth factor (GF) of pure NH_4NO_3 and $(NH_4)_2SO_4$ particles as a function of RH above their deliquescence RH. As shown in Fig. R1, for the deliquescent pure NH_4NO_3 and $(NH_4)_2SO_4$ particles, the hygroscopic growth factor under the same RH was comparable.

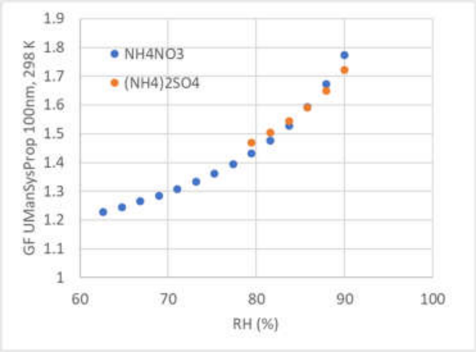


*Fig. R1. Calculated hygroscopic growth factor (GF) at 298 K with 100 nm dry particle size for pure NH_4NO_3 and $(NH_4)_2SO_4$ as a function of relative humidity (RH) from UManSysProp (*http://umansysprop.seaes.manchester.ac.uk/index*). Here, the co-condensation of water and NH_4NO_3 was not considered in the calculation.*

The original sentence has been revised as shown below.

As one of the main hydrophilic compounds in atmospheric aerosol particles, the ability of water uptake is comparable between deliquescent $(NH_4)_2SO_4$ and NH_4NO_3 particles with same sizes and ambient RH (Kreidenweis and Asa-Awuku, 2014;Wu et al., 2016), (http://umansysprop.seaes.manchester.ac.uk/).

Q5. Lines 312-313: It can be understood that in their calculation the authors ignore the interaction between dissolved organic components and the activity of NO_3^-. However, small organic acids affect the aerosol hygroscopicity. Can the authors provide the potential impact of such small organic acids on their calculation?

In this study, the aerosol liquid water was calculated based on the measurements of the particle number size distribution, hygroscopicity by H-TDMA, ambient RH and T. Here, the hygroscopicity measurement gives an bulk hygroscopic growth of given particle size. Therefore, the estimated aerosol liquid water has already considered the contribution from organic compounds. Then, the aerosol liquid water was used as input of E-AIM model to calculate the equilibrium vapor pressure of HNO_3 and NH_3 over wet particles.

Q6. Molar fraction of nitrate over total of HNO_3 + NO_3^- highly depends on particle pH (e.g., Nah et al., 2018). The authors attributed a strong positive correlation between particulate nitrate and aerosol liquid water to the feedback loop between them, but no particle pH effect has been discussed. Can you exclude the possibility that increased particle pH would lead to an increase in particulate nitrate?

Nah et al., Atmospheric Chemistry and Physics 18.15 (2018): 11471-11491.

Good point. We agree with the reviewer that the higher pH of aerosol particles is favorable for the equilibrium of HNO_3 into the particle phase (Nah et al., 2018). Therefore, We calculated aerosol pH using ISORROPIA II and found out that the aerosol pH is not the driving factor for particulate nitrate formation in the investigated case.

A detailed discussion has been added into the Sec. 3.2 (Line 318~330, clean manuscript) as shown below.

"Aerosol pH is also an important factor on the particulate nitrate formation, higher pH is favorable for the equilibrium of HNO_3 into the particle phase (Nah et al., 2018). pH of the fine aerosol particles was calculated by ISORROPIA Ⅱ (Fountoukis and Nenes, 2007) during the investigated period. The model was running in 'forward mode' with chemical composition of NR-PM1 (NO_3^-, SO_4^{2-}, Cl^-, NH_4^+) and gas precursors (HNO_3, HCl, NH_3) by GAC-IC as inputs. And the model was running in 'metastable mode', assuming no solid existed in the system. Generally, the fine aerosol particles became more acidic with pH dropping from ~8 down to ~4 when NR-PM_1 mass concentration increased from ~12 μg/m^3 up to >300 μg/m^3 as shown in Figure 5 and Figure 6. This declining trend of pH is not favorable for the HNO_3 partitioning into the particle phase (Nah et al., 2018). However, a clear enhanced trend of molar ratio of particulate nitrate in the total nitrate as a function of NR-PM_1 mass concentration was observed correspondingly (as shown in Figure 5 and Figure 6). Therefore, in this case the increase of aerosol liquid water is more likely to be the driving factor of particulate nitrate formation compared to the influence of pH."

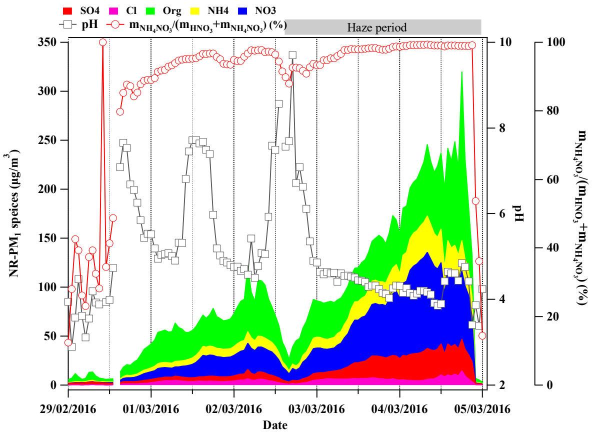


Figure 5 in the revised manuscript (revised from Figure 3 in the old version) The time series of chemical composition measured by HR-ToF-AMS (left axis), calculated aerosol pH by ISORROPIA II (inner right axis) and molar ratio of particulate nitrate in the total nitrate (gas+particle phase) shown on outer right axis.

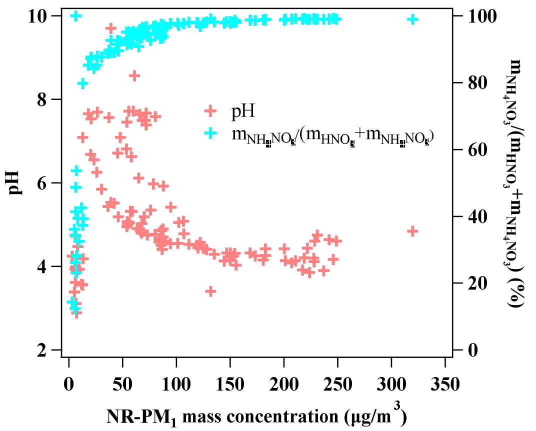


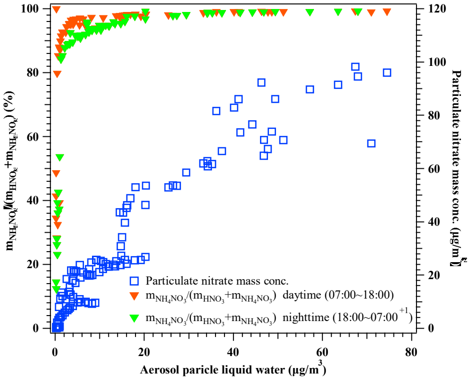
Figure 6 in the revised manuscript. The pH of the fine aerosol particles (left axis) and the molar ratio of particulate nitrate in the total nitrate (gas+particle phase) (right axis) as a function of NR-PM$_1$ mass concentrations.

Q7. If the mutual effect of both nitrate and aerosol particle liquid water is the determine factor for increasing nitrate, why did the mass concentration of ammonium nitrate reach a plateau at aerosol liquid water of > 20 µg/m^3?

Thanks so much for your comment on this point. I made a mistake by using the PM$_{2.5}$ nitrate mass concentration from GAC-IC measurement as a function of PM$_1$ aerosol liquid water. The revised figure was shown in revised Figure 4 below, a clear co-increase of particulate nitrate and aerosol liquid water was observed, which has been shown in Figure 1.

The previous description (Line 319~322, original manuscript) has been revised in the manuscript, as shown below.

"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 μg/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 μg/m^3."



Revised Figure 4 in the manuscript. The relationship between aerosol particle liquid water and the molar ratio of particulate nitrate in the total nitrate, $\boldsymbol{m_{NH_4NO_3}/(m_{HNO_3}+m_{NH_4NO_3})}$ *(left axis) during* *the nighttime 18:00~07:00^{+1} (green solid triangle) and the daytime at 07:00 ~ 18:00 (red solid triangle), and mass concentration of particulate nitrate as a function of aerosol liquid water (right axis) during the period of February 29 to March 5, 2016. Here, particulate nitrate was measured by HR-ToF-AMS and the HNO_3 in the gas phase was measured by GAC-IC. Aerosol liquid water was calculated by H-TDMA-derived method.*

Q8. Finally, an increase in RH also leads to increasing aerosol liquid water. As shown in Fig. 1, the increased nitrate is coincident with the elevated RH during the haze period. How do the authors discriminate the mutual effect from this elevated RH effect?

The aerosol liquid water is determined by the ambient RH and chemical composition. So, the variations of ambient RH has been included in the changes of aerosol liquid water. We demonstrated the increasing of ambient RH as a prerequisite of the mutual promotion effect between particulate nitrate and liquid water.

Minor comments:

Q1. Lines 109-113: Is the discussion about NO_3^-/SO_4^{2-} in China?

This discussion is based on NO_3^-/SO_4^{2-} in Beijing. This has been clarified in the manuscript.

Q2. Line 123: Need to be more explicit about how the reactive uptake o precursors and the thermodynamic equilibrium of ammonium nitrate change. Enhancing or increasing?

Here, changing represents enhancing. This sentence has been clarified in the update version as "This leads to an increased aerosol liquid water content (Wu et al., 2018), which will enhance the particulate nitrate formation by increasing the reactive uptake of precursors and the thermodynamic equilibrium of ammonium nitrate (Cheng et al., 2016;Wang et al., 2016;Wang et al., 2017;Yun et al., 2018;Yue et al., 2019)."

