Response to Referee #1 (Dr. Rodney Weber)

This paper assesses the composition of $PM_{2.5}$ in Seoul under different transport & meteorological conditions. The separation of data collection into periods when Seoul was impacted or not by upwind transport from China, combined with local ventilation conditions over Seoul, is clever and insightful. The result is that clear differences in the aerosol composition and processes can be identified. The authors show that highest $PM_{2.5}$ concentrations occur when species transported from China are present and when there is little dispersion over Seoul, as might be expected. The unique feature is they find that these periods have enhanced inorganic aerosol concentrations and investigate a number of possible feedbacks that could explain the enhanced aerosol concentrations under these conditions, all related to aerosol liquid water levels (ALW). This includes enhanced SO_2 oxidation to form sulfate and especially the uptake of HNO_3 to form particle NO_3^-. The specific contributions of China (SO_2 / sulfate) vs Seoul (NO_x / NH_3) on these interactions is also identified. This allows a unique assessment of possible control strategies to reduce $PM_{2.5}$ mass. The main issue with this paper is the lack of NH_3 and HNO_3 data that are required to run the thermodynamic model. The authors should more fully assess this limitation through a detailed sensitivity analysis, but my suspicion is it will not significantly change the result.

We appreciate the reviewer for valuable comments and suggestions. As indicated in the following point-by-point responses, we have incorporated the reviewer's comments and suggestions into the revised manuscript. We have conducted additional analyses, modified texts, figures, and tables, and added several new figures (Figs. 4 and 5) and references in the revised version. Each response to the reviewer is in blue, and the change in the manuscript is in red.

During the revision process, we found that the molar concentrations of Ca^{2+} and Mg^{2+} in the ISORROPIA input data were mistakenly applied by 2-time values. We have corrected those input data errors and newly conducted simulations. As a result, average and standard deviation of ALW (both W_i and W_o), ionic strength, pH, oxidation/partitioning ratios [SOR, $\varepsilon(NO_3^-)$, and $\varepsilon(NH_4^+)$] in Table 2 have been slightly changed. By the changes in results, several figures (Figs. 6a, g, and h, Fig 7, Fig. 8, Fig. 10, and Fig. 11 in the revised version) have also been modified. However, such changes are negligible and did not affect our conclusions.

We also corrected average and standard deviation of NH_3 concentrations in Table 2, because the unit of original version were μg m^{-3}. NH_3 are now represented by unit of ppb in the revised version. Sect. 2.2 and Sect. 2.3 were exchanged with each other to keep consistency of the order of figures and text contents.

Specific Comments:

The use of acronyms made the paper, at times, difficult to follow for me. Where it is possible, it might be better to just write out the term. A list (table) defining them could also be useful. For example, in this study SIA is just sulfate, nitrate and ammonium.

Thanks for the comment. We tried to reduce the usage of acronyms in the revised version.

Potential NO_3^- sampling issues? Were samples gas denuded; seems not but maybe use of Teflon filters minimizes this possible positive artifact? Since particle NO_3^- is a large component of this paper, and it is known to be difficult to measure using filters due to evaporation, this issue should be discussed. That is, is it possible that ammonium nitrate is significantly under-measuring in this study?

As the reviewer pointed out, we did not employ both a denuder and backup filters for $PM_{2.5}$ sampling on Teflon filters. Therefore, there are possibilities of both positive and negative artifacts by absorption of gas-phase nitric acid on the filter and evaporation of ammonium nitrate. Although both artifacts may partly compensate each other, previous evaluation studies showed that the major concern of nitrate measurement on Teflon filter is the negative artifact (Ashbaugh and Eldred, 2004; Chow et al., 2005). Nie et al. (2010) reported large nitrate loss (~75%) at the lower nitrate concentrations (< 10 μg m^{-3}) but much smaller nitrate loss (~10%) at the higher nitrate concentrations (> 10 μg m^{-3}) attributable to formation of particle cake, even in summertime (temperature range of 22–34°C) in Beijing. Considering that the evaporative loss of nitrate was minimal in winter, they expected small to moderate sampling artifacts for conventional sampling method (un-denuded filter sampling without backup filters) in polluted eastern China.

