Local formation of sulfates contributes to the urban haze with regional transport origin

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Keywords: East Asian haze, regional transport, gas–particle partitioning of semivolatile inorganic species

Abstract
Urban particle pollution is affected by not only the emissions of pollutants and secondary aerosol formation through atmospheric chemistry on a local scale, but also the regional transport of particles and precursor gases from highly polluted upwind areas. However, this regional impact on urban particle formation is not well understood. Wintertime haze events occur at Seoul, Korea through the combination of regional transport from China and local formation at Seoul. We perform thermodynamic model simulations based on inorganic component measurements of haze particles collected at Seoul and Deokjeok Island (upwind background). Results suggest that in the downwind area (Seoul) the local formation of sulfates increases the mass concentrations of transported particles through the gas–particle partitioning of semivolatile nitric acid (HNO$_3$) and ammonia (NH$_3$). Therefore, this synergetic effect of the local sulfate formation on urban haze with regional transport must be considered in implementing effective particle reduction controls for urban sustainability.

1. Introduction

Urban air pollution with high concentrations of particulate matter with a diameter below 2.5 µm (PM$_{2.5}$) poses a risk to human health and the environment [1, 2]. However, implementing reduction strategies for urban sustainability is challenging because it requires decreasing the emissions of the pollutants that form particles through physical/chemical processes in the atmosphere but the scientific knowledge of the particle formation is considerably limited. A large fraction of PM$_{2.5}$ is secondary particles, which are formed through complicated atmospheric reactions in the multiphase including the gas and particle phase. Nonetheless, secondary particle formation has been extensively studied, which has improved the understanding of atmospheric chemistry. High levels of SO$_2$ emissions rapidly form sulfate particles through aqueous-phase reactions in aerosol liquid water (ALW). This results in high PM$_{2.5}$ concentrations during Chinese haze events [3, 4]. High levels of volatile organic compounds (VOCs) and NO$_x$ emissions form organic and nitrate particles through photochemistry during Los Angeles smog events [5]. These high-concentration urban particles are considered to be formed on a local scale (10–100 km) [6] under stagnant meteorological conditions with relatively low boundary layer height [5]. Therefore, typical PM$_{2.5}$ reduction strategies are developed based on local emissions.

High PM$_{2.5}$ concentrations in polluted urban areas can be the regional source of downwind air pollution owing to long lifetimes of PM$_{2.5}$ [6, 7]. Thus, downwind urban areas also suffer from the high PM$_{2.5}$ concentrations owing to the combination of regional and local sources. Consequently, it is necessary to estimate the local and regional contributions to PM$_{2.5}$ levels for establishing PM$_{2.5}$ reduction strategies. Our previous study [8] shows that wintertime haze events at Seoul, Korea are a good example of high-concentration PM$_{2.5}$ caused by the combination of the regional transport of PM$_{2.5}$ from China and the local stagnation at Seoul due to synoptic conditions (supplementary information S1, figure S1 stacks.iop.org/ERL/15/084034/mmedia). Receptor models [9] and regional air quality models coupled
with weather prediction models [10] have been used to investigate the local and regional contributions to particle formation at Seoul. It is feasible to establish PM$_{2.5}$ reduction strategies based on these approaches. However, potential synergetic effects of the combination of local formation and regional transport are still not well understood. This is because regional effects of transported particles and precursor gases on the gas–particle partitioning and atmospheric chemistry in downwind urban areas are largely unexplored.

In this work, we hypothesize that particles are the sulfate–ammonium–nitrate–water system and that thermodynamic equilibriums are maintained between the gas phase and particle phase (i.e. gas–particle partitioning) and in the aqueous phase within particles because East Asian haze particles mainly contain inorganics (e.g. sulfates, ammoniums and nitrates) [8, 11, 12] and ALW [13]. Then, we show that the increase in sulfate concentrations influences particle formation using a thermodynamic model [14], which simulates the increase in ammonium and ALW concentrations in PM$_{2.5}$ during the wintertime multiday haze event at Seoul (February 24–28, 2014, [PM$_{2.5}$ average] = 116 µg m$^{-3}$). We perform sensitivity analyses for describing the response of the total inorganic PM$_{2.5}$ to inorganic precursor concentrations ([H$_2$SO$_4$]$_{\text{total}}$, [NH$_3$]$_{\text{total}}$ and [HNO$_3$]$_{\text{total}}$) [11, 15, 16] because these analyses are useful for implementing particle reduction strategies.