Q3. Line 279: theoretical calculations of what?

Here, the theoretical calculations of condensational loss rate of N_2O_5 and HNO_3. This has been clarified in the update version.

Q4. Line 293: Please use either liquify or liquefy for consistency.

Thanks for your kindness. This has already been corrected in the update version.

Q5. Line 346: HNO3 instead of particulate nitrate?

Thanks for your kindness. This has already been corrected in the update version.

Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the Reactive Uptake of Gaseous Compounds by Organic-Coated Aqueous Aerosols: Theoretical Analysis and Application to the Heterogeneous Hydrolysis of N2O5, The Journal of Physical Chemistry A, 110, 10435-10443, 10.1021/jp062403c, 2006.

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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 μg/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 μg/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."

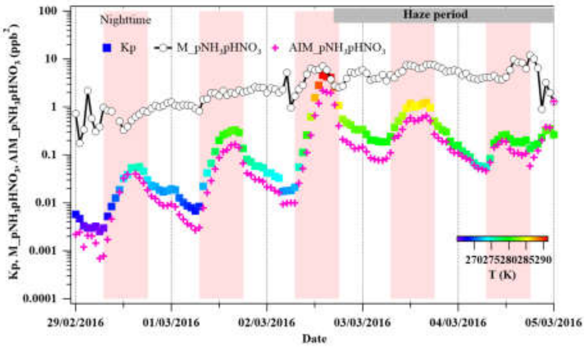

Figure 3 in the old version. The comparison of the calculated temperature-dependent dissociation constant of NH_4NO_3 (Kp) (Seinfeld. and Pandis., 2006) in the absence of liquid water, the product of equilibrium vapor pressure of gaseous NH_3 and HNO_3 from E-AIM, and the product of mixing ratios of 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)."

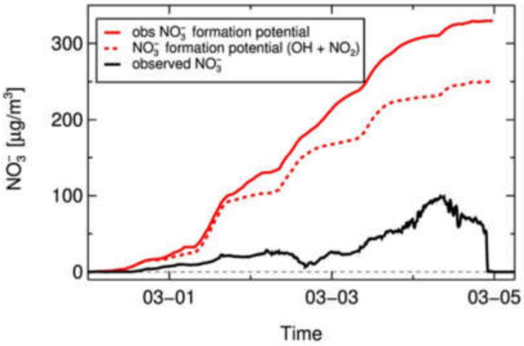

Fig. R1. Calculated contributions from HNO_3 (·OH+NO_2) shown as dashed red line and total particulate nitrate formation potential (solid red line) by box model during the same observational period. The difference between these two was the N_2O_5 contribution. This figure is sourced from the Figure S13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

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Mutual promotion ~~effect~~ between aerosol particle liquid water and ~~nitrate~~particulate nitrate enhancement~~formation~~ ~~lead~~leads to severe nitrate-dominated particulate matter pollution and low visibility

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Abstract. As has been the case in North America and Western Europe, the SO_2 emissions substantially reduced in North China Plain (NCP) in recent years. A dichotomy of reductions in SO_2 and NO_x concentrations result in the frequent occurrences of nitrate (pNO_3^-)-dominated particulate matter pollution over NCP. In this study, we observed a polluted episode with the ~~nitrate~~particulate nitrate mass fraction in non-refractory PM_1 (NR-PM_1) up to 44% during wintertime in Beijing. Based on this typical pNO_3^--dominated haze event, the linkage between aerosol water uptake and pNO_3^- ~~formation~~enhancement, further impacting on visibility degradation, have been investigated based on field observations and theoretical calculations. During haze development, as ambient relative humidity (RH) increased from ~10% up to 70%, the aerosol particle liquid water increased from ~1 µg/m^3 at the beginning to ~75 µg/m^3 at the fully-developed haze period. The aerosol liquid water further increased the aerosol surface area and volume, enhancing the condensational loss of N_2O_5 over particles. ~~Without considering the water uptake, the particle surface area and the volume concentrations increased by a factor of 4.1 and 4.8, respectively, during the development of haze event. Taking water uptake into account, the wet particle surface area and volume concentrations enhanced by a factor of 4.7 and 5.8, respectively. As a consequence, the hygroscopic growth of particles facilitated the condensational loss of dinitrogen pentoxide (N_2O_5) and nitric acid (HNO_3) to particles contributing pNO_3^-.~~ From the beginning to the fully-developed haze, the condensational loss of N_2O_5 increased by a factor of 20 when only considering aerosol surface area and volume of dry particles, while increasing by a factor of 25 considering extra surface area and volume due to water uptake. Furthermore, aerosol liquid water favored the thermodynamic equilibrium of HNO_3 into the particle phase under the supersaturated HNO_3 and NH_3 in the atmosphere. All ~~Similarly, the condensational loss of HNO_3 increased by a factor of~~

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~~2.7~2.9 and 3.1~3.5 for dry and wet aerosol surface area and volume from the beginning to the fully-developed haze period.~~ ~~a~~Above results demonstrated that the pNO_3^- ~~formation~~ is ~~further~~ enhanced by aerosol water uptake with elevated ambient RH during haze development, in turn, facilitating the aerosol taking up water due to the hygroscopicity of ~~nitrate~~particulate nitrate salt. Such mutual promotion ~~effect~~ between aerosol particle liquid water and ~~nitrate~~particulate nitrate enhancement~~formation~~ can rapidly degrade air quality and halve visibility within one day. Reduction of nitrogen-containing gaseous precursors, e.g., by control of traffic emissions, is essential in mitigating severe haze events in NCP.

1 Introduction

Aerosol particle hygroscopicity plays an important role in air quality deterioration and cloud formation (Yu, 2009;Fitzgerald, 1973;Kreidenweis and Asa-Awuku, 2014;Wang and Chen, 2019;McFiggans et al., 2006) and can also directly influence aerosol measurements (Chen et al., 2018a). In atmospheric environments influenced by anthropogenic activities, particulate secondary inorganic compounds are often dominated by ~~ammonium~~ particulate sulfate ~~$((NH_4)_2SO_4)$~~ and ~~ammonium~~ nitrate ~~(NH_4NO_3)~~ (Heintzenberg, 1989), which originate from the oxidation of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) via multiple chemical pathways ~~via well-established chemical pathways~~ (Calvert et al., 1985;Cheng et al., 2016;Wang et al., 2016;Gen et al., 2019a, b). The abundance of secondary inorganic components is one of the most important factors determining particle hygroscopicity (Swietlicki et al., 2008), thereby governing the aerosol liquid water content under ambient moist conditions. Increased aerosol particle liquid water could accelerate secondary inorganic and organic aerosol formation by decreasing the kinetic limitation of mass transfer of gaseous precursors and providing more medium for multiphase reactions (Mozurkewich and Calvert, 1988;Cheng et al., 2016;Wang et al., 2016;Ervens et al., 2011;Kolb et al., 2010).

Sulfuric acid (H_2SO_4) is formed from the oxidation of SO_2 via gaseous and multiphase reactions. H_2SO_4 is subsequently fully or partly neutralized by gaseous NH_3 taken up on particles, resulting in the formation of $(NH_4)_2SO_4$ and / or NH_4HSO_4. Any remaining NH_3 is available to neutralize HNO_3 to form particulate NH_4NO_3 (Seinfeld. and Pandis., 2006) (and further excess NH_3 can neutralize any available HCl to form particulate NH_4Cl). Over the past several decades, substantial efforts have reduced emissions of both SO_2 and NO_x improving the local and regional air quality all over the world. For example, SO_2 and NO_x emissions were reduced by 82% and 54% in the majority of European Environment Agency member countries between 1990 and 2016 (https://www.eea.europa.eu/data-and-maps/indicators/main-anthropogenic-air-pollutant-emission s/assessment-4). In consequence, an increasing trend of NO_3^-/SO_4^{2-} molar ratio was observed in long-term measurements at Leipzig, Germany (Spindler et al., 2004) and at some other European sites from the European Monitoring and Evaluation Programme (EMEP) (Putaud et al., 2004).

In the recent years, China has also managed to reduce SO_2 emissions by 75% ~~since~~ during 2007~2015 (Li et al., 2017a) and declined by ~15.1% per year during 2013~2017 (Vu et al., 2019), whereas NO_x emissions declined only by ~10% between 2011 and 2015 (de Foy et al., 2016) and by ~ 4.3% per year during 2013~2017 (Vu et al., 2019). The strict emission control reduced the $PM_{2.5}$ mass concentration and the corresponding chemical components in China significantly (Vu et al., 2019). The annual mean $PM_{2.5}$ mass loading decreased by 39.6% during 2013~2017 in Beijing-Tianjin-Hebei region, and the SO_4^{2-} and NO_3^- mass concentrations in the $PM_{2.5}$ declined by 40% and 34% respectively during 2015~2017 in Beijing (Vu et al., 2019). However, NH_3 emissions have been observed by satellites to increase by ~30% from 2008 to 2016 over the North China Plain (NCP) (Liu et al., 2018).~~,~~ The faster reduction rate of SO_2 than NO_x emissions in conjunction with elevated NH_3 level, made it reasonable of ~~Similar with European countries, the~~ switching dominant inorganic component in fine aerosol particles ~~has switched~~ from sulfate to nitrate in the recent years similar like European countries (Sun et al.,