In this study, average temperature of two *regional transport* (V-T and S-T) groups are much lower than summer (~9°C), and average nitrate concentrations of these two groups are high (> 10 μg m^{-3}). In addition, although average nitrate concentrations of the *local ventilation with no regional transport* (V-nT) group are very low (~2 μg m^{-3}), the cold temperature (~3°C) can prevent evaporation of ammonium nitrate from the Teflon filter. Therefore, we expected potential nitrate loss for these three groups to be small enough (< 20%). The *local stagnation with no regional transport* (S-nT) group is probably most affected by evaporation because of its low nitrate concentration (~5 μg m^{-3}) with moderate temperature (~15°C). However, nitrate loss of this group would not be as much as that of the summertime Beijing (~75%) reported by Nie et al. (2010).

We further examined the sensitivity of our results by potential negative artifacts in NO_3^- through the ISORROPIA simulations using hypothetical NH_4^+ and NO_3^- concentrations considering evaporative nitrate loss [from 0% (no loss) to 80% loss of ammonium nitrate from the filter samples] together with the average concentrations of $PM_{2.5}$ components for each categorized group summarized in Table 2 (Fig. S8). Note that the results from the 0% nitrate loss assumption do not exactly same as the values in Table 2, because Table 2 shows the average of measured and predicted data for each group while Fig. S8 is obtained from the simulations using the average inorganic concentrations. If we assumed a 20% nitrate loss [NO_3^- and excess $NH_4^+ = (NH_4^+ / SO_4^{2-} - 1.5) \times SO_4^{2-}$; Pathak et al., 2004] for the V-nT, V-T, and S-T groups and a 50% nitrate loss for the S-nT group based on above discussion, the nitrate fraction in $PM_{2.5\ \mathrm{dry}}$ of the S-nT group becomes comparable to that of the *regional transport* (V-T and S-T) groups (Fig. S8a). However, inorganic ALW (W_i), $\varepsilon(NO_3^-)$, and $\varepsilon(NH_4^+)$ of the V-T and S-T groups are still larger than that of the S-nT group (Figs. S8b, d, and e), and this supports an important role of the transported wet particles in the formation of $PM_{2.5}$ inorganic species. In conclusion, therefore, potential negative artifacts induced by the un-denuded filter sampling method without backup filters do not significantly change the conclusions of this study.

To clarify the effect of potential errors from the sampling artifacts on our results, we added the following paragraph to the end of Line 90 on page 3 (as the third paragraph in Sect. 2.1).

Note that the $PM_{2.5}$ sampling on Teflon filter for inorganic ions was conducted without both a denuder and backup filters, and thus there could be potential sampling artifacts on the results, particularly negative artifacts in semivolatile ammonium nitrate (Ashbaugh and Eldred, 2004; Chow et al., 2005). Nie et al. (2010) reported that summertime nitrate loss on Teflon filter from the un-denuded filter sampling without backup filters is to be ~75% at lower nitrate concentrations (< 10 μg m^{-3}) but only ~10% at higher nitrate concentrations (> 10 μg 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 group does not change our conclusion (Fig. S8).