2. Methods

2.1. Sites and sample analyses

All information regarding sites and sample analyses can be found in Seo et al [8]. Korea is a geographical neighbor of China, east of the Yellow Sea [17]. Thus, owing to the prevailing westerlies (figure S2(A)) the air quality in Korea is frequently influenced by that in China, which experiences severe air pollution owing to rapid industrialization. Seoul, the megacity in Korea (~10 million people), experiences severe haze events that are dominated by secondary particles [18, 19] under the synoptic conditions, which cause the combination of the regional transport of pollutants from China and the local stagnation at Seoul [8]. The regional and local contributions to particle formation at Seoul are investigated by measuring PM$_{2.5}$ at Seoul and Deokjeok Island (upwind background) (figure S2(B)) from 24 February to 9 March 2014 through 24-h sampling filter collections followed by ion chromatography (IC) and elemental carbon/organic carbon (EC/OC) analyses (S2). During the haze event (24–28 February 2014), daily concentrations of PM$_{2.5}$ and inorganic components, along with wind speed and direction, indicate that PM$_{2.5}$ at Seoul is influenced by regional transport through Westerlies (figure S3). The concentrations of PM$_{2.5}$ and sulfates at Deokjeok Island (figures S3(A) and (B)) are initially comparable to those at Seoul, indicating the strong influence of regional transport in the early haze period. Then the concentrations become smaller later, indicating that the local formation takes over. The nitrate concentration in Seoul is always higher than that in Deokjeok Island, indicating the local formation of nitrates at Seoul. Note that on February 26, the concentrations of PM$_{2.5}$ and nitrates (figures S3(A) and (B)) are similar because of the abrupt occurrence of an east wind (figure S3(C)).

2.2. Thermodynamic equilibrium

2.2.1. Thermodynamic model

The ISORROPIA-II thermodynamic model [14] is used to predict the pH of PM$_{2.5}$ and the gas–particle partitioning of the inorganic components of PM$_{2.5}$ (i.e. NH$_3$–NH$_4^+$ and HNO$_3$–NO$_3^-$). pH is defined as the activity of the hydrogen ion (aH$^+$); therefore, pH = −log aH$^+$, which is the product of the activity coefficient (γ) and the hydrogen ion (H$^+$) concentration in the aqueous phase (i.e. aH$^+ = γ[H^+]$). [H$^+$] is the molality concentration (i.e. the mole of H$^+$ divided by the mass of ALW in 1 m$^{-2}$ air) and γ is assumed to be unity [20]. ALW is the water uptake by hygroscopic particles based on relative humidity (RH) and it is estimated using the thermodynamic model. As the haze particles are mainly inorganic, the ALW due to only inorganics is considered [11]. The forward mode is used for determining pH and the gas–particle partitioning of HNO$_3$ and NH$_3$. This is because the reverse mode tends to predict unrealistically high concentrations for inorganic gases and either too low or too high pH. But the forward mode constrains the output values, which are likely to be more realistic [11, 12, 16, 21, 22]. The inputs (S3) are the concentration of the total NH$_3$ (i.e. [NH$_3$]$_{\text{total}}$ = [NH$_3$] + [NH$_4^+$]), where NH$_3$ exists in the gas-phase and NH$_4^+$ in the particle-phase), the concentration of the total HNO$_3$ (i.e. [HNO$_3$]$_{\text{total}}$ = [HNO$_3$] + [NO$_3^-$], where HNO$_3$ exists in the gas-phase and NO$_3^-$ in the particle-phase), and the concentration of the total H$_2$SO$_4$ (i.e. [H$_2$SO$_4$]$_{\text{total}}$ = [SO$_4^{2-}$] + [HSO$_4^-$], where all ions exist in the particle-phase). Finally, the metastable state is used because the PM$_{2.5}$ during the haze event is expected to be deliquesced. This haze PM$_{2.5}$ contains a high fraction (~80%) of inorganic components (sulfates, ammoniums, and nitrates), and the stable state mode in ISORROPIA-II would predict no water uptake because the average RH during the haze event (59% RH) is below deliquescence RH (DRH) for inorganic salts (e.g. DRH for (NH$_4$)$_2$SO$_4$ is 80% RH at 25 °C). However, the PM$_{2.5}$ also contains organic components (~20%), which still enable particles to take up water below DRH [23–26]. Therefore, we expect that water uptake into PM$_{2.5}$, the pH of PM$_{2.5}$ and the gas–particle partitioning of NH$_3$ and HNO$_3$ are due to the metastable state of particles (wet particles). Note that in ISORROPIA-II the outputs of
ALW, pH, and gas- and particle-phase inorganic concentrations are obtained by the inputs of inorganic concentrations with the metastable mode. And these outputs are not corrected by the additional hygroscopicity of organic components [11].