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2015;Hu et al., 2017;Hu et al., 2016;Wu et al., 2018;Guo et al., 2014;Huang et al., 2014;Huang et al., 2010;Ge et al., 2017;Xu et al., 2019a;Xie et al., 2019;Li et al., 2018). Field measurements in Beijing show that annually averaged NO_3^-/SO_4^{2-} molar ratio of NR-PM_1 (non-refractory PM_1) in 2012 (1.3~1.8) (Sun et al., 2015) has significantly increased compared to that in 2008 (0.9~1.5) (Zhang et al., 2013). Comparably, the NO_3^-/SO_4^{2-} molar ratio of $PM_{2.5}$ in Beijing increased substantially, from 1.5 before 2013 to 3.33 in 2017 (Xu et al., 2019a). ~~Model simulations have also shown that the simulated annual mass concentration of nitrate and its mass fraction in secondary inorganic components over North China increased by 17~19% and 7% respectively, while the sulfate mass and fraction decreased by 10~19% and 6% between 2006 and 2015 under the assumption of constant NH_3 emissions (Wang et al., 2013). However, NH_3 emissions have been observed by satellites to increase by ~30% from 2008 to 2016 over the North China Plain (NCP) (Liu et al., 2018), further increasing the potential for nitrate formation (Wang et al., 2013).~~

Over the NCP region, heavy haze events are typically associated with enhanced ambient RH levels. This leads to an increased aerosol liquid water content (Wu et al., 2018), which will ~~influence~~ enhance the particulate nitrate formation by ~~changing~~ increasing the reactive uptake of precursors and the thermodynamic equilibrium of ammonium nitrate (Cheng et al., 2016;Wang et al., 2016;Wang et al., 2017;Yun et al., 2018;Yue et al., 2019). To date, few studies reported aerosol liquid water content over NCP region (Wang et al., 2018;Bian et al., 2014;Cheng et al., 2016;Wu et al., 2018;Ge et al., 2019). However, the observational and theoretical analysis of the relationship between particulate nitrate enhancement ~~formation~~ and associated liquid water during haze events in China has been infrequently reported (Wu et al., 2018).

In this study, a self-amplification effect between particulate nitrate and liquid water is demonstrated by examining a nitrate-dominated fine particle Beijing pollution episode. The facilitation of particulate nitrate ~~formation~~ enhancement by abundant aerosol liquid water is subsequently theoretically explored through the impacts of liquid water on thermodynamic equilibrium and heterogeneous reactions. Finally, the corresponding impacts on light extinction coefficient, and visibility degradation are estimated. These results improve our quantitative understanding of the development of haze events over the NCP and on formulating emission reduction strategies, as well as may also provide insights for other polluted regions.

2 Measurements and Methods

2.1 Location and instrumentation

Measurements were conducted within the framework of the BEST-ONE (Beijing winter finE particle STudy- Oxidation, Nucleation, and light Extinctions) field campaign from January 1 to March 5, 2016, at the Huairou site (40.42°N, 116.69°E), located in a rural environment, north of Beijing, China. Detailed information about the sampling site was described in Tan et al. (2018). A weather station (Met one Instrument Inc., USA) was performed to measure meteorological parameters (ambient RH, temperature, wind speed, wind direction) and detailed aerosol particle physical and chemical properties were recorded using a suite of state-of-the-science instrumentation. Hygroscopic growth factor (HGF) of sub-micrometer aerosol particles was measured using a Hygroscopicity-Tandem Differential Mobility Analyzer (H-TDMA, TROPOS, Germany) (Wu et al., 2011;Massling et al., 2011;Wang et al., 2018;Wu et al., 2016;Liu et al., 1978) and data retrieval followed the $TDMA_{inv}$ method in Gysel et al. (2009). The hygroscopicity parameter (κ) was estimated using by the κ-Köhler approach (Petters and Kreidenweis, 2007;Köhler, 1936). Size-resolved NR-PM_1 was recorded by an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometry (HR-ToF-AMS, Aerodyne Research, Inc., USA) (DeCarlo et al., 2006). Regular calibration procedures followed as reported in Jayne et al. (2000) and Jimenez et al. (2003) and composition dependent correction followed as in Middlebrook et al. (2012). Gaseous HNO_3 and NH_3 were measured using Gas-Aerosol Collector (GAC) coupled with Ion Chromatography (IC) (Dong et al., 2012). Mass concentration of equivalent black carbon in aerosol particles (Petzold et al., 2013) was recorded by Multi Angle Absorption Photometer (MAAP, Model 5012, Thermo Fisher Scientific, USA) with a laser wavelength of 670 nm (Petzold and Schönlinner, 2004). Furthermore, particle number size distribution (PNSD) in the size range of 3 nm~10 μm was measured using a Mobility Particle Size Spectrometer (MPSS, Model 3776+3085 3775+3081, TSI, USA), following the recommendations described in Wiedensohler et al. (2012) and an Aerodynamic Particle Size Spectrometer (APS, Model 3021, TSI, USA) (Wu et al., 2008;Pfeifer et al., 2016). Detailed description on H-TDMA, HR-ToF-AMS and GAC-IC can be found in the supporting information.

2.2 Estimation of aerosol particle liquid water

Given the absence of direct liquid water measurement, size-resolved liquid water was calculated using the corresponding HGFs measured at RH=90% (50, 100, 150, 250, 350 nm in stokes diameter), PNSD data (3 nm~10 μm) and meteorological parameters (RH, T), following the method proposed in Bian et al. (2014), referred to below as H-TDMA-derived liquid water. Briefly, the measured PNSD with 57 size bins were fitted using a four-mode lognormal distribution. The classification of four modes and the fitting results are shown in Table S1 and Figure S4. Good agreement between measured values and fitted PNSD was achieved, which indicates the reliability of the four-mode lognormal fitting method. Based on four-mode lognormal fitting results, the particle number size distribution and number fractions of each mode can be obtained. It has been assumed that particles from the same mode have constant particle hygroscopicity (κ). Under the assumption of constant particle hygroscopicity in each mode (shown in Table S1), the κ values for each mode (κ_1, κ_2, κ_3) can be calculated by ~~equation~~Eq. [1] from the known number fraction of fitted four modes and the κ values of measured particle size from H-TDMA measurement.

$$\kappa = \sum_{i=1}^{4} \kappa_i f_i \quad [1]$$

Here, κ_i and f_i represent the κ value and the particle number fraction of the i mode. Then, the calculated κ values for each mode and the derived number fraction of each size bin were used to obtain the κ distribution for each size bin. Figure S5 shows the comparison of calculated sized-resolved κ distribution and the κ measured by H-TDMA, the good agreement showed the reliability of the method. Then, based on κ-Kölher theory (Petters and Kreidenweis, 2007;Köhler, 1936), the size-resolved *HGF*s at ambient RH were calculated. Finally, liquid water of size-resolved particles can be derived by calculating the differentials between the dry and wet PNSD of aerosol particles in ~~equation~~Eq. [2]:

$$\text{Liquid water} = \frac{\pi}{6} N_j D_{p,j}^3 \left(HGF\left(D_p, RH\right)^3 - 1\right) * \rho_w \qquad [2]$$

where j represents the bin number of measured PNSD, N_j and $D_{p,j}$ represent the number concentration and the diameter of dry particles of the j^{th} bin, respectively, while, *HGF* and ρ_w, are the hygroscopic growth factor of aerosol particles and water density (1 g/cm^3), respectively.

2.3 Condensation rate of trace gases

The condensation rate (*k*) of trace gases (dinitrogen pentoxide, N_2O_5~~ and nitric acid, HNO_3 in the constrained conditions~~, referred as k_N_2O_5~~ and k_HNO_3 below~~) was calculated by the method of Schwartz (1986), shown in ~~equation~~Eq. [3]. In order to illustrate the influences of the dry and wet PNSD due to water uptake on condensation rate of gases, the PNSD of the dry and wet particles (obtained by applying the HGF estimated from H-TDMA-derived liquid water method) were used.

$$k = \frac{4\pi}{3}\int_0^{\infty}\left(\frac{r^2}{3D_g} + \frac{4r}{3C_g\gamma}\right)^{-1} r^3 \frac{dN}{dlogr}\, dlogr \qquad [3]$$

$$C_g = \sqrt{\frac{3RT}{M}} \qquad [4]$$

Where, *r* represents radius of the particles, D_g represents the binary diffusion coefficient evaluated following Maitland (1981) (1.18*e^{-5} m^2/s). C_g is the kinetic velocity of the gas molecules, calculated in ~~equation~~Eq. [4]. Here, R and M are the ideal gas constant (8.314 kg.m^2/mol/K/s^2) and molar mass of the gas, respectively while T represents the ambient temperature. dN/dlogr is the number size distribution and γ is the uptake coefficient of the gas.

