



Synergistic enhancement of urban haze by nitrate uptake into transported hygroscopic particles in the Asian continental outflow

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Received: 18 December 2019 – Discussion started: 6 February 2020

Revised: 21 May 2020 – Accepted: 3 June 2020 – Published: 30 June 2020

Abstract. Haze pollution is affected by local air pollutants, regional transport of background particles and precursors, atmospheric chemistry related to secondary aerosol formation, and meteorological conditions conducive to physical, dynamical, and chemical processes. In the large, populated and industrialized areas like the Asian continental outflow region, the combination of regional transport and local stagnation often exacerbates urban haze pollution. However, the detailed chemical processes underlying the enhancement of urban haze induced by the combined effect of local emissions and transported remote pollutants are still unclear. Here, we demonstrate an important role of transported hygroscopic particles in increasing local inorganic aerosols, by studying the chemical composition of PM_{2.5} collected between October 2012 and June 2014 in Seoul, a South Korean megacity in the Asian continental outflow region, using the ISOR-ROPIA II thermodynamic model. PM_{2.5} measured under the condition of regional transport from the upwind source areas in China was higher in mass concentration and richer in secondary inorganic aerosol (SIA) species (SO₄^{2−}, NO₃[−], and NH₄⁺) and aerosol liquid water (ALW) compared to that measured under non-transport conditions. The secondary inorganic species and ALW were both increased, particularly in cases with high PM_{2.5} levels, and this indicates inorganic species as a major driver of hygroscopicity. We conclude that the urban haze pollution in a continental outflow region like Seoul, particularly during the cold season, can be exacerbated by ALW in the transported particles, which enhances the nitrate partitioning into the particle phase in NO_x- and

NH₃-rich urban areas. This study reveals the synergistic effect of remote and local sources on urban haze pollution in the downwind region and provides insight into the nonlinearity of domestic and foreign contributions to receptor PM_{2.5} concentrations in numerical air quality models.

1 Introduction

Fine particulate matter (under 2.5 μm in diameter; PM_{2.5}) in urban areas consists of inorganic species (SO₄^{2−}, NO₃[−], and NH₄⁺) and organic matter (OM) produced by the gas-to-particle conversion of anthropogenic and biogenic precursors (Seinfeld and Pandis, 2016). These particles pose a public health problem due to their adverse effects on the human respiratory and cardiovascular systems (Pope and Dockery, 2006). Consequently, many countries have tried to mitigate urban haze pollution by reducing local precursor emissions (van der A et al., 2017; Kim and Lee, 2018). However, since air pollution is also influenced by transported air pollutants, it is difficult to achieve improved air quality in megacities located in large, populated, and industrialized areas by controlling local emissions (Seo et al., 2018). Synoptic weather conditions cause stagnation and long-range transport that can lead to the accumulation of particles and gaseous precursors from local and remote sources. It can also change local meteorological factors to favorable conditions for secondary aerosol production, such as photo-oxidation and aqueous-

phase processing (Sun et al., 2014; Zheng et al., 2015; Seo et al., 2017). Therefore, a better understanding of the combined effects of local emissions, regional transport, and meteorological conditions on urban haze pollution is required to establish appropriate mitigation strategies.

One key aerosol component that affects the formation and growth of haze particles is aerosol liquid water (ALW), which is ubiquitous and abundant in tropospheric fine particles (Nguyen et al., 2016). ALW not only increases the mass of secondary organic aerosols (SOAs) by facilitating the partitioning of gas-phase water-soluble OM into the condensed phase, followed by aqueous-phase reactions (Asa-Awuku et al., 2010; Carlton and Turpin, 2013; McNeill, 2015; Marais et al., 2016), but it also enhances the secondary inorganic aerosol (SIA) mass via nitrate formation through HNO_3 uptake and N_2O_5 hydrolysis (Zhang et al., 2015; Wang et al., 2017) and via sulfate production through the aqueous oxidation of SO_2 (Cheng et al., 2016; Wang et al., 2017). Studies of urban haze in the North China Plain reported a simultaneous elevation of the relative humidity (RH), ALW, and SIA, which indicates the hygroscopic properties of inorganic species and the role of ALW in mass transfer into the particles (Liu et al., 2017; Tie et al., 2017; Wu et al., 2018). Combined with the ambient temperature and particle pH, ALW is critical for gas–particle partitioning of inorganic and water-soluble organic acid gases (Guo et al., 2018; Nah et al., 2018). Therefore, regional transport of wet particles to the precursor-rich urban environment will affect haze pollution downwind.

The South Korean capital city of Seoul and its metropolitan area is one of the highly populated megacities in East Asia, with a population of 25 million people, 9 million vehicles, and nearly half of the national gross domestic product, and it has suffered from episodic haze events, particularly during the cold season (Seo et al., 2017, 2018). Although the Seoul metropolitan area is a large anthropogenic emission source of nitrogen oxides (NO_x), ammonia (NH_3), and volatile organic compounds (VOCs) (NIER, 2018), the effect of transported air pollutants from China cannot be ignored, because of its location downwind from the major emission source region in China like the North China Plain and Yangtze River Delta (Fig. S1 in the Supplement). In particular, severe multiday haze events in the Seoul metropolitan area mostly occur with a specific synoptic pattern, such as an eastward-moving high-pressure system, which induces regional transport of air pollutants from China and, subsequently, local stagnation (Seo et al., 2017, 2018). Therefore, the haze pollution in Seoul becomes severe primarily by the accumulation of local and transported air pollutants. However, a recent numerical modeling study on regional contribution to the particulate concentration in Seoul reported a discrepancy between responses to the reduction in domestic and foreign emissions (Kim et al., 2017), and this implies additional production and growth of local haze particles by non-

linear interactions between local emissions and transported pollutants.

In this study, we explore the combined effects of local and remote sources, ALW and particle pH, and meteorological factors on the formation and growth of urban haze particles, based on daily measurement of $\text{PM}_{2.5}$ chemical compositions in Seoul, backward trajectory analysis, and the ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007). Different chemical compositions and characteristics of Seoul haze according to the regional transport from China and the local stagnation in the Seoul metropolitan area is investigated from the perspective of inorganic partitioning and water uptake processes. An effective strategy for $\text{PM}_{2.5}$ reduction in Seoul is further discussed using ambient NO_x and NH_3 levels and analytic calculation of the HNO_3 – NO_3^- partitioning ratio as a function of ALW, pH, and temperature.

2 Data and methods

2.1 Measurements and chemical analysis

Daily $\text{PM}_{2.5}$ sampling was conducted on 210 days between October 2012 and June 2014 at the Korea Institute of Science and Technology (KIST) site in northeastern Seoul (37.603° N, 127.047° E; 58 m above sea level; Fig. S1). $\text{PM}_{2.5}$ samples for determining inorganic and carbonaceous species were collected on 47 mm Teflon filters (Pall Corporation, Port Washington, NY, USA) with a Teflon-coated aluminum cyclone (URG Corporation, Chapel Hill, NC, USA) at a flow rate of 16.7 L min^{-1} and on $203 \times 254 \text{ mm}$ quartz fiber filters (Whatman, Maidstone, UK) with a high-volume air sampler (flow rate of 1000 L min^{-1} ; Andersen Instruments, Atlanta, GA, USA), respectively.

The concentrations of inorganic ions (SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , K^+ , Ca^{2+} , Na^+ , and Mg^{2+}) were measured using a 2000i/SP ion chromatograph (Dionex, Sunnyvale, CA, USA) after sonicating the Teflon filter sample for 30 min in a mixture of 0.5 mL of ethanol and 14.5 mL of distilled deionized water. Using a piece of the quartz fiber filter sample ($10 \times 15 \text{ mm}$), the concentrations of organic carbon (OC) and elemental carbon (EC) were measured using a thermal–optical carbon aerosol analyzer (Sunset Laboratory, Tigard, OR, USA) based on National Institute for Occupational Safety and Health (NIOSH) method 5040 (Birch and Cary, 1996). We also identified 17 *n*-alkanes (C_{20} – C_{36}), 15 polycyclic aromatic hydrocarbons (PAHs; C_{14} – C_{24}), 19 monocarboxylic acids (C_6 – C_{20}), 19 dicarboxylic acids (C_3 – C_{11}), and 10 sugars (C_5 – C_6 and C_{12}) using the extract from one half of the quartz fiber filter sample and a 7890A gas chromatograph (Hewlett Packard, Palo Alto, CA, USA) coupled to a 5975C mass selective detector (Agilent, Santa Clara, CA, USA). The OM/OC ratios derived from the measured OM and OC concentrations were used to estimate the total OM concentration. The organic compounds identified

in this study constitute $\sim 5\%$ of the total OM. The analytical procedures used herein are described in detail elsewhere (Seo et al., 2017; Kim et al., 2018). In this study, out of 210 sampling days, 118 daily data that include not only inorganic species but also OM based on the identified organic compounds' information were selected and utilized (Fig. S2).

Note that the PM_{2.5} sampling on a Teflon filter for inorganic ions was conducted without either a denuder or backup filters, and thus there could be potential sampling artifacts in the results, particularly negative artifacts in semi-volatile ammonium nitrate (Ashbaugh and Eldred, 2004; Chow et al., 2005). Nie et al. (2010) reported that summertime nitrate loss on a Teflon filter from the un-denuded filter sampling without backup filters is $\sim 75\%$ at lower nitrate concentrations ($< 10 \mu\text{g m}^{-3}$) but only $\sim 10\%$ at higher nitrate concentrations ($> 10 \mu\text{g m}^{-3}$) due to the formation of particle cake. Considering small evaporative loss in the cold season and the high nitrate concentration in Seoul, we expected small to moderate sampling errors in this study. Sensitivity tests considering potential ammonium nitrate loss from the filter samples show that the assumption of 20 % nitrate loss for the high concentrations with low-temperature groups and 50 % nitrate loss for the low concentrations with moderate-temperature groups does not change our conclusion (Fig. S3).

The hourly concentrations of SO₂, NO₂, CO, O₃, and PM₁₀ at 34 air quality monitoring sites in Seoul (Fig. S1) provided by the Korea Ministry of Environment were averaged over all sites for each day to obtain representative daily concentrations of each species for Seoul (Korea Environment Corporation, 2019). The hourly meteorological data of temperature, RH, wind speed, and solar irradiance at the Seoul weather station (37.571° N, 126.966° E) managed by the Korea Meteorological Administration (KMA) were averaged for each day and used in our analysis (KMA, 2019). Boundary layer height (BLH) was derived from the European Centre for Medium-Range Weather Forecasts Reanalysis Interim (ERA-Interim) data (Dee et al., 2011; <http://apps.ecmwf.int/datasets/data/interim-full-daily/>, last access: 23 October 2019) at a grid point in Seoul (37.5° N, 127.0° E).

2.2 Categorization of measurements

To categorize the daily measurements according to (1) local atmospheric conditions (stagnation or ventilation) and (2) regional impact (transport of pollutants from upwind source area), we used the 72 h backward trajectories from 500 m above the sampling site, obtained with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model (<https://ready.arl.noaa.gov>; Stein et al., 2015) for every hour of each measurement day. We defined a local source area (Seoul metropolitan area) and two major upwind source areas in China (North China Plain and Yangtze River Delta) based on the satellite tropospheric NO₂ column density distribution (Fig. 1a) and calculated the average residence time of daily 24 trajectories in the Seoul metropolitan area (t_{SMA})

and the two source areas in China (t_{CHN}). The daily average residence time in each area shows different source characteristics such as the smaller sulfur-to-nitrogen emission ratio in Seoul (~ 0.06 ; 4.5 kt of SO_x and 71.1 kt of NO_x in 2010; NIER, 2018) compared with that of the Jing–Jin–Ji region in the North China Plain (~ 0.71 ; 2010 kt of SO₂ and 2830 kt of NO_x in 2010; Li et al., 2017). For example, t_{CHN} is highly correlated not only with particulate SO₄^{2−} and NO₃[−] concentrations but also with their precursor (SO₂ and NO₂) concentrations, while t_{SMA} has statistically significant correlation only with NO₂ concentration (Fig. S4).