2.2.2. Gas–particle partitioning of HNO₃ and NH₃

During the haze period (24–28 February 2014), the average PM$_{2.5}$ concentrations were 116 µg m$^{-3}$ in Seoul and 84 µg m$^{-3}$ in Deokjeok Island (upwind background). Additionally, both types of particles were inorganic rich (~80% of [PM$_{2.5}$]$_{total}$) (figure 1(A)). Among the particle components at Seoul, the increase in nitrates is the most prominent (figure 1(B)). As we hypothesize that East Asian PM$_{2.5}$ is the sulfate-ammonium-nitrate-water system maintained by thermodynamic equilibriums, nitrates are expected to be formed via the gas–particle partitioning of HNO$_3$ with NH$_3$. High levels of ALW and NH$_3$ concentrations and low temperatures during wintertime significantly enhance the nitrate uptake in East Asia [11, 13, 27]. During the multi-day haze period at Seoul under NH$_3$-rich conditions at 59% RH and 279 K, the thermodynamic model predicts ~100% uptake of HNO$_3$ into particles as nitrates (S4, figure S4(A)). This is consistent with recent field studies for wintertime Chinese haze [11, 28]. To verify thermodynamic equilibriums during the haze event, additional daily simulations are conducted (figure S4(B)). The inorganic species measurements (inputs) are almost identical to simulation results (outputs). Furthermore, the HNO$_3$ uptake each day is ~100%. Note that NH$_3$ gas is assumed to be 10 ppb, which will be discussed in the next section.

Sensitivity analyses are performed for the gas–particle partitioning of NH$_3$ and HNO$_3$ in Seoul with the increase in gas-phase NH$_3$ concentrations. Note that the concentration of sulfates during the haze event (37.01 µg m$^{-3}$) is used. Results show almost no change in the nitrate or ammonium concentrations in the particle phase (figure 1(C)). Therefore, during wintertime in East Asia, almost all the HNO$_3$ initially produced in the gas phase from the atmospheric oxidation of NO$_x$ is partitioned into particles as nitrates. Because NH$_3$ is excessive in East Asia, the same molar concentration of NH$_3$ as that of nitrates is partitioned into particles as ammoniums, and the
leftover NH3 remains in the gas phase. In other words, HNO3 is a limiting agent owing to NH3 richness, and almost all gas-phase HNO3 converts to particles because the forward reaction of the equilibrium for producing ammoniums and nitrates in the aequous phase of particles is dominant (equation (1)):

\[
\text{NH}_3^{\text{gas}}, \text{excess} + \text{HNO}_3^{\text{gas}} \rightarrow \text{NH}_4^+ + \text{NO}_3^- \text{ (in ALW)} \tag{1}
\]

The pH of particles is an important parameter for the gas–particle partitioning of HNO3 and NH3. The particle fraction of the total HNO3 increases as the particles become more neutral. First, the pH of particles increases with gas-phase NH3. Then, above ~10 ppb of NH3, pH plateaus at ~4 owing to the buffering effect of NH4–NH4+ partitioning (figure 1(C)) [16]. Note that there must be 1 × 10^5 ppb of NH3 in order for particles to be at pH 7. Although an ammonia-rich environment at Seoul does not fully neutralize acidic particles, the level of pH is sufficient for the complete uptake of HNO3 into particles [16, 28].