The uptake coefficient of N_2O_5 was estimated following the method proposed in Chen et al. (2018b) and Chang et al. (2016) and references therein. The influences of RH, temperature, multiple inorganic particle compositions, secondary organic aerosol (SOA) and primary organic aerosol (POA) are considered. The uptake suppression effect of N_2O_5 due to the presence of ~~secondary organic aerosol~~ ~~(~~SOA~~)~~ was considered following the method in Anttila et al. (2006). Based on our source apportionment using Positive matrix factorization (SoFi tool, ME2, Francesco Canonaco, PSI), two oxygenated organic aerosol factors (OOA), usually interpreted as SOA, and three POA~~primary organic aerosol~~ factors ~~(POA)~~ were determined. The fraction of SOA in the total organic aerosol (OA) was 60%~90% during the observed period, which is quite consistent with the results of a previous study in Beijing (Huang et al., 2014). Hence, 75% was used as the ratio of SOA/OA in our model to ~~calculate uptake coefficient of the N_2O_5, where~~estimate the suppression effect of SOA on the uptake of N_2O_5 ~~was estimated~~ following the work of Anttila et al. (2006). T~~Additionally, t~~he reaction of chloride with N_2O_5 was not considered in this study due to its limited mass concentration (on average 5% of the PM_1 mass concentration during the marked haze period), which ~~might~~ could cause minor uncertainty in the $k\_N_2O_5$ calculation. The detailed information regarding the estimation γ_{N2O5} is given in Chen et al. (2018b), and influences of different chemical components on γ_{N2O5} is summarized in the Table 1 of Chen et al. (2018b). ~~For the estimation of γ_{HNO3}, it was reported that the γ_{HNO3} on the solid and deliquesced inorganic compound such like sodium chloride were 0.01~0.03 (Fenter et al., 1994;Leu et al., 1995;Beichert and Finlayson-Pitts, 1996) and >0.2 (even 0.5) (Guimbaud et al., 2002;Abbatt and Waschewsky, 1998), respectively. Therefore, γ_{HNO3}=0.01 and γ_{HNO3}=0.5 are selected to calculate the lower and upper limit of condensation rate of HNO_3 in the atmosphere.~~

2.4 Equilibrium of NH_4NO_3

The equilibrium dissociation constant of NH_4NO_3 (Kp) under dry conditions was calculated as a function of ambient temperature (Seinfeld. and Pandis., 2006) in the following ~~equation~~Eq. [5].

$$lnK_p = 84.6 - \frac{24220}{T} - 6.1ln\left(\frac{T}{298}\right) \qquad [5]$$

Taking into account the associated liquid water, the equilibrium vapor pressure of HNO_3 and NH_3 was calculated by employing the Extended-Aerosol Inorganic Model (E-AIM) Model II H^+ - NH_4^+ - SO_4^{2-} - NO_3^- - H_2O (Clegg et al., 1998) using HR-ToF-AMS data, NH_3 from GAC-IC, and meteorological parameters (RH, T). In this calculation, a simplified ion pairing scheme was performed to ensure the ion balance of the input chemical composition following the method in Gysel et al. (2007).

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2.5 Light extinction coefficient and visibility calculation

Size-resolved chemical composition of the NR-PM_1 from HR-ToF-AMS, mass concentration of equivalent black carbon from MAAP, PNSD data and the H-TDMA-derived liquid water were used to calculate light extinction coefficient (including light absorption and scattering) and visibility degradation of size-resolved particles by the Mie scattering theory described in Barnard et al. (2010). Here, size-resolved equivalent black carbon mass concentration was inferred by the particle mass size distribution measurement from single particle soot photometer in PKUERS. The method of re-distribution of liquid water and HR-ToF-AMS data has been described in the supporting information (Text S1, HR-ToF-AMS introduction section). Thus, with the re-distributed datasets as the input of the Mie scattering theory, the light extinction coefficient for atmospheric particles in the absence and presence of liquid water with a size range of 100~2500 nm in stokes diameter can be derived. Due to lack of measurements on aerosol particle morphology and mixing state, we assume particles are spherical as described in Barnard et al. (2010). To perform Mie calculation, the complex reflective index of each component is given in Table 1 of Barnard et al. (2010) and references therein. This method shows good agreement with measurements in Mexico City and is consistent as the regional atmospheric chemistry model WRF-Chem. Here, Ext_550nm_wet and Ext_550nm_dry represent the calculated light extinction coefficient for particles in the presence and absence of liquid water at an incident light wavelength of 550 nm. The corresponding visibility degradation (VIS) for dry/wet particles was calculated from the light extinction coefficient following the Koschmieder ~~equation~~Eq. [6].

$$\mathrm{VIS} = \frac{3.912}{Ext\_5\ 5\,0nm} \qquad [6]$$

3 Results and Discussion

3.1 Nitrate-dominated fine particulate matter pollution

Figure 1 illustrates a summary of chemical composition of NR-PM_1, ambient RH, size distribution and total aerosol particle liquid water, size distribution and total aerosol surface area concentration during the period of February 29 to March 5, 2016 in the BEST-ONE campaign. During this period, polluted episodes occurred under stagnant meteorological conditions with low wind speed (Figure S6) and elevated ambient RH (Figure 1a). As marked ‘haze period’ in Figure 1, an obvious increase of NR-PM_1 was observed. The secondary inorganic components (sulfate, nitrate and ammonium) were dominant components of the NR-PM_1, accounting for up to 73% during the 'haze period'. Particularly, nitrate was the major contributor of the secondary inorganic components and accounted for up to ~44% of NR-PM_1 mass, while sulfate contributed for ~12% on average.

In the recent decade, severe haze events with high aerosol mass loading occurred frequently in Beijing during wintertime (Hu et al., 2016;Hu et al., 2017;Sun et al., 2014;Sun et al., 2015). To mitigate the air pollution, the Beijing government implemented strict emission controls. The total mass loading of particulate matter has reduced substantially in the recent years (http://sthjj.beijing.gov.cn/). With decreasing in PM mass concentration, the mass fraction of particulate nitrate during these haze events in Beijing enhanced substantially. In 2014, the highest fraction of nitrate in PM_1 was reported as ~20% and increased to ~35% in 2016 (Xu et al., 2019b), which is comparable to the ratio (44%) in this study. The particulate nitrate became more dominant in secondary inorganic compounds other than particulate sulfate with the air quality improvement over NCP.

As one of the main hydrophilic compounds in atmospheric aerosol particles, the ability of water uptake ~~at 90% RH of particulate NH_4NO_3~~ is comparable between deliquescent ~~with particulate~~ $(NH_4)_2SO_4$ and NH_4NO_3 particles with same sizes and ambient RH (Kreidenweis and Asa-Awuku, 2014;Wu et al., 2016), (http://umansysprop.seaes.manchester.ac.uk/). However, compared to $(NH_4)_2SO_4$, NH_4NO_3 particles have a lower deliquescence RH (62%, 298 K) than $(NH_4)_2SO_4$ (80%, 298 K) (Kreidenweis and Asa-Awuku, 2014)~~,~~ and easily ~~liquify~~ liquefy (Li et al., 2017b). In addition, NH_4NO_3 particles are semi-volatile, the co-condensation of semi-volatile compounds and water (Topping et al., 2013;Hu et al., 2018) could be significant. Therefore, the switching from sulfate-dominated to nitrate-dominated

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aerosol chemistry may impact on aerosol water uptake. The interaction between aerosol particle liquid water and particulate nitrate formation and visibility degradation should be reconsidered.

3.2 Mutual promotion ~~effects~~ between liquid water and particulate nitrate enhancement~~formation~~

~~In the following discussion, the high fraction of particulate nitrate during the 'haze period' is elucidated by theoretical calculations considering the uptake of N_2O_5 and HNO_3, and the thermodynamic equilibrium of NH_4NO_3.~~ 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). In the following discussion, the enhancement of particulate nitrate during the 'haze period' is elucidated by theoretical calculations of condensational loss rate of N_2O_5, and the thermodynamic equilibrium of NH_4NO_3 and HNO_3. In particular, the role of aerosol water uptake in particulate nitrate formation is comprehensively investigated.

N_2O_5 is an important gaseous precursor for ~~nitrate~~particulate nitrate formation via its hydrolysis to form HNO_3 during nighttime (Brown et al., 2006). Liquid water can enhance aerosol surface areas and volumes, thereby increasing the available heterogeneous reacting medium. Across the development of 'haze period', the estimated liquid water increased from ~1 μg/m^3 at the beginning (~~2th~~ March 2, 14:00~18:00 p.m.) to ~75 μg/m^3 when the haze was fully developed (~~4th~~ March 4, 4:00~8:00 a.m.). The total surface area and volume concentrations of particles were increased by the liquid water by 2~3% at the beginning and by up to~~about~~ ~25 and ~40% in the fully-developed haze compared to the 'dry'

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values, respectively (see Figure S7 and S8). Additionally, from the beginning to the fully-developed haze, the uptake coefficient of N_2O_5 was enhanced by a factor of 9 from 0.002 to 0.018, and the k_N_2O_5 increased by a factor of 20 (dry particles); while, considering the increased particle surface area and volume due to water uptake, the respective value of enhanced k_N_2O_5 was by a factor of 25 (Figure 2a). Apart from providing extra reacting medium, the abundant liquid water can liquefy the aerosol particles and may reduce any kinetic limitation of mass transfer for reactive gases (Koop et al., 2011;Shiraiwa et al., 2011) and impact thermodynamic equilibrium of semi-volatile compounds (Kulmala et al., 1993;Topping et al., 2013) to contribute to secondary aerosol formation. Our previous study provided the observational evidence that particles may have transitioned from the solid phase to the liquid phase as RH increased from 20% to 60% during wintertime in Beijing (Liu et al., 2017). In this study, the ambient RH increased from ~10% up to 70% during the haze period, suggesting a likely transition of particles from the solid to liquid phase. Such phase transition may facilitate particulate nitrate formation by increasing diffusion coefficients of dissolved precursors.

