



Mutual promotion effect between aerosol particle liquid water and nitrate formation lead 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 SO₂ emissions substantially
40 reduced in North China Plain (NCP) in recent years. A dichotomy of reductions in SO₂ and NO_x
concentrations result in the frequent occurrences of nitrate (pNO₃⁻)-dominated particulate matter
pollution over NCP. In this study, we observed a polluted episode with the nitrate mass fraction in non-
refractory PM₁ (NR-PM₁) up to 44% during wintertime in Beijing. Based on this typical pNO₃⁻-
dominated haze event, the linkage between aerosol water uptake and pNO₃⁻ formation, further
45 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/m³ at the beginning to ~75 μg/m³ at the
fully-developed haze period. 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
50 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 (N₂O₅) and nitric acid (HNO₃) to particles
contributing pNO₃⁻. From the beginning to the fully-developed haze, the condensational loss of N₂O₅
increased by a factor of 20 when only considering aerosol surface area and volume of dry particles,
55 while increasing by a factor of 25 considering extra surface area and volume due to water uptake.
Similarly, the condensational loss of HNO₃ increased by a factor of 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. Above results
demonstrated that the pNO₃⁻ 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



60 hygroscopicity of nitrate salt. Such mutual promotion effect between aerosol particle liquid water and
nitrate 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.

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1 Introduction

80 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 sulfate ((NH₄)₂SO₄) and ammonium nitrate (NH₄NO₃) (Heintzenberg,
85 1989), which originate from the oxidation of sulfur dioxide (SO₂) and nitrogen oxides (NO_x) via well-
established chemical pathways (Calvert et al., 1985). 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
90 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 (H₂SO₄) is formed from the oxidation of SO₂ via gaseous and multiphase reactions. H₂SO₄
is subsequently fully or partly neutralized by gaseous NH₃ taken up on particles, resulting in the
95 formation of (NH₄)₂SO₄ and / or NH₄HSO₄. Any remaining NH₃ is available to neutralize HNO₃ to
form particulate NH₄NO₃ (Seinfeld. and Pandis., 2006) (and further excess NH₃ can neutralize any
available HCl to form particulate NH₄Cl). Over the past several decades, substantial efforts have
reduced emissions of both SO₂ and NO_x improving the local and regional air quality all over the world.



For example, SO₂ and NO_x emissions were reduced by 82% and 54% in the majority of European
100 Environment Agency member countries between 1990 and 2016 ([https://www.eea.europa.eu/data-and-](https://www.eea.europa.eu/data-and-maps/indicators/main-anthropogenic-air-pollutant-emissions/assessment-4)
[maps/indicators/main-anthropogenic-air-pollutant-emissions/assessment-4](https://www.eea.europa.eu/data-and-maps/indicators/main-anthropogenic-air-pollutant-emissions/assessment-4)). In consequence, an
increasing trend of NO₃⁻/SO₄²⁻ 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 recent years, China has also managed to reduce
105 SO₂ emissions by 75% since 2007 (Li et al., 2017a), whereas NO_x emissions declined only by ~10%
between 2011 and 2015 (de Foy et al., 2016). Similar with European countries, the dominant inorganic
component in fine aerosol particles has switched from sulfate to nitrate in the recent years (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., 2019a;Xie et al., 2019;Li et al., 2018). Field measurements show that
110 annually averaged NO₃⁻/SO₄²⁻ molar ratio of NR-PM₁ (non-refractory PM₁) 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 NO₃⁻/SO₄²⁻ molar ratio of PM_{2.5} 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
115 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 NH₃ emissions (Wang et al., 2013).
However, NH₃ 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).



120 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 the particulate nitrate formation by changing 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
125 (Wang et al., 2018; Bian et al., 2014; Cheng et al., 2016; Wu et al., 2018). However, the observational and theoretical analysis of the relationship between particulate nitrate 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
130 nitrate formation by abundant 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.

135 **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.

140 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
145 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-PM₁ was recorded by an Aerodyne High-
Resolution Time-of-Flight Aerosol Mass Spectrometry (HR-ToF-AMS, Aerodyne Research, Inc., USA)
150 (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 HNO₃ and NH₃ 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
155 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 μ m 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).



160 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.

170 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 ($\kappa_1, \kappa_2, \kappa_3$) can be calculated by equation [1] from the known number fraction of fitted four modes and the κ values of measured particle size from H-TDMA

175 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



180 distribution and the κ measured by H-TDMA, the good agreement showed the reliability of the method. Then, based on κ -Köhler 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 [2]:

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

185 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/cm³), respectively.