3. Results and discussions

3.1 Partitioning shift of local HNO3 and NH3 towards particles by sulfate particles

This study aims to assess the effect of the local sulfate formation on urban haze influenced by regional transport. To achieve this, we demonstrate that the transported particles from Deokjeok Island (upwind background) act as seed particles and the local sulfate formation in Seoul increases the mass concentration through the gas–particle partitioning of local semivolatile HNO3 and NH3 at Seoul (downwind) during the haze event (figure S2(B)). Thus, it is important to determine the concentration of the total HNO3 and total NH3 at Seoul without the influence of regional transport. No gas-phase concentration data for HNO3 and NH3 are available during the haze event at Seoul and Deokjeok Island. Hence, the total HNO3 is assumed to be nitrate particles, as discussed in the previous section. In addition, we assume that the gas-phase NH4+ concentration at Seoul is maintained at 10 ppb based on the measurements performed in 2010–2011 [27].

Our estimation (S5) indicates that under no influence of regional transport, 8 ppb of the total HNO3 and 18 ppb of the total NH3 would exist locally at Seoul during the haze event. Thermodynamic model simulations for the gas–particle partitioning of the total local HNO3 (8 ppb) and the total local NH3 (18 ppb) shifted by transported PM2.5 in Seoul agree well with nitrates and ammoniums measured in Seoul PM2.5 during the haze event. If we assume that the transported particles are Deokjeok Island PM2.5, then the concentrations of nitrates and ammoniums are 32.40 µg m⁻³ and 19.70 µg m⁻³, respectively (figure 2(A)). The errors in the simulated nitrate and ammonium concentrations compared to the actual measured composition data for Seoul PM2.5 (figure 2(C)) are ~5% and ~12%, respectively. The higher concentrations of sulfates at Seoul compared to Deokjeok Island during the haze event suggest the additional local sulfate formation at Seoul while Deokjeok Island PM2.5 is transported to Seoul (figure 1(B)). It should be noted that SO2 rapidly forms sulfates via aqueous-phase reactions with transition metal ions, NOx or H2O2 [3, 4, 28, 29] and gradually via gas-phase reactions with OH radicals [30]. Therefore, the sulfate formation from both pathways on a local scale (10–100 km) is possible because Deokjeok Island is located ~80 km away from Seoul. Then, the difference between the sulfate concentrations at Seoul and Deokjeok Island (∆SO4 = 8 µg m⁻³) can be viewed as the additional local sulfate formation at Seoul during the haze event. A thermodynamic model simulation was performed with the input of the sulfate concentration in Seoul PM2.5 (= [Sulfates]Deokjeok Island + ∆SO4). Results show that the ammonium concentration is predicted more accurately (figure 2(B)). Compared to the errors obtained in the previous simulations, the error of the simulated nitrate concentration is similar (4%), whereas the error in the simulated ammonium concentration reduces significantly (1%). The simulations predict the gas-phase concentrations of NH3 and HNO3 at 7.35 ppb and 0.08 ppb, respectively. These values still support our hypotheses of an NH3 concentration at 10 ppb and the complete uptake of HNO3 into particles (figure 2(B)). The simulation predicts the pH of Seoul PM2.5 as 3.37. We simulate the thermodynamic model for the other three high-concentration haze events at Seoul and find that the pH of particles is 3–4 (S6, figure S5(B)). This pH range is slightly lower than that of Chinese haze particles (pH 4–5) [11] but higher than Eastern US haze particles (pH 0–2) [16]. Changing the concentration of sulfates affects the gas–particle partitioning of NH3 with ~100% HNO3 uptake, leading to change in the total PM2.5 concentrations and the composition of PM2.5, including inorganic and ALW concentrations and particle pH.