To illustrate the facilitation of particulate nitrate ~~formation~~ 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. T~~First, t~~he dissociation constant of NH_4NO_3 (*Kp*) in dry condition was calculated using Eq.~~equation~~ [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, t~~T~~he equilibrium vapor pressure of HNO_3 and NH_3 over particles was calculated by E-AIM Model II (www.aim.env.uea.ac.uk)~~ taken into account the liquid water~~. Note that this calculation

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assumes negligible interaction between dissolved organic components and the activity of NO_3^-. In the presence of aerosol associated water~~, the HNO_3 equilibrium vapor pressure dropped from its dry values to effectively zero, indicating liquid water significantly favored greater partitioning to particulate nitrate.~~ 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 t~~T~~he measured ~~partial pressure~~ product of the NH_3 and HNO_3 partial pressure (2.55~9.63 ppb^2) was supersaturated compared to~~greater than~~ the equilibrium values in both dry and deliquescent particles. ~~*Kp* nearly all the time (Figure 3).~~ In this case, the partitioning of gaseous NH_3 and HNO_3 in the atmosphere ~~were supersaturated and would tend to partition~~ into the ~~the dry~~ particle phase could be accelerated and leaded particulate nitrate enhancement as increasing of ambient RH ~~phase gradually even in the absence of liquid water~~. 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 µg/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

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Formatted: Font: Not Italic, No underline, Font color: Auto aerosol liquid water was higher than ~20 µg/m^3. ~~The presence of liquid water under ambient RH can supress the HNO3 equilibrium vapor pressure to nearly zero, changing equilibrium and facilitate the partitioning of nitrate substantially.~~ ~~The equilibrium vapor pressure of HNO3 over particles was calculated by E-AIM Model II (www.aim.env.uea.ac.uk) taken into account the liquid water. Note that this calculation assumes negligible interaction between dissolved organic components and the activity of NO3-. In the presence of aerosol associated water, the HNO3 equilibrium vapor pressure dropped from its dry values to effectively zero, indicating liquid water significantly favored greater partitioning to particulate nitrate.~~ ~~The negligible equilibrium vapor pressure of HNO3 resulted in essentially no HNO3 evaporation back to the gas phase and irreversible uptake of HNO3 can be assumed under the ambient RH and NH3 concentration. This enabled the simplified treatment of the irreversible condensation rate following Schwartz (1986) used below. As shown in Figure 4, the partitioning ratio (molar ratio between particulate and total nitrate) increasing with RH was observed during the development of haze, and 98% of nitrate was present as particle phase when the haze was fully developed with liquid water increasing from 1 µg/m3 to ~75 µg/m3.~~The function between the particulate nitrate fraction in the total nitrate is given in Figure 4. 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 explains the slightly underestimation of the particulate fraction during nighttime when aerosol liquid water is less than 10 µg/m^3 (Figure 4). However, the general 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.

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Except for aerosol liquid water, aerosol pH is also an important factor on the particulate nitrate formation, higher pH is favorable for the equilibrium of HNO_3 into the particle phase (Nah et al., 2018). pH of the fine aerosol particles was calculated by ISORROPIA II (Fountoukis and Nenes, 2007)~~(Fountoukis and Nenes, 2007)~~ during the investigated period. The model was running in 'forward mode' with chemical composition of NR-PM$_1$ (NO_3^-, SO_4^{2-}, Cl^-, NH_4^+) and gas precursors (HNO_3, HCl, NH_3) by GAC-IC as inputs. And the model was running in 'metastable mode', assuming no solid existed in the system. Generally, the fine aerosol particles became more acidic with pH dropping from ~8 down to ~4 when NR-PM$_1$ mass concentration increased from ~12 μg/m^3 up to >300 μg/m^3 as shown in Figure 5 and Figure 6. This declining trend of pH is not favorable for the HNO_3 partitioning into the particle phase (Nah et al., 2018). However, a clear enhanced trend of molar ratio of particulate nitrate in the total nitrate as a function of NR-PM$_1$ mass concentration was observed correspondingly (as shown in Figure 5 and Figure 6). Therefore, in this case the increase of aerosol liquid water is more likely to be the driving factor of particulate nitrate formation compared to the influence of pH.

~~Furthermore, the presence of aerosol associated water was substantially enhanced by the uptake rate of HNO_3, which could dominate the gaseous HNO_3 partitioning into particle phase throughout the haze developing. Because the negligible equilibrium vapor pressure suggests that HNO_3 condensation loss was not limited by thermodynamic equilibrium but limited by its uptake rate. The condensation (or uptake) rate of HNO_3 (k_HNO_3) can be calculated using equations [3-4]. Here, the lower and upper limit of k_HNO_3 were calculated assuming the uptake coefficient (γ) of HNO_3 in the range of 0.01 to 0.5 (Fenter et al., 1994;Leu et al., 1995;Beichert and Finlayson-Pitts, 1996;Abbatt and Waschewsky, 1998;Guimbaud et al., 2002). As shown in Figure 2b and 2c, the lower (upper) limit of k_HNO_3~~

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~~increased by a factor of 2.9 (2.7) for dry PNSD and 3.5 (3.1) for wet PNSD from the beginning to fully-developed haze period. As one can see, the liquid water facilitated the rate of HNO_3 uptake and hence the particulate nitrate formation.~~

~~The above analyses quantify the effect of the increased aerosol surface area and volume concentrations resulting from the water uptake on the particulate nitrate formation through increased uptake of N_2O_5 and HNO_3. Such an effect becomes more pronounced with the increasing pollution throughout the haze event owing to the simultaneously increasing ambient RH. Owing to its hygroscopicity, the increased ammonium nitrate mass fraction led to a further increase in aerosol surface area and volume concentrations through additional increase in liquid water, further enhancing uptake of condensable vapors.~~

It is worth noting that a similar co-condensation effect between water vapor and semi-volatile organic components (Topping and McFiggans, 2012;Topping et al., 2013;Hu et al., 2018) could promote the haze formation as well, for which there may be some evidence in the current case. Such a co-condensation effect will lead to the enhancement of semi-volatile organic and inorganic (e.g., nitrate) material with the increasing RH in a developing haze. The associated water will favor partitioning of both ~~particulate nitrate~~HNO_3 and semi-volatile organic materials to the particle phase depending on the organic solubility, providing a linkage between the development of increasing organic and inorganic particle mass.

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3.3 The key role of liquid water on visibility degradation

Aerosol particles grow up in size as ambient RH increases, further enhances their extinction coefficient and impacts visibility (Zhao et al., 2019;Kuang et al., 2016). In this section, size-resolved extinction coefficient of aerosol particles was estimated, and the influences of liquid water on the extinction coefficient and visibility were quantitatively evaluated. As shown in Figure ~~5a~~7a, the total light extinction coefficient of dry and wet aerosol particles enhanced by a factor of 4.3 and 5.4, respectively, from the beginning to a fully-developed haze. Correspondingly, the calculated visibility without considering liquid water degraded significantly from ~10 km to less than 2 km within 48 hours during the marked 'haze period'. The contribution of aerosol associated water to visibility impairment was negligible in the beginning (2%), while it was significant (up to 24%) in the fully-developed haze (Figure ~~5b~~7b). This indicates that liquid water facilitated visibility degradation during haze development.

The influences of liquid water on visibility degradation varied with aerosol particle size. The size-resolved chemical composition data showed that the inorganic species, mainly ~~nitrate~~particulate nitrate, were dominant components in the aerosol particles within the size range of 300~700 nm (Figure S3). Correspondingly, the particles in this size range contained most of the liquid water (50~80% of the total aerosol liquid water content of PM_1). According to discussion in Sec. 3.2, the mutual promotion effect between liquid water and particulate nitrate can promote their ~~formation~~mass loading enhancement. Aerosol particles in this size range experienced the most significant enhancement of light extinction due to water uptake (Figure ~~6a~~ 8a and ~~6b~~8b) and contributed 70~88% of the total extinction coefficient of the total NR-PM_1 (Figure S9). In conclude, the rapid ~~nitrate~~particulate nitrate enhancement~~formation~~

enhanced the aerosol extinction coefficient during haze developing, while the aerosol water uptake further enhanced the visibility degradation by increasing extinction coefficient and promoting ~~nitrate~~particulate nitrate ~~formation~~enhancement.

It is worth noting that the enhanced dimming effect will further shallower the planetary boundary layer (PBL), which, in turn, depresses the dilution of water vapor and particulate matter in the atmosphere, hence leads to a higher RH and aerosol particle mass loading (Tie et al., 2017). Such effect is beyond the scope of this study.

4 Conclusions and implication

In this study, we observed a particulate nitrate-dominated (up to 44% of non-refractory PM_1 mass concentration) particulate matter pollution episode, which is typical during winter haze in Beijing, China. A clear co-increase of aerosol particle liquid water and particulate nitrate was observed, demonstrating the mutual promotion ~~effect~~ between them via observation-based theoretical calculations.

As shown in Figure ~~7~~9, the water uptake by hygroscopic aerosols increased the aerosol surface area and volume, ~~favoring the thermodynamic equilibrium of ammonium nitrate and~~ enhancing the condensational loss of N_2O_5 ~~and HNO_3~~ over particles and favoring the thermodynamic equilibrium of HNO_3 into the particle phase under the supersaturated ambient HNO_3 and NH_3. The enhanced particulate nitrate ~~formation~~ from the above pathways increased the mass fraction of particulate nitrate, which had a lower deliquescence RH than sulfate and resulted in more water uptake at lower ambient RH (Kreidenweis and Asa-Awuku, 2014). Hence, the increased aerosol particle surface area and

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volume concentrations due to water uptake, in turn facilitates particulate nitrate ~~formation~~enhancement. Hence, a feedback loop between liquid water and particulate nitrate enhancement is built up. Therefore the enhanced particulate nitrate components can accelerate the feedback compared with sulfate-rich pollution over the NCP region in the past (Hu et al., 2016). This self-amplification can rapidly degrade air quality and halve visibility within one day. Our results highlight the importance of reducing the particulate nitrate and its precursors (e.g. NO_x) for mitigation of haze episodes in NCP region.

Data availability

The observational dataset of the BEST-ONE campaign can be accessed through the corresponding author Z. Wu (zhijunwu@pku.edu.cn).

The E-AIM model can be accessed via http://www.aim.env.uea.ac.uk/aim/aim.php.