Since the medians of both t_{SMA} (for all measurement days) and t_{CHN} (for the measurement days with $t_{\text{CHN}} \neq 0$ h) were ~ 6 h, we applied 6 h as a reference trajectory residence time to categorize daily measurement data into relatively stronger and weaker influences through the local stagnation in the Seoul metropolitan area (with t_{SMA}) and the regional transport from China (with t_{CHN}). The measurement days were classified into one of four groups and summarized in Table 1: (i) “local ventilation with no regional transport” (V-nT), in which the trajectories did not originate from the source areas in China and were also not stagnant in the Seoul metropolitan area ($t_{\text{SMA}} < 6$ h and $t_{\text{CHN}} = 0$ h; $n = 9$ d); (ii) “local stagnation with no regional transport” (S-nT), in which the trajectories did not originate from the source areas in China but were stagnant in the Seoul metropolitan area ($t_{\text{SMA}} \geq 6$ h and $t_{\text{CHN}} = 0$ h; $n = 15$ d); (iii) “local ventilation with regional transport” from the Chinese source area (V-T), in which the trajectories originated from the source areas in China but were not stagnant in the Seoul metropolitan area ($t_{\text{SMA}} < 6$ h and $t_{\text{CHN}} \geq 6$ h; $n = 15$ d); and (iv) “local stagnation with regional transport” from the Chinese source area (S-T), in which the trajectories originated from the source areas in China and were also stagnant in the Seoul metropolitan area ($t_{\text{SMA}} \geq 6$ h and $t_{\text{CHN}} \geq 6$ h; $n = 21$ d). The trajectory density distribution in the North China Plain and Yangtze River Delta areas were characterized for each group, with few trajectories for the no regional-transport (V-nT and S-nT) groups but relatively dense trajectories for the regional-transport (V-T and S-T) groups (Fig. 1b–d).

Despite the various potential factors like emissions, atmospheric chemistry, and meteorology that can affect the gas and particulate air quality, the simple categorization according to the residence time of backward trajectories could reveal different characteristics in chemical species and meteorological factors associated with the local stagnation and the regional transport of air pollutants. For example, the average concentrations of primary gaseous pollutants (SO₂, NO₂, and CO) of the “local stagnation with regional transport” (S-T) group are significantly higher than those of the “local stagnation with no regional transport” (S-nT) group ($p \leq 0.001$), although average local meteorological factors between the two groups do not show significant differences (Table 2 and Figs. 2 and 3). On the other hand, the lower wind speed and shallower BLH were seen in the local stagnation (S-T

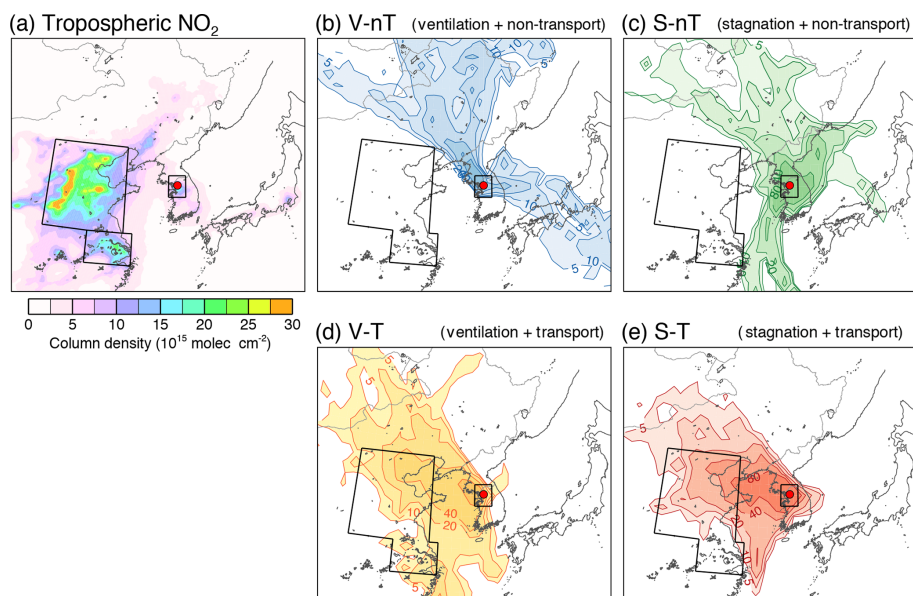


Figure 1. (a) Tropospheric NO_2 column density obtained from the Ozone Monitoring Instrument (OMI) onboard the EOS-Aura satellite, averaged for 2012–2014, and the major anthropogenic emission areas defined in this study (North China Plain, NCP: $33\text{--}41^\circ\text{N}$, $112\text{--}121^\circ\text{E}$; Yangtze River Delta, YRD: $30\text{--}33^\circ\text{N}$, $117\text{--}122^\circ\text{E}$; and Seoul metropolitan area, SMA; $36.5\text{--}38.5^\circ\text{N}$, $126\text{--}128^\circ\text{E}$). (b–e) Trajectory frequency (number of endpoints in each $1^\circ \times 1^\circ$ grid cell per number of trajectories, %) derived from the HYSPLIT 72 h backward trajectories obtained 500 m above the Korea Institute of Science and Technology (KIST) site and average chemical compositions of particulate matter under $2.5\text{ }\mu\text{m}$ in diameter ($\text{PM}_{2.5}$) for the (b) “local ventilation with no regional transport” (V-nT) group, (c) “local stagnation with no regional transport” (S-nT) group, (d) “local ventilation with regional transport” (V-T) group, and (e) “local stagnation with regional transport” (S-T) group. Seoul is marked with a solid red circle.

Table 1. List of four categorized groups of daily $\text{PM}_{2.5}$ measurements in this study.

Categories	Acronyms	Trajectory residence time in the Chinese source area (t_{CHN})	Trajectory residence time in the Seoul metropolitan area (t_{SMA})
“local ventilation with no regional transport”	V-nT	$t_{\text{CHN}} = 0\text{ h}$	$t_{\text{SMA}} < 6\text{ h}$
“local stagnation with no regional transport”	S-nT	$t_{\text{CHN}} = 0\text{ h}$	$t_{\text{SMA}} \geq 6\text{ h}$
“local ventilation with regional transport”	V-T	$t_{\text{CHN}} \geq 6\text{ h}$	$t_{\text{SMA}} < 6\text{ h}$
“local stagnation with regional transport”	S-T	$t_{\text{CHN}} \geq 6\text{ h}$	$t_{\text{SMA}} \geq 6\text{ h}$

and S-nT) groups compared with the local-ventilation (V-T and V-nT) groups (Fig. 2), and the “local stagnation with regional transport” (S-T) group shows significantly higher levels of SO_2 , NO_2 , and CO in comparison with the “local ventilation with regional transport” (V-T) group, probably related to accumulation in the stagnant condition. Note that although the present study used a part of total daily data for which OM concentrations are available ($n = 118$), composite averages and differences in meteorological variables and air pollutant concentrations among the four categorized groups using the total daily data including the OM-unavailable dates ($n = 210$) showed the same characteristics as shown in Figs. 2 and 3 (Fig. S5).

2.3 Prediction of ALW content and pH

The ISORROPIA II thermodynamic model was run in forward mode to estimate ALW content associated with inorganic species, pH, and the equilibrium gas–particle partitioning based on the daily $\text{PM}_{2.5}$ ionic compositions, RH, and temperature. ISORROPIA II uses total (gas- plus aerosol-phase) measurements as inputs, under the metastable assumption (no solid precipitates). Recent validation studies demonstrate that the forward mode is influenced less by measurement errors and gives a more accurate pH than the reverse mode, which uses only the aerosol-phase composition as an input (Hennigan et al., 2015; Song et al., 2018).

The forward mode of ISORROPIA II requires the total NH_3 (gas-phase NH_3 plus particulate NH_4^+), total HNO_3 (HNO_3 plus particulate NO_3^-), and total Cl (gas-phase HCl

Table 2. The average and standard deviation of PM_{2.5} chemical composition, meteorological factors, related gas concentrations, thermodynamic model results and gas-particle partitioning ratios, and mass concentration ratios to wet PM_{2.5} (PM_{2.5} wet) for the “local ventilation with no regional transport” (V-nT) group, the “local stagnation with no regional transport” (S-nT) group, the “local ventilation with regional transport” (V-T) group, and the “local stagnation with regional transport” (S-T) group and *p* values derived from Welch’s *t* test for the composite differences between the S-T and S-nT groups and between the S-T and V-T groups.

Components		Composite average and standard deviation				<i>p</i> values from Welch’s <i>t</i> test	
	Units	(V-nT) (<i>n</i> = 9)	(S-nT) (<i>n</i> = 15)	(V-T) (<i>n</i> = 15)	(S-T) (<i>n</i> = 21)	(S-T) minus (S-nT) (transport effect)	(S-T) minus (V-T) (stagnation effect)
Meteorological factors							
<i>T</i>	(°C)	2.6 ± 13.2	15.2 ± 11.5	9.4 ± 6.0	9.3 ± 8.5	<i>p</i> = 0.104	<i>p</i> = 0.967
RH	(%)	45.9 ± 10.0	53.5 ± 10.2	61.0 ± 9.3	51.8 ± 11.7	<i>p</i> = 0.632	<i>p</i> = 0.013
WS	(m s ^{−1})	3.5 ± 0.7	2.4 ± 0.6	3.2 ± 0.9	2.4 ± 0.7	<i>p</i> = 0.824	<i>p</i> = 0.009
SI	(W m ^{−2})	167 ± 41	172 ± 53	154 ± 64	137 ± 67	<i>p</i> = 0.094	<i>p</i> = 0.445
BLH ^a	(m)	770 ± 177	550 ± 210	666 ± 277	457 ± 165	<i>p</i> = 0.165	<i>p</i> = 0.016
Gaseous species							
SO ₂	(ppb)	4.6 ± 0.6	5.2 ± 2.0	6.6 ± 2.2	8.8 ± 2.7	<i>p</i> < 0.001	<i>p</i> = 0.012
NO ₂	(ppb)	27.4 ± 4.1	41.6 ± 11.7	41.2 ± 9.5	57.3 ± 12.5	<i>p</i> < 0.001	<i>p</i> < 0.001
CO	(ppm)	0.42 ± 0.05	0.55 ± 0.26	0.66 ± 0.28	0.89 ± 0.31	<i>p</i> = 0.001	<i>p</i> = 0.026
O ₃	(ppb)	24.6 ± 7.0	20.1 ± 11.9	23.1 ± 10.5	15.5 ± 9.0	<i>p</i> = 0.219	<i>p</i> = 0.031
NH ₃ ^b	(ppb)	4.9 ± 4.1	10.5 ± 3.0	10.2 ± 3.4	11.0 ± 4.3	<i>p</i> = 0.668	<i>p</i> = 0.499
PM _{2.5} components							
PM _{2.5} dry	(μg m ^{−3})	19.9 ± 4.8	34.4 ± 20.7	53.3 ± 33.7	72.2 ± 31.9	<i>p</i> < 0.001	<i>p</i> = 0.100
SO ₄ ^{2−}	(μg m ^{−3})	3.3 ± 0.7	5.8 ± 4.1	10.8 ± 7.6	16.7 ± 11.2	<i>p</i> < 0.001	<i>p</i> = 0.069
NO ₃ [−]	(μg m ^{−3})	1.7 ± 1.4	5.4 ± 7.3	12.1 ± 11.2	17.6 ± 12.1	<i>p</i> < 0.001	<i>p</i> = 0.166
NH ₄ ⁺	(μg m ^{−3})	1.6 ± 0.5	3.4 ± 3.6	6.9 ± 5.7	10.8 ± 6.9	<i>p</i> < 0.001	<i>p</i> = 0.075
EC	(μg m ^{−3})	1.4 ± 0.6	1.7 ± 0.6	1.6 ± 0.6	2.1 ± 0.8	<i>p</i> = 0.128	<i>p</i> = 0.036
OM	(μg m ^{−3})	10.1 ± 4.4	15.3 ± 10.1	15.0 ± 7.0	22.9 ± 8.6	<i>p</i> = 0.025	<i>p</i> = 0.005
W _i	(μg m ^{−3})	2.7 ± 1.4	7.4 ± 7.5	23.7 ± 24.9	22.2 ± 18.6	<i>p</i> = 0.003	<i>p</i> = 0.853
W _o	(μg m ^{−3})	0.9 ± 0.4	2.2 ± 1.7	3.1 ± 2.7	3.3 ± 2.3	<i>p</i> = 0.087	<i>p</i> = 0.833
Carbonaceous analysis							
O/C	(atomic ratio)	0.55 ± 0.11	0.55 ± 0.07	0.54 ± 0.04	0.55 ± 0.07	<i>p</i> = 0.883	<i>p</i> = 0.622
OM/OC	(mass ratio)	1.87 ± 0.15	1.87 ± 0.10	1.86 ± 0.05	1.87 ± 0.08	<i>p</i> = 0.927	<i>p</i> = 0.632
OC/EC	(mass ratio)	4.2 ± 1.7	4.8 ± 2.4	5.7 ± 2.5	6.2 ± 2.1	<i>p</i> = 0.071	<i>p</i> = 0.510
ISORROPIA II analysis							
Ionic strength	(<i>M</i>)	54.3 ± 16.2	42.2 ± 17.6	30.6 ± 10.3	47.1 ± 22.7	<i>p</i> = 0.470	<i>p</i> = 0.006
pH		3.1 ± 0.6	3.2 ± 0.7	3.5 ± 0.5	3.5 ± 0.7	<i>p</i> = 0.186	<i>p</i> = 0.808
Oxidation/partitioning							
SOR	(molar ratio)	0.13 ± 0.04	0.19 ± 0.07	0.25 ± 0.09	0.28 ± 0.12	<i>p</i> = 0.006	<i>p</i> = 0.439
ε(NO ₃ [−])	(molar ratio)	0.83 ± 0.28	0.67 ± 0.31	0.93 ± 0.09	0.90 ± 0.19	<i>p</i> = 0.017	<i>p</i> = 0.481
ε(NH ₄ ⁺)	(molar ratio)	0.40 ± 0.27	0.25 ± 0.14	0.43 ± 0.18	0.52 ± 0.18	<i>p</i> < 0.001	<i>p</i> = 0.150