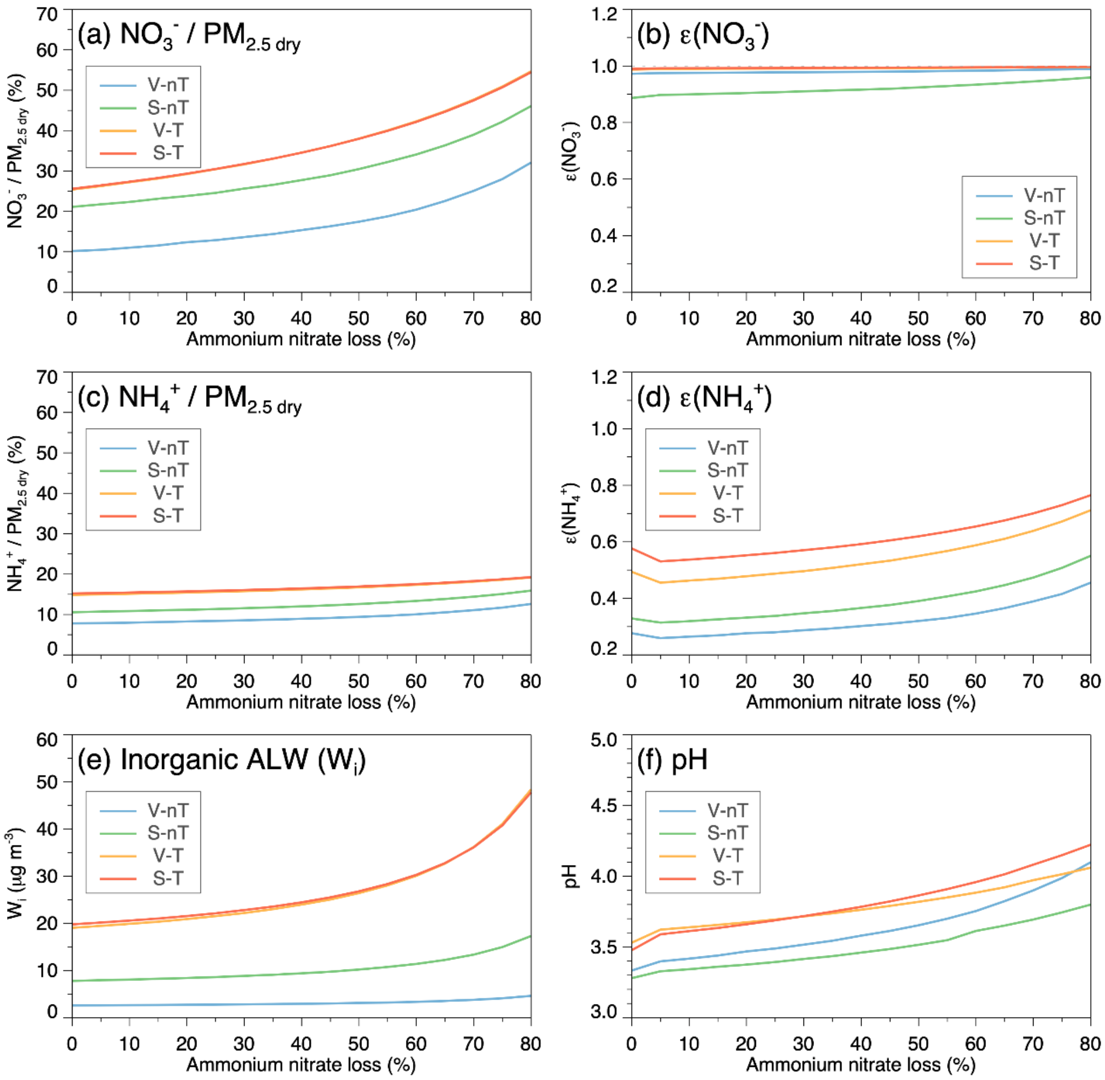

Figure S8: Sensitivity of (a) nitrate fraction in dry $PM_{2.5}$ (NO_3^- / $PM_{2.5\ dry}$), (b) nitrate partitioning ratio [$\varepsilon(NO_3^-)$], (c) ammonium fraction in dry $PM_{2.5}$ (NH_4^+ / $PM_{2.5}$), (d) ammonium partitioning ratio [$\varepsilon(NH_4^+)$], (e) inorganic ALW (W_i) content, and (f) pH to the hypothetical ammonium nitrate loss during the sampling on Teflon filters. Average $PM_{2.5}$ components (Table 2) with extrapolated concentrations of NO_3^- and excess NH_4^+ [$NH_4^+{}_{excess}$ = (NH_4^+ / SO_4^{2-} − 1.5) × SO_4^{2-}; Pathak et al., 2004], considering the hypothetical ammonium nitrate loss from 0% to 80%, were employed in the ISORROPIA simulations. Sensitivity curves in blue, green, yellow, and red colors 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.