Author contributions

Z.W., Y.W. and Y.C. conceived the study. Y.Z., M.H., and A.K.S developed BEST-ONE field campaign program. Y.W., Z.W., D.S., Z.D., S.H.S., R.S., G.I.G., P.S., T.H., K.L., L.Z., C.Z., A.K.S., Y.Z., and M.H. participated in this campaign and collected the dataset. Y.W. conducted aerosol particle liquid water calculation under guide of Y.B. and thermodynamic equilibrium of particulate ammonium nitrate under guidance of G.M. Y.C. calculated the uptake coefficient of N_2O_5, optical properties and visibility. Y.W. and Y.C. cowrite the manuscript with the inputs from all co-authors. Z.W., G.M., A.K.S., S.H.S., G.I.G., P.S., T.H., A.V., and A.W. proofread and help improve the manuscript. All authors discussed the results.

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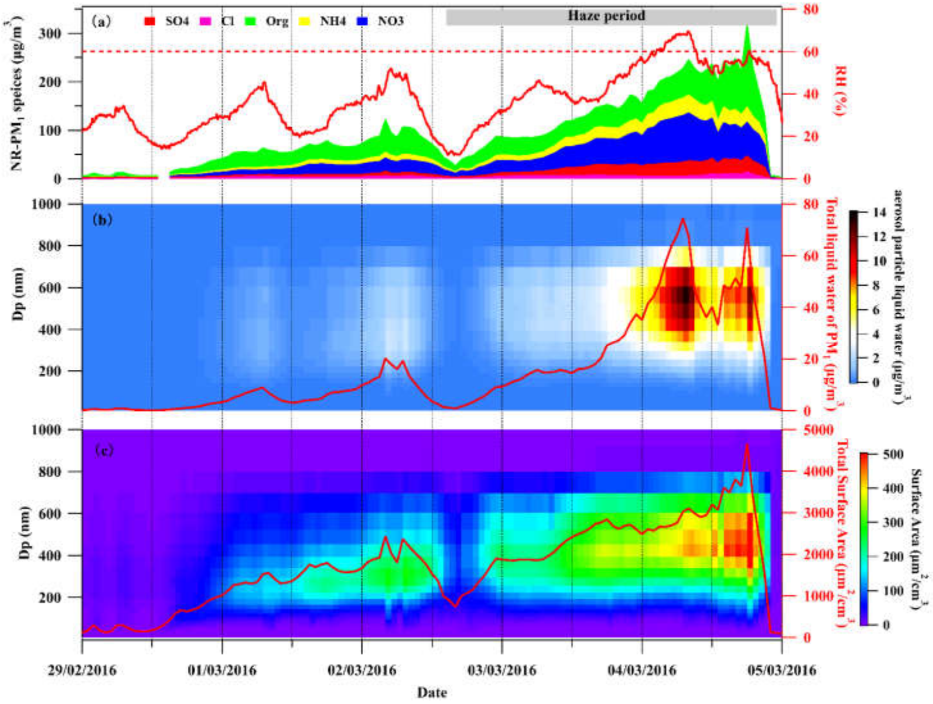
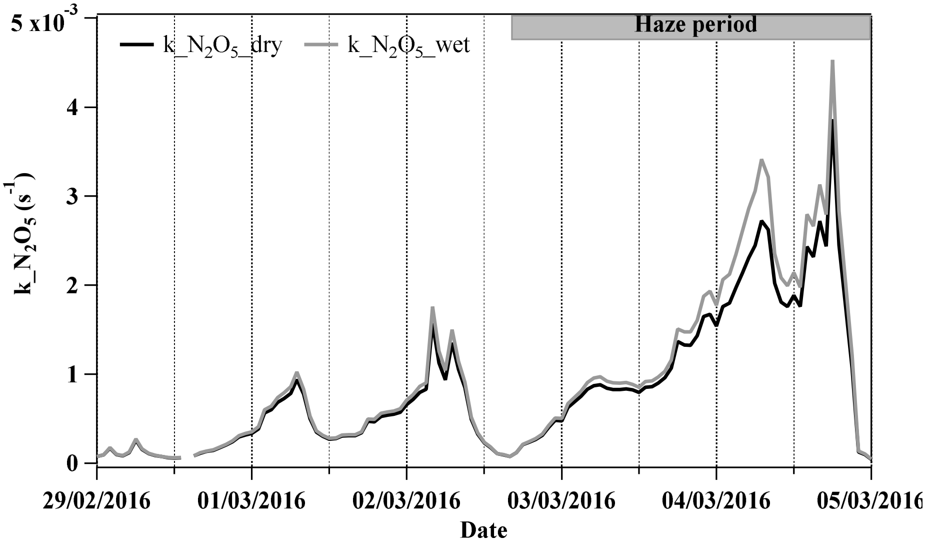


Figure 1: The time series of (a) NR-PM$_1$ chemical composition measured by the HR-ToF-AMS and ambient RH (red solid line), (b) size-segregated aerosol particle liquid water and the total mass concentration of liquid water with smaller than 1 µm in aerodynamic diameter (red solid line), (c) size-segregated aerosol particle surface area and total aerosol particle surface area without considering particle hygroscopic growth during February 29 to March 5, 2016.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k_N$_2$O$_5$_wet
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4
3
2
1
0
k_N$_2$O$_5$ (s^{-1})
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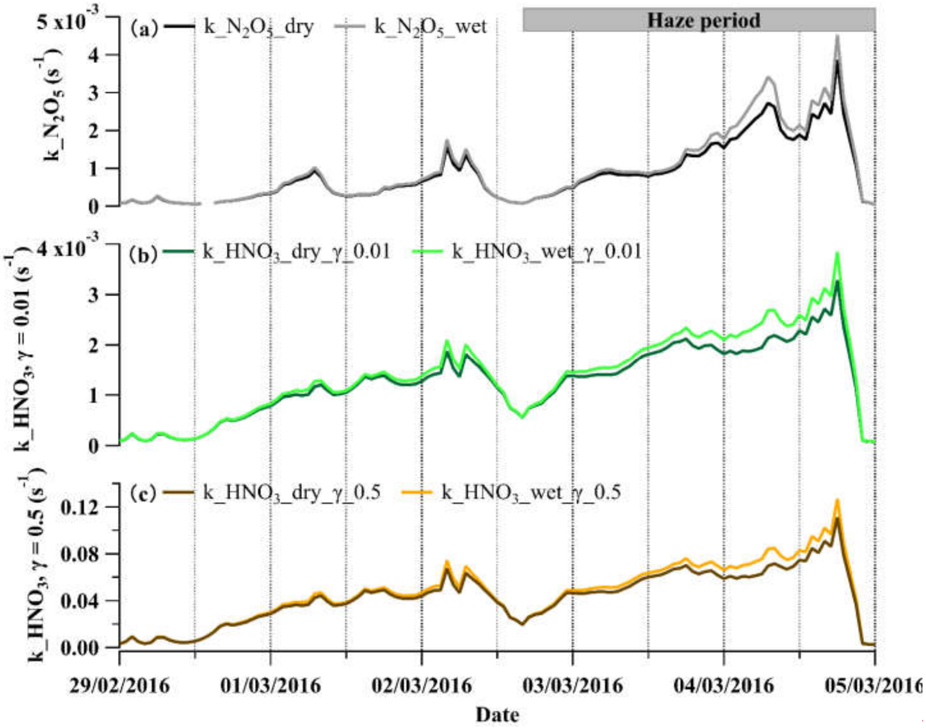
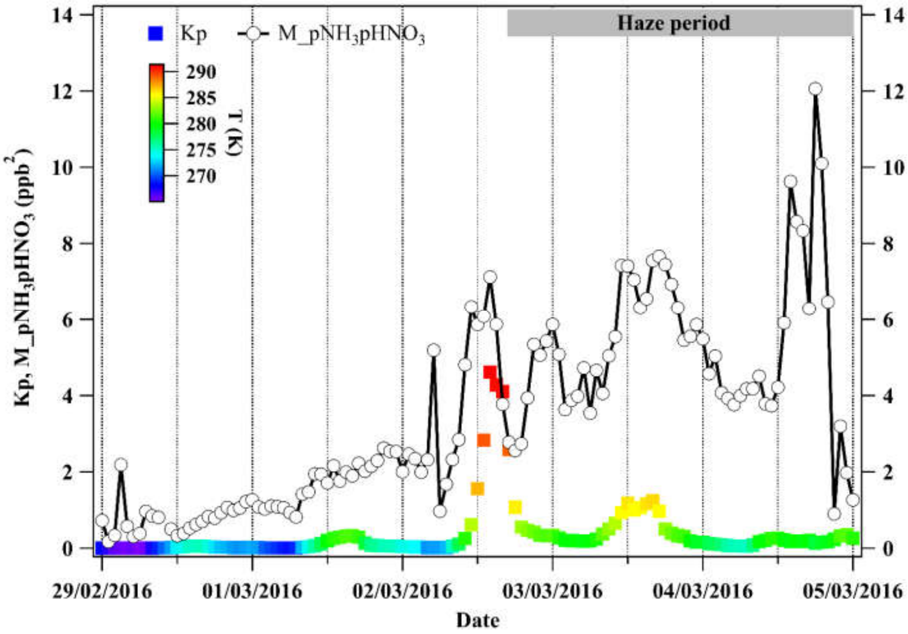


Figure 2: The time series of ~~(a)~~ condensational loss rate of N_2O_5 ($k\_N_2O_5$) with the calculation of dry particle number size distribution (PNSD) and wet PNSD~~, (b-c) condensation rate of HNO_3 (k_HNO_3) with the calculation of dry and wet PNSD under the assumption of γ=0.01 and γ=0.5, respectively~~ during February~~February~~ 29 to~~ March~~March 5,~~ 5,~~ 2016.



