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Multiday haze in the East Asia: Transport and chemical aging of hygroscopic particles

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Abstract. East Asian countries (Korea and China) have been experiencing exceedingly high concentrations of particulate matter (PM), which threaten health and potentially alter climate. However, the formation of East Asian PM is poorly understood. Furthermore, during the winter high PM concentrations at Seoul, Korea often occur via the combination of the transport of Chinese haze through the prevailing Westerlies and the local formation at Seoul, and this complicates the PM formation. A severe multiday haze event occurred at Seoul during February 24-28, 2014, and the synoptic meteorological conditions suggest the combination of the transport and the local formation (Seo et al., 2017). PM at Seoul and Deokjeok Island during this haze period was sampled and analyzed. Deokjeok Island provides background for Seoul PM since it is upwind and emission free. We hypothesize that transported PM from China (PM at Deokjeok Island) is hygroscopic (thus contains water due to high RH) and undergoes multiphase photochemical aging at Seoul. To validate our hypothesis, we conducted smog chamber experiments. In a humid smog chamber, photochemistry of NO_x initiates the hygroscopic growth of particles, and aerosol liquid water in turn facilitates aqueous chemistry forming organonitrates and oligomers. This multiphase chemistry provides chemical insights of chemical aging during a haze event in East Asia. NO_x effects on photochemical aging of particles are substantial. Even a few ppb of NO_x form nitrates in aerosol liquid water, and acidify neutral particles. NO_x reduction is not likely to be an effective strategy for nitrate- and acidity-related health issues.

1 Introduction

East Asian countries (China and Korea) have suffered from exceedingly high concentrations of particulate matter (PM), which risk population health and potentially alter climate. This pollution is a consequence of rapid urbanization and industrialization, yet it is “unprecedented” (Kulmala, 2015): Its composition and formation pathways are different from the previous smog in London or Los Angeles (LA). A recent study reports that secondary organic aerosol (SOA) and secondary inorganic aerosol (SIA) are dominant during haze events in China, and it also reports that aqueous chemistry in aerosol liquid water (ALW) may play a role for SOA formation and certainly does for SIA (e.g., sulfate or nitrate) formation due to the high relative humidity (RH) and the hygroscopic nature of particles in East Asia (Huang et al., 2014). SOA, which is formed via atmospheric reactions (oxidation or oligomerization) of organic precursors emitted into the gas phase, has been extensively studied in field, lab and modeling areas. Gas-particle partitioning of semivolatile organic compounds has been fundamental for theorizing SOA formation (Seinfeld and Pankow, 2003; Robinson et al., 2007). This view helps us understand LA smog driven by photochemistry of volatile organic compounds (VOCs) with NO_x at low RH (Haagen-Smit, 1952; Haagen-Smit et al., 1953; Haagen-Smit, 1963; George et al., 1999). At high RH, however, hygroscopic particles take up water leading to aqueous chemistry. In ALW, water soluble organic compounds form highly oxidized products with OH radicals or oligomers via acid catalysis, and organic-inorganic oligomers with inorganic constituents (e.g., organosulfates or organosulfate oligomers) (Tan et al., 2009; Loeffler et al., 2006; Surratt et al., 2007; Lim et al., 2010). SOA formation via aqueous chemistry has been directly observed in the atmosphere (Gilardoni et al., 2016; El-Sayed et al., 2015): Highly oxygenated SOA in Beijing, China is formed through aqueous chemistry (Xu et al., 2017). SIA is dominantly formed in the aqueous phase (Seinfeld and Pandis, 2016). In the London smog episode (December 5-8, 1952), sulfates formed via oxidation of SO_2 in fog droplets presumably with H_2O_2 (Zhang et al., 2015; Wang et al., 2016). In current Chinese haze episodes, NO_x or transition metal ions, depending on the acidity of particles, helps oxidizing SO_2 to H_2SO_4 in ALW (Wang et al., 2016; Cheng et al., 2016; Guo et al., 2017). Therefore, aqueous chemistry that leads to the formation, interactions, and hygroscopic impacts of organic/inorganic constituents of particles is a hint to unveil haze particle formation in East Asia, which is currently poorly understood.

Severe multiday haze with high PM concentrations (PM2.5 > 100 $\mu g/m^3$) during winter and spring is a national health concern not only in China and but also in Korea. While China emits the largest anthropogenic air pollutants in the world (Lin et al., 2014), Korea, which is a geographical neighbor across Yellow Sea to the East, is often influenced through the prevailing Westerlies and meteorological stagnant conditions (Fig. 1A) (Seo et al., 2017). Seoul, the megacity in Korea with a population of ~ 10 million, emits NO_x and anthropogenic VOCs (NIER), and experiences severe haze events, whose formation is dominantly secondary (Kim et al., 2018; Park et al., 2014). The combination of the regional transport of air pollutants from China and the local formation of secondary aerosols in Seoul complicates our understanding of particle formation and aging in East Asia.

The goal of this work is to provide chemical insights of particle aging in East Asia when PM formed in China is transported to Seoul, Korea, encountering another urban environment with a different air quality. We hypothesize that multiphase reactions, including the gas phase and the aqueous phase in ALW, are the main particle aging process. In other words, our hypothesis is that haze particles at Seoul are chemically aged particles from Deokjeok Island through multiphase reactions including aqueous chemistry. We focus on particles at Deokjeok Island and Seoul during the multiday haze event (February 24-28, 2014) (Seo et al., 2017). Since Deokjeok Island is emission free and upwind of Seoul, particles at this area are considered the surrogate of Chinese haze particles (Fig. 1B). For better understanding of chemical aging processing of transported particles, we have conducted a smog chamber experiments for photochemical aging of wet aerosols that contain glyoxal as an organic precursor and ammonium sulfates or sulfuric acids. Then, we validate our hypothesis with chamber study results, and discuss the formation and chemical aging of East Asian PM further.

2 Method

2.1 Field Sampling Method

Descriptions can be found elsewhere (Seo et al., 2017). In summary, 24-hr sampling PM2.5 was collected on 47 mm Teflon filter (Zefluor^{TM}, Pall Corp.) through a Teflon-coated aluminium cyclone with a cut size of 2.5 μM and the flow rate of 16.7 L/min (URG Corp.). Mass concentrations of PM2.5 were measured using the Mettler MT5 microbalance (Mettler-Toledo) after 24 hr sitting on the Teflon filter in a desiccator. Then, particle samples were extracted with the mixture solution of ethanol (0.5 mL) and Milipore water (14.5 mL) for 30 minute sonication. The ion compositions of particles (e.g., sulfate, nitrate, chloride, ammonium, sodium, potassium, calcium) were analyzed using ion chromatography (Dionex 2000i/SP). For carbonaceous and organic compound analyses, PM2.5 samples were collected on 203 mm × 254 mm quartz fiber filters (Whatman Inc.) through a high-volume air sampler with the flow rate of 1000 L/min (Anderson Instruments Inc.). Then, a piece of quartz fiber filter (10 mm × 15 mm) and a thermal/optical analyzer (Sunset Laboratory) were used for elemental carbon (EC) and organic carbon (OC) analysis. Lastly, individual organic compounds (e.g., alkanes, polycyclic aromatic hydrocarbons (PAHs), fatty acids, sugars, dicarboxylic acids) were identified and quantified by gas chromatography coupled to mass spectrometry (GC-MS). The PM2.5 samples were extracted with the mixture solution of dichloromethane and methanol (3:1; volume ratio) for 1 hr, and spiked with 11 isotopically-labeled surrogated standards, then blown down to 100 mL with a Zymark TurboVap 500 concentrator (Zymark Corporation) under pure N_2 steam at 40 ^oC. This extract was filtered and further blown down to the final volume, 0.5 mL with N_2. The final extract was analyzed using GC-MS (Hewlett Packard 7890A coupled to Agilent 5975C mass selective detector). 1 μL of the sample was injected at 240 ^oC in the splitless mode and analyzed in the electron impact (EI) mode at 70 eV. Fragment ions were scanned from m/z 40 to 550.

Filtered PM2.5 samples were also analyzed using High Resolution-Quadrupole-Time Of Flight- Mass Spectrometry (HR-Q-TOF-MS). The samples were extracted with either Milipore water for 20 minute sonication. Water extract was injected into HR-Q-TOF-MS for chemical composition analysis.

2.2 Chemicals

Glyoxal solution (Simga-Aldrich) 40 % in H_2O (by weight), hydrogen peroxide (Kanto Chemical Co. Inc.) 30 % in H_2O (by weight), ammonium sulfate (Sigma-Aldrich) 99.999 % (by weight), sulfuric acid (Junsei Chemical Co. Inc.) 95.0 % in H_2O (by volume), and nitric acid (Sigma-Aldrich) 70 % in H_2O (by weight).