2.3 Condensation rate of trace gases

The condensation rate (k) of trace gases (dinitrogen pentoxide, N₂O₅ and nitric acid, HNO₃ in the
 190 constrained conditions, referred as $k_{\text{N}_2\text{O}_5}$ and k_{HNO_3} below) was calculated by the method of Schwartz (1986), shown in equation [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.

$$k = \frac{4\pi}{3} \int_0^\infty \left(\frac{r^2}{3D_g} + \frac{4r}{3C_g v} \right)^{-1} r^3 \frac{dN}{d \log r} d \log r \quad [3]$$

195 $C_g = \sqrt{\frac{3RT}{M}} \quad [4]$

Where, r represents radius of the particles, D_g represents the binary diffusion coefficient evaluated following Maitland (1981) (1.18*10⁻⁵ m²/s). C_g is the kinetic velocity of the gas molecules, calculated in



equation [4]. Here, R and M are the ideal gas constant ($8.314 \text{ kg.m}^2/\text{mol.K/s}^2$) and molar mass of the gas, respectively while T represents the ambient temperature. $dN/d\log r$ is the number size distribution
200 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 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, 205 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 calculate uptake coefficient of the N_2O_5 , where the suppression effect of SOA on the uptake of N_2O_5 was
210 estimated following the work of Anttila et al. (2006). Additionally, 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_{10} mass concentration during the marked haze period), which might cause uncertainty in the $k_{\text{N}_2\text{O}_5}$ calculation. The detailed information regarding the estimation $\gamma_{\text{N}_2\text{O}_5}$ is given in Chen et al. (2018b). For the estimation of γ_{HNO_3} , it was reported that the γ_{HNO_3} on the solid and deliquesced inorganic compound
215 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, $\gamma_{\text{HNO}_3}=0.01$ and $\gamma_{\text{HNO}_3}=0.5$ 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

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

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

Taking into account the associated liquid water, the equilibrium vapor pressure of HNO_3 was calculated by employing the Extended-Aerosol Inorganic Model (E-AIM) Model II $\text{H}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{H}_2\text{O}$ (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).

2.5 Light extinction coefficient and visibility calculation

Size-resolved chemical composition of the NR-PM_{10} 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 [6].

$$\text{VIS} = \frac{3.912}{\text{Ext}_{550\text{nm}}} \quad [6]$$

3 Results and Discussion

3.1 Nitrate-dominated fine particulate matter pollution

Figure 1 illustrates a summary of chemical composition of NR-PM₁, 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-PM₁ was observed. The secondary inorganic components (sulfate, nitrate and ammonium) were dominant components of the NR-PM₁, 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-PM₁ 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 PM₁ 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 NH₄NO₃ is comparable with particulate (NH₄)₂SO₄ (Kreidenweis and Asa-Awuku, 2014; Wu et al., 2016). However, compared to (NH₄)₂SO₄, NH₄NO₃ particles have a lower deliquescence RH (62%, 298 K) than (NH₄)₂SO₄ (80%, 298 K) (Kreidenweis and Asa-Awuku, 2014), and easily liquify (Li et al., 2017b). In addition, NH₄NO₃ 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 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 nitrate 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 . 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 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 $\sim 1 \mu\text{g}/\text{m}^3$ at the beginning (2th March, 14:00~18:00 p.m.) to $\sim 75 \mu\text{g}/\text{m}^3$ when the haze was fully developed (4th March, 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 about 25~40% in the fully-developed haze compared to the ‘dry’ 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 $k_{\text{N}_2\text{O}_5}$ 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 $k_{\text{N}_2\text{O}_5}$ was 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 nitrate formation in the presence of liquid water, we performed the theoretical calculation of equilibrium between particulate NH_4NO_3 and gaseous HNO_3 under dry and ambient conditions, respectively. First, the dissociation constant of NH_4NO_3 (K_p) was calculated using equation [5] without considering the influence of the liquid water. K_p ranged from 0.06 (275.3 K) to 4.61 (291.5 K) ppb^2 during the ‘haze period’. The measured partial pressure product (2.55~9.63 ppb^2) was greater than the equilibrium K_p nearly all the time (Figure 3). In this case, gaseous NH_3 and HNO_3 in the atmosphere were supersaturated and would tend to partition into the dry particle phase gradually even in the absence of liquid water. The presence of liquid water under ambient RH can suppress the HNO_3 equilibrium vapor pressure to nearly zero, changing equilibrium and facilitate the partitioning of nitrate substantially. The equilibrium vapor pressure of HNO_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 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 negligible equilibrium vapor pressure of HNO_3 resulted in essentially no HNO_3 evaporation back to the gas phase and irreversible uptake of HNO_3 can be assumed under the ambient RH and NH_3 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
320 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 $1 \mu\text{g}/\text{m}^3$ to $\sim 75 \mu\text{g}/\text{m}^3$.

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
325 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,
330 1998; Guimbaud et al., 2002). As shown in Figure 2b and 2c, the lower (upper) limit of k_{HNO_3}
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
335 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
340 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)
345 material with the increasing RH in a developing haze. The associated water will favor partitioning of both particulate nitrate 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.

3.3 The key role of liquid water on visibility degradation

350 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, the total light extinction coefficient of dry and wet aerosol particles enhanced by a factor of 4.3 and 5.4, respectively, from the
355 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). This indicates that liquid water facilitated visibility degradation during haze development.