3.2. Inorganic PM2.5 response to precursor concentration controls

To establish effective PM2.5 reduction strategies, it is important to control the emissions of the relevant species forming particles through gas–particle partitioning. Because the PM2.5 at Seoul is inorganic rich, we focus on sulfates, nitrates, and ammoniums in particles. We perform sensitivity analyses for examining the gas–particle partitioning of HNO3–NO3⁻ and NH3–NH4⁺, the ALW uptake into PM2.5, and the pH of PM2.5 at Seoul. The sulfate, the total NH3, and the total HNO3 concentrations are considered as inputs to the thermodynamic model. We assume that
only inorganic components contribute to ALW formation and particle pH because the PM$_{2.5}$ at Seoul and Deokjeok Island is inorganic-rich [11, 22].

3.2.1. Sulfate control
Sulfates are persistently formed in Chinese haze particles [3, 8], and they do not undergo gas–particle partitioning because of extremely low volatility (i.e. sulfates always stay in the particle phase). The difference between the sulfate concentrations at Deokjeok Island and Seoul ($\Delta$SO$_4$ ~8 $\mu$g m$^{-3}$) may represent the local formation of sulfates at Seoul during the haze event, as discussed earlier. However, a part of the SO$_2$ at Seoul could have been transported from China owing to the higher concentrations of SO$_2$ at Deokjeok Island compared to Seoul during the first three days of the haze event (figure S6(C)). In particular, the SO$_2$ concentration at Deokjeok Island is the highest on the first day of the haze event. Furthermore, the level of SO$_2$ in China is 20–80 ppb during the wintertime haze period [3]. Therefore, we cannot rule out the possibility that a part of the sulfates at Seoul is formed from transported SO$_2$ during the haze event.

We have conducted sensitivity analyses for the Seoul PM$_{2.5}$ during the haze to investigate the effect of sulfates on the gas–particle partitioning of NH$_3$ and HNO$_3$. The particle-phase concentration of nitrates (34 $\mu$g m$^{-3}$) and the concentration of the total NH$_3$ (30 $\mu$g m$^{-3}$) are fixed inputs for the thermodynamic model while the sulfate concentration is a variable input that ranges from 0 to 100 $\mu$g m$^{-3}$ (figure 3(A)). At ~40 $\mu$g m$^{-3}$ of sulfates, which is the actual sulfate concentration at Seoul, particles are composed of ~100% of the total HNO$_3$ and ~70% of the total NH$_3$ in the particle phase as nitrates and ammoniums, respectively. In addition, ALW is ~50 $\mu$g m$^{-3}$ and pH ~3 (‘a’ arrow in figure 3(A)). A decrease in the sulfate concentration results in more evaporation of ammonium into NH$_3$ gas (figure 3(B)), no evaporation of nitrates (figure 3(C)) and a gradual increase in pH (figure 3(A)). It is interesting to estimate the reduction in the mass concentration of PM$_{2.5}$ at Seoul if there were no transported PM$_{2.5}$ during the haze event. We assume that 11 $\mu$g m$^{-3}$ of sulfates would be locally formed at Seoul in the absence of transported particles (S7). At 11 $\mu$g m$^{-3}$ of sulfates (73% decrease), 60% of the total NH$_3$ evaporates; therefore,
the particle mass concentration is 88 µg m$^{-3}$, (37% decrease) and pH ~4 ('d' arrow from 'a' arrow in figure 3(A)). However, it should be noted that transported SO$_2$ can form sulfates at Seoul. Thus, our assumption of 11 µg m$^{-3}$ of sulfates is likely to be the upper limit for the local-only sulfate concentration at Seoul. When the sulfate concentration approaches 0 µg m$^{-3}$, ~33% of the total NH$_3$ and ~100% of the total HNO$_3$ remain as ammoniums and nitrates in the particle phase, respectively, at pH ~5. As the sulfate concentration increases above 40 µg m$^{-3}$, nitrates start to evaporate into HNO$_3$ in the gas phase but more NH$_3$ is partitioned into particles as ammoniums. Additionally, the particles are acidified rapidly first then gradually at the end (pH ~ 0).