2.3 Chamber Method

Descriptions can be found elsewhere (Lim et al., 2016). In summary, 5 m^3 PTFE smog chamber at Korea Institute of Science and Technology (KIST), Seoul, Korea was used. Initially clean and dry air (< 0.5 ppb NMHC, < 5 % RH, ~ 40 particles, and ~ 0.01 $\mu g/m^3$) filled the chamber at 20-25 ^oC and atmospheric pressure. Ammonium sulfate aerosols (AS aerosols) were made by atomizing the solution of glyoxal (1 mM), H_2O_2 (200 µM), and $(NH_4)_2SO_4$ (0.012 M) through a collison atomizer with 35 psi. Similarly, sulfuric acid aerosols (SA aerosols) were made by atomizing the solution of glyoxal (1 mM), H_2O_2 (200 µM), and H_2SO_4 (0.012 M). Atomized aerosols were passed through a diffusion dryer (3062-NC, TSI) with the residence time of ~ 5 s to minimize the water content. Then, atomized aerosols with mass concentrations of 70-180 $\mu g/m^3$ and the geometric mean diameter of 70-90 nm were introduced into the chamber.

Photooxidation was initiated by turning on tropospheric UV lights (340-400 nm, and the peak intensity at 359 nm). During the irradiation, OH is generated by H_2O_2 photolysis in ALW of wet aerosols. Then, this OH undergoes partitioning: It not only reacts in the aqueous phase, but also evaporates into the gas phase. In smog chamber experiments, OH concentrations were atmospheric (OH concentrations in the aqueous phase and in the gas phase are ~ 3×10^{-14} M and ~ 1×10^6 molecules/cm^3, respectively). Glyoxylic acid and formic acid, products of the glyoxal-OH reaction, are also partitioned into the gas phase. The humidity of chamber was controlled by the KIST humidifier up to ~ 90 %. RH and temperature were measured using a Kimo AMI 300 multifunction meter. Size distributions were measured using a scanning mobility particle sizer (SMPS) comprised of TSI 3080 differential mobility analyzer, TSI Model 3010 Condensation Particle Counter, and software (Aerosol Instrument Manager). The mass concentrations were corrected for the particle wall loss using the first order decay rate (0.004-0.010 min^{-1}) determined from the mass concentrations measured for 1 hour after UV lights were turned off (Lim and Ziemann, 2009). No vapor wall loss was expected since only atomized solutions were introduced into the chamber. All experiments were conducted in moderate O_3 and NO_x conditions (Supplementary Table 1), and their concentrations were measured using an NO-NO_2-NO_x Analyzer (Thermo Scientific Model 42i) and an Ozone Analyzer (Thermo Scientific Model 49i).

Aerosols were collected on blank Teflon filter (25 mm, 1.0 µm, Pall Corporation) for 10-20 minutes at a sampling rate of 10 LPM at 0-180 minute reaction times. The filter samples were extracted with 5 mL of Milipore water (18.2 Ω) for 20 minute sonication. The chemical compositions of the aerosol samples were analyzed using HR-Q-TOF-MS (Waters, Synapt G2). The diluted aerosol samples with methanol (50: 50 = methanol: water by volume) were introduced to the electrospray ionization source by direct infusion, with a flow rate of 2.5 mL/h. The capillary voltage and the capillary temperature were -2500 V and 350 ^oC, respectively for the negative mode. For the positive mode, the capillary voltage and the capillary temperature were 2500 V and 250 ^oC, respectively.

Organic compounds (CHO), organonitrogens (CHNO), organosulfates (CHOS), and organonitrogen sulfates (CHNOS) were analyzed both in the negative and the positive mode of HR-Q-TOF-MS. In the negative mode, carboxylic acids, organonitrates, and organosulfates are detected as $[M - H]^-$. Some organonitrates are detected as $[M + Cl]^-$. In the positive mode, glyoxal, glyoxal oligomers, and reduced organonitrogens like imines are detected as $[M + H]^+$ or $[M + Na]^+$. Elemental formulas were assigned by MIDAS Formula Calculator (version 1.2.3) with the lowest uncertainty and chemically reasonable structures.

3 Results and Discussion

3.1 Multiday Haze Event

The synoptic meteorological conditions indicate the haze period (February 24-28) and clean period (March 1-9) (Fig. 2). The lower tropospheric circulation and the aerosol optical depth (AOD) patterns (Fig. 2) show clear influence of synoptic-scale meteorology on the air quality in Seoul. In both haze and clean periods, the North China Plain (NCP) was under the influence of high pressure, which provides stable and stagnant conditions; secondary production and accumulation of aerosols resulted in the high AOD over this region. During the haze period (Fig. 2A), a zonally elongated high pressure system extending from the Western North Pacific caused weak but steady transport of aerosols and gaseous precursors from the NCP to the Korean Peninsula across the Yellow Sea. Low winds and warm temperature in Seoul also helped local production of aerosols in this period. During the clean period (Fig. 2B), on the other hand, a developing cyclone over the Sea of Okhotsk increased the southwest-northeast pressure gradient over the Korean Peninsula and prevented transboundary transport of pollutants from the NCP. Strong and cold northwesterly winds transported clean air from the north and interrupted local formation of aerosols.

During the haze period the average PM2.5 concentrations were 116 $\mu g/m^3$ in Seoul and 84 $\mu g/m^3$ in Deokjeok Island (Fig. 3A). The boundary layer height at Seoul was ~ 400 m. High NO_2 levels in Seoul (as high as ~ 80 ppb; average 68 ppb) and low NO_2 levels in Deokjeok Island during the haze period (Fig. 3B) clearly indicate that NO_x is a main contributor of particle formation at Seoul in a local scale. High fractions of NO_3^-, SO_4^{2-}, and highly oxygenated organic compounds (O/C ~ 0.6, OM/OC ~ 1.9; Fig. 4) (Jimenez et al., 2009) suggest that haze particles are hygroscopic. At high RH (Fig. 3E), there must exist ALW in particles, which can be estimated by using an aerosol thermodynamic model (Wexler and Clegg, 2002). Estimated ALW fraction of particles is substantial (Fig. 5). Note that the method of estimating ALW fraction of particles is described in Supplementary Material S1.

Particle formation in Seoul is locally driven by NO_x. A strong correlation of mass concentrations between NO_2 and NO_3^- (R^2 ~ 0.8) in Seoul indicates that NO_3^- in particles is originated from NO_2 through HNO_3 formation (Fig. 6A). This is expected to be a local process since the lifetime of NO_2 by OH reactions to form HNO_3 is only ~ 1 day, and a recent field study supports that NO_x is a major contributor of OH reactivity in Seoul (Kim et al., 2016b). Another strong correlation between NO_2 and wet PM2.5 mass suggests that aqueous chemistry in ALW is a dominant process (Fig. 6A). The ratio of two slopes of NO_2-Nitrate and NO_2-Wet PM2.5 (Fig. 6) represents the concentration of NO_3^- in wet particles. The value of 3.5 M based on this ratio agrees well with the measurement-based molar concentration during the haze period (3.3 M) and during the clean period (2.4 M) at Seoul (Table S2). The modest correlation between NO_2 and NO_3^- in Deokjeok Island (Fig. 6B) reflects no

NO_x emission source in the area, thus supports that NO_x-HNO_3 chemistry is a local process at Seoul. However, low levels of SO_2 (< 10 ppb) and O_3 (< 20 ppb) at Seoul during the haze period (Fig. 3C and D) suggest that local SO_2–H_2SO_4 chemistry (He et al., 2014; Wang et al., 2016; Taatjes et al., 2013) is of minor importance. The low SO_2 emission at Seoul (< 10 ppb) results in an unrealistically high molar ratio of SO_4^{2-} in wet PM2.5 to SO_2 during the haze period (~ 1.4), which exceeds the ratio observed in China (< 1.2) (Wang et al., 2016). Therefore, sulfate may not be formed locally but transported regionally.

The oxygen-to-carbon ratio (O/C) and the organic mass-to-organic carbon ratio (OM/OC) (Aiken et al., 2008) were estimated based on identified organic compounds (e.g., carboxylic acids, fatty acids, monocarboxylic acids, PAHs, and alkanes), which were ~ 8 % of total organic compounds in particles in Seoul and Deokjeok Island (Fig. 4). The previous study shows that the smaller ratio (OM/OC = 1.6) represents fresh particles typically in urban areas, and the higher ratio (OM/OC = 2.1) represents oxygenated (or aged) particles typically in rural areas since rural areas are located downwind of polluted urban areas (Turpin and Lim, 2001). However, the ratios for Seoul (OM/OC = 1.93) and Deokjeok Island (OM/OC = 2.04) during the haze period indicate that particles in both areas have been already aged (Note that during the clean period, OM/OC for both particles in Seoul and Deokjeok Island was 1.83). The Korea Peninsula is downwind of air pollution from China through Westerlies and particles are aged through the transport (Kim et al., 2016a). Aqueous chemistry is likely to be a main aging process since dicarboxylic acids are known to be common aqueous chemistry products with high O/C (Lim et al., 2010), and are dominant organic components of haze particles in Seoul and Deokjeok Island. It should be pointed out that during the clean day O/C was 0.51 for both PM in Seoul and Deokjeok Island, indicating semivolatile oxygenated organic aerosol (SV-OOA), and the fraction of dicarboxylic acids of PM is much smaller than the one of haze PM. During the clean days (non-haze days) dominant SOA formation is expected to be local gas-particle partitioning of semivolatile organic compounds (fresh SOA).