^a Reanalysis data from the ERA-Interim at 37.5° N, 127.0° E. ^b Statistically reconstructed data based on Phan et al. (2013). *T*: temperature; RH: relative humidity; WS: wind speed; SI: solar irradiance; BLH: boundary layer height; EC: elemental carbon; OM: organic matter; W_i: aerosol liquid water (ALW) content associated with inorganic species; W_o: ALW content associated with OM; OC: organic carbon; SOR: sulfur oxidation ratio; ε(NO₃[−]): nitrate partitioning ratio; ε(NH₄⁺): ammonium partitioning ratio.

plus particulate Cl[−]) concentrations, as well as the particulate SO₄^{2−}, K⁺, Ca²⁺, Na⁺, and Mg²⁺ concentrations. However, the ambient NH₃, HNO₃, and HCl data were not available for this study. To overcome this problem with the input

data, we used statistically reconstructed NH₃ data and then estimated HNO₃ using a thermodynamic model.

Firstly, the daily NH₃ concentrations in Seoul from January 2012 to December 2014 were reconstructed using the statistical characteristics of a year-long record of NH₃ at

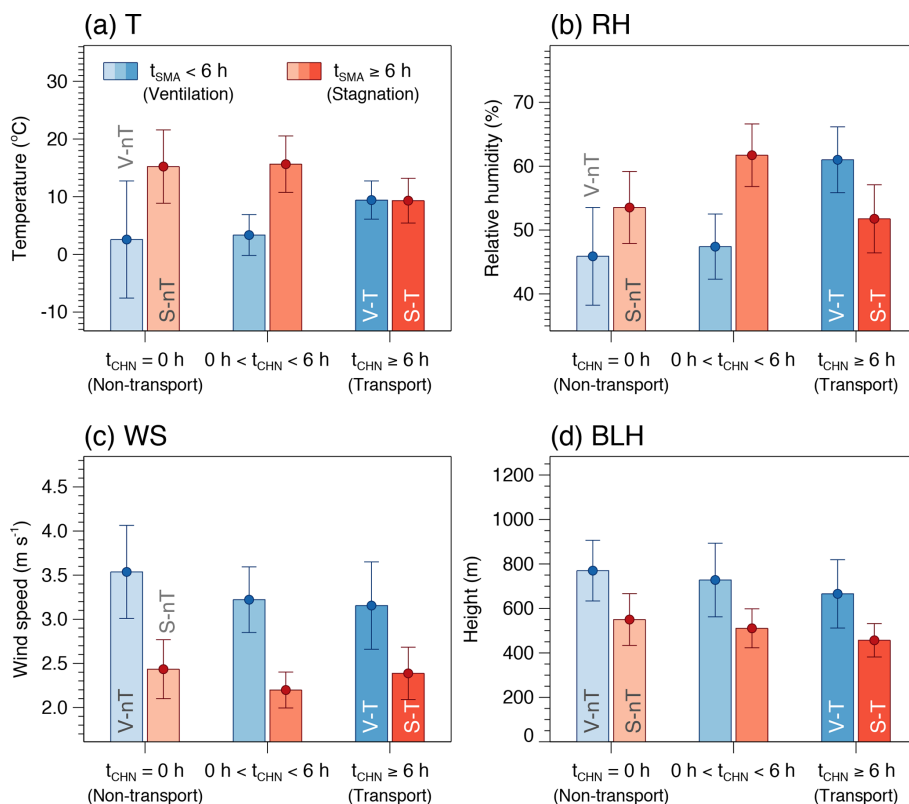


Figure 2. Averages and confidence intervals at 95 % of (a) temperature (T), (b) relative humidity (RH), (c) wind speed (WS), and (d) boundary layer height (BLH) for the six case groups categorized by the ranges of the average daily residence time of backward trajectories in the Seoul metropolitan area (t_{SMA}) and in the North China Plain and Yangtze River Delta (t_{CHN}).

the Gwangjin site (37.545° N, 127.096° E) in Seoul for the preceding year (346 d between September 2010 and August 2011; Phan et al., 2013). There were small interannual changes in the estimated NH_3 emission in Seoul (Fig. S6; NIER, 2018), and the two sites both share similar environments located downwind from the downtown core under the prevailing westerlies and surrounded by residential and small urban green areas (Fig. S1). Therefore, we assumed that the statistical characteristics of both sites and periods would be similar despite the temporal gap (~ 1 – 3 years) and spatial distance (~ 7.8 km) between this study and Phan et al. (2013). We built a multiple linear regression model of NH_3 that retains statistical characteristics of the measured NH_3 such as the annual average and standard deviation of 10.9 ± 4.25 ppb and the significant linear correlations ($p < 0.05$) with temperature, RH, wind speed, and SO_2 , NO_2 , and CO concentrations (Text S1 and Table S1 in the Supplement). The reconstructed NH_3 concentration is seasonally high during the warm season as reported by Phan et al. (2013) and shows high peaks on the polluted days with stagnant condition in the cold season (Fig. S7).

In the next step, the ISORROPIA II calculation was performed, using the reconstructed NH_3 and measured NH_4^+ as the total equivalent NH_3 , and the measured NO_3^- alone

as the total HNO_3 , to estimate the HNO_3 – NO_3^- partitioning ratio. Then, using both the measured NO_3^- and the ratio between the HNO_3 and NO_3^- predicted from the initial result, we estimated the ambient HNO_3 . Note that we regarded the $\text{HNO}_3/\text{NO}_3^-$ ratio as approximately independent of the total HNO_3 . Although the nitrate partitioning depends on temperature, ALW content, and pH in general, the $\text{HNO}_3/\text{NO}_3^-$ ratio is affected only by pH because both temperature and ALW are independent variables in this step. In the existence of excess NH_3 as we assumed for Seoul (~ 10 ppb at the first step), changes in pH by total HNO_3 are limited owing to the buffering effect of NH_3 – NH_4^+ partitioning (Weber et al., 2016; Guo et al., 2018; Lim et al., 2020). The pH, nitrate partitioning ratio [$\varepsilon(\text{NO}_3^-) = \text{NO}_3^-/(\text{HNO}_3 + \text{NO}_3^-)$], and the ammonium partitioning ratios [$\varepsilon(\text{NH}_4^+) = \text{NH}_4^+/(\text{NH}_3 + \text{NH}_4^+)$] from the ISORROPIA simulations with and without gas-phase HNO_3 information show negligible differences to each other (Fig. 4d–f), unlike the significant role of additional NH_3 information in increasing pH and $\varepsilon(\text{NO}_3^-)$ and decreasing $\varepsilon(\text{NH}_4^+)$ (Fig. 4a–c).

Finally, we repeated the ISORROPIA simulation with both total NH_3 and total HNO_3 estimated from the previous steps. Here we did not consider HCl – Cl^- partitioning because the

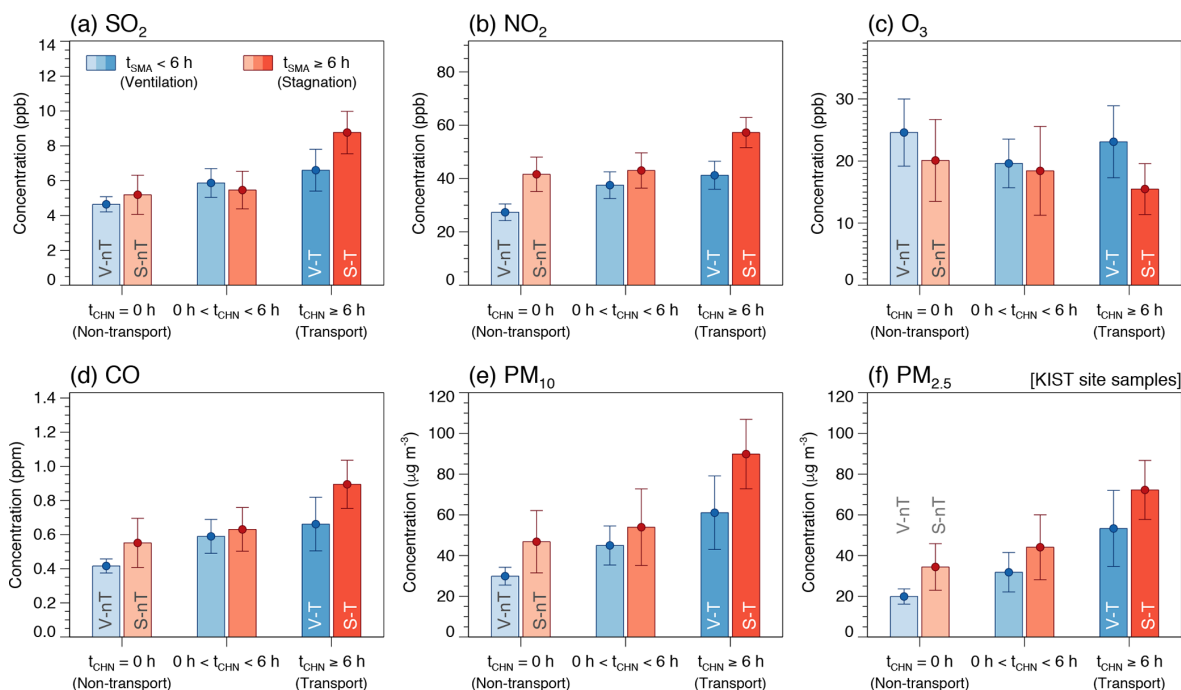


Figure 3. Averages and confidence intervals at 95 % of daily average concentrations of (a) SO_2 , (b) NO_2 , (c) O_3 , (d) CO , and (e) PM_{10} , together with (f) $\text{PM}_{2.5}$ measured at the KIST site in this study (dry $\text{PM}_{2.5}$) for the six case groups categorized by ranges of the average daily residence time of backward trajectories in the Seoul metropolitan area (t_{SMA}) and in the North China Plain and Yangtze River Delta (t_{CHN}).

Cl^- fraction in dry $\text{PM}_{2.5}$ ($\sim 1\%$ on average) is significantly smaller than the NO_3^- and NH_4^+ fractions ($\sim 18\%$ and $\sim 12\%$ on average, respectively).

Although there are uncertainties in the reconstructed NH_3 and HNO_3 due to lack of direct measurements, their impact on the estimation of inorganic ALW and particle pH is small enough to utilize them for the thermodynamic analysis in this study. The good agreement between the predicted and statistically reconstructed NH_3 concentrations ($R^2 \sim 0.95$), as well as between the predicted and measured SO_4^{2-} , NO_3^- , and NH_4^+ concentrations ($R^2 > 0.95$; Fig. S8), ensures small errors in water contents of individual inorganic species. Since water uptake by inorganic aerosol in ISORROPIA II is based on the Zdanovskii–Stokes–Robinson (ZSR) mixing rule (Stokes and Robinson, 1966), which approximates the water content of a mixture as a sum of water contents of individual salts at the same RH (Fountoukis and Nenes, 2007), the expected error in W_i induced by potential errors in NH_3 and HNO_3 would also be small. Regarding pH, the buffering effect of semi-volatile NH_3 partitioning reduces the sensitivity of pH to excess NH_3 in the NH_3 -rich conditions like Seoul (Weber et al., 2016; Guo et al., 2018; Lim et al., 2020). We conducted ISORROPIA simulations with various NH_3 levels (0–50 ppb) applied to all the measurement days as fixed values to further explore the sensitivity of pH, $\varepsilon(\text{NO}_3^-)$, and $\varepsilon(\text{NH}_4^+)$ to NH_3 . Good correlations between results from the daily varied- NH_3 simulation and the fixed- NH_3 simulations show that potential errors induced by the estimation of daily

NH_3 levels will be small if NH_3 concentrations are nonzero (Fig. 5a, c, and e). The slopes of pH, $\varepsilon(\text{NO}_3^-)$, and $\varepsilon(\text{NH}_4^+)$ curves to the increase in fixed- NH_3 level become gradually flat at over 5 ppb (Fig. 5b, d, and f), and this indicates that the potential errors in reconstructed NH_3 will not significantly change the results in this study.