3.2.2. HNO$_3$ control

HNO$_3$ and NO$_x$ gases are local contributors to particle formation. HNO$_3$ is the main atmospheric oxidation sink for NO$_x$. HNO$_3$ is not expected to be regionally transported. Almost all HNO$_3$ is partitioned into particles as nitrates at China and Seoul owing to the NH$_3$-rich, humid and cold conditions. NO$_x$ in Seoul during the haze event is considered to contribute to the local formation of HNO$_3$ (NO$_2$ + OH $\rightarrow$ HNO$_3$) because the lifetime of NO$_2$ by OH reactions is ~1 d, and the formation of HNO$_3$ is a major sink for NO$_x$ [31]. The NO$_2$ levels at Deokjeok Island during the haze event are mostly below 10 ppb, which is considerably lower than those at Seoul. This suggests that NO$_2$ is not likely to be transported from China. The level on February 26 is atypically high (~30 ppb) because of the influence of Seoul through an abrupt local East Wind event [8]. Furthermore, the lower O$_3$ concentrations at Seoul (with higher NO$_2$) compared to Deokjeok Island (with lower NO$_2$) (figures S6(B) & (D)) indicate NO$_x$ titration in Seoul owing to local O$_3$-NO$_x$-VOC
chemistry. Therefore, the formation of HNO₃ from NOₓ and the uptake of HNO₃ into particles as nitrates are local processes.

A decrease in the total HNO₃ results in more evaporation of ammoniums in the particle phase. However, ~100% of the total HNO₃ remains in the particle phase (figures 4(A) and (B)). The particle mass concentrations decrease almost linearly with the total HNO₃ input (figure 4(A)). The arrow (figure 4(A)) indicates the mass concentrations of the Seoul PM₂.₅ during the haze event, and 50% reduction in the total HNO₃ leads to 20% decrease in the particle mass concentration. Clearly, particle mass decreases with HNO₃ (NO₂). Note that a decrease in PM₂.₅ by HNO₃ reduction is comparable to that by sulfate reduction because the same decrease (50%) in sulfates results in 29% reduction in the particle mass concentration. A decrease in the total HNO₃ does not significantly change the acidity, and pH ranges between 3 and 4 (figure 4(A)).

3.2.3. NH₃ control

NH₃ is a local contributor to particle formation owing to the relatively short lifetime (<3 d). Seoul is an NH₃-rich area with ~10 ppb (gas-phase only) based on one-year measurement considering anthropogenic and agricultural sources [27].

Sensitivity analysis shows that the relationship between NH₃ reduction and PM₂.₅ reduction is non-linear although 50% reduction in the total NH₃ results in ~30% decrease in the particle mass concentration (figure 5(A)). The total NH₃ (~40 ppb during the haze event) must be decreased by more than 10 ppb to provide significant particle reduction. Note that 10 ppb is the gas-phase concentration of NH₃, which is the excess NH₃ from the reaction with HNO₃ (equation (1)). A decrease in the total NH₃ below 30 ppb results in ~100% uptake of NH₃ gas into particles as ammoniums and the evaporation of nitrates (figures 5(B) and (C)). In these conditions, Seoul becomes NH₃ poor [12] and particles become

Figure 4. Thermodynamic simulations for ammonium, nitrate and ALW concentrations and pH varied by the total HNO₃ concentration input (A). Gas–particle partitioning of NH₃ (B) and HNO₃ (C) according to the total HNO₃ concentration input. The arrow in (A) indicates the total HNO₃ concentration during the Seoul haze event.
highly acidic, reaching a pH of \(-0.5\) (figure 5(A)). This result is consistent with other studies for urban areas in the United States and China, suggesting that although NH\(_3\) reduction is the most effective method for decreasing the total PM\(_{2.5}\), particles become acidic under these conditions [11, 15]. An increase in the total NH\(_3\) beyond 40 ppb results in no change in particle mass and only the accumulation of NH\(_3\) gas. Particles are not completely neutralized because of the buffering effect of NH\(_3\)-NH\(_4^+\) partitioning [11, 16] (figures 5(B) and 1(C)).