360 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, 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_{10}). According to discussion in Sec. 3.2, the mutual promotion effect between liquid
365 water and particulate nitrate can promote their formation. Aerosol particles in this size range experienced the most significant enhancement of light extinction due to water uptake (Figure 6a and 6b) and contributed 70~88% of the total extinction coefficient of the total NR- PM_{10} (Figure S9). In conclude, the rapid nitrate formation enhanced the aerosol extinction coefficient during haze developing, while the aerosol water uptake further enhanced the visibility degradation by increasing
370 extinction coefficient and promoting nitrate formation.

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.



375 4 Conclusions and implication

In this study, we observed a nitrate-dominated (up to 44% of non-refractory PM_{10} 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.

380 As shown in Figure 7, 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. 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,
385 2014). Hence, the increased aerosol particle surface area and volume concentrations due to water uptake, in turn facilitates particulate nitrate formation. Hence, a feedback loop between liquid water and particulate nitrate 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
390 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).

395 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
400 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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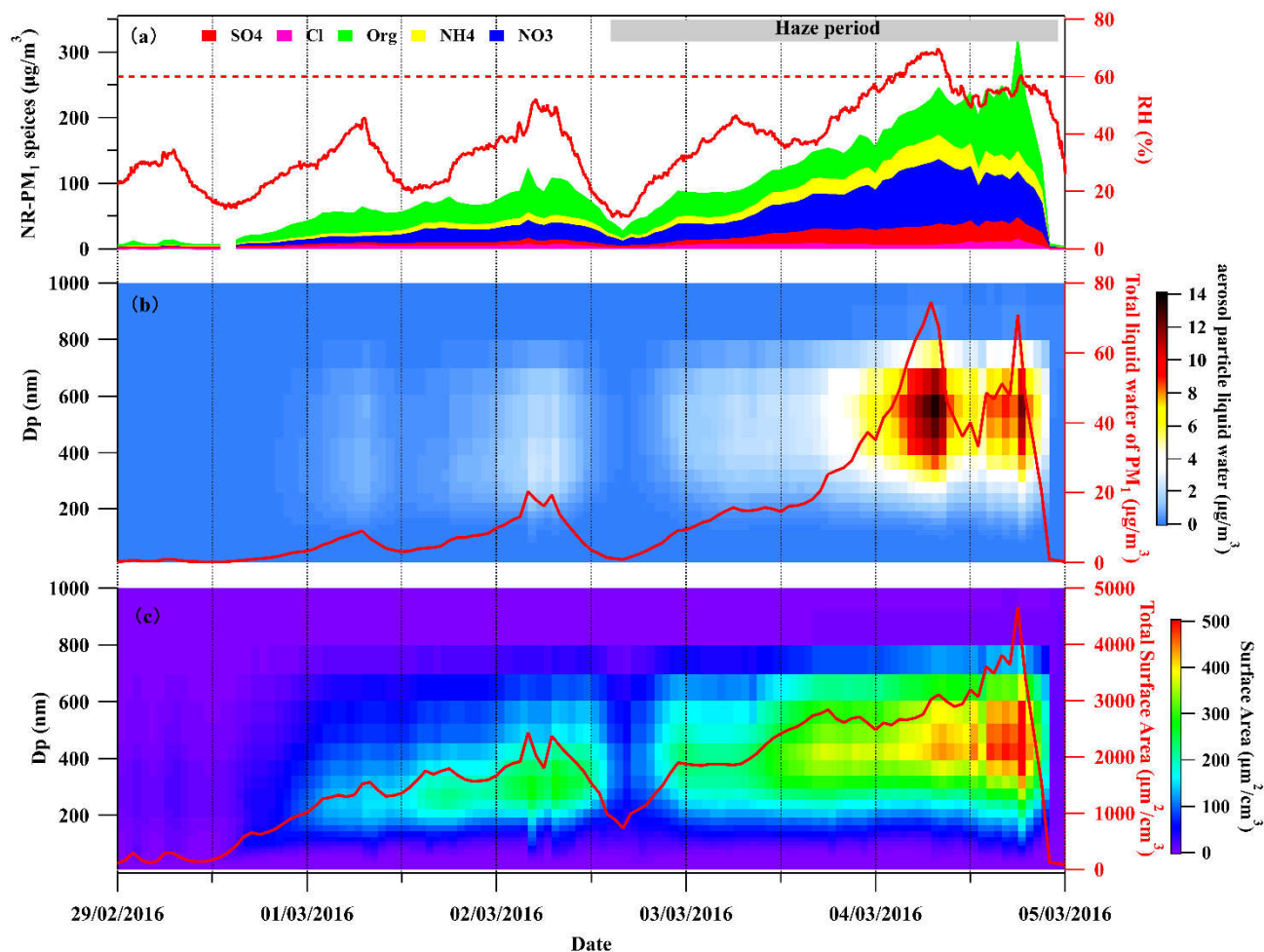


Figure 1: The time series of (a) NR-PM₁ chemical composition measured by the HR-ToF-AMS and ambient RH (red solid line), (b) size-segregated aerosol particle liquid water and the total mass concentration of liquid water with smaller than 1 μm in aerodynamic diameter (red solid line), (c) size-segregated aerosol particle surface area and total aerosol particle surface area without considering particle hygroscopic growth.