Ashbaugh, L. L. and Eldred R. A.: Loss of particle nitrate from Teflon sampling filters: Effects on measured gravimetric mass in California and in the IMPROVE network, J. Air Waste Manage. Assoc., 54, 93–104, https://doi.org/10.1080/10473289.2004.10470878, 2004.

Chow, J. C., Watson, J. G., Lowenthal, D. H., and Magliano, K. L.: Loss of $PM_{2.5}$ nitrate from filter samples in central California, J. Air Waste Manage. Assoc., 55, 1158–1168, https://doi.org/10.1080/10473289.2005.10464704, 2005.

Nie, W., Wang, T., Gao, X., Pathak, R. K., Wang, X., Gao, R., Zhang, Q., Yang, L., and Wang, W.: Comparison among filter-based, impactor-based and continuous techniques for measuring atmospheric fine sulfate and nitrate, Atmos. Environ., 44, 4396–4403, https://doi.org/10.1016/j.atmosenv.2010.07.047, 2010.

Pathak, R. K., Yao, X., and Chan, C. K.: Sampling artifacts of acidity and ionic species in $PM_{2.5}$, Environ. Sci. Technol., 38, 254–259, https://doi.org/10.1021/es0342244, 2004.

Regarding the estimated NH_3 and effect on pH. A sensitivity test is warranted, as noted by another reviewer. This could include discussing $\varepsilon(NH_4^+)$ and $\varepsilon(NO_3^-)$. Table 2 suggests that with $\varepsilon(NH_4^+)$ values ranging from 0.23 to 0.5, there may be some sensitivity to $[NH_3]$. But as noted, this may not contribute to much change in pH. Furthermore given Fig 9, in some situations this may not have a large effect on predicted NO_3^-. The point is, the epsilon data for NH_4^+ and NO_3^- can be used to help assess the sensitivity of the predictions to uncertainties in gas phase species that were not measured; eg, one could make a graph of $\varepsilon(NH_4^+)$ similar to Fig 9 and then show the data for a range of estimated NH_3 and HNO_3 around the predicted values.

Following the reviewer's suggestion, we conducted sensitivity tests for pH and inorganic partitioning ratios $[\varepsilon(NO_3^-)$ and $\varepsilon(NH_4^+)]$ and represented the results as Fig. 5 in the revised version. As the reviewer expected, the changes in pH, $\varepsilon(NO_3^-)$, and $\varepsilon(NH_4^+)$ by NH_3 is not significant when NH_3 concentration is larger than 5 ppb.

Various NH_3 levels from 0 ppb to 50 ppb are applied for all the measurement days as fixed values (no day-to-day variations in NH_3) in our sensitivity tests. Figs. 5a, c, and e show good correlations between the results from simulation with daily varied NH_3 (average of 10.9 ppb) and that with daily fixed NH_3 if it was not 0 ppb. This indicates that the potential errors in pH and partitioning ratios from the day-to-day estimation seem to be limited. Figs. 5b, d, and f show that the average pH and partitioning ratios for each categorized group become flattened over the 5 ppb of NH_3. Therefore, the potential errors from the estimation of NH_3 do not change our conclusion.

We added the content related to the sensitivity test for NH_3 to Line 130 on page 5 of the original manuscript as follows:

We conducted ISORROPIA simulations with various NH_3 levels (0–50 ppb) applied for all the measurement days as fixed values to further explore the sensitivity of pH, $\varepsilon(NO_3^-)$, and $\varepsilon(NH_4^+)$ to NH_3. Good correlations between results from the daily varied NH_3-simulation and the fixed NH_3-simulations shows that potential errors induced by the estimation of daily NH_3 levels will be small if NH_3 concentrations are nonzero (Figs. 5a, c, and e). Increasing pH and $\varepsilon(NO_3^-)$ and decreasing $\varepsilon(NH_4^+)$ by the increase in fixed NH_3 level become flatten over the range from a half to 2 times of the average NH_3 concentration in Seoul (~5–20 ppb; Phan et al., 2013) (Figs. 5b, d, and f), and this indicates that the potential errors in reconstructed NH_3 will not significantly change the results in this study.