4. Conclusions and implications

Downwind particle formation aided by transported seed particles is synergetic because transported particles are added to downwind areas and shift the gas–particle partitioning of semivolatile inorganic compounds toward particles. And the local sulfate formation shifts the partitioning toward particles even more. In this work, we view particles as the sulfate-ammonium-nitrate system maintained by thermodynamic equilibriums. Therefore, the pH of particles is an important parameter that reflects thermodynamic equilibriums. The haze condition at Seoul can be described by \(~100\%\) HNO\(_3\) uptake in an ammonia-rich environment, and in this condition, the local sulfate formation increases mass concentrations of particles. A pH of 3–4 for haze PM\(_{2.5}\) reflects this condition (‘a’ in figure 3(A)). The PM\(_{2.5}\) at Seoul in other haze events can be also viewed as the sulfate-ammonium-nitrate system maintained by thermodynamic equilibriums (figure S5(A)). The same pH range (pH \(~3–4\)) for other haze events under the same synoptic conditions (figure S5B) also reflects \(~100\%\) HNO\(_3\) uptake in an ammonia-rich environment, thus, the same synergetic effect of the local sulfate formation on urban haze.

Regional and local species are summarized in table 1. Urban clean air strategies can be implemented
by controlling the emissions of NO\textsubscript{x} or NH\textsubscript{3} on a local scale and SO\textsubscript{2} on a local/regional scale. NO\textsubscript{x} and NH\textsubscript{3} reductions must be considered carefully. Seoul is the NO\textsubscript{x}-titration region (figures S6(B) & (D)), which implies that a decrease in NO\textsubscript{x} may increase the O\textsubscript{3} concentration. NH\textsubscript{3} reduction risks sustainability because (1) the acidification of particles by NH\textsubscript{3} reduction (below a pH of 2 in figure 5(A)) results in adverse health effects; and (2) NH\textsubscript{3} reduction requires the control of agricultural activities (e.g. land (fertilizer), domesticated animal waste), which are directly related to sustaining food production [32]. Furthermore, NH\textsubscript{3} control is difficult because natural processes are largely involved in NH\textsubscript{3} emissions. On the other hand, the sulfate reduction strategy only focuses on decreasing SO\textsubscript{2} emissions because it minimizes the negative effects of NO\textsubscript{x}/NH\textsubscript{3} reductions.

According to our sensitivity analyses, the sulfate reduction in particles is as effective as the total HNO\textsubscript{3} reduction for decreasing haze particle mass concentrations. Reducing the sulfates and the total HNO\textsubscript{3} is an effective method to decrease the total PM\textsubscript{2.5} as it results in not only a sulfate/nitrate decrease in particles, but also the ammonium evaporation in particles (figures 3(B) and 4(B)). The maximum reduction in PM\textsubscript{2.5} that can be achieved by the sulfate reduction (37 \( \mu \)g m\textsuperscript{-3} \( \rightarrow \) 11 \( \mu \)g m\textsuperscript{-3}; ‘a’ to ‘b’ in figure 6) is 53 \( \mu \)g m\textsuperscript{-3} (141 \( \mu \)g m\textsuperscript{-3} \( \rightarrow \) 88 \( \mu \)g m\textsuperscript{-3}). The maximum reduction in PM\textsubscript{2.5} that can be achieved by the total HNO\textsubscript{3} reduction (12 ppb \( \rightarrow \) 4 ppb; ‘a’ to ‘c’ in figure 6) is 41 \( \mu \)g m\textsuperscript{-3} (141 \( \mu \)g m\textsuperscript{-3} \( \rightarrow \) 100 \( \mu \)g m\textsuperscript{-3}). Note that the level of the total HNO\textsubscript{3} cannot be lower than ~4 ppb because the total HNO\textsubscript{3} formed locally at Seoul without the influence of regional transport is ~8 ppb.