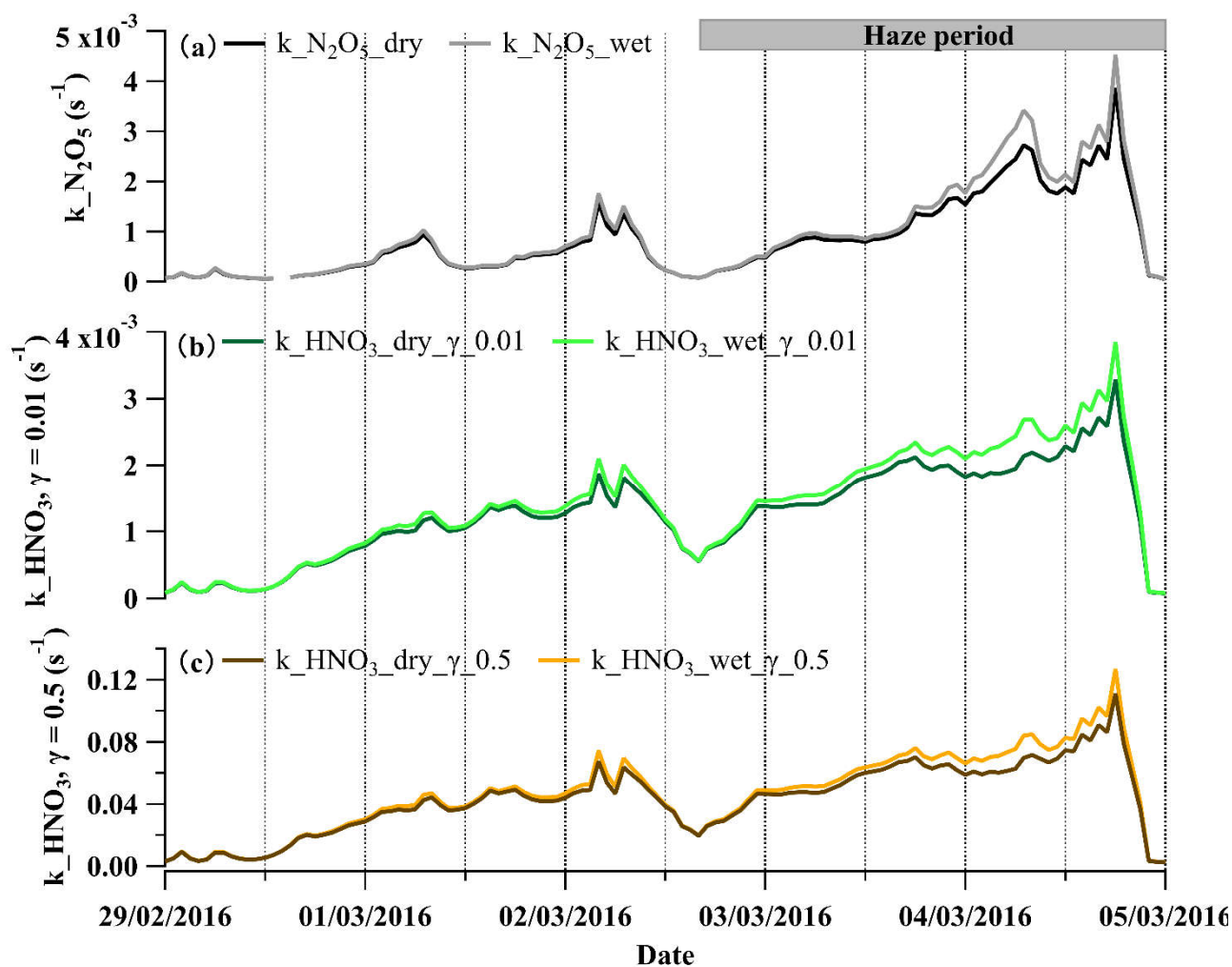


Figure 2: The time series of (a) condensation rate of N_2O_5 ($k_{\text{N}_2\text{O}_5}$) with the calculation of dry particle number size distribution (PNSD) and wet PNSD, (b-c) condensation rate of HNO_3 (k_{HNO_3}) with the calculation of dry and wet PNSD under the assumption of $\gamma=0.01$ and $\gamma=0.5$, respectively during February 29 to March 5, 2016.