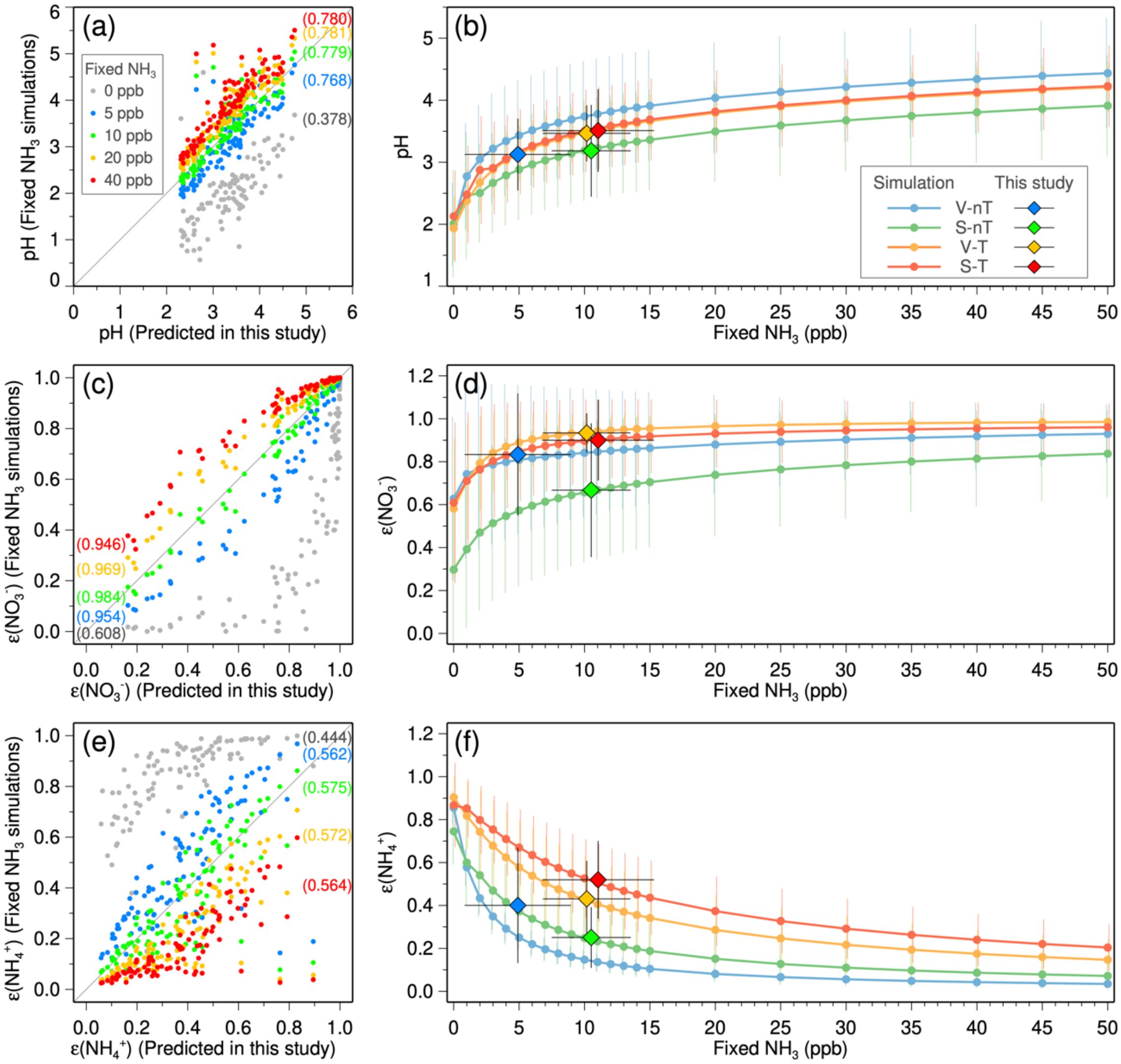

Figure 5: Sensitivity of (a–b) predicted pH, (c–d) nitrate partitioning ratio [$\varepsilon(NO_3^-) = NO_3^- / (HNO_3 + NO_3^-)$], and (e–f) ammonium partitioning ratio [$\varepsilon(NH_4^+) = NH_4^+ / (NH_3 + NH_4^+)$] to gas-phase ammonia ($NH_3$) concentrations. (a, c, and e) Comparisons between the simulation in this study (using the daily reconstructed NH_3 concentrations) and the simulations with the various fixed NH_3 levels (colored dots in gray, blue, green, yellow, and red for 0 ppb, 5 ppb, 10 ppb, 20 ppb, 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, and f) Average (solid circles) and standard deviation (vertical bars) of pH, $\varepsilon(NO_3^-)$, and $\varepsilon(NH_4^+)$ 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 NH_3 levels from 0 ppb to 50 ppb. Averages and standard deviations of the reconstructed NH_3 concentrations and obtained pH, $\varepsilon(NO_3^-)$, and $\varepsilon(NH_4^+)$ 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.

Line 319, one could be more specific here, with $\varepsilon(NO_3^-)$ near or at 1 there is a direct relation between NO_x control and particle NO_3^-.

We added following sentence behind the line 319:

Such a direct relationship between NO_x control and nitrate aerosol is significant at the condition of $\varepsilon(NO_3^-)$ close to 1.

Sulfate is a large component of the SIA. How does sulfate play a role in this feedback mechanism (see next)?

The idea of feedback (or sometimes called co-condensation) leading to more uptake of NH_3 and HNO_3 by the added liquid water is not a new concept. I suggest the authors think about it some more and add a deeper discussion. It happens for any semi-volatile acidic species that when partitioned to the particle phase significantly increases the water uptake, which then raises the pH and allows more uptake. Examples include HCl / Cl^- & HNO_3 / NO_3^-. Since sulfate is not semi-volatile and highly hygroscopic the semivolatile species involved that is driving this feedback process must generally have significantly higher concentrations then sulfate, or more precisely, contribute comparable or more to AWC than sulfate, otherwise the feedback does not exist. For example, in this study if sulfate was significantly larger then nitrate, would nitrate levels increase due to uptake of water? Probably not because sulfate would then control the overall AWC. One could play around with sulfate concentrations to see when this happens. The process discussed here is very similar to that discussed in Guo et al. (2017). Also, as another example, see Topping et al (2013).

Guo, H., J. Liu, K. D. Froyd, J. Roberts, P. R. Veres, P. L. Hayes, J. L. Jimenez, A. Nenes, and R. J. Weber (2017), Fine particle pH and gas-particle phase partitioning of inorganics in Pasadena, California, during the 2010 CalNex campaign, Atm. Chem. Phys., 17, 5703–5719.

Topping, D., P. Connolly, and G. McFiggans (2013), Cloud droplet number enhanced by co-condensation of organic vapours, Nature Geoscience, 6, 443–446.

We appreciate the reviewer's comment and suggestion on this. As the reviewer pointed out, the significant nitrate concentration compared to sulfate can promote the feedback mechanism including water and nitrate uptake into the particle together with pH increase. This relationship can be also found in our results. For example, the nitrate-to-sulfate molar ratio is largest in the *local stagnation with regional transport* (S-T) group (1.87), followed by the *local ventilation with regional transport* (V-T) group (1.60), the *local stagnation with no regional transport* (S-nT) group (1.29), and the *local ventilation with no regional transport* (V-nT) group (0.81). Because inorganic ALW, pH, and $\varepsilon(NO_3^-)$ are high in the *regional transport* (V-T and S-T) groups followed by the S-nT and V-nT groups (Table 2), this feedback process explains the synergistic effect of transported (wet) particle on the nitrate uptake.

We added the content related to the feedback mechanism to Line 285 on page 9 of the original manuscript as follows:

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 by dilution effect on hydrogen ions. 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 uptake more ALW. However, if SO_4^{2-} is dominant in the particle, such a feedback process will be weakened because sulfate is non-volatile (Guo et al., 2017). The average nitrate-to-sulfate 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 $\varepsilon(NO_3^-)$ 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 particle on high NO_3^- and ALW fractions.