3.2 Photochemical Aging of Wet Aerosols

We have conducted smog chamber experiments of photochemistry of wet aerosols containing glyoxal, $(NH_4)_2SO_4$ (or H_2SO_4,), and H_2O_2 in the presence of NO_x and O_3 at high (> 70 % RH) and low (< 5 % RH) humid conditions (Lim et al., 2016). AS aerosols (the atomized aqueous solution of glyoxal, $(NH_4)_2SO_4$, and H_2O_2) or SA aerosols (the atomized aqueous solution of glyoxal, H_2SO_4, and H_2O_2) were introduced into a 5 m^3 PTFE smog chamber for photooxidation or dark reactions. Initial concentrations of particle mass, NO_x, O_3 (and no SO_2) in the smog chamber are relevant to a moderate haze condition at Seoul.

During the irradiation in the smog chamber, NO_x eventually yields HNO_3 via NO_2 reactions with OH (Scheme 1). The conversion of NO to NO_2 is possible by the reactions with peroxy radicals ($ROO^•$) (i.e., $NO + ROO^• \rightarrow NO_2 + RO$) and HO_2 (i.e., $NO + HO_2 \rightarrow NO_2 + OH$). $ROO^•$ is from gas-phase OH reactions of evaporated less water soluble organic products (e.g., glyoxylic acid, formic acid) from glyoxal-OH reactions in ALW. In the aqueous phase, photolysis of H_2O_2 in the presence of glyoxal generates ~ 10^{-14} M of OH radical concentration and in the gas phase, 10^5-10^6 molecules/cm^3 according to an aqueous chemistry full kinetic model (Lim et al., 2013; Lim and Turpin, 2015; Lim et al., 2016), and these concentrations of OH in the aqueous phase and the gas phase are atmospheric (Arakaki et al., 2013; Finlayson-Pitts and Pitts Jr, 1999). The aqueous-phase OH reactions of glyoxal also generate HO_2 (Lim et al., 2010) with ~ 10^{-7} M in the aqueous phase according to the aqueous-phase kinetic model. Due to the modest solubility (H = 4000 M/atm), some HO_2 in the aqueous phase evaporates to the gas phase (~ 10^9 molecules/cm^3) and contributes to the formation of NO_2.

Photochemically formed HNO_3 (i.e., $NO_2 + OH \rightarrow HNO_3$) is taken up into ALW. Dominant peaks at m/z$^-$ 62 (NO_3^-), 147 ($Na^+(NO_3^-)_2$, nitrate cluster) and 226 ($Ca^{2+}(NO_3^-)_3$, nitrate cluster) in HR-Q-TOF-MS analysis for photochemical aging of AS aerosol in the humid chamber (Fig. 7) confirm nitrate uptake into ALW. Note that we have previously reported m/z$^-$ 147 and 226 as organonitrates (Lim et al., 2016), but we correct here that they are actually nitrate clusters, not organonitrates since pure nitric acid has peaks at m/z$^-$ 147 and 226 (Fig. S1).

The nitrate uptake drives two things: 1) interaction with organics; and 2) water uptake resulting in the hygroscopic growth due to the hygroscopic nature of nitrates. Organonitrates appear at m/z$^-$ 154 and 162 in Fig. 8A. Organonitrates are formed by non-radical reactions of glyoxal and HNO_3 in the aqueous phase (Fig. 8B). These two peaks at m/z$^-$ 154 and 162 are confirmed by HR-Q-TOF-MS analysis for a standard solution of glyoxal and HNO_3 (Fig. S2). The gas-phase organonitrate formation is not likely to happen because OH reactions of glyoxylic and formic acid form are expected form neither alkyl nitrate (via $ROO^\bullet$ + NO) nor alkyl peroxyacetyl nitrate (via $ROO^\bullet + NO_2$) (Lim et al., 2016; Orlando and Tyndall, 2001). Besides organonitrate formation, aqueous chemistry yielded oxalic acid (m/z$^-$ 89; the main product from glyoxal + OH), organosulfates (m/z$^-$ 283), organic acid (m/z$^-$ 265), nitrooxy organosulfates (m/z$^-$ 198 and 402) (Lim et al., 2016) (Fig. 7). It is also worth considering HNO_3 formation through the uptake of N_2O_5 into ALW during the irradiation although N_2O_5 is the nighttime sink of NO_x. (It is formed via the dark reaction of NO_2 and NO_3). The photolysis of NO_2 in our chamber system has been measured by actinometric experiments previously ($k_{photo} = 0.55\ min^{-1}$) (Lee, 2007). A model simulation predicts dominant photochemical HNO_3 formation (~ 0.36 ppb) with minor N_2O_5 formation (~ 0.05 ppb) at the end of the irradiation (Fig. S3A). For ambient conditions, photochemical HNO_3 formation is still a dominant sink for NO_x and at the end of daytime the photochemical HNO_3 concentration reaches the NO_2 concentration (Fig. S3B).

During the irradiation, photochemically aged AS aerosols in the humid chamber take up water (Fig. 9A). Using AS aerosols and SA aerosols in humid and dry conditions, we observed the particle mass growth only for AS aerosols in the humid chamber. This growth was due to water uptake since it occurred in the humid chamber, not in the dry chamber. The growth was not due to an organic partitioning since no VOC was added into the chamber initially. SMPS analyses support the hygroscopic growth by showing that the process is condensation, not nucleation (Fig. S4). Smog chamber experiments for different conditions were conducted (Fig. S5). Despite humid conditions, the absence of glyoxal results in no hygroscopic growth. Glyoxal is the source of peroxy radicals and HO_2 that convert NO to NO_2, and NO_2 is eventually oxidized to HNO_3. The absence of H_2O_2 also results in no hygroscopic growth (Fig. S5). H_2O_2 is the source of OH radicals required for aqueous-phase photochemical products from glyoxal (peroxy radicals and HO_2) and the gas-phase photooxidation of NO_2 forming HNO_3, which is accumulated back in wet aerosols. The lack of either glyoxal or H_2O_2 in aerosols shuts off HNO_3 formation.

Therefore, the main drive for water uptake is nitrates, which are indeed hygroscopic. The hygroscopic growth and nitrate uptake are well correlated since the particle mass concentrations measured by SMPS increase as nitrate/nitrate cluster peaks (m/z^- 62, 147, and 226), and organonitrate peaks (m/z^- 154) in mass spectra increase (Fig. 9B). The organonitrate peak, m/z^+ 154, decays after ~ 1 hour irradiation since this simplest organonitrate, which contains only one glyoxal monomer and one nitrooxy group, is likely to form more complicated organic-inorganic oligomers.

3.3 Photochemical Aging Simulations

3.3.1 Smog Chamber Simulations

HNO_3 uptake is particularly significant in neutral particles mainly due to the dissociation of the equilibrium ($HNO_3 \rightleftharpoons H^+ + NO_3^-$). It is well established that the effective Henry's law equilibrium constant for HNO_3 ($H^*_{HNO_3}$) depends on the acidity of ALW due to the large dissociation constant (K_{HNO3}) (Seinfeld and Pandis, 2016).

$$H^*_{HNO_3} = H_{HNO_3}\frac{K_{HNO_3}}{[H^+]} = \frac{2.46e6}{[H^+]} \qquad \text{(Equation 1)}$$

where H_{HNO3} = 1.6e5 M/atm, and K_{HNO3} = 15.4 M.

Total nitrates ($[NO_3^-]_T = [NO_3^-] + [HNO_3]$) are mostly nitrates ($[NO_3^-]$ due to nearly complete dissociation of HNO_3:

$$[NO_3^-] = H^*_{HNO_3}P_{HNO_3} = \frac{2.46e6}{[H^+]}P_{HNO_3} \qquad \text{(Equation 2)}$$

where P_{HNO3} is the partial pressure of HNO_3 in the gas phase.

According to (Equation 2), the nitrate uptake depends on the particle acidity: the nitrate uptake favors neutral particles over acidic particles. However, it should be noted that HNO_3 uptake acidifies the particles. Rapid HNO_3 uptake into initially neutral AS aerosols (pH 5 for Experiment #4 and #5, Table S1) occurs in the beginning of photooxidation. Nitrate accumulation takes up water and acidifies particles at the same time, so after the chamber reaction the accumulated nitrate concentration is ~ 1 M and pH is ~ 2 (Experiment #4 and #5, Table S1). However, acidification, in turn, slows down HNO_3 uptake, and eventually stops it when particles become highly acidic. No hygroscopic growth for SA aerosols has been observed since SA aerosols are already highly acidic (~ pH -1) so suppress HNO_3 uptake (Note that $[NO_3^-]$ is ~ 10^{-3} M for

SA aerosols, but [NO_3^-] is ~ 1 M for AS aerosols, Table S1). Figure 10 illustrates nitrate and water uptake and the particle acidification of AS aerosols in the humid chamber during the 3 hour irradiation (Experiment #4 and #5, Table S1). The method of ALW, pH and nitrates estimations is described in Supplementary Material S1. Note that organonitrate formation has not been consider since the quantification of organonitrates is beyond the scope.

3.3.2 Atmospheric Simulations

We have simulated multiphase photochemical aging of the haze particles at Deokjeok Island to validate our hypothesis of NO_x effects on hygroscopic particles as an aging process at Seoul. NO_2 at Seoul (average 68 ppb) is assumed to be completely oxidized to HNO_3 in the gas phase by OH (therefore, [HNO_3] = 68 ppb). Note that in the smog chamber peroxy radicals and HO_2 that convert NO to NO_2 are originated from the aqueous phase reactions: however, in the atmosphere peroxy radicals and HO_2 are more likely to be formed through gas-phase reactions of VOCs-HO_x-NO_x. The local oxidation on/in organic particles at Seoul was not considered because of similar O/C ratios of Seoul and Deokjeok Island particles (Fig. 4). Due to the hygroscopic growth, the final amount of simulated ALW is adjusted to the amount of ALW in haze particles at Seoul while other particle components remain in particles. The chemical aging simulation includes HNO_3 and water uptake based on the thermodynamic model and the equilibrium model (Supplementary Material S1).

Figure 11 illustrates the chemical aging simulation of haze PM at Deokjeok Island under the same NO_x and RH conditions at Seoul in comparison with the haze PM measurement in Seoul. The simulated concentration of NO_3^- (32 $\mu g/m^3$) agrees well with the measured one (34 $\mu g/m^3$). Acidification due to HNO_3 uptake reaches pH 0.4, which is slightly higher than the measured pH 1.2. The simulated OM (18 $\mu g/m^3$), which is Deokjeok Island OM by itself, is close to the measured OM (20 $\mu g/m^3$), confirming the minor importance of local SOA formation. The discrepancy between total mass concentrations of the simulated PM and the measured PM (15 $\mu g/m^3$ underprediction) is mainly because the formation of ammonium (9 $\mu g/m^3$ underprediction) and sulfate (9 $\mu g/m^3$ underprediction) is not included in the simulation (if we include ammonium and sulfate formation, the simulated mass concentration becomes 216 $\mu g/m^3$, which is very close to the measured one, 213 $\mu g/m^3$). Ammonia emission in Seoul is as low as SO_2 emission (below 10 ppb), and is mainly from agriculture. Therefore, agricultural ammonia in Gyeonggi County, which surrounds Seoul, may affect the chemical aging of particles during the transport from Deokjeok Island to Seoul by producing ammonium in ALW and lowering the acidity of particles. Although we hypothesize that SO_2-H_2SO_4 chemistry is not important locally, there still forms 9 $\mu g/m^3$ of sulfates (24 % of total sulfates), whose concentration is not minor. One possible pathway is that sulfates have formed during the regional transport from China to Korea through the gas-phase OH reactions of SO_2 and SO_2 has been dissipated.

4 Conclusions and Atmospheric Implications

Photooxidation at high NO_x/humidity initiates HNO_3 uptake into wet particles, which in turn take up water leading to hygroscopic growth. HNO_3 uptake is significant particularly for neutral wet particles due to the rapid dissociation of dissolved HNO_3. Since hygroscopic nitrates are replenished in wet particles, water uptake is significant. Consequently, aqueous chemistry leading to SOA/SIA formation is more important than currently thought. Previously, we have reported the formation of oligomers and inorganic-organic compounds from glyoxal through condensed-phase reactions in wet particles (Lim et al., 2016). And here we report that glyoxal and dissolved HNO_3 form organonitrates, which may increase nitrate concentrations by suppressing the evaporation of dissolved HNO_3 due to the semivolatile nature, resulting in more organonitrates (and oligomers) in the condensed phase. Since Seoul is a photochemically active and humid urban area, we interpret the haze particle formation at Seoul as chemical aging of haze PM at Deokjeok Island, which is upwind, providing chemical insights of the chemical aging process in East Asia. This work suggests several atmospheric implications.

4.1 LA smog vs. East Asian haze

NO_x affects particle formation and aging differently by geographical regions. In dry urban areas like Los Angeles, photochemically formed HNO_3 from NO_x becomes NH_4NO_3 by the gas phase reaction with NH_3, then undergoes gas-particle partitioning due to semivolatile nature (Pusede et al., 2016), or NO_x affects SOA formation through daytime photochemistry and nighttime NO_3 radical reactions in the gas phase as it forms semivolatile organonitrates that are partitioned into particles (Rollins et al., 2012; Haagen-Smit, 1952). However, in humid urban areas like Seoul or East Asian cities, HNO_3 is immediately partitioned into neutral wet particles and initiates hygroscopic growth (Hodas et al., 2014) that facilitates aqueous chemistry presumably via acid catalysis due to the acidity enhancement by HNO_3, and forms oligomers and organonitrates in the aqueous phase. Clearly, acidification of neutral particles is a marker for HNO_3 uptake from photochemistry of NO_x. The low pH of haze particles in Seoul, while haze particles in Deokjeok Island and clean-day particles in Seoul and Deokjeok Island are neutral (Fig. 4), supports HNO_3 uptake into transported neutral particles from Deokjeok Island, which is originated from China since haze particles at China are also neutral (Wang et al., 2016).

4.2 NO_x Reduction Strategy at Seoul

Uptake of nitrates and water is significant in East Asian cities characterized by high NO_x, humidity and photochemistry. Nitrate accumulation and acidification give rise to public health issues (EPA; Dockery et al., 1996). Besides, the nitrate is a dominant component that constitutes 16 % of Seoul haze particles (Fig. 4) (~ 30 % if ALW is excluded). NO_x is a major pollutant in Seoul, and emitted via fossil fuel combustion (vehicle exhaust). Even a few ppb of NO_x (NO_2) concentration acidifies particles to pH ~ 2 and forms ~ 2 M of nitrates (Fig. 12); therefore, NO_x reduction strategy may not be an effective solution.

4.4 SO_2-Sulfate Chemistry at China

NO_x effects on the hygroscopic growth of particles provide an insight of sulfate formation in Chinese urban areas. The current understanding is that NO_x helps the conversion of SO_2 to sulfates in ALW (Wang et al., 2016; Cheng et al., 2016). But this is challenged by Guo et al. (2017), who claim that the acidity of Chinese haze particles is higher than the prediction by Wang et al., thus favors transition metal ions over NO_x for sulfate formation. Our finding suggests that at high NO_x

conditions in urban areas HNO_3 formed from photooxidation during the daytime (and N_2O_5 during the nighttime) will dissolve and acidify particles effectively. Therefore, SO_2 conversion to sulfates may occur under acidic conditions. However, it should be noted that the substantial hygroscopic growth by nitrate uptake may affect the particle acidity. Furthermore, organonitrate formation also affects the acidity. For example, under highly acidic conditions (presumably by sulfuric acid formation) nitrates form HNO_3, which forms organonitrates as remaining in particles, instead of fully evaporating to the gas phase. Organonitrates act as a HNO_3 reservoir in particles, thus can generate HNO_3 back (through hydrolysis) if particles undergo the hygroscopic growth. Therefore, the hygroscopicity of particles and the interaction of organics with inorganics need to be considered further for East Asian particle formation.

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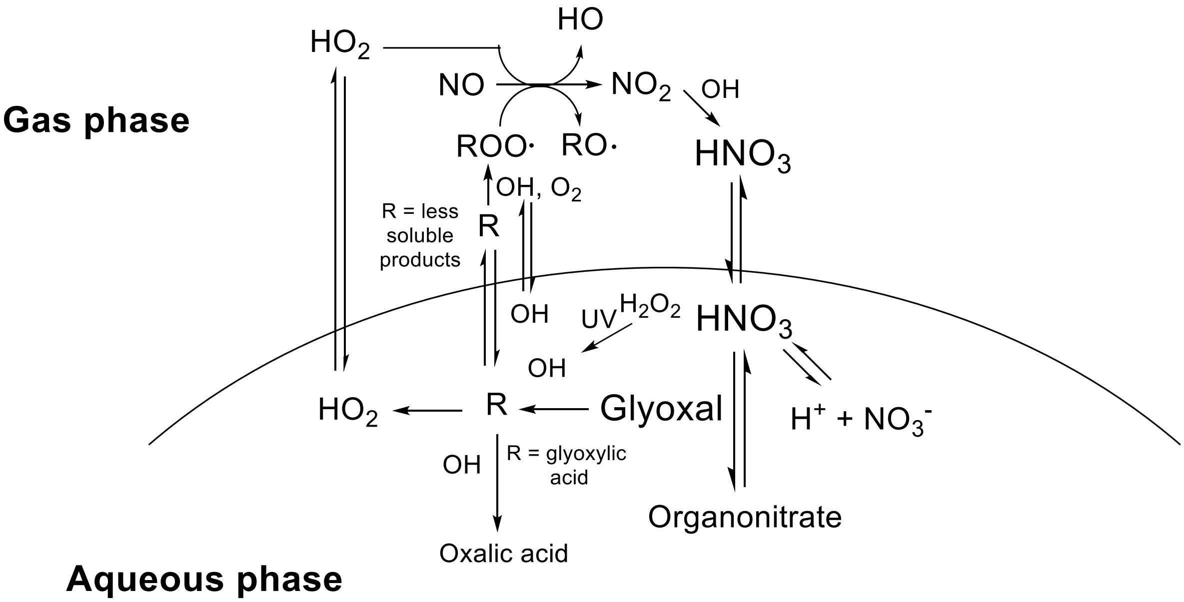
Discussion started: 16 April 2018



Scheme 1: Photochemical nitric acid formation through multiphase reactions

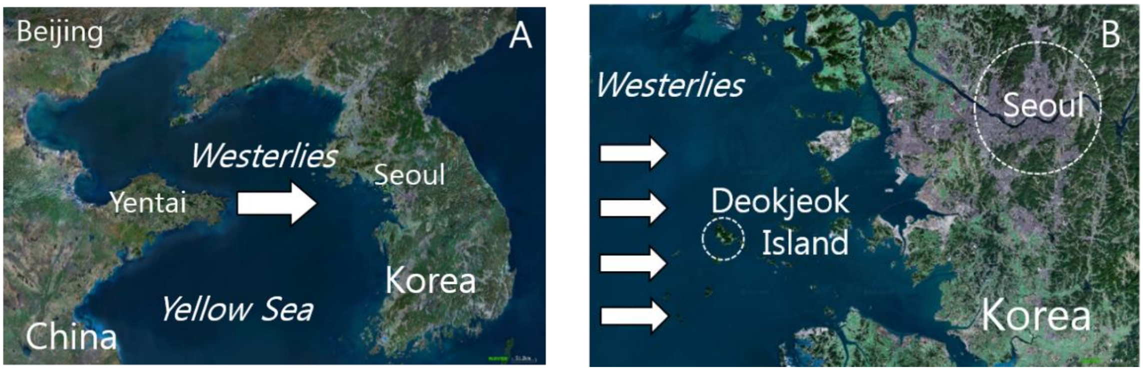
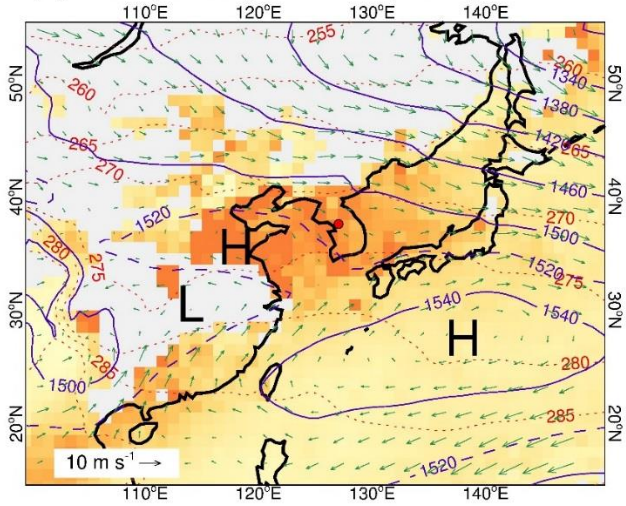


Figure 1: The map of South/North Korea and China (A) and the zoomed-in map of Seoul (37.603ºN, 127.047ºE) and Deokjeok Island (37.233ºN, 126.149ºE) in South Korea (B) (Naver Map). Chinese-origin haze transported to Korea (Seoul) through Westerlies according to synoptic meteorological conditions during the multiday haze event. Deokjeok island is a gateway (or equivalent to a gate way) of the transported haze and serves as a background to Seoul haze since Deokjeok Island is emission free.

(a) Haze period (Feb 24-28, 2014)



(b) Clean period (Mar 5-9, 2014)

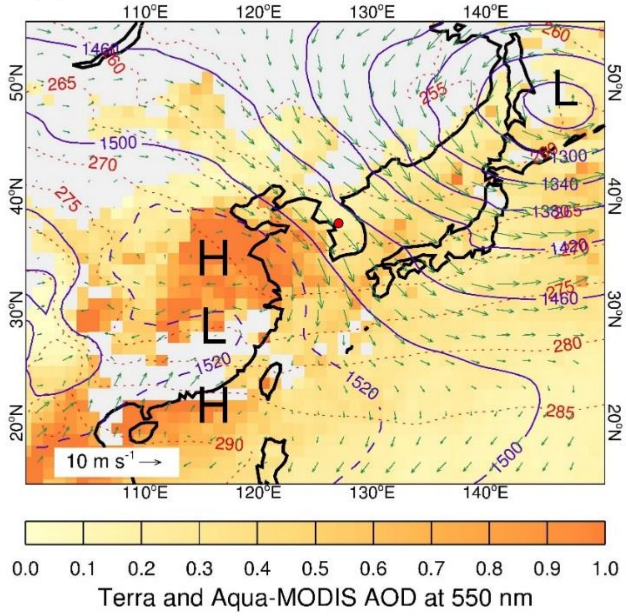


Figure 2: Synoptic meteorological conditions in the lower troposphere (850 hPa; about 1.5 km altitude) and the aerosol optical depth (AOD) over East Asia for the haze period (A) and the clean period (B). Geopotential height (purple contour, gpm), temperature (red/dotted contour, K), and wind (green arrows) at 850 hPa from the ERA-Interim reanalysis and the Terra and Aqua-MODIS AOD at 550 nm were averaged for each 5-day period. Seoul is marked as red filled circles.

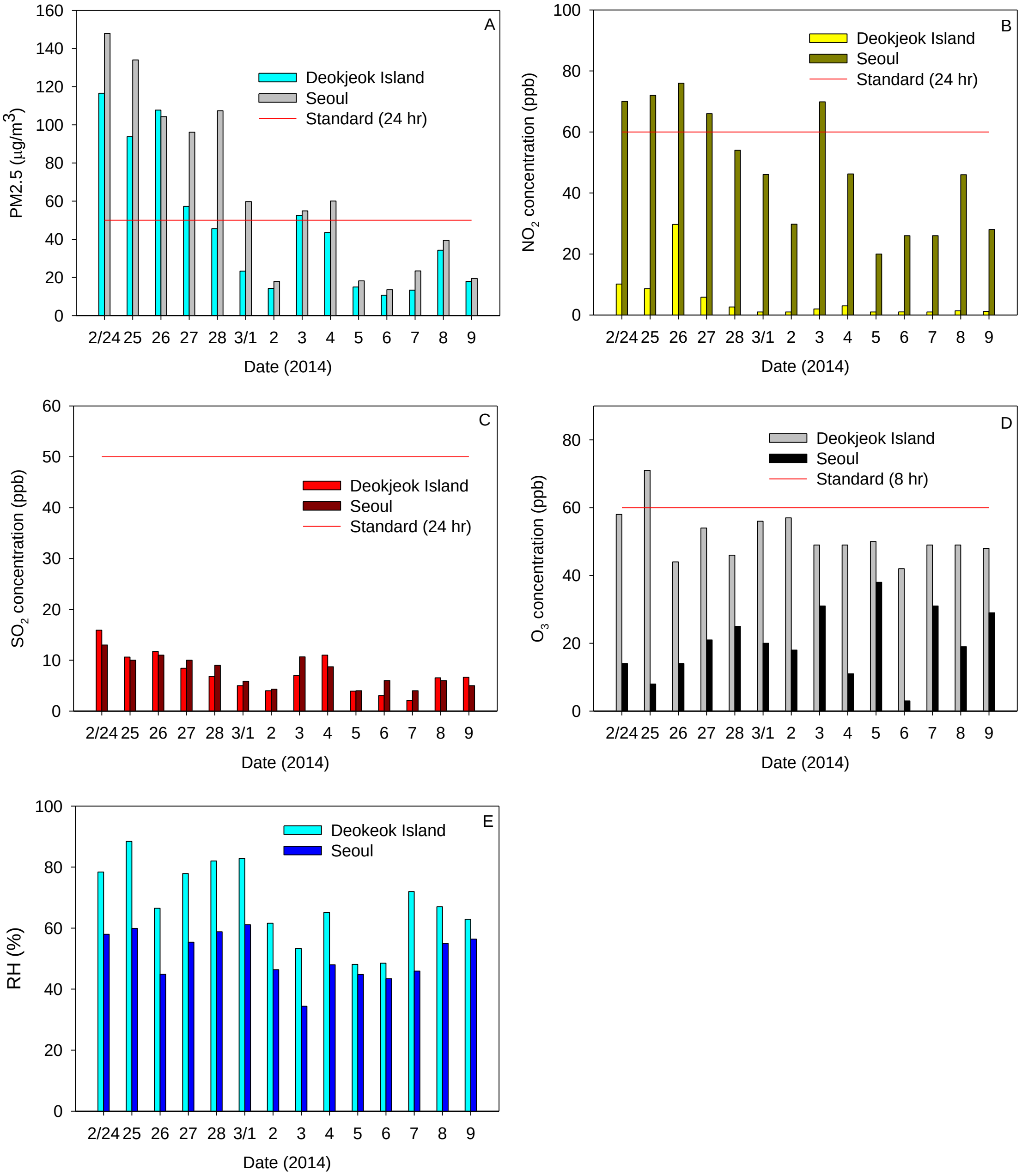


Figure 3: Air quality (A, B, C, and D) and RH (E) at Seoul and Deokjeok Island from February 24 to March 9, 2014.

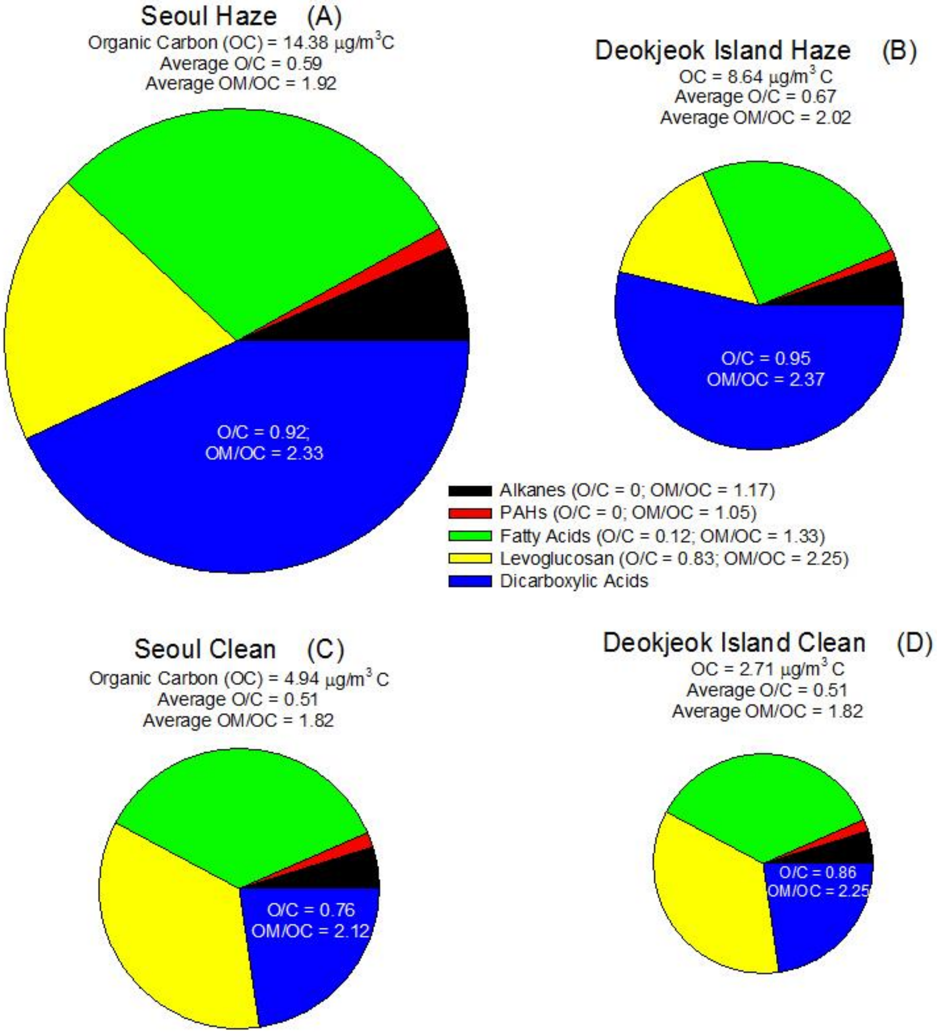


Figure 4: Organic components in particles at Seoul (A) and Deokjeok Island (B) during the haze period, and organic components at Seoul (C) and Deokjeok Island (D) during the clean period: These organic components are ~ 8 % of identified organic carbon. 5 **Average O/C refers to the average oxygen-to-carbon ratio of identified organic components. Average OM/OC refers to the average organic mass-to-organic carbon ratio of identified organic compounds. O/C and OM/OC values for components are constants except for dicarboxylic acids, whose values have been noted in the blue portions of pie charts.**

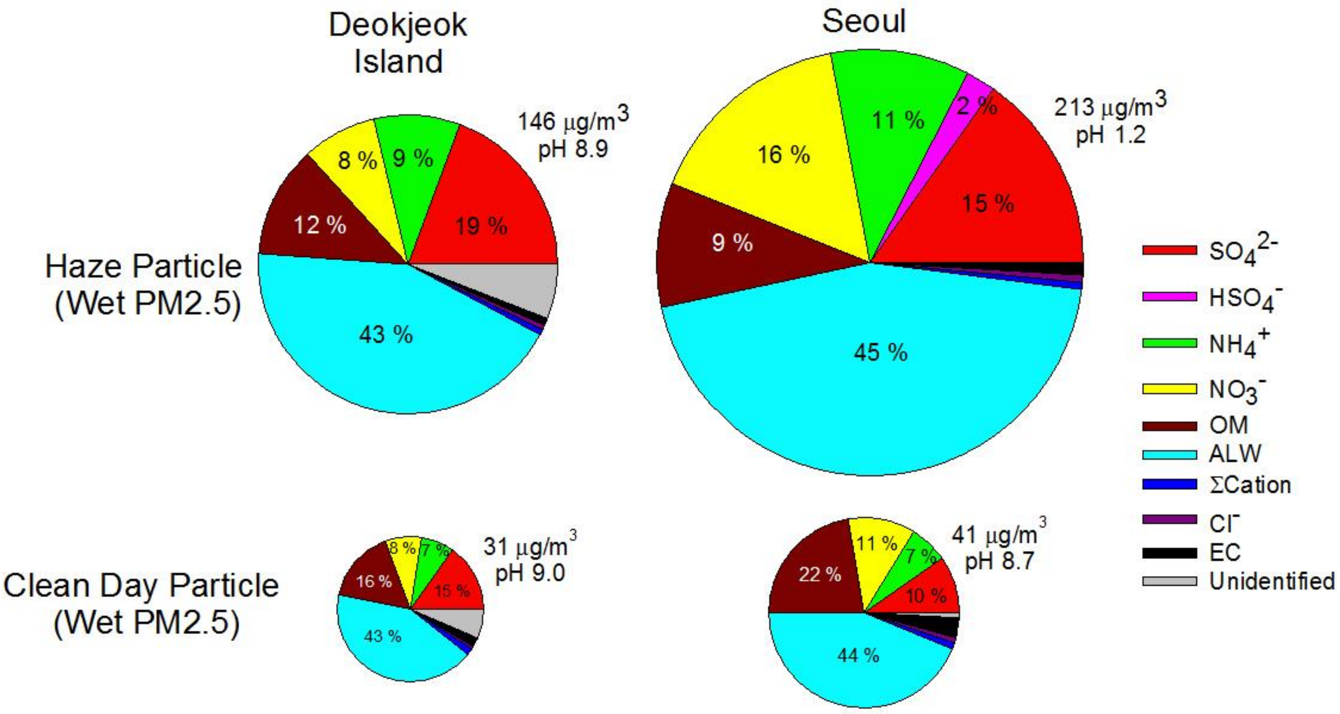


Figure 5: Chemical component distributions of hygroscopic particles (Wet PM2.5) at Seoul and Deokjeok Island during the haze and clean day periods. ALW was estimated by using an aerosol thermodynamic mode (Wexler and Clegg, 2002) at 70% RH. Σ Cation is the sum of cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}). No organonitrate has been estimated.

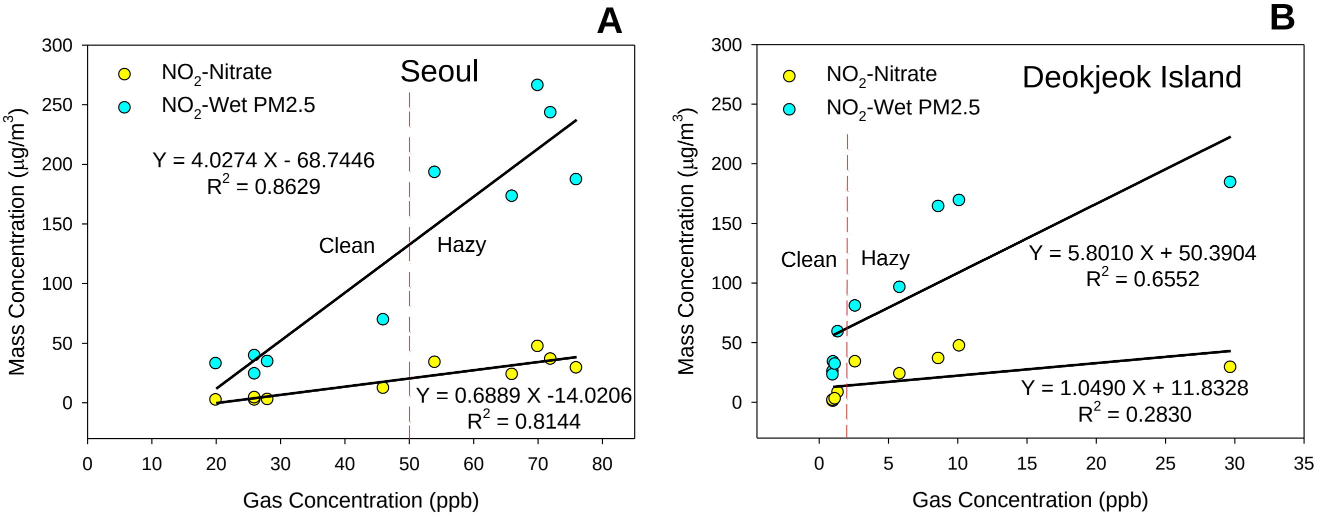


Figure 6: Correlations of NO_2-Nitrate and NO_2-Wet PM2.5 in Seoul (B) and Deokjeok Island (C). "Hazy" represents the haze period of February 24-28, 2014. "Clean" represents the period of March 5-9, 2014 after the haze event.

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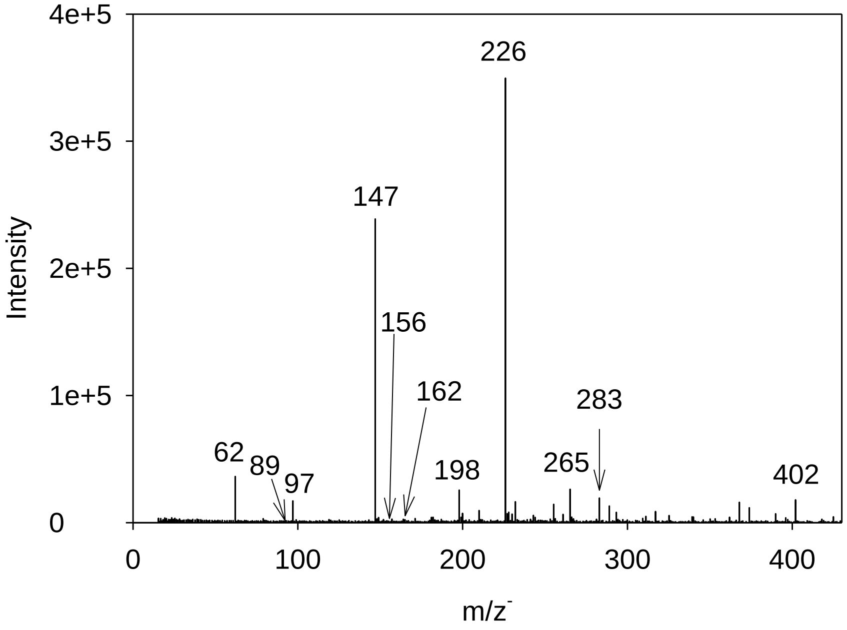

5 **Figure 7: The negative mode HR-Q-TOF-MS spectrum for photo-aged AS aerosols after 3 hours in the humid chamber: m/z$^-$ 62 (nitrate), 89 (oxalate), 97 (sulfate), 147 (nitrate cluster), 156 (organonitrate), 162 (organonitrate) and 226 (nitrate cluster).**

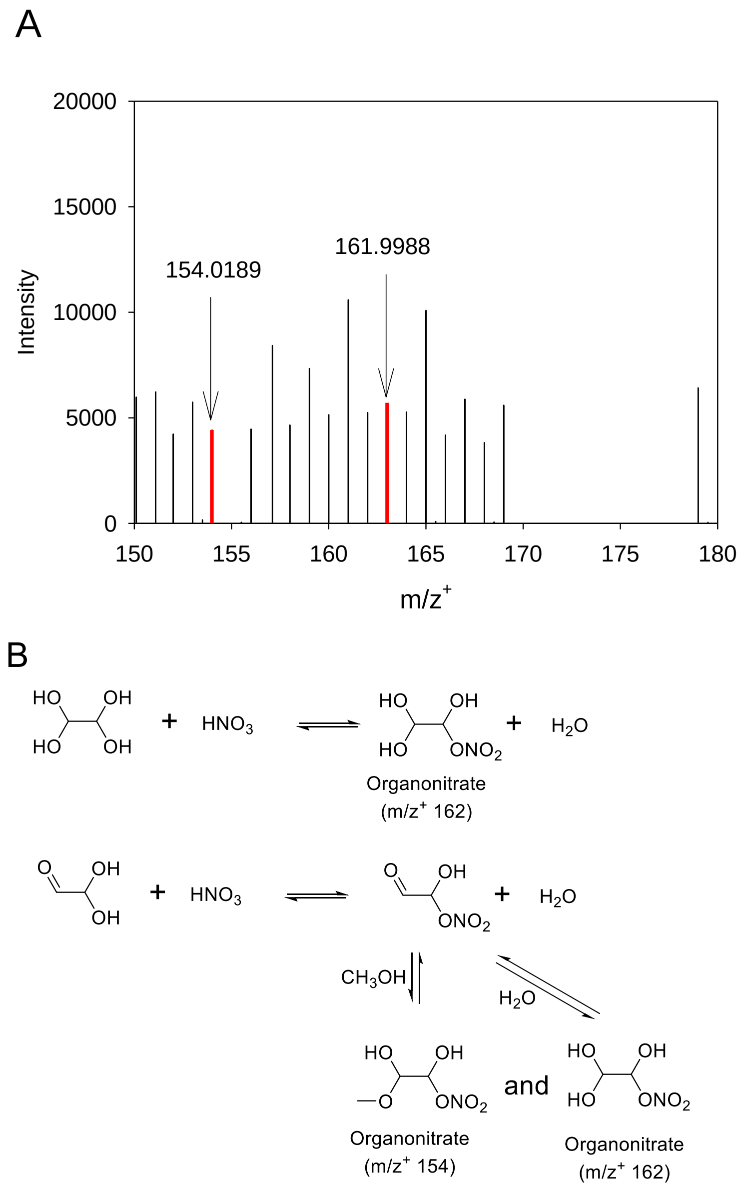

Figure 8. (A) The positive mode of HR-Q-TOF-MS after 30 minute irradiation. Organonitrates are in red (m/z^+ 154 and 162). (B) The formation of organonitrate by the reaction of the dehydrated/monohydrated glyoxal with HNO_3. In the top reaction, the dehydrated with HNO_3 forms the organonitrate (C2H5N1O6) at m/z^+ 162. In the bottom reaction, the monohydrated glyoxal with HNO_3 forms the two types of organonitrates. The organonitrate (C3H7N1O6) at m/z^+ 154 forms through the hemiacetal formation with methanol and the other organonitrate (C2H5N1O6) at m/z^+162 forms through the hydration since the eluent of the HR-Q-TOF-MS is the mixture of methanol/water (50/50).

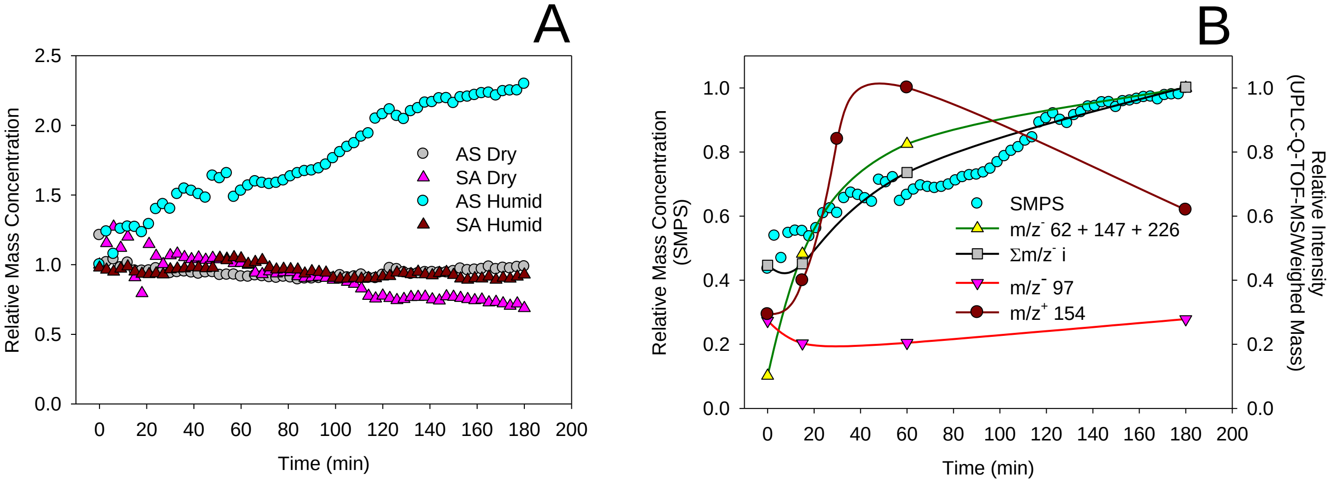

Fig. 9: (a) Relative mass concentrations of photo-aged AS aerosols in the dry chamber (AS Dry) and in the humid chamber (AS Humid), and SA aerosols in the dry chamber (SA Dry) and in the humid chamber (SA Humid). (b) The relative mass concentration from SMPS (SMPS), the relative intensity of the sum of nitrate and nitrate cluster peaks at m/z^- 62, 147, and 226 (m/z^- 62 + 147 + 226), the relative intensity of the sum of all negative ions (Σ m/z^- i) from photochemical aging of AS aerosols in the humid chamber, the relative intensity of m/z^- 97 (m/z^- 97, sulfate) and the relative intensity of m/z^+ 154 (m/z^+ 154, organonitrate) are plotted. Note that the relative mass concentrations (SMPS) were obtained by the raw mass concentrations divided by the highest raw mass concentrations (at 3 hours). Note also that the relative intensity was obtained by the raw intensity divided by the weighed mass of collected particles on the filter, then normalized except for m/z^- 97, whose lowest intensity was adjusted to 0.2.

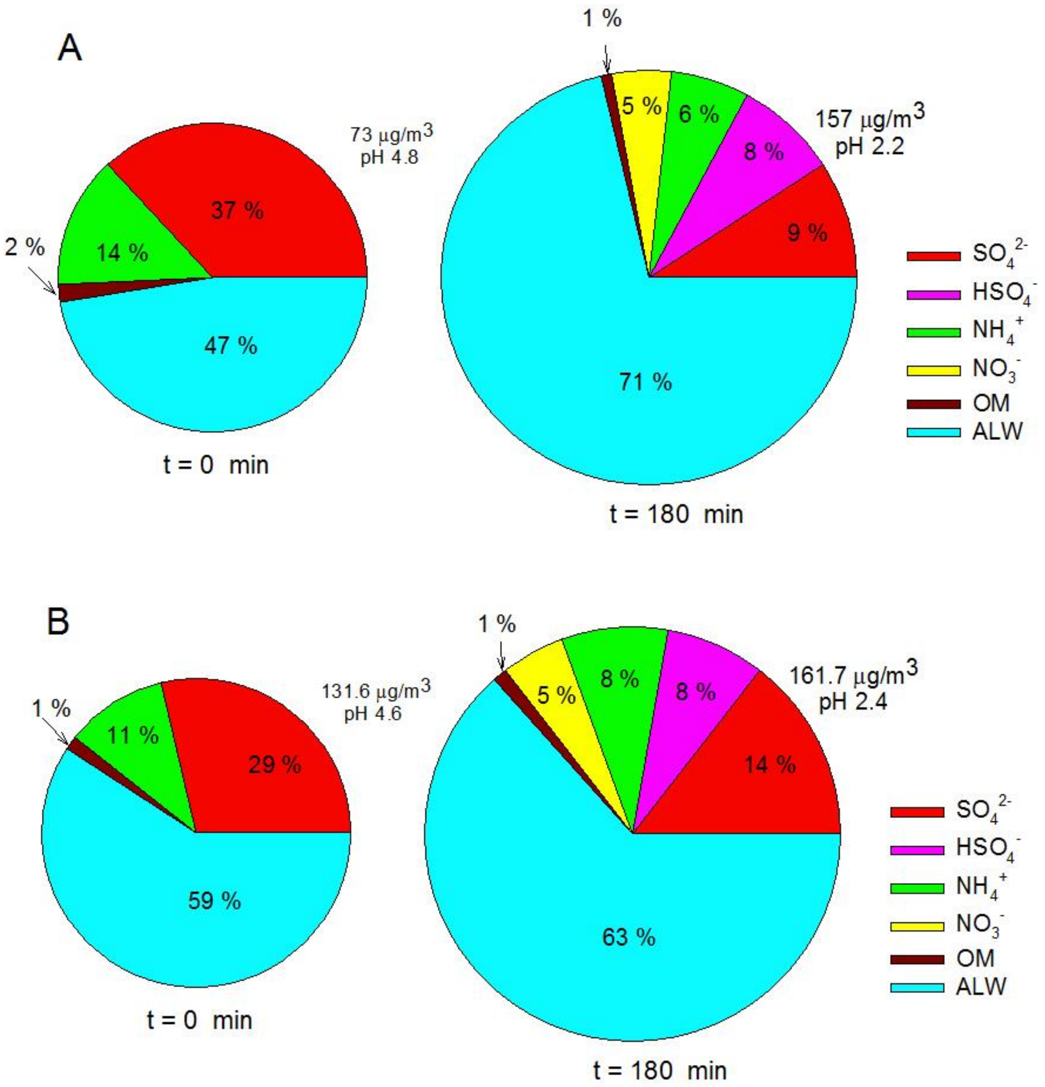

Fig. 10: Hygroscopic growth of chamber particles, particle acidification, and nitrate accumulation in particles during 3 hour photooxidation of AS aerosols in the humid chamber from Experiment #4 (A) and from Experiment #5 (B).

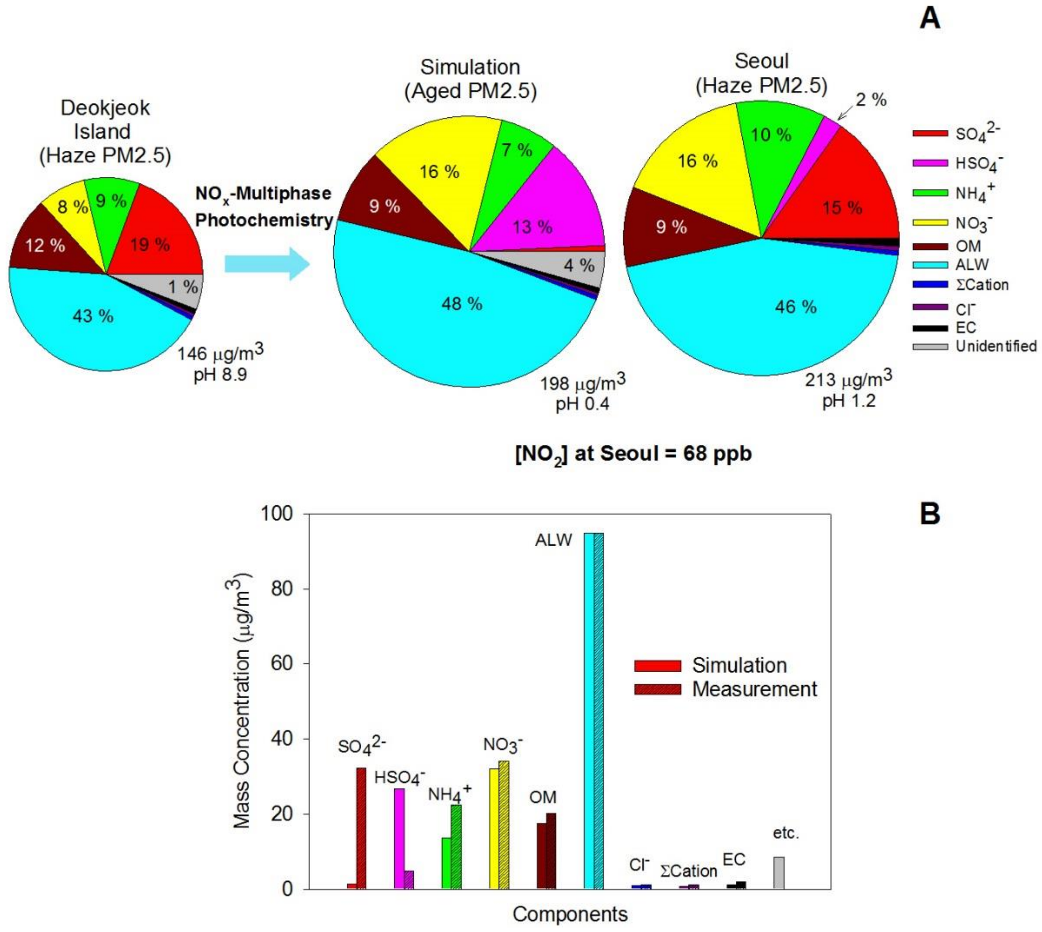

Fig. 11: PM simulation vs. PM measurement at Seoul during the multiday haze event (February 24-28, 2014). PM2.5 at Seoul has been simulated by photochemically aging PM2.5 at Deokjeok Island under the same NO_x and RH conditions as Seoul.

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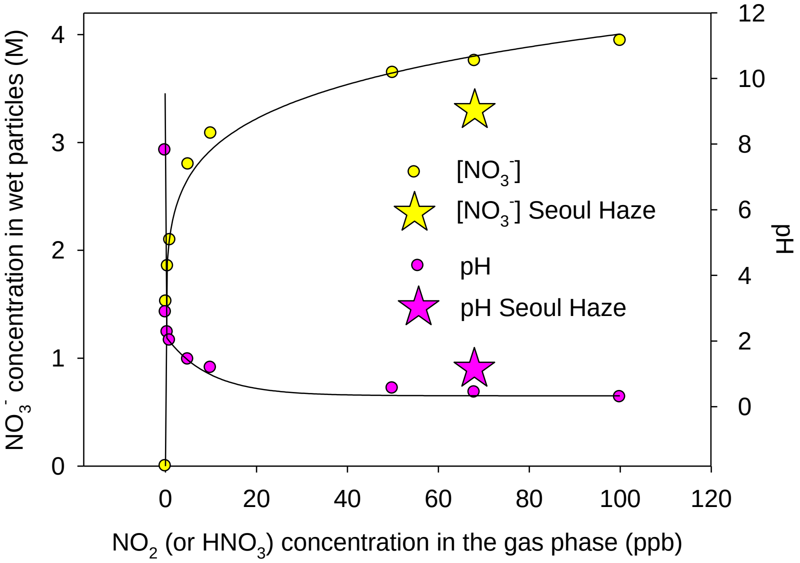

Fig. 12: Simulated plots of NO_3^- concentration (yellow) and pH (pink) vs. gaseous NO_2 (or HNO_3)