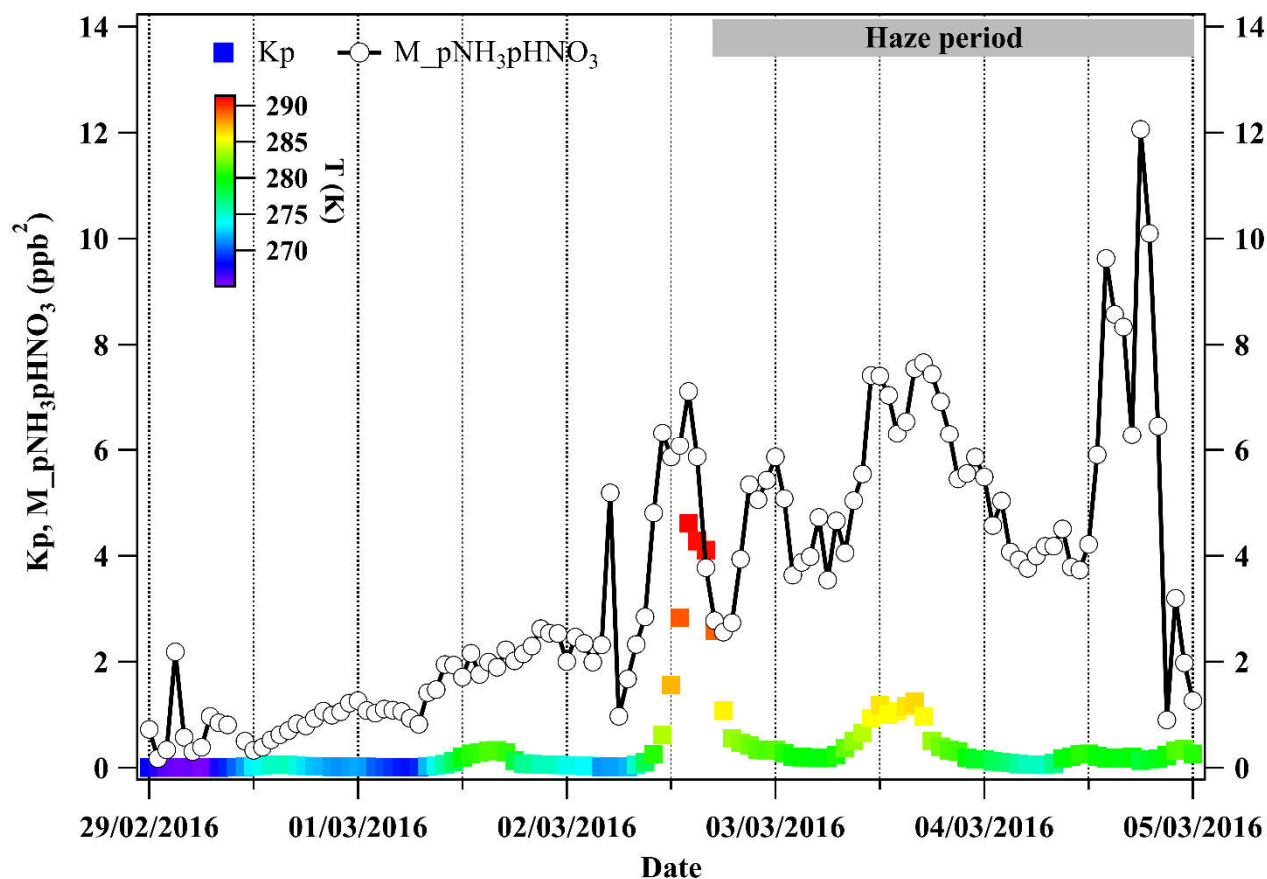


Figure 3: The comparison of the calculated temperature-dependent dissociation constant of NH_4NO_3 (K_p) (Seinfeld. and Pandis., 2006) in the absence of liquid water and the product of mixing ratios of gaseous NH_3 and HNO_3 measured by GAC-IC ($M_{\text{pNH}_3\text{pHNO}_3}$). Here, K_p is colored by the ambient temperature ranging 265~293K during February 29 to March 5, 2016.