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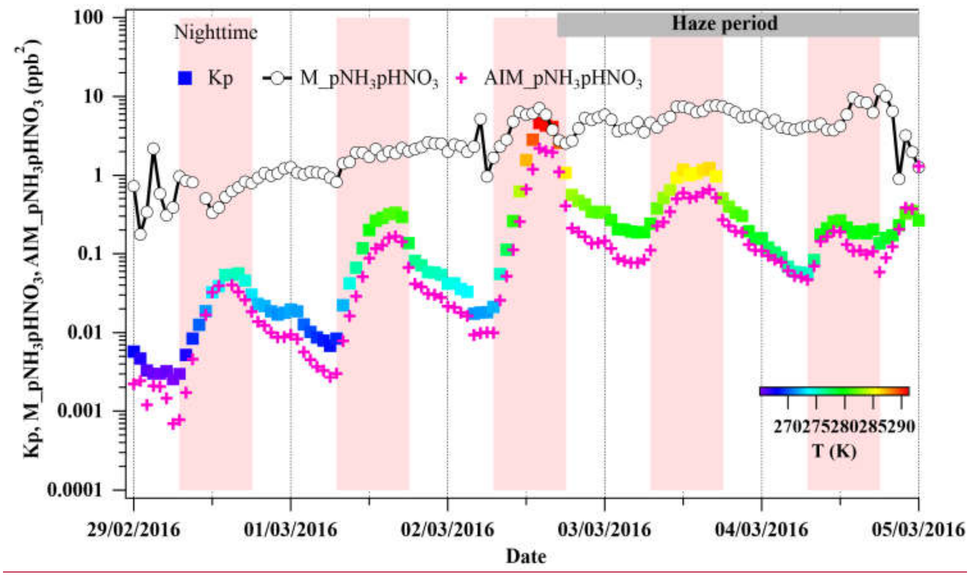

Figure 3: The comparison of the calculated temperature-dependent dissociation constant of NH_4NO_3 (Kp) (Seinfeld. and Pandis., 2006) in the absence of liquid water, the product of equilibrium vapor pressure of gaseous NH_3 and HNO_3 from E-AIM (AIM_pNH$_3$pHNO$_3$), and the product of mixing ratios of gaseous NH_3 and HNO_3 measured by GAC-IC (M_pNH$_3$pHNO$_3$). Here, Kp is colored by the ambient temperature ranging 265~293K during February 29 to March 5, 2016~~during February 29 to March 5, 2016~~.

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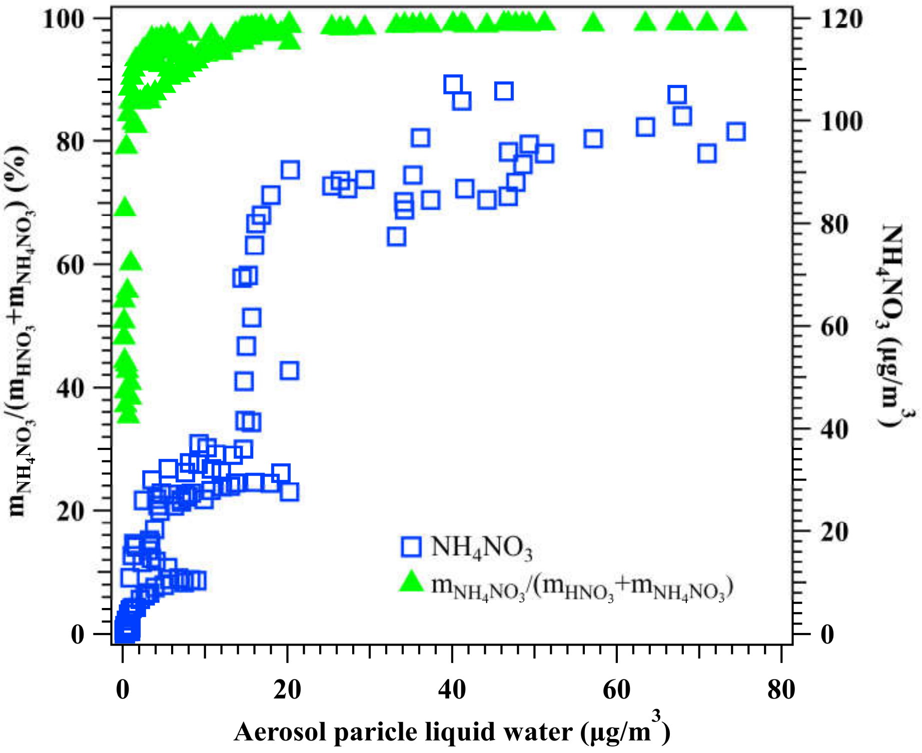

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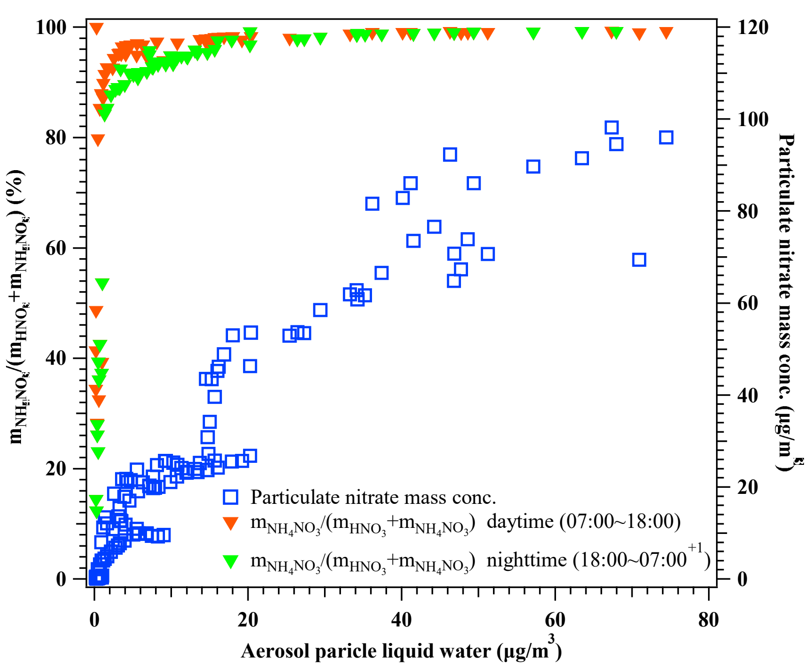

Figure 4: The relationship between aerosol particle liquid water and the molar ratio of particulate nitrate in the total nitrate, $m_{NH_4NO_3}/(m_{HNO_3}+m_{NH_4NO_3})$ (left axis) during the nighttime 18:00~07:00+1 (green solid triangle) and the daytime at 07:00 ~ 18:00 (red solid triangle), a~~and~~nd mass concentration of particulate nitrate ~~NH_4NO_3 in the particle phase~~ as a function of aerosol liquid water (right axis) during the period of ~~February~~, during February 29 to March 5, 2016 ~~29 to March 5, 2016~~. Here, particulate nitrate~~, NH_4NO_3 in the particle phase~~ was measured by HR-ToF-AMS and the HNO_3 in the gas phase was measured by GAC-IC. Aerosol l~~L~~iquid water was calculated by H-TDMA-derived method.

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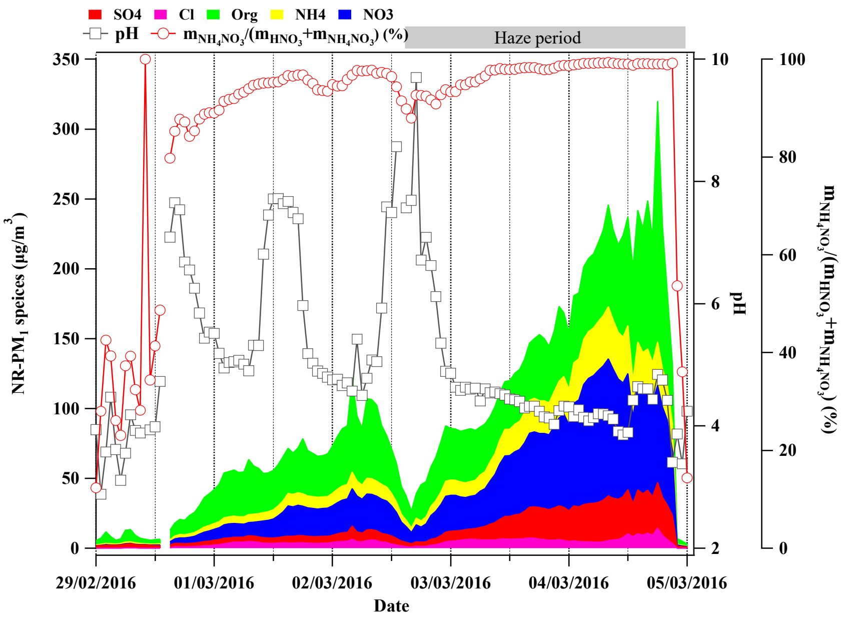

Figure 5. The time series of chemical composition measured by HR-ToF-AMS (left axis), calculated aerosol pH by ISORROPIA II (inner right axis) and molar ratio of particulate nitrate in the total nitrate (gas+particle phase) shown on outer right axis during February 29 to March 5, 2016.