Limitations in this work include the unavailability of NH\textsubscript{3} and HNO\textsubscript{3} data and the uncertainty of the organic contribution to the PM\textsubscript{2.5} formation during the haze event. According to recent measurements of the NH\textsubscript{3} concentrations conducted in Seoul in January 2018 ([NH\textsubscript{3}] = 5–20 ppb) [33], the pH of PM\textsubscript{2.5} at Seoul is still 3–4 (figure 1(C)). The pH is well constrained because of the buffering effect of NH\textsubscript{3}–NH\textsubscript{4}\textsuperscript{+} partitioning, so the error is not expected to be significant. Despite no direct measurement for HNO\textsubscript{3}, our sensitivity tests for HNO\textsubscript{3}-NO\textsubscript{x} partitioning in East Asian haze conditions (low temperature, high RH, and NH\textsubscript{3} richness) show that ~100% of the total HNO\textsubscript{3} is nitrates (figures 1(C), 2(A) and (B), 3(C), and figures S4(A) and (B)). Although the organic contribution to the PM\textsubscript{2.5} formation is not considered in this work, in figure 1(B), the increase

| Local Species (Non-transported) | Regional Species (Transported) |
|---------------------------------|---------------------------------|
| **Species** | **Source** | **Sink** | **Species** | **Source** | **Sink** |
| NH\textsubscript{3} | Agricultural activity | Partitioning into particles | ‘SO\textsubscript{2}’ | Coal combustion | Gas-phase OH oxidation to H\textsubscript{2}SO\textsubscript{4} (slow) |
| HNO\textsubscript{3} | Oxidation of NO\textsubscript{x} | Partitioning into particles | PM\textsubscript{2.5} (Inorganic PM\textsubscript{2.5} + Organic PM\textsubscript{2.5}) | Local fine particle formation (mainly secondary) | Dry deposition for PM\textsubscript{2.5} (O/C increase of organic PM due to chemical aging during transport) |
| NO\textsubscript{x} | Combustion, Vehicle exhaust | Photo-oxidation to HNO\textsubscript{3} (major) & Organonitratre formation (minor) | NH\textsubscript{4}\textsuperscript{+} | Partitioning from NH\textsubscript{3} | Partitioning into NH\textsubscript{3} & Dry deposition |
| VOCs | Anthropogenic: Aromatics, alkanes | Atmospheric oxidation (e.g. OH, NO\textsubscript{3}, O\textsubscript{3} reactions) | Organic PM\textsubscript{2.5} | SOA formation from VOC | Partitioning into gaseous semi volatile compounds & Dry deposition |

\textsuperscript{a} SO\textsubscript{2} is also considered a local species because it can rapidly form H\textsubscript{2}SO\textsubscript{4} through aqueous chemistry at a local scale. This happens in both upwind and regionally transported downwind areas.

\textsuperscript{b} NO\textsubscript{x} can also be regionally transported.

\textsuperscript{c} PM\textsubscript{2.5} is composed of inorganic PM\textsubscript{2.5} and organic PM\textsubscript{2.5}.

\textsuperscript{d} Wet deposition is not considered because of no rain/snow during the haze event.
in organics is significant. Therefore, organic formation needs to be studied. In particular, secondary organic aerosol formation in the aqueous phase warrants further study because haze particles are deliquesced. Furthermore, the effects of organics on hygroscopicity, pH, and the liquid-solid particle phase of particles, and organosulfate/organonitrate formation in particles warrant further study.

Acknowledgments

This work was 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) (2017M3D8A1090654 and 2019M3D8A1070941). This work was also supported by the Brainpool Fellowship from MSIT (152S-5-2-1416), and the Korea Institute of Science and Technology (KIST) Institutional Program (Atmospheric Environment Research Program, Contract No. 2E30111-20-092). We thank Rodney J. Weber and Shaojie Song for helpful discussions.

Author contributions

Y B L initiated the investigation. Y B L performed thermodynamic modelling analyses. J S performed the analyses for synoptic meteorological conditions and the field study. J Y K initiated the field study sampling at Deokjeok Island and Seoul. H C J provided IC and EC/OC analyses for PM$_{2.5}$ collected at Seoul and Deokjeok Island. Y B L wrote the paper with input from J S, J Y K, and Y P K. All authors discussed and contributed to writing the paper.

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Data availability statement

Additional data and information can be found in supplementary information.
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