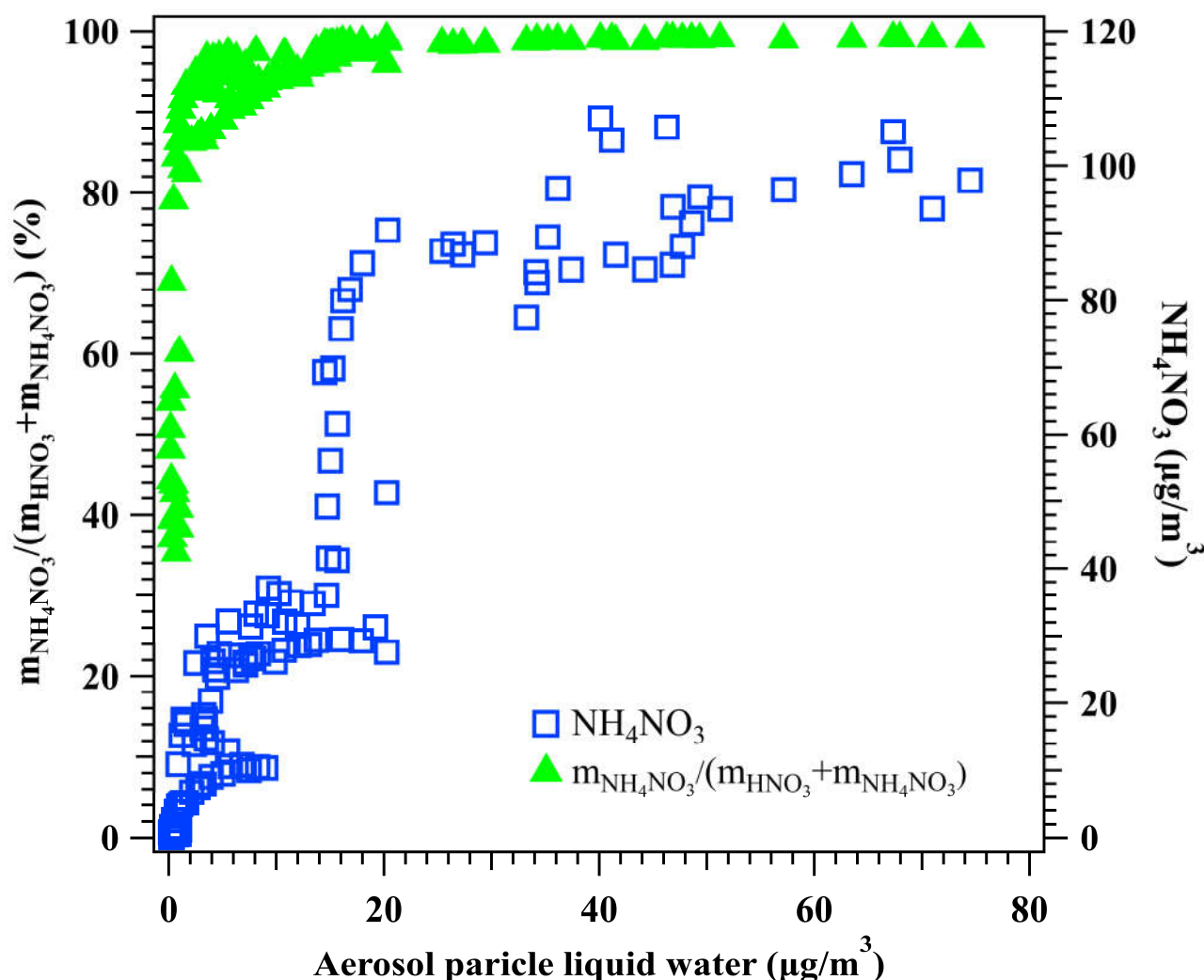
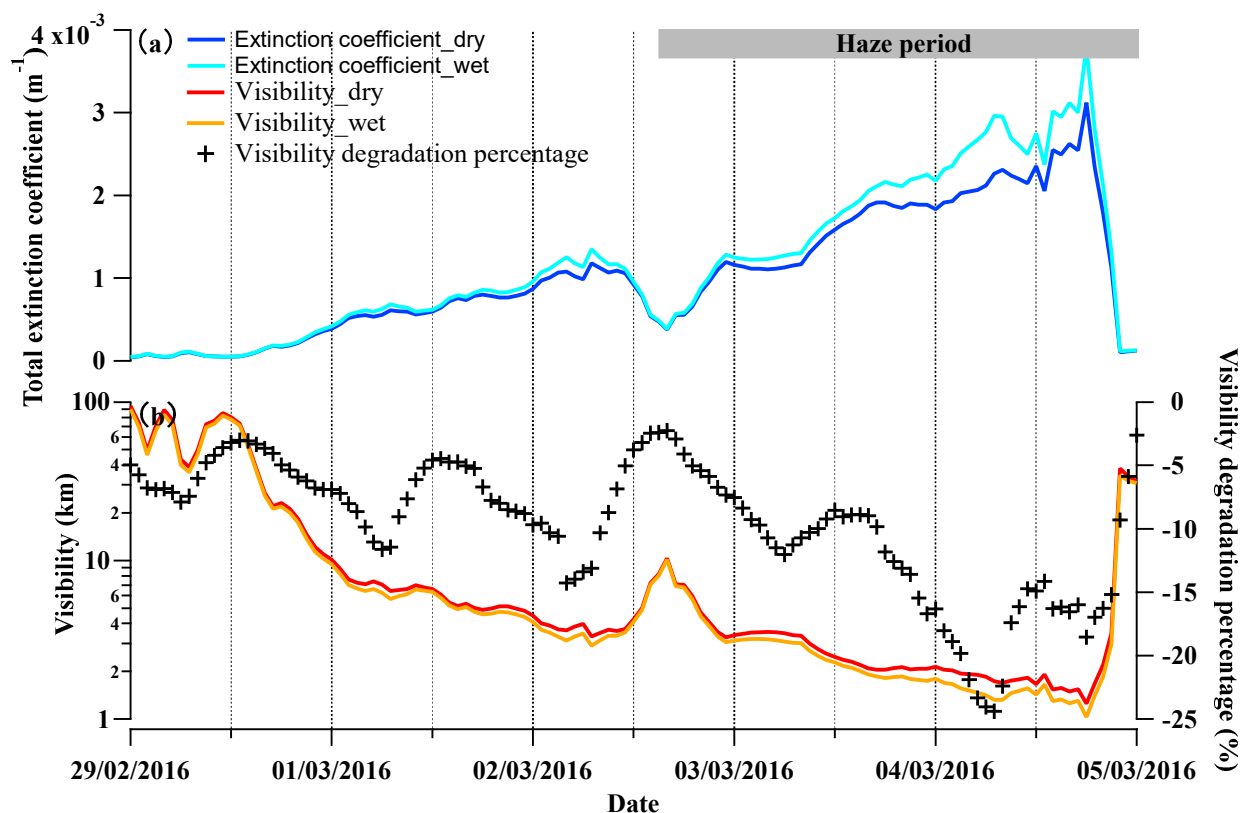


Figure 4: The relationship between aerosol particle liquid water and $m_{\text{NH}_4\text{NO}_3}/(m_{\text{HNO}_3} + m_{\text{NH}_4\text{NO}_3})$ (left axis) and mass concentration of NH_4NO_3 in the particle phase (right axis) during the period of February 29 to March 5, 2016. Here, NH_4NO_3 in the particle phase was measured by HR-ToF-AMS and the HNO_3 in the gas phase was measured by GAC-IC. Liquid water was calculated by H-TDMA-derived method.



720 **Figure 5:** 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. Visibility degradation percentage is
 (Visibility_wet-Visibility_dry)/Visibility_dry, representing the visibility degradation in the
 725 presence of liquid water.

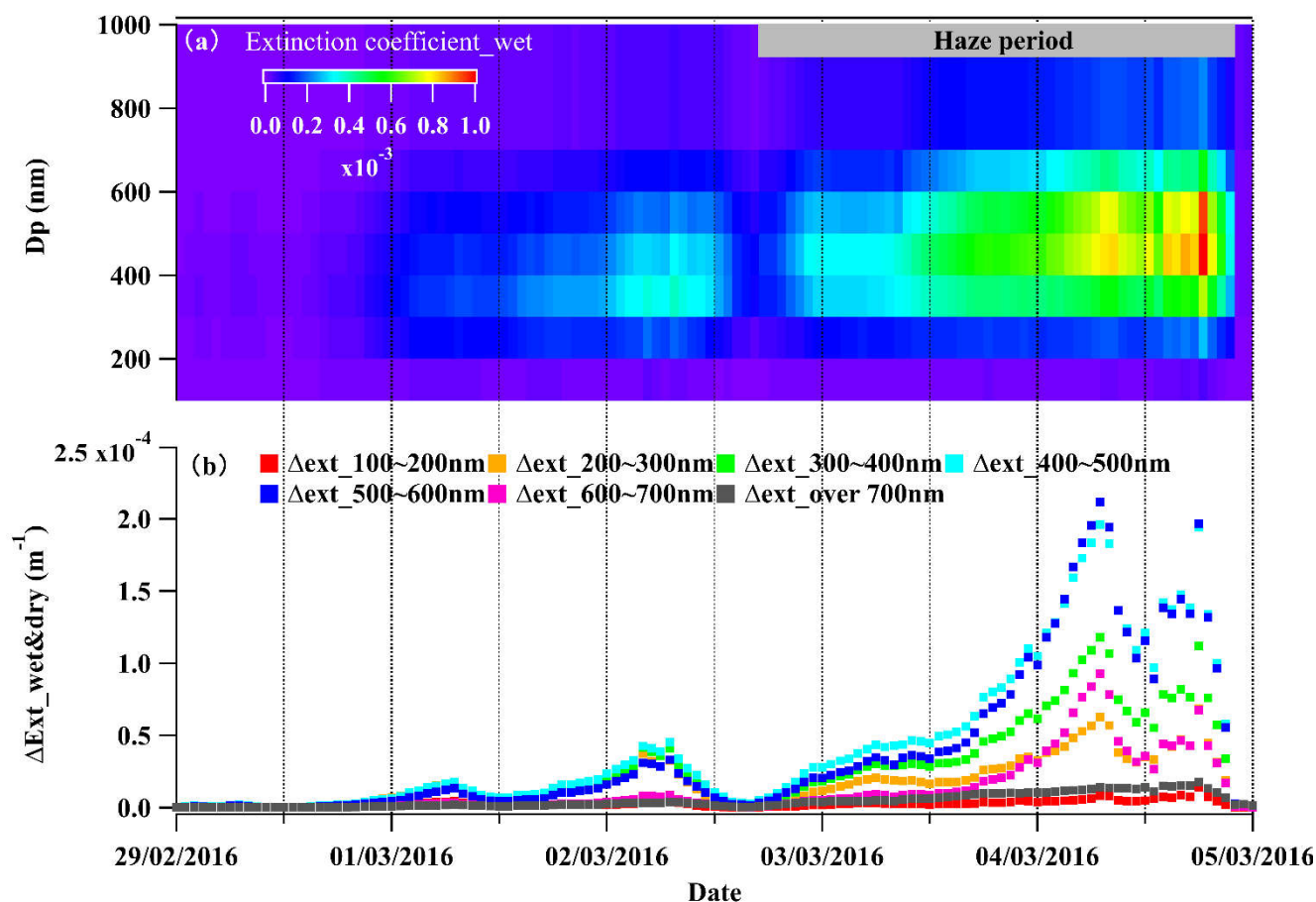


Figure 6: (a) Size-segregated light extinction coefficient at wavelength of 550 nm for wet particles (Extinction coefficient_{wet}), (b) size-segregated difference between Extinction coefficient_{wet} and Extinction coefficient_{dry}, representing light extinction coefficient difference with and without considering liquid water.

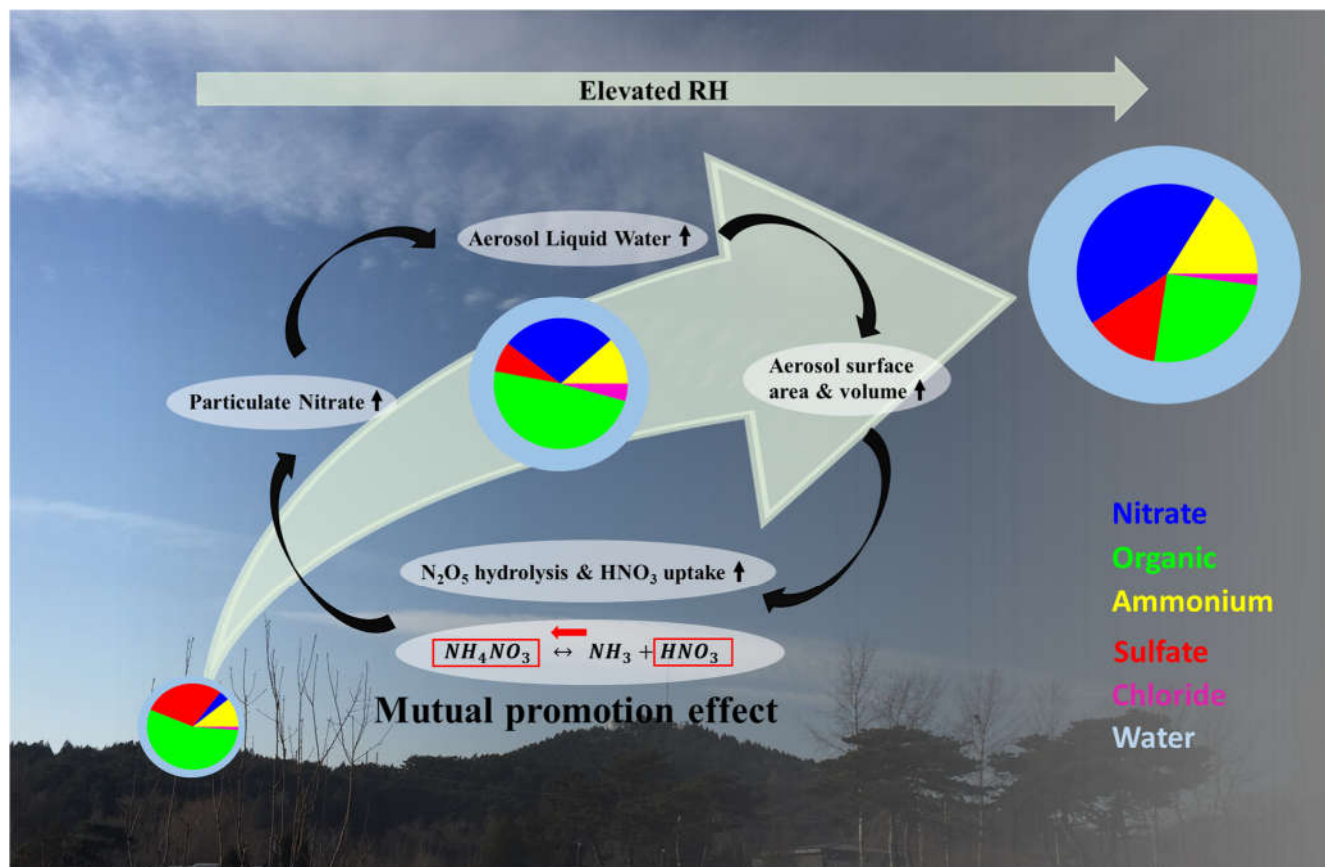


Figure 7: The scheme of the mutual promotion effect between aerosol liquid water and particulate nitrate

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