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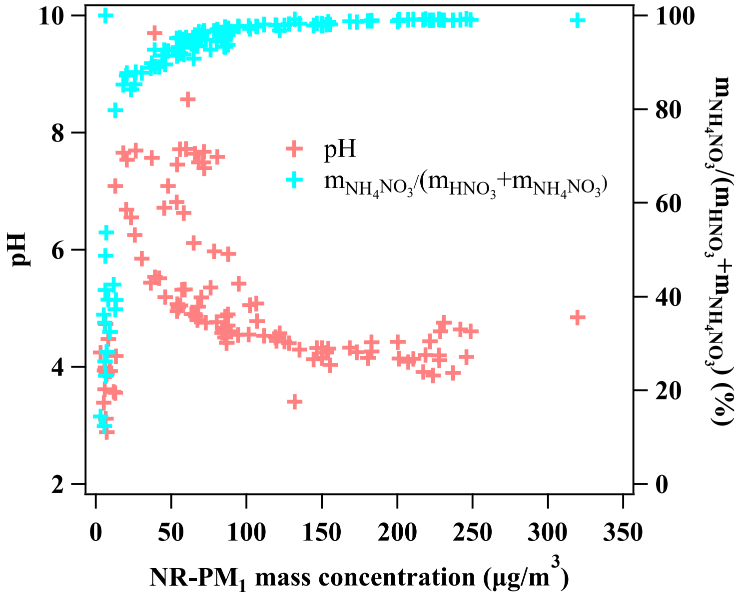

Figure 6. The pH of the fine aerosol particles (left axis) and the molar ratio of particulate nitrate in the total nitrate (gas+particle phase) (right axis) as a function of NR-PM_1 mass concentrations.

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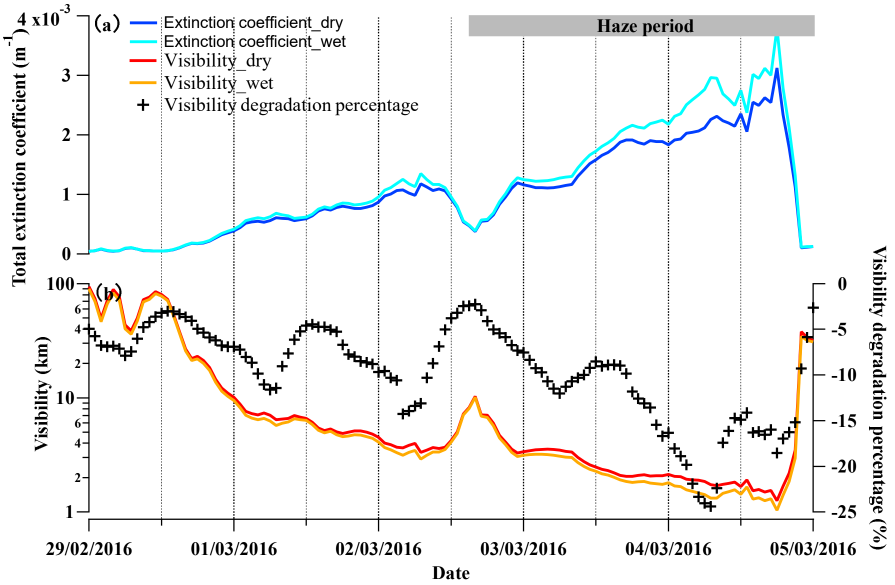


Figure ~~5~~7: The time series of (a) calculated total extinction coefficient at wavelength of 550 nm with the consideration of dry and wet PNSD, referred as Extinction coefficient_dry and Extinction coefficient_wet, (b) calculated visibility with the consideration of dry and wet PNSD, referred as Visibility_dry and Visibility_wet, respectively during February 29 to March 5, 2016. Visibility degradation percentage is (Visibility_wet-Visibility_dry)/Visibility_dry, representing the visibility degradation in the presence of liquid water.

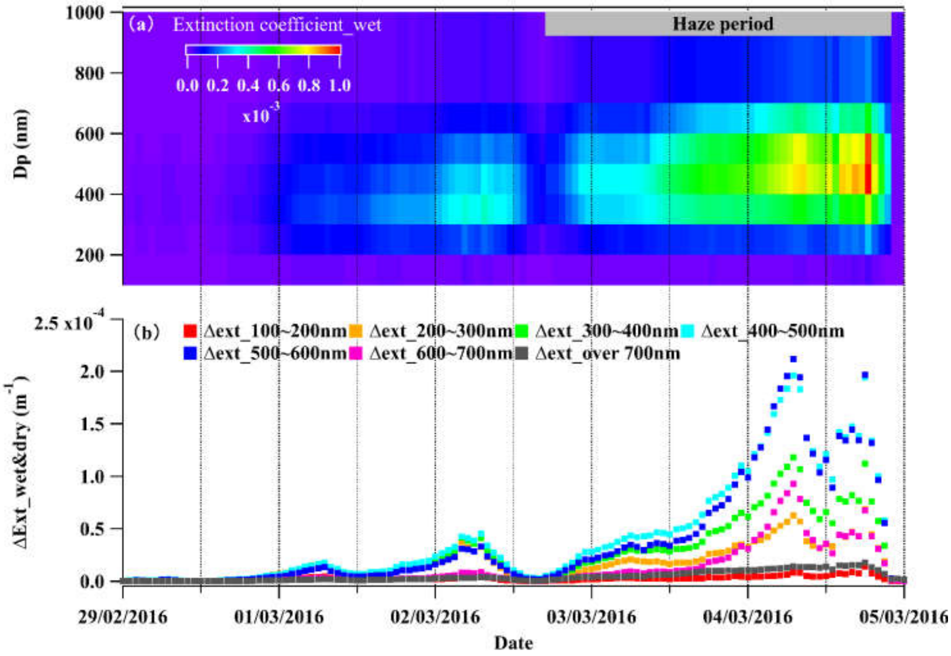
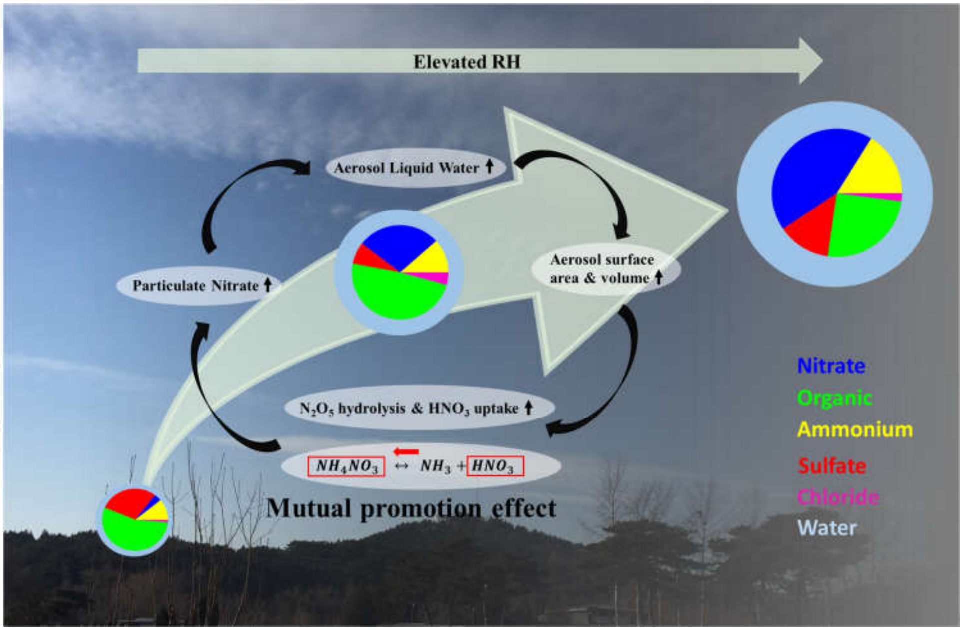


Figure ~~6~~8: (a) Size-segregated light extinction coefficient at wavelength of 550 nm for wet particles (Extinction coefficient_wet), (b) size-segregated difference between Extinction coefficient_wet and Extinction coefficient_dry, representing light extinction coefficient difference with and without considering liquid water during February 29 to March 5, 2016.



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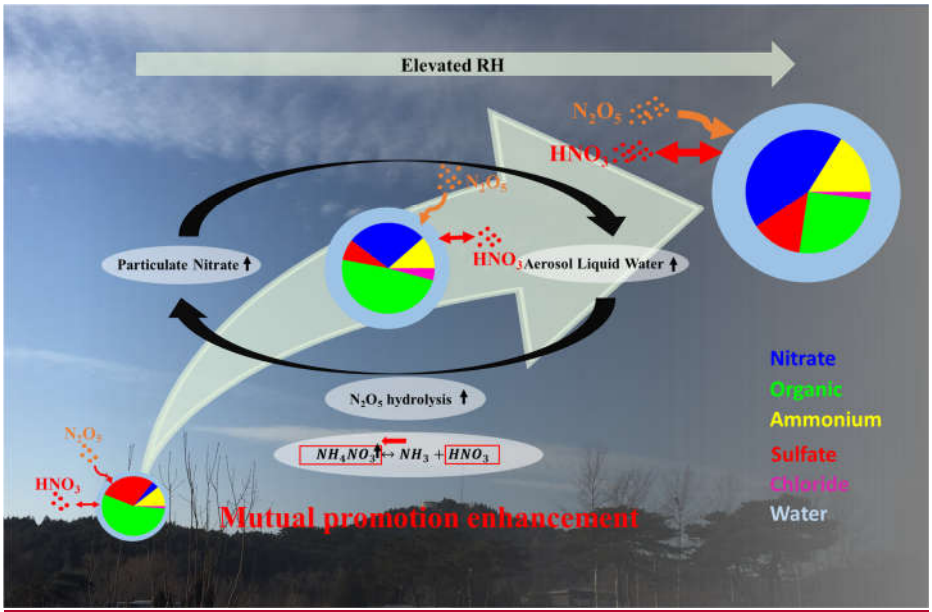

Figure ~~7~~9: The scheme of the mutual promotion effect between aerosol liquid water and particulate nitrate

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