Since ALW content associated with OM (W_o) is not considered in ISORROPIA II, we estimated it according to κ -Köhler theory and the ZSR mixing rule (Nguyen et al., 2015, and references therein) using the following equation:

$$W_o = V_o \kappa_{\text{org}} \frac{a_w}{1 - a_w}, \quad (1)$$

where V_o is the volume of OM ($\mu\text{m}^3 \text{cm}^{-3}$), which is obtained from OM concentration ($\mu\text{g m}^{-3}$) divided by a typical organic density of 1.4 g cm^{-3} (Turpin and Lim, 2001), κ_{org} is the hygroscopicity parameter (dimensionless) calculated from the parameterized relationship of $\kappa_{\text{org}} = (0.29 \pm 0.05) \cdot (\text{O/C})$ for the range of O/C from 0.3 to 0.6 (Chang et al., 2010), and a_w is water activity (dimensionless) that is assumed to be equivalent to RH (Nguyen et al., 2016).

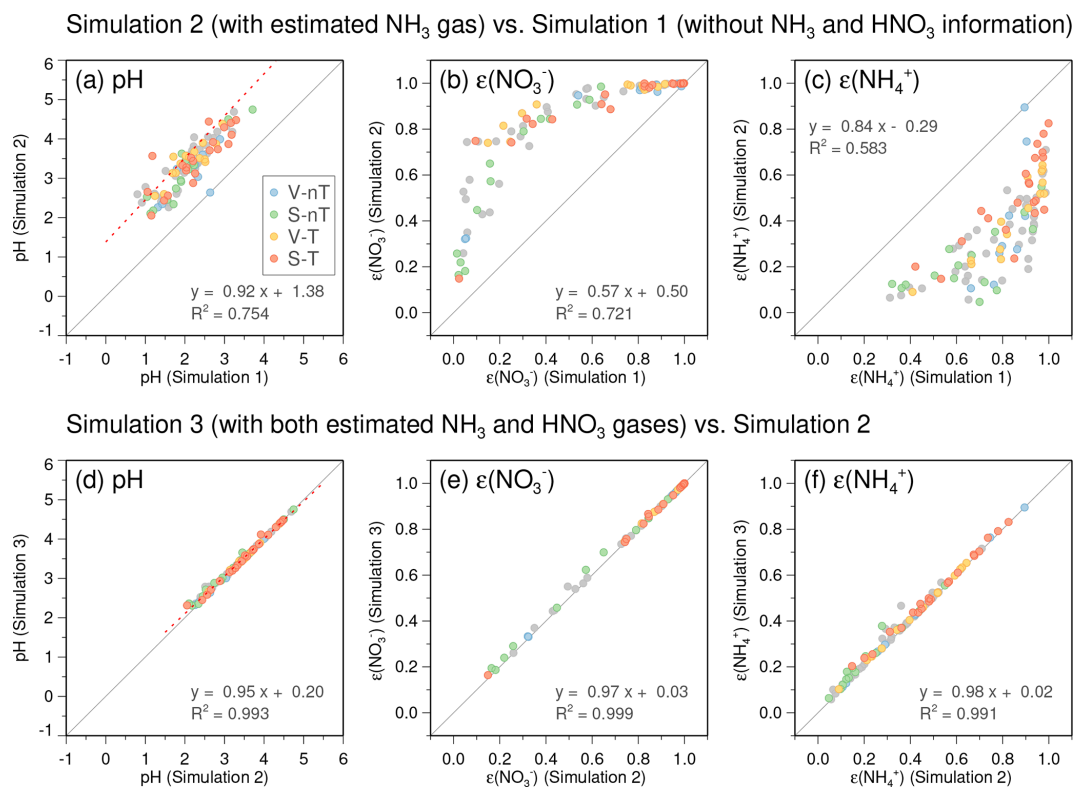


Figure 4. Comparisons of the predicted pH, nitrate partitioning ratio [$\epsilon(\text{NO}_3^-) = \text{NO}_3^- / (\text{HNO}_3 + \text{NO}_3^-)$], and ammonium partitioning ratio [$\epsilon(\text{NH}_4^+) = \text{NH}_4^+ / (\text{NH}_3 + \text{NH}_4^+)$] between (a–c) the simulation without gas-phase NH₃ and HNO₃ information (using NH₄⁺ and NO₃[−] as the total NH₃ and total HNO₃; Simulation 1) and the simulation with reconstructed NH₃ (using NH₃ + NH₄⁺ as the total NH₃ but only NO₃[−] as the total HNO₃; Simulation 2) and between (d–f) Simulation 2 and the simulation with both estimated gas-phase NH₃ and HNO₃ information (this study; Simulation 3). Filled circles in light blue, light green, light yellow, and light red colors represent daily data and belong to the “local ventilation with no regional transport” (V-nT) group, “local stagnation with no regional transport” (S-nT) group, “local ventilation with regional transport” (V-T) group, and “local stagnation with regional transport” (S-T) group, respectively. Gray solid lines indicate a 1-to-1 relationship.

3 Results and discussion

3.1 Effects of regional transport and local stagnation on PM_{2.5} composition

Average concentrations of PM_{2.5} and chemical components were highest in the “local stagnation with regional transport” (S-T) group (e.g., PM_{2.5, dry} of 72.2 μg m^{−3}) and lowest in the “local ventilation with no regional transport” (V-nT) group (e.g., PM_{2.5, dry} of 19.9 μg m^{−3}), and the average concentrations for the “local ventilation with regional transport” (V-T) group and the “local stagnation with no regional transport” (S-nT) groups (e.g., PM_{2.5, dry} of 53.3 and 34.4 μg m^{−3}, respectively) were located between those of the S-T and V-nT groups (Table 2 and Fig. 3f). The composite difference between the regional-transport (V-T and S-T) groups and no regional-transport (V-nT and S-nT) groups reveals the regional effect of transported haze particles and precursors from the North China Plain and Yangtze River Delta, while that between the local-stagnation (S-T and S-nT) groups and

local-ventilation (V-T and V-nT) groups shows the effect of accumulation or diffusion of both local and transported pollutants in the Seoul metropolitan area. Thus, the significant difference in each PM_{2.5} component between the S-T and V-nT groups (Fig. 6) indicates both contributions of local stagnant conditions over the Seoul metropolitan area and regional transport from the Chinese source area to the exacerbation of haze pollution in Seoul.

The average concentrations of gaseous precursors like SO₂ and NO₂ for the S-T group were about 2 times higher than those for the V-nT group (Fig. 3), while SO₄^{2−}, NO₃[−], NH₄⁺, and inorganic ALW increased by 5–10 times (Fig. 6). In contrast, average OM concentration for the S-T group was 2 times higher than that for the V-nT group, similarly to CO, and organic ALW of the S-T group showed a relatively smaller increase (~4 times of the V-nT group) than inorganic ALW (~8 times of the V-nT group). Therefore, the PM_{2.5} increase in Seoul seems to be induced not only by the physical and dynamical processes like transport or accumulation of air pollutants but also by the chemical process like

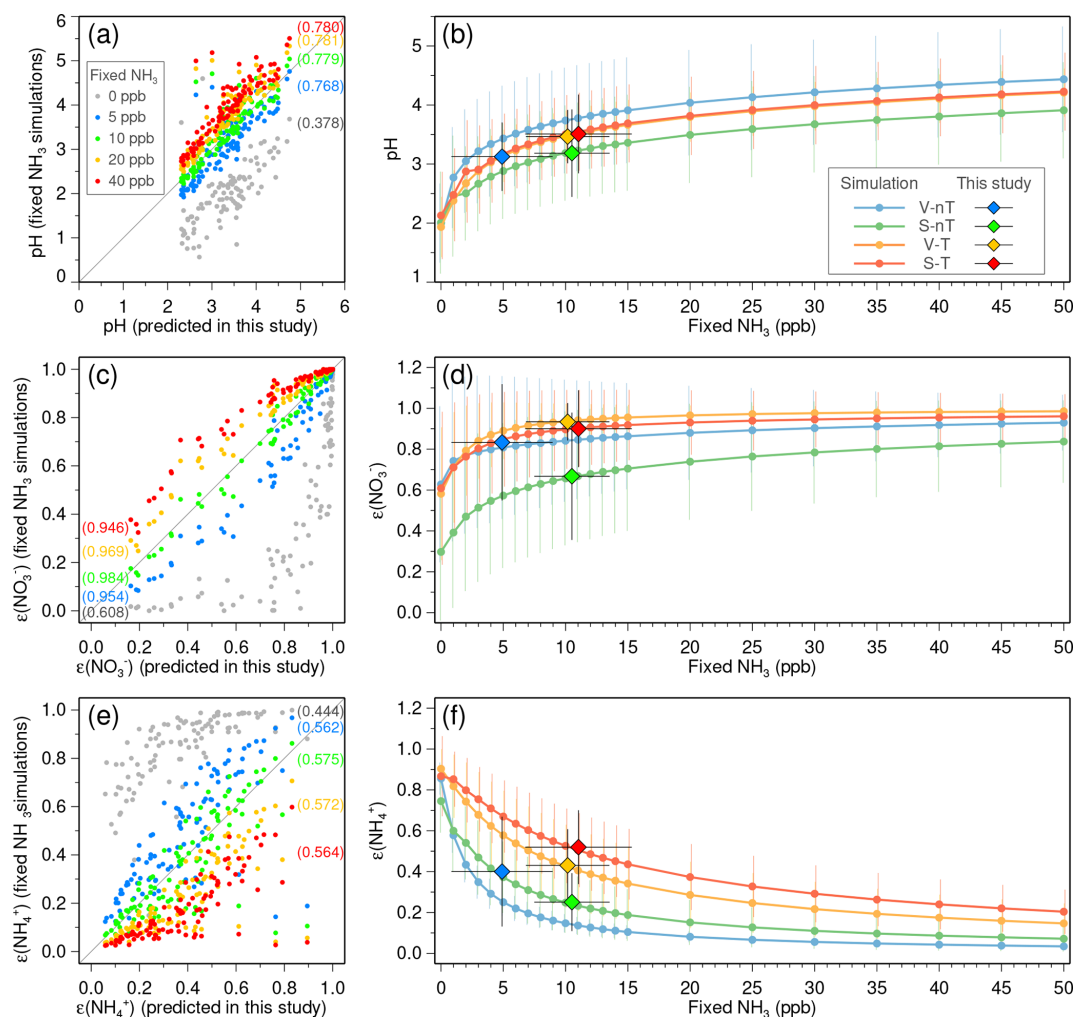


Figure 5. Sensitivity of (a–b) predicted pH, (c–d) nitrate partitioning ratio [$\epsilon(\text{NO}_3^-) = \text{NO}_3^- / (\text{HNO}_3 + \text{NO}_3^-)$], and (e–f) ammonium partitioning ratio [$\epsilon(\text{NH}_4^+) = \text{NH}_4^+ / (\text{NH}_3 + \text{NH}_4^+)$] to gas-phase ammonia (NH₃) concentrations. (a, c, e) Comparisons between the simulation in this study (using the daily reconstructed NH₃ concentrations) and the simulations with the various fixed-NH₃ levels (colored dots in gray, blue, green, yellow, and red for 0, 5, 10, 20, and 40 ppb, respectively). Values in round brackets are the R -squared values of the linear regressions. Gray solid lines indicate a 1-to-1 relationship. (b, d, f) Average (solid circles) and standard deviation (vertical bars) of pH, $\epsilon(\text{NO}_3^-)$, and $\epsilon(\text{NH}_4^+)$ for the “local ventilation with no regional transport” (V-nT) group (light blue), “local stagnation with no regional transport” (S-nT) group (light green), “local ventilation with regional transport” (V-T) group (light yellow), and “local stagnation with regional transport” (S-T) group (light red) with respect to the various fixed-NH₃ levels from 0 to 50 ppb. Averages and standard deviations of the reconstructed NH₃ concentrations and obtained pH, $\epsilon(\text{NO}_3^-)$, and $\epsilon(\text{NH}_4^+)$ for the V-nT, S-nT, V-T, and S-T groups are represented as blue, green, yellow, and red diamonds with horizontal and vertical bars.

secondary aerosol formation, particularly related to the increase in inorganic species and ALW.

