Response to Referee #2

General comments:

Seo et al. combined measurements of $PM_{2.5}$ mass and composition (from filter collection) in Seoul, Korea, with thermodynamic modeling in ISORROPIA II and back trajectory analysis. They find that particles influenced by regional transport from source areas in China have higher mass, higher inorganic aerosol content and higher water content. Specifically, the highest concentrations are observed in air masses under locally stagnant conditions affected by regional transport. They conclude that the synergistic effects of local stagnation and regional transport affect $PM_{2.5}$ concentrations and composition.

Except for a few English usage issues, the manuscript is well written and within the scope of Atmospheric Chemistry and Physics. While the measurements are local, the main conclusion(s) are likely applicable to other regions and are therefore of broader interest. I have one major and several minor comments and concerns which should be addressed before publication.

We appreciate the reviewer for careful reading and helpful comments that improve our manuscript. 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 and references in the revised version of manuscript. 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 $\mu g\ m^{-3}$. 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.

Major comments:

In section 2.2, the author describes reconstructing concentrations of HNO_3 and NH_3 for their thermodynamic modeling analysis. I have two main issues with this:

1. In my opinion, the current version of the manuscript does not sufficiently justify the methods of reconstruction. For NH_3, the authors seem to assume that the concentrations at the Gwangjin site are the same as the concentrations at the KIST site, and that they did not change between years. Please describe why these are reasonable assumptions.

Since there were no NH_3 measurements in Seoul for the analysis period of 2012–2014, we had to reconstruct NH_3 concentrations for the thermodynamic model simulations in some way. Fortunately, we found a year-long measurement (2010–2011) of NH_3 at the Gwangjin site (37.545°N, 127.096°E, 7.8 km southeastward away from the KIST site) in Seoul reported by Phan et al. (2013). Although the NH_3 data reported by Phan et al. (2013) has some spatiotemporal gaps (~1 to 3 years) to data in this study measured at the KIST site (37.603°N, 127.047°E), we assumed that both two site data shares statistical characteristics like annual average NH_3 level, standard deviation, and correlations with meteorological factors (temperature, RH, and wind speed) and anthropogenic gas pollutants (SO_2, NO_2, and CO), as mentioned in Text S1. Our assumption is based on (i) the small interannual changes in the estimated NH_3 emissions in Seoul from the Clean Air Policy Support System (CAPSS) inventory (Lee et al., 2011; NIER, 2018) (Fig. S5) and (ii) the similar environment of both two sites that are located downwind of the downtown core in the prevailing westerlies in Seoul and surrounded mainly by residential areas and small urban green areas (modified version of Fig. S1).

To clarify the justification of the NH_3 reconstruction based on the data by Phan et al. (2013), we added the following sentences to the end of Line 111 on page 4 of the original version as follows:

There were small interannual changes in the estimated NH_3 emission in Seoul (Fig. S5; NIER, 2018), and both two sites 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 two sites and periods would be similar despite the temporal gap (~1–3 yr) and spatial distance (~7.8 km) between this study and Phan et al. (2013).

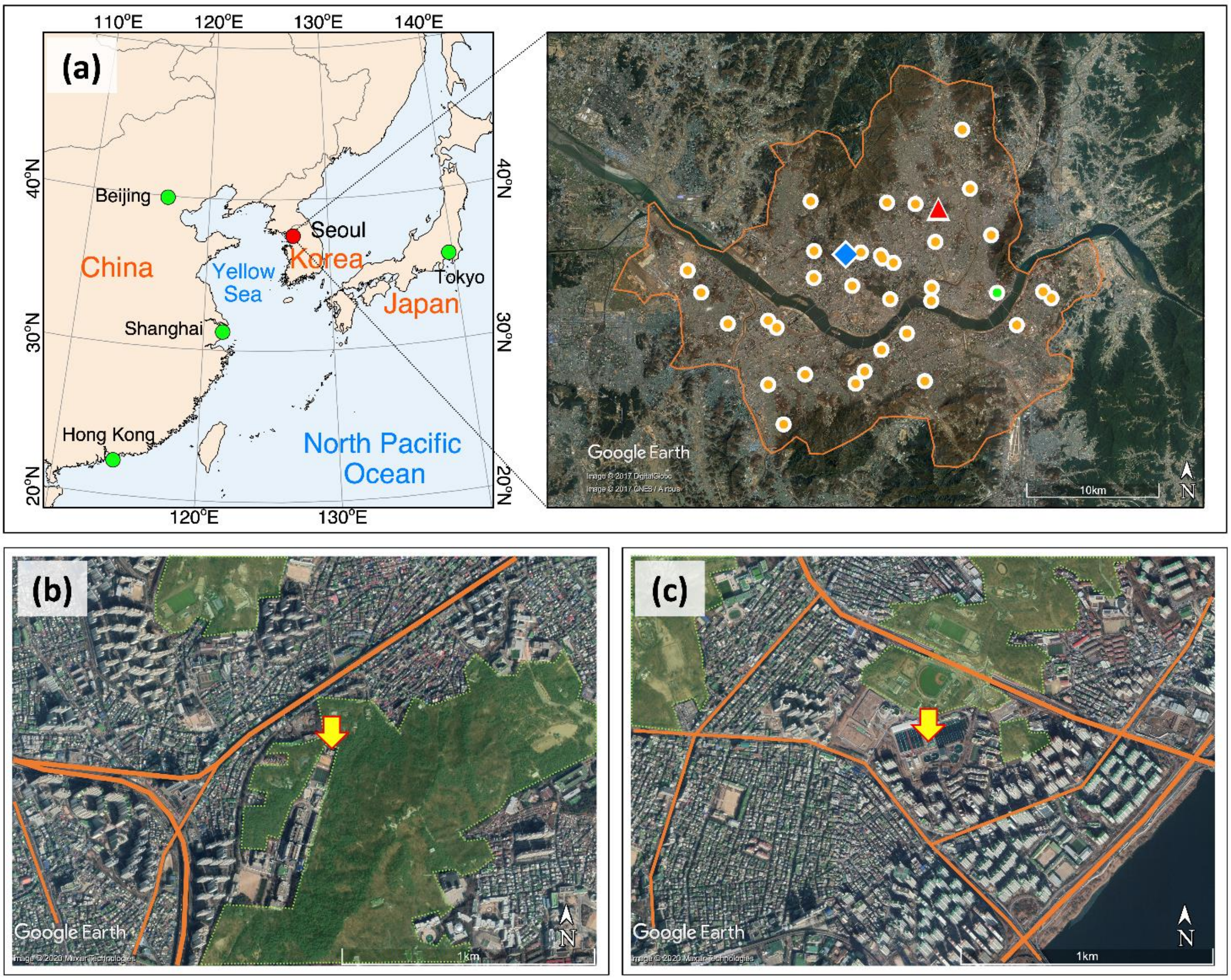


Figure S1: (a) The locations of Seoul (left panel) and the Korea Institute of Science and Technology (KIST) $PM_{2.5}$ sampling site (red triangle), the Korea Meteorological Administration (KMA) weather station (blue diamond), and Korea Ministry of Environment (KMOE) air quality monitoring sites (34 solid circles in yellow and green) in Seoul (right panel). The solid circle in green indicates the Gwangjin site at which a year-long NH_3 measurement was conducted by Phan et al. (2013). (b–c) Satellite maps of (b) the KIST $PM_{2.5}$ sampling site (37.603°N, 127.047°E) utilized in this study and (c) the Gwangjin site (37.545°N, 127.096°E) for NH_3 measurement in Phan et al. (2013). Yellow arrows are the sampling locations, areas shaded by light green are urban green areas, and lines in orange are the main roads. The background satellite images are courtesy of Google Earth.