A statistically significant difference ($p < 0.05$) between the S-T and S-nT groups (effect of regional transport in the local stagnant condition) was observed in SIA species (SO_4^{2-} , NO_3^- , and NH_4^+), OM, and ALW (both W_i and W_o), and that between the S-T and V-T groups (effect of local stagnation in the regional-transport condition) was seen for EC and OM (Table 2). Thus, although both regional transport and local stagnation can induce high concentrations of PM_{2.5} and its chemical components of the S-T group, the

effect of regional transport is more significant for the increase in inorganic species and water content, while the effect of local stagnation is more significant for the increase in carbonaceous species. The sulfur oxidation ratio [$\text{SOR} = \text{SO}_4^{2-} / (\text{SO}_2 + \text{SO}_4^{2-})$], nitrate partitioning ratio [$\epsilon(\text{NO}_3^-)$], and ammonium partitioning ratio [$\epsilon(\text{NH}_4^+)$] of the S-T group, which were significantly higher than that of the S-nT group ($p < 0.05$) but did not clearly differ from that of the V-T group, indicate that the increase in SIA through the regional-transport effect is closely associated with the enhanced oxi-

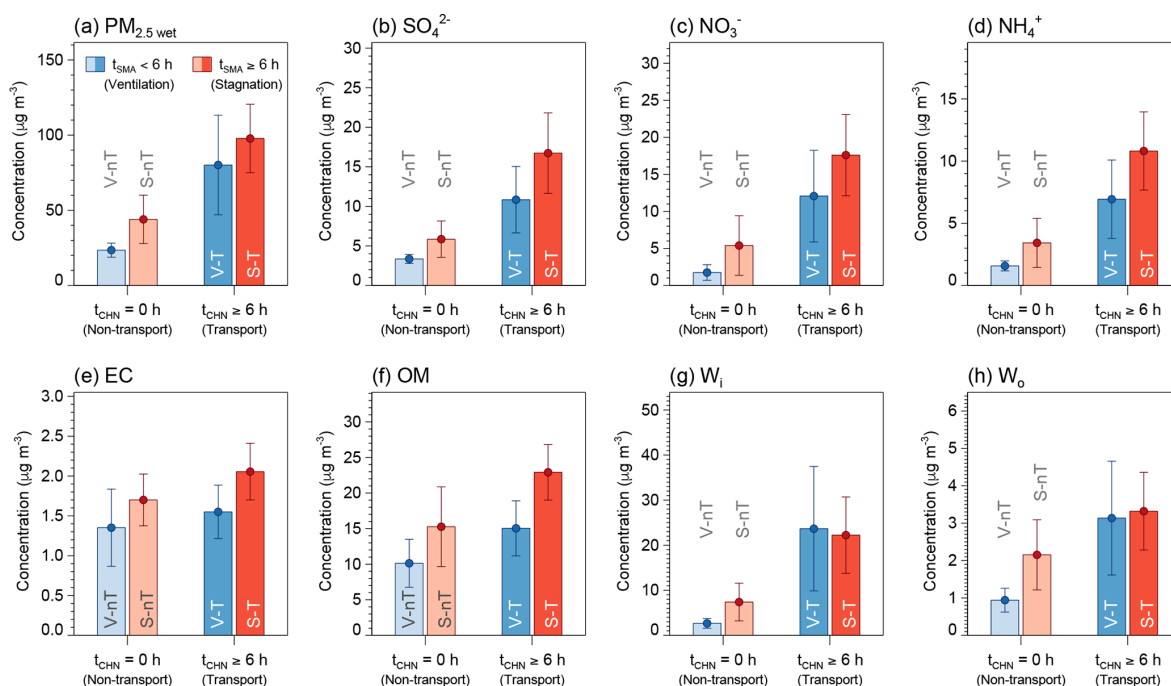


Figure 6. Average concentrations and confidence intervals at 95 % of (a) wet $\text{PM}_{2.5}$ ($\text{PM}_{2.5 \text{ wet}}$), (b) sulfate (SO_4^{2-}), (c) nitrate (NO_3^-), (d) ammonium (NH_4^+), (e) elemental carbon (EC), (f) organic matter (OM), (g) inorganic ALW (W_i), and (h) organic ALW (W_o) for the “local ventilation with no regional transport” (V-nT) group (light blue), “local stagnation with no regional transport” (S-nT) group (light red), “local ventilation with regional transport” (V-T) group (darker light blue), and “local stagnation with regional transport” (S-T) group (darker light red) categorized by ranges of the average daily residence time of backward trajectories in the Seoul metropolitan area (t_{SMA}) and in the North China Plain and Yangtze River Delta (t_{CHN}).

dation (e.g., from NO_x to HNO_3) or partitioning of inorganic species into the particle phase.

Note that OM concentration seems to be increased by both effects of regional transport and local stagnation (Table 2 and Fig. 6f). However, the average estimates of the O/C ratio (~ 0.55) and OM/OC ratio (~ 1.87), which are in between semi-volatile oxygenated OA (SV-OOA) and low-volatility oxygenated OA (LV-OOA), are similar for the four categorized groups (Table 2). Together with weak correlations of the O/C ratio with wind speed ($r = -0.093$) and BLH ($r = -0.172$) in total daily data ($n = 118$), this suggests that aging and oxidation of SOA in Seoul was not much dependent on external conditions like stagnation or transport. Rather, significant correlations of the O/C ratio with temperature ($r = -0.531$) and solar irradiance ($r = -0.370$) indicate the winter-high/summer-low seasonality of the secondary fraction in OA. Such temperature-dependent SOA fraction can be also found in OC/EC ratio ($r = -0.638$ for temperature and $r = -0.469$ for solar irradiance), which can be regarded as an index for secondary OC, and is consistent with partitioning theory (Takekawa et al., 2003).

3.2 Fractional changes of ALW and SIA by effects of regional transport and local stagnation

The chemical mass fraction of $\text{PM}_{2.5}$ is expected to be affected by source characteristics (emissions) and chemical process (secondary aerosol formation), but not by the physical and dynamical processes (transport and accumulation), which affect the mass concentration of $\text{PM}_{2.5}$. Thus, the mass fraction of each component is helpful to understand the source and chemical characteristics of each categorized group.

In terms of the component fraction, $\text{PM}_{2.5}$ of the “local stagnation with regional transport” (S-T) group can be characterized by inorganic-rich, wet particles, while that of the “local ventilation with no regional transport” (V-nT) group was relatively organic-rich and drier (Fig. 7). Estimated wet $\text{PM}_{2.5}$ (including ALW of both W_i and W_o ; $\text{PM}_{2.5 \text{ wet}}$) of the S-T group contained larger fractions of SIA species (SO_4^{2-} , NO_3^- , and NH_4^+) and ALW but a smaller OM fraction (46 % SIA, 23 % OM, and 26 % ALW) than that of the V-nT group (29 % SIA, 43 % OM, and 15 % ALW). Comparisons with the “local ventilation with regional transport” (V-T) group (37 % SIA, 19 % OM, and 33 % ALW) and the “local stagnation with no regional transport” (S-nT) group (34 % SIA, 35 % OM, and 21 % ALW) show that the effect

of regional transport increases inorganic and water fractions, while the effect of local stagnation raises organic fraction of the total $\text{PM}_{2.5 \text{ wet}}$. Note that the increase in ALW fraction from the V-nT (15 %) to V-T (33 %) groups is much larger than that from the S-nT (21 %) to S-T (26 %) groups because of the significantly higher increase in RH from the V-nT (46 %) to V-T (61 %) groups compared to that from the S-nT (54 %) to S-T (52 %) groups. The relationship between RH and ALW, as well as hygroscopic properties of Seoul haze particles, will be further discussed in the next section.

The SO_4^{2-} fraction of dry $\text{PM}_{2.5}$ (excluding W_i and W_o ; $\text{PM}_{2.5 \text{ dry}}$) was $\sim 17\%$ for the no regional-transport (V-nT and S-nT) groups and about 20 % and 23 % for the V-T and S-T groups, respectively. The SO_4^{2-} fraction in the no regional-transport groups is close to the background fraction of SO_4^{2-} in $\text{PM}_{2.5 \text{ dry}}$ in Seoul, and this fraction is comparable to the “local sulfate source” contribution of 21.7 % (mostly in the form of ammonium sulfate and equivalent to the SO_4^{2-} contribution of $\sim 16\%$) identified by the previous source apportionment study on $\text{PM}_{2.5}$ in Seoul (Kim et al., 2016). A previous field study conducted on the multi-day haze episode showed that the SO_4^{2-} concentration at the upwind background site over the Yellow Sea (Deokjeok Island; 37.233° N, 126.149° E) was nearly the same as Seoul SO_4^{2-} at the regional-transport stage of haze or the clean period and even kept $\sim 50\%$ of the Seoul SO_4^{2-} concentration at the local-stagnation stage of the haze episode (Seo et al., 2017). Thus, together with considering the small SO_2 emission in the Seoul metropolitan area compared to the North China Plain (Li et al., 2017; NIER, 2018) and the SO_2 increase through the regional-transport effect (regional-transport groups minus no regional-transport groups; $\sim 2\text{--}4$ ppb), the majority of SO_4^{2-} in the regional-transport (V-T and S-T) groups seems to be directly transported from China or produced during the transport from China before arriving at the Seoul metropolitan area.

The NO_3^- fraction of $\text{PM}_{2.5 \text{ dry}}$ was only $\sim 9\%$ for the V-nT group but increased to 16 % and 23 % for the S-nT and V-T groups and reached more than 24 % for the S-T group. Interestingly, the fractional increase through the local-stagnation effect (local-stagnation groups minus local-ventilation groups; $\sim 2\text{--}7\%$) is much smaller than that through the regional-transport effect (regional-transport groups minus no regional-transport groups; $\sim 9\text{--}14\%$) despite the same increase in NO_2 concentration (~ 15 ppb; Table 2) through two different effects. Seoul is one of the largest sources of NO_x in Korea, but the previous study using satellite NO_x column data with the Lagrangian model demonstrated that the Chinese contribution to the NO_2 columns over Korea reaches up to $\sim 50\text{--}70\%$ (Lee et al., 2014). However, the impact of regional transport on the increase in NO_3^- fraction, which is ~ 2 times higher than that of the local stagnation, indicates a nonlinear effect of regional transport on the NO_3^- increase in Seoul haze.

The NH_4^+ fraction of $\text{PM}_{2.5 \text{ dry}}$ was 8 % for the V-nT group, 10 % for the S-nT group, 13 % for the V-T group, and 15 % for the S-T group. The higher fractional increase in NH_4^+ through the regional-transport effect (T-minus nT-groups; 5 %) compared to that through the local-stagnation effect (S-minus V-groups; 2 %) results from the higher increase in both SO_4^{2-} and NO_3^- aerosols related to the regional-transport effect.

3.3 Synergistic effect of transported hygroscopic particles on SIA in the cold season

The high-concentration, inorganic-rich, and wet particles (high SIA and ALW fractions of $\text{PM}_{2.5 \text{ wet}}$) mostly belong to the regional-transport (V-T and S-T) groups, of which backward trajectories originated from the upwind regional source area (the North China Plain and Yangtze River Delta), while relatively low-concentration, organic-rich dry particles (high OM fraction of $\text{PM}_{2.5 \text{ wet}}$) belong to the “local ventilation with no regional transport” (V-nT) group (Fig. 8a and b). The ALW fraction is a function of RH and also increases with the SIA fraction at the same RH (Fig. 8c), similar to the Beijing haze (Wu et al., 2018). This indicates that Seoul haze is hygroscopic and the major driver of its hygroscopicity is inorganic species. Since the SIA fraction was relatively higher in the regional-transport groups compared to that in the no regional transport groups, the hygroscopic properties of $\text{PM}_{2.5}$ in Seoul were more clearly revealed in the regional-transport groups (Fig. 8d). Therefore, the ALW fraction in the transported particles (e.g., the regional-transport groups) was higher than that in the particles of local origin (e.g., the “local stagnation with no regional transport” (S-nT) group).

The concentrations of SO_4^{2-} , NO_3^- , and NH_4^+ increase with their gas-phase precursors (SO_2 , NO_2 , and NH_3) in Seoul, except for the V-nT group. However, the regression slopes of the SO_4^{2-} , NO_3^- , and NH_4^+ with respect to their precursors in the regional-transport groups are steeper than the slope of the S-nT group (Fig. 9). Such a higher sensitivity of the increase in SO_4^{2-} , NO_3^- , and NH_4^+ to the gas-phase precursors of the regional-transport groups is related to the higher ratios of sulfur oxidation (SOR) and partitioning [$\varepsilon(\text{NO}_3^-)$ and $\varepsilon(\text{NH}_4^+)$] compared to the S-nT group (Fig. 10b, f, and j). Since the average concentrations of total sulfur ($= \text{SO}_2 + \text{SO}_4^{2-}$), total HNO_3 , and total NH_3 are highest in the “local stagnation with regional transport” (S-T) group due to a combination of remote precursors transported from China and local precursors accumulated in the stagnant condition (Fig. 10a, e, and i), the high SOR, $\varepsilon(\text{NO}_3^-)$, and $\varepsilon(\text{NH}_4^+)$ of the regional-transport groups induced the highest average SO_4^{2-} , NO_3^- , and NH_4^+ concentrations of the S-T group (Table 2).

The SOR, $\varepsilon(\text{NO}_3^-)$, and $\varepsilon(\text{NH}_4^+)$ averaged for four range classes of temperature and inorganic ALW (W_i) show that all the ratios increased with W_i (Fig. 10d, h, and l), and $\varepsilon(\text{NO}_3^-)$ and $\varepsilon(\text{NH}_4^+)$ decreased with temperature (Fig. 10g and k).

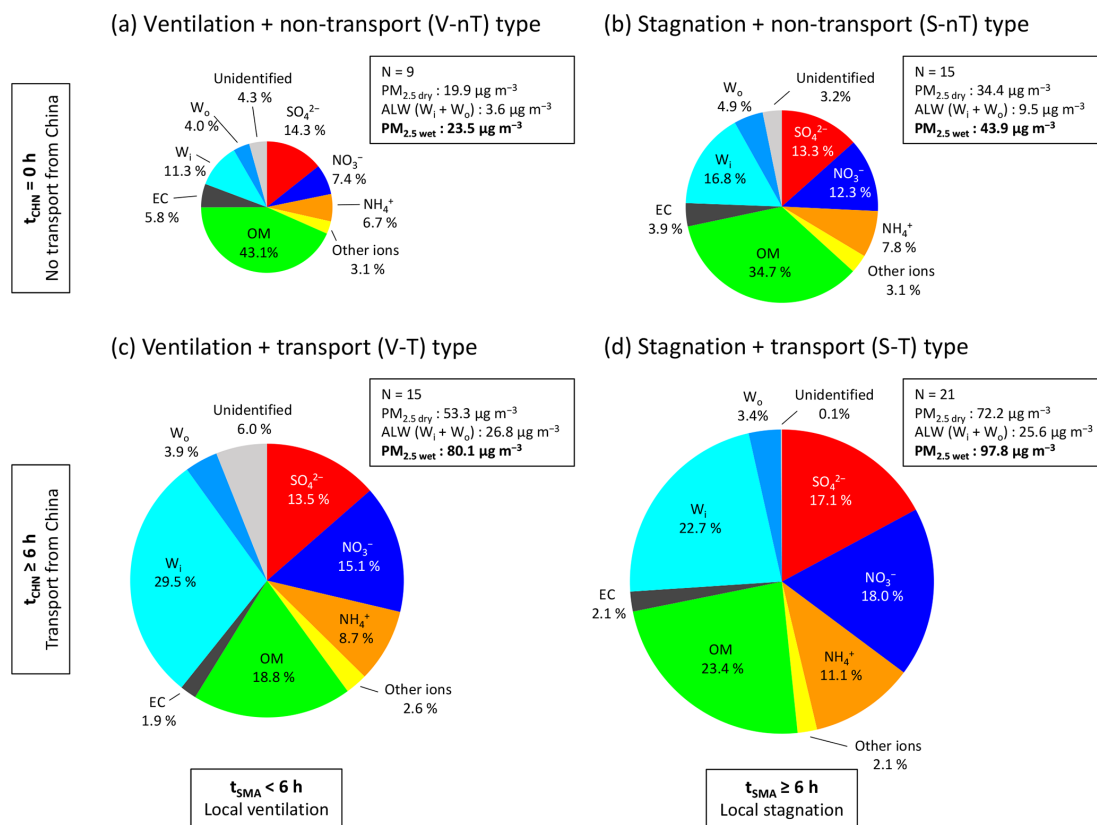


Figure 7. Average chemical compositions of wet $\text{PM}_{2.5}$ ($\text{PM}_{2.5 \text{ wet}}$) for the (a) “local ventilation with no regional transport” (V-nT) group, (b) “local stagnation with no regional transport” (S-nT) group, (c) “local ventilation with regional transport” (V-T) group, and (d) “local stagnation with regional transport” (S-T) group. Fractional species are sulfate (red), nitrate (dark blue), ammonium (orange), organic matter (green), elemental carbon (black), inorganic ALW (light blue), organic ALW (darker light blue), and other ions (chloride, sodium, potassium, magnesium, and calcium; yellow). The size of each circle is proportional to the $\text{PM}_{2.5 \text{ wet}}$ concentration.

Changes in W_i from the S-nT group ($\sim 7 \mu\text{g m}^{-3}$ on average; W_{i1}) to the regional-transport groups ($> 20 \mu\text{g m}^{-3}$ on average; W_{i3}) increase SOR, $\varepsilon(\text{NO}_3^-)$, and $\varepsilon(\text{NH}_4^+)$ by approximately up to 20 % for each ratio. This implies that the transported haze particles in the regional-transport groups, which are richer in inorganics and more hygroscopic than the local haze particles of the S-nT group (Fig. 8), promote SIA production. The aqueous-phase oxidation of SO_2 via H_2O_2 , O_3 , NO_2 , and transition metal ion (TMI) pathways (Harris et al., 2013; Cheng et al., 2016; Wang et al., 2016) and the partitioning of HNO_3 and NH_3 via dissolution and dissociation in the wet particles (Seinfeld and Pandis, 2016) are effective ways to produce SO_4^{2-} , NO_3^- , and NH_4^+ . Therefore, ALW in the hygroscopic particles can synergistically increase the inorganic species in a precursor-rich urban area like Seoul.

In terms of the synergistic increase in NO_3^- with ALW, the ratio between NO_3^- and SO_4^{2-} can be an important factor. Hygroscopic uptake of ALW by both SO_4^{2-} and NO_3^- can increase pH through a dilution effect on hydrogen ions (H^+). Because NO_3^- is a semi-volatile hygroscopic species, the higher pH increased by ALW allows more partitioning

of HNO_3 gas into the particle phase and takes up more ALW. However, if SO_4^{2-} is dominant in the particle, such a feedback process will be weakened because SO_4^{2-} is non-volatile (Guo et al., 2017). The average NO_3^- -to- SO_4^{2-} molar ratios of the regional-transport groups (1.87 for the S-T group and 1.60 for the V-T group) are higher than that of the no regional-transport groups (1.29 for the S-nT group and 0.81 for the V-nT group). Since ALW, pH, and $\varepsilon(\text{NO}_3^-)$ in the regional-transport (V-T and S-T) groups are higher than those in the no regional-transport (V-nT and S-nT) groups, this feedback process can explain the synergistic effect of transported particles on the high NO_3^- and ALW fractions.

Note that the partitioning of HNO_3 and NH_3 is also dependent on temperature (T) (Fig. 10g and k). Changes in T from the S-nT group ($\sim 15^\circ\text{C}$ on average; T_3) to the regional-transport groups ($\sim 9^\circ\text{C}$ on average; T_2) can also increase $\varepsilon(\text{NO}_3^-)$ and $\varepsilon(\text{NH}_4^+)$ by approximately 20 % for each, similar to the effect of inorganic ALW. In Korea, the regional transport of air pollutants from the NCP area is usually accompanied by westerly or northwesterly continental outflow, which induces cold advection, during the cold season

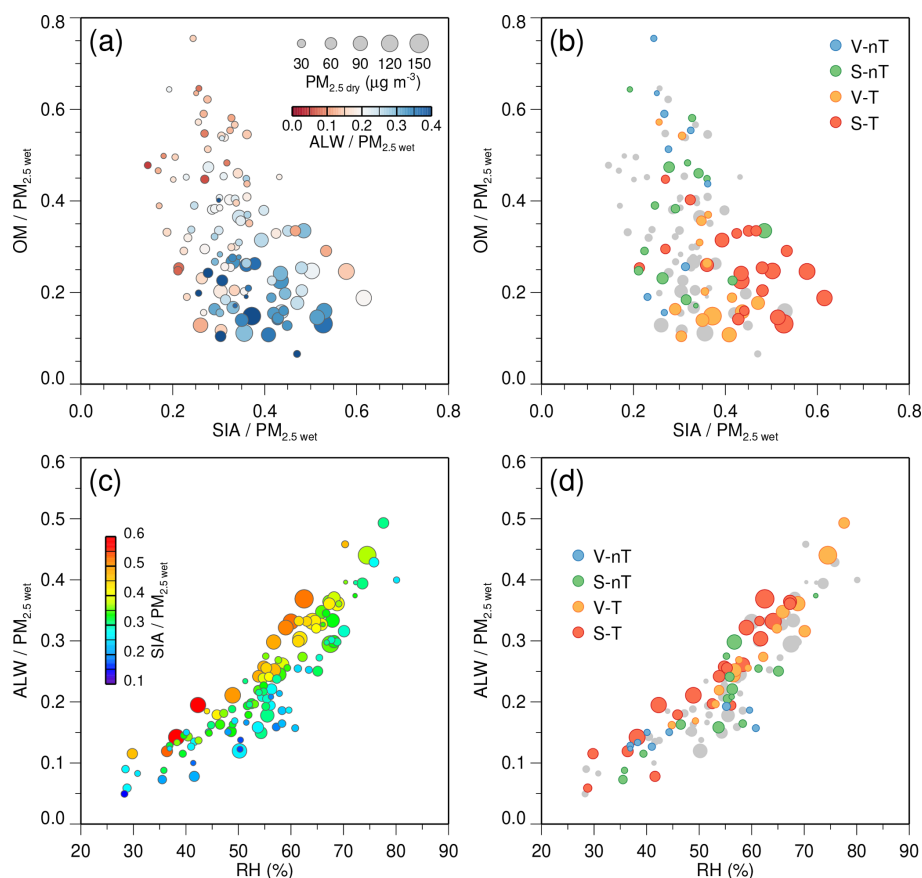


Figure 8. (a–b) Scatterplots of the secondary inorganic aerosol (SIA) fraction to wet $\text{PM}_{2.5}$ ($\text{SIA}/\text{PM}_{2.5 \text{ wet}}$) ratio versus the organic matter (OM) fraction to wet $\text{PM}_{2.5}$ ($\text{OM}/\text{PM}_{2.5 \text{ wet}}$) ratio, colored according to (a) the aerosol liquid water (ALW) to wet $\text{PM}_{2.5}$ ($\text{ALW}/\text{PM}_{2.5 \text{ wet}}$) ratio and (b) the categories for each case. (c–d) Scatterplots of $\text{ALW}/\text{PM}_{2.5 \text{ wet}}$ versus relative humidity (RH), colored according to (c) $\text{SIA}/\text{PM}_{2.5 \text{ wet}}$ ratio and (d) the categories. The size of each circle is proportional to the dry $\text{PM}_{2.5}$ ($\text{PM}_{2.5 \text{ dry}}$) concentration.

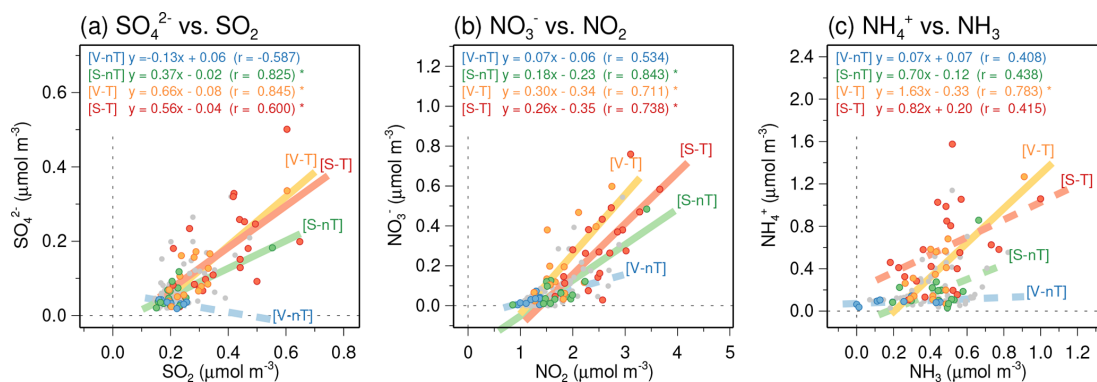


Figure 9. Scatterplots of (a) SO_4^{2-} versus SO_2 , (b) NO_3^- versus NO_2 , and (c) NH_4^+ versus the reconstructed ammonia (NH_3). Filled circles in blue, green, yellow, and red colors represent daily data belonging to the “local ventilation with no regional transport” (V-nT) group, “local stagnation with no regional transport” (S-nT) group, “local ventilation with regional transport” (V-T) group, and “local stagnation with regional transport” (S-T) group, respectively. The statistically significant linear regression slopes ($p < 0.01$) for each group are represented by solid lines.

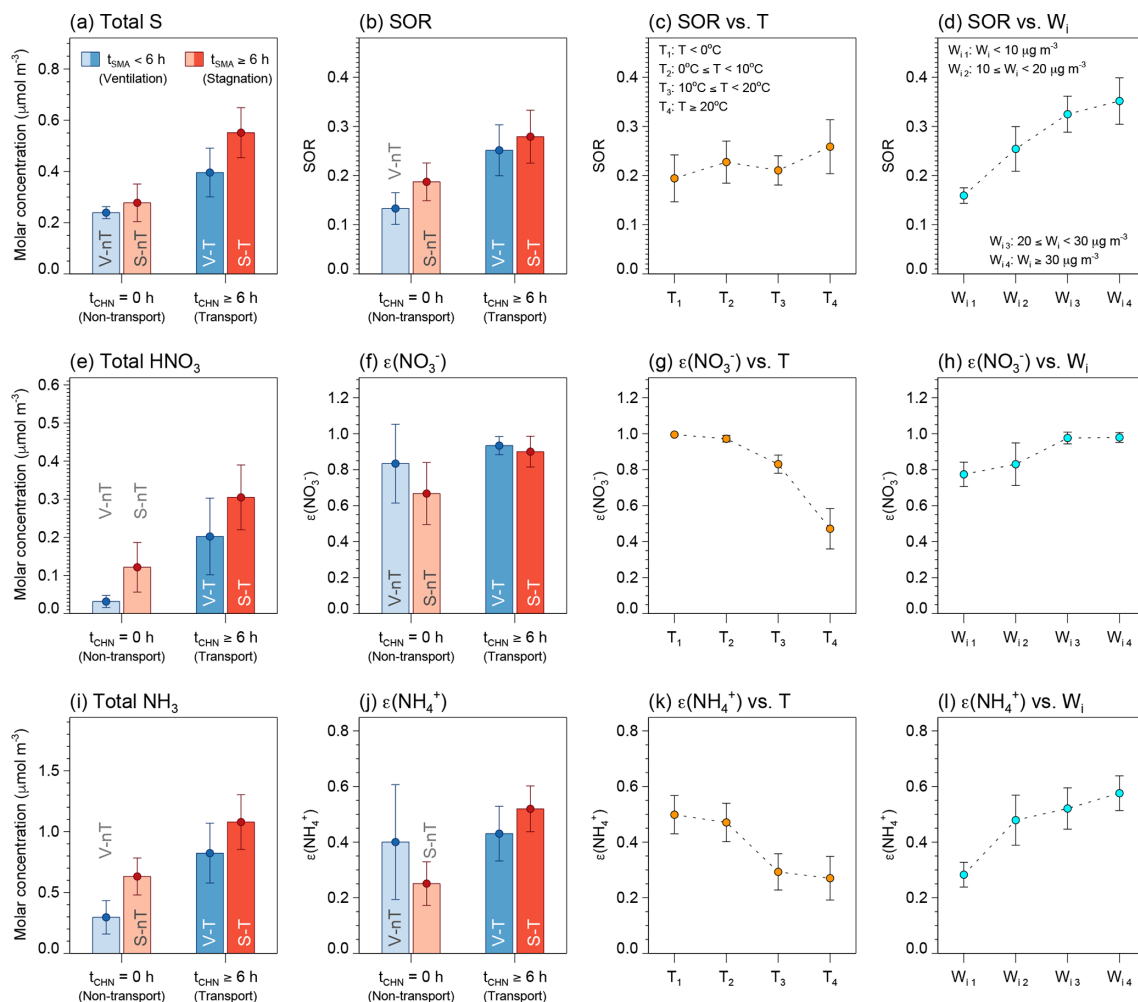


Figure 10. Average concentrations and confidence intervals at 95 % of (a) total sulfur ($= \text{SO}_2 + \text{SO}_4^{2-}$), (b–d) sulfur oxidation ratio (SOR), (e) total HNO_3 ($= \text{HNO}_3 + \text{NO}_3^-$), (f–h) nitrate partitioning ratio [$\varepsilon(\text{NO}_3^-)$], (i) total NH_3 ($= \text{NH}_3 + \text{NH}_4^+$), and (j–l) ammonium partitioning ratio [$\varepsilon(\text{NH}_4^+)$]. (a–b, e–f, i–j) Average for the “local ventilation with no regional transport” (V-nT) group (light blue), “local stagnation with no regional transport” (S-nT) group (light red), “local ventilation with regional transport” (V-T) group (darker light blue), and “local stagnation with regional transport” (S-T) group (darker light red). (c, g, k) Average for the temperature (T) ranges of $T < 0^\circ\text{C}$ (T_1 ; $n = 19$), $0^\circ\text{C} \leq T < 10^\circ\text{C}$ (T_2 ; $n = 31$), $10^\circ\text{C} \leq T < 20^\circ\text{C}$ (T_3 ; $n = 30$), and $T \geq 20^\circ\text{C}$ (T_4 ; $n = 19$). (d, h, l) Average for the inorganic ALW (W_i) ranges of $W_i < 10 \mu\text{g m}^{-3}$ (W_{i1} ; $n = 58$), $10 \mu\text{g m}^{-3} \leq W_i < 20 \mu\text{g m}^{-3}$ (W_{i2} ; $n = 14$), $20 \mu\text{g m}^{-3} \leq W_i < 30 \mu\text{g m}^{-3}$ (W_{i3} ; $n = 12$), and $W_i \geq 30 \mu\text{g m}^{-3}$ (W_{i4} ; $n = 15$).

(Kim et al., 2018). The lower temperature of the S-T group ($\sim 9^\circ\text{C}$) compared to the S-nT group ($\sim 15^\circ\text{C}$) could lead to the higher sensitivity of the SIA increase to the precursor concentrations in the S-T group (Fig. 9). Interestingly, the increasing SOR through temperature (and also irradiance) is not as significant as that through inorganic ALW (Figs. 10c) despite the high-temperature and strong-irradiance conditions conducive to photochemical oxidation of SO_2 in summer. This implies that the observed high SO_4^{2-} in the S-T group resulted not only from the photochemical gas-phase oxidation but also considerably from the aqueous-phase oxidation of SO_2 in the transported wet particles.

3.4 Effect of NO_x and NH_3 control on mitigating haze pollution in Seoul

The $\varepsilon(\text{NO}_3^-)$ can be analytically calculated according to the solubility and dissociation of gas-phase HNO_3 and represented as a sigmoid function (S curve) of pH (Guo et al., 2018; Nah et al., 2018) by the following equation:

$$\varepsilon(\text{NO}_3^-) = \frac{H_{\text{HNO}_3}^* W_i RT (0.987 \times 10^{-14})}{\gamma_{\text{H}^+} \gamma_{\text{NO}_3^-} 10^{-\text{pH}} + H_{\text{HNO}_3}^* W_i RT (0.987 \times 10^{-14})}, \quad (2)$$

where 0.987×10^{-14} is the unit conversion factor from atmospheric pressure and micrograms to SI units, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), W_i ($\mu\text{g m}^{-3}$) is the ALW content associated with inorganic species, and $H_{\text{HNO}_3^*}$ is the effective Henry's law constant (products of Henry's law constant for HNO_3 gases and the acid dissociation constant for $\text{HNO}_3 \leftrightarrow \text{NO}_3^- + \text{H}^+$) dependent on temperature and pH ($\text{mol}^2 \text{ kg}^{-2} \text{ atm}^{-1}$ on a molality basis; Clegg et al., 1998). The product of activity coefficients, $\gamma_{\text{H}} \gamma_{\text{NO}_3^-}$, is dependent on both temperature and ionic strength (Kusik and Meissner, 1978; Kim et al., 1993). In this study, daily $\gamma_{\text{H}} \gamma_{\text{NO}_3^-}$ was obtained based on daily average ambient temperature and ionic strength from ISORROPIA II and ranged from 0.135 to 0.734, with an average of 0.333 ± 0.150 .

The S curve of $\varepsilon(\text{NO}_3^-)$ as a function of pH is useful for examining the role of inorganic ALW and temperature in HNO_3 – NO_3^- partitioning and provides insights into the potential HNO_3 partitioning by a change in particle pH. In Fig. 11, both a decrease in temperature and an increase in ALW can shift the $\varepsilon(\text{NO}_3^-)$ curves toward a lower pH, so more HNO_3 can exist in the particle phase. Almost 100 % of the total HNO_3 exists in the particle phase at the higher pH (> 4) in Seoul. Since the gas-phase HNO_3 largely formed by the reaction of NO_2 with hydroxyl radicals (OH) is highly water-soluble (Seinfeld and Pandis, 2016), the transported wet particles (the regional-transport (V-T and S-T) groups) can easily take up HNO_3 gas into the aerosol solution in the NO_x -rich (~ 60 ppb) environment of Seoul (Vellingiri et al., 2015), particularly during the cold season. Note that ALW can additionally enhance the nitrate radical (NO_3)– N_2O_5 pathway and heterogeneous N_2O_5 hydrolysis (Bertram et al., 2009). In addition, the high NH_3 level (~ 10 ppb) in Seoul (Phan et al., 2013) helps further to increase the uptake of HNO_3 gas into the aerosol solution (Guo et al., 2018).

To reduce ammonium nitrate aerosols in Seoul, therefore, two ways can be suggested; the NO_x control and the NH_3 control. As shown in Fig. 9b, the observed NO_3^- concentration is highly correlated with the NO_2 level, and this implies that the NO_x control will be an effective way to reduce total HNO_3 and NO_3^- concentrations. Such a direct relationship between NO_x control and nitrate aerosol is significant at the condition of $\varepsilon(\text{NO}_3^-)$ close to 1. Because of the higher $\varepsilon(\text{NO}_3^-)$ of the transported wet particles, the NO_x reduction will more effectively reduce NO_3^- in the regional-transport groups compared to the “local stagnation with no regional transport” (S-nT) group. For example, the potential NO_3^- reduction by a 10 ppb decrease in ambient NO_2 concentration deduced from the linear regression in Fig. 9b can be estimated as being $\sim 8 \mu\text{g m}^{-3}$ for the “local ventilation with regional transport” (V-T) group, $\sim 7 \mu\text{g m}^{-3}$ for the “local stagnation with regional transport” (S-T) group, and $\sim 5 \mu\text{g m}^{-3}$ for the “local stagnation with no regional transport” (S-nT) group. On the other hand, the NH_3 control to achieve the low $\varepsilon(\text{NO}_3^-)$ by lowering the particle pH from the current level

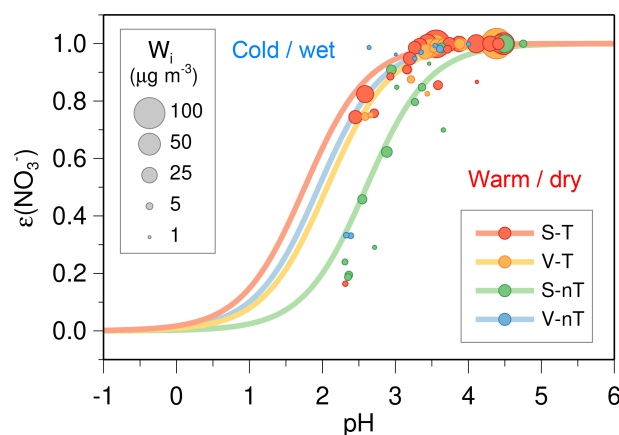


Figure 11. The calculated sigmoid curves (S curves) and observed ambient gas-particle partitioning ratios (solid circles) for nitrate [$\varepsilon(\text{NO}_3^-)$] plotted against the ISORROPIA-predicted particle pH. The blue, green, yellow, and red circles represent the “local ventilation with no regional transport” (V-nT) group, “local stagnation with no regional transport” (S-nT) group, “local ventilation with regional transport” (V-T) group, and “local stagnation with regional transport” (S-T) group, respectively, and the size of each circle is proportional to the concentration of inorganic ALW (W_i). The curves were calculated based on the median values of temperature (T), W_i , and the product of activity coefficient ($\gamma_{\text{H}} \gamma_{\text{NO}_3^-}$) for each group; $T = 0.6^\circ \text{C}$, $W_i = 2.2 \mu\text{g m}^{-3}$, and $\gamma_{\text{H}} \gamma_{\text{NO}_3^-} = 0.146$ for the V-nT group; $T = 17.5^\circ \text{C}$, $W_i = 5.6 \mu\text{g m}^{-3}$, and $\gamma_{\text{H}} \gamma_{\text{NO}_3^-} = 0.295$ for the S-nT group; $T = 11.6^\circ \text{C}$, $W_i = 16.6 \mu\text{g m}^{-3}$, and $\gamma_{\text{H}} \gamma_{\text{NO}_3^-} = 0.458$ for the V-T group; $T = 6.9^\circ \text{C}$, $W_i = 18.0 \mu\text{g m}^{-3}$, and $\gamma_{\text{H}} \gamma_{\text{NO}_3^-} = 0.400$ for the S-T group.

(pH of ~ 3.5 on average) for the S-T group may cost more than that for the S-nT group because the $\varepsilon(\text{NO}_3^-)$ in the S-nT group (green circles) starts to decrease rapidly at $\text{pH} < 3.5$, while that in the regional-transport groups (yellow circles for the V-T group and red circles for the S-T group) remains relatively high ($\sim 80\%$) at the lower pH (~ 2.5) (Fig. 11). Since the haze pollution in Seoul usually becomes severe with the regional transport of hygroscopic wet particles (e.g., the S-T group), a greater reduction in the NH_3 emissions should be required for the higher-concentration S-T group compared to the lower-concentration S-nT group. However, the benefit of reducing $\text{PM}_{2.5}$ mass concentration by an NH_3 control can be canceled out by the adverse effects of strong particle acidity on human health (Fang et al., 2017).

4 Conclusions

Based on $\text{PM}_{2.5}$ chemical speciation, gaseous pollutants, and meteorological data in Seoul together with backward trajectory analysis, the present study investigated chemical compositions and characteristics of urban haze particles in the

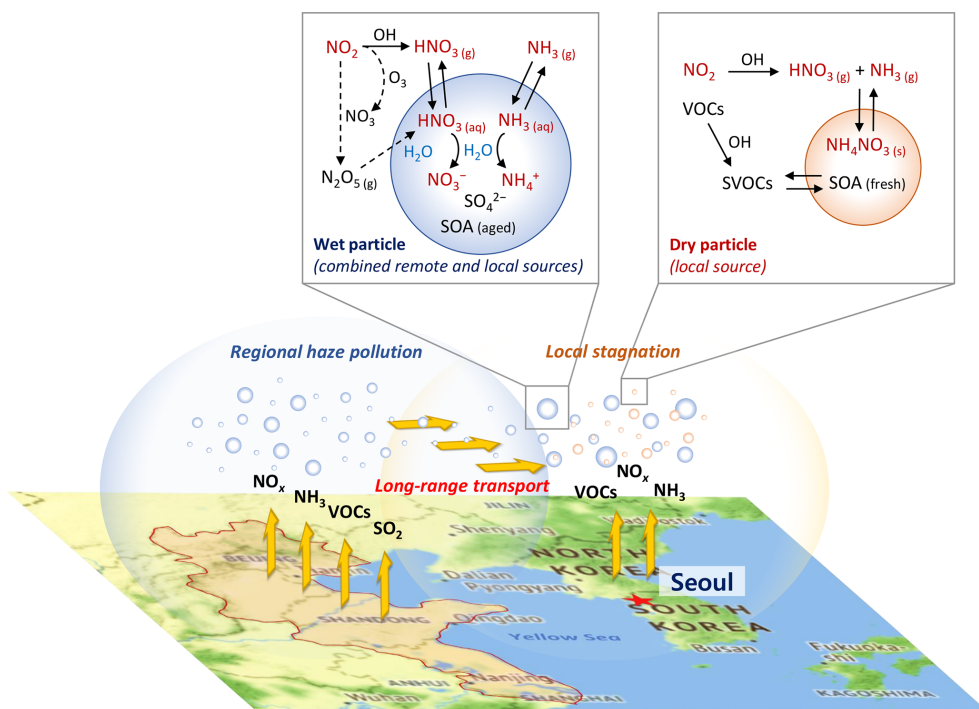


Figure 12. Schematic of synergistic nitrate partitioning to the particle phase aided by wet particles transported from the remote source area (North China Plain and Yangtze River Delta) in a high NO_x and NH_3 urban area (Seoul metropolitan area) during the cold season in East Asia. The background map was derived from © Google Maps.

Asian continental outflow region, according to physical and dynamical conditions such as local stagnant condition in the urban area and regional transport of air pollutants from the remote source area. Although various factors like local emissions of primary pollutants and secondary precursors, atmospheric chemistry related to the secondary formation and aging of aerosols, and meteorological conditions can affect the urban haze pollution, a simple categorization by average residence times of backward trajectories within the local (Seoul metropolitan area) and remote (North China Plain and Yangtze River Delta) source areas showed clearly distinguishable characteristics in concentration and fractional composition of $\text{PM}_{2.5}$ among the local-stagnation/ventilation groups and the regional-transport/non-transport groups. In particular, ALW content associated with inorganic species and particle pH estimated by the ISORROPIA II thermodynamic model helped to show different hygroscopic and inorganic partitioning properties of Seoul haze by the categorized groups.

The measurement group of “local stagnation with regional transport” (S-T) from China is characterized by higher $\text{PM}_{2.5}$ concentration ($72 \pm 32 \mu\text{g m}^{-3}$ of $\text{PM}_{2.5}$ dry) and more inorganic-rich and wetter particles (46 % SIA, 23 % OM, and 26 % ALW in $\text{PM}_{2.5}$ wet) in comparison to the measurement group of “local ventilation with no regional transport” (V-nT; $20 \pm 5 \mu\text{g m}^{-3}$ of $\text{PM}_{2.5}$ dry and 29 % SIA, 43 % OM, and 15 % ALW in $\text{PM}_{2.5}$ wet). An increase in SIA from the “local

ventilation with no regional transport” (V-nT) group to the “local stagnation with regional transport” (S-T) group (~ 7 times from ~ 7 to $45 \mu\text{g m}^{-3}$) is larger than the OM increase (~ 2 times from 10 to $23 \mu\text{g m}^{-3}$) but relates closely to the increase in inorganic ALW (~ 7 times from ~ 3 to $22 \mu\text{g m}^{-3}$), indicating inorganic species as a major driver of hygroscopicity. The larger increase in SIA species (SO_4^{2-} from ~ 3 to $17 \mu\text{g m}^{-3}$ and NO_3^- from ~ 2 to $18 \mu\text{g m}^{-3}$) compared to the increase in gaseous precursors (SO_2 from 5 to 9 ppb and NO_2 from 27 to 57 ppb) suggests that there is not only the accumulation of local and transported particles but also additional chemical processes for the SIA production in the combination of regional transport and local stagnant conditions.

Further comparisons with the “local stagnation with no regional transport” (S-nT) group and the “local ventilation with regional transport” (V-T) group shows the stronger influence of regional transport rather than local stagnation on the high oxidation and partitioning ratios (SOR, $\varepsilon(\text{NO}_3^-)$, and $\varepsilon(\text{NH}_4^+)$) associated with the SIA increase. SOR, $\varepsilon(\text{NO}_3^-)$, and $\varepsilon(\text{NH}_4^+)$ were raised up to ~ 20 % by the increase in inorganic ALW in the Seoul haze condition, and this demonstrates an important role of ALW of the transported hygroscopic particles in increasing the SIA fraction. In addition, $\varepsilon(\text{NO}_3^-)$ and $\varepsilon(\text{NH}_4^+)$ are decreased through temperature, and thus the transported wet particles can efficiently convert the gas-phase HNO_3 and NH_3 into the particle-phase NO_3^- and NH_4^+ during the cold season. Therefore, the synergistic ef-

fect of transported wet particles and local precursors on the SIA increase and high PM_{2.5} concentration in Seoul can be most prominent in the cold season, when the continental outflow dominates East Asia and helps transboundary transport of air pollutants to Korea. Since SO₂ emissions in Seoul are small, the increased SO₄^{2−} in the regional-transport condition is likely to be transported from the remote source areas in China or produced during the transport. On the other hand, the high-NO_x (~ 60 ppb) and NH₃-rich (~ 10 ppb) conditions in Seoul can promote the uptake of HNO₃ into the wet particle.

Most of the severe haze events in Seoul occur in the local stagnant conditions combined with transport of the preceding regional haze (Seo et al., 2017). The transported regional haze particles with a high inorganic fraction and abundant ALW readily take up HNO₃ and NH₃ gases under the high NO_x and NH₃ conditions of the urban area and consequently reduce the air quality more than local haze formation without regional transport (Fig. 12). Considering both the high $\varepsilon(\text{NO}_3^-)$ of the transported wet particles and the low pH required to decrease $\varepsilon(\text{NO}_3^-)$ in the combined regional-transport–local-stagnation condition, NO_x control rather than NH₃ control may be a more effective PM_{2.5} reduction strategy in Seoul.

Our results provide insight into the nonlinear effects of the transported particles and local precursors on urban haze pollution in the regional air quality modeling system. For example, domestic and foreign contributions to PM₁₀ concentration over the Seoul metropolitan area estimated by the brute force method approach show a discrepancy between reductions in domestic and foreign emissions, in particular during the cold season (Kim et al., 2017). The synergistic enhancement of urban haze pollution by the combination of regional and local sources makes a precise estimation of domestic and foreign contributions difficult. This study also shows a need for international cooperation in air quality management.

Code availability. The ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007) is available on the website of the Laboratory of atmospheric processes and their impacts (LAPI) in the EPFL (<https://www.epfl.ch/labs/lapi/isorro피아/iso-code-repository/>, last access: 25 June 2020). The HYSPLIT model (Stein et al., 2015) is available on the website managed by the NOAA Air Resources Laboratory (<https://www.ready.noaa.gov/HYSPLIT.php>, last access: 25 June 2020).

Data availability. Daily PM_{2.5} measurements, chemical analysis, meteorological factors, and ISORROPIA II result data utilized in this study are available at https://drive.google.com/open?id=1hJrwViP_qx23dTuBxLapbWhAn5LrTXMI (last access: 25 June 2020). The hourly data of SO₂, NO₂, CO, O₃, and PM₁₀ concentrations at 34 air quality monitoring sites in Seoul for the analysis period are available on the website managed by the Korea Environment Corporation (2019; <https://www.airkorea.or.kr/web/>

[last_amb_hour_data?pMENU_NO=123](https://www.airkorea.or.kr/web/)). The hourly meteorological data of temperature, sea level pressure, relative humidity, wind speed, and solar irradiance at the Seoul weather station for the same period can be found on the website of the KMA (2020; <https://data.kma.go.kr/data/grnd/selectAsosRltmList.do?pgmNo=36>). The ERA-Interim data (Dee et al., 2011) can be accessed via the European Centre for Medium-Range Weather Forecasts (ECMWF) data server (<http://apps.ecmwf.int/datasets/data/interim-full-daily/>, last access: 25 June 2020).

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/acp-20-7575-2020-supplement>.

Author contributions. JS initiated the investigation and performed thermodynamic modeling analyses. JS and YBL extensively discussed the concept. HCJ conducted the field measurement and provided chemical analyses. DY and JYK provided additional feedback on the paper. JS prepared the paper with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. This research was supported by the Korea Institute of Science and Technology (KIST) and the National Strategic Project – Fine Particle of the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (MSIT), the Ministry of Environment (ME), and the Ministry of Health and Welfare (MOHW) (2017M3D8A1090654). Yong Bin Lim was supported by NRF (2019M3D8A1070941). Daeok Youn was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (MOE) (2015R1D1A3A01020130) and Korea Environment Industry & Technology Institute (KEITI) funded by the Korea Ministry of Environment (ME) (2018001310004). The authors are grateful to the editor and two referees for their valuable and constructive comments and suggestions.

Financial support. This research has been supported by the National Strategic Project – Fine Particle of the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (MSIT), the Ministry of Environment (ME), and the Ministry of Health and Welfare (MOHW) (grant no. 2017M3D8A1090654), the National Research Foundation of Korea (NRF) (grant no. 2019M3D8A1070941), the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (MOE) (grant no. 2015R1D1A3A01020130), and the Korea Environment Industry & Technology Institute (KEITI) funded by the Ministry of Environment (ME) (grant no. 2018001310004).

Review statement. This paper was edited by Barbara Ervens and reviewed by Rodney Weber and one anonymous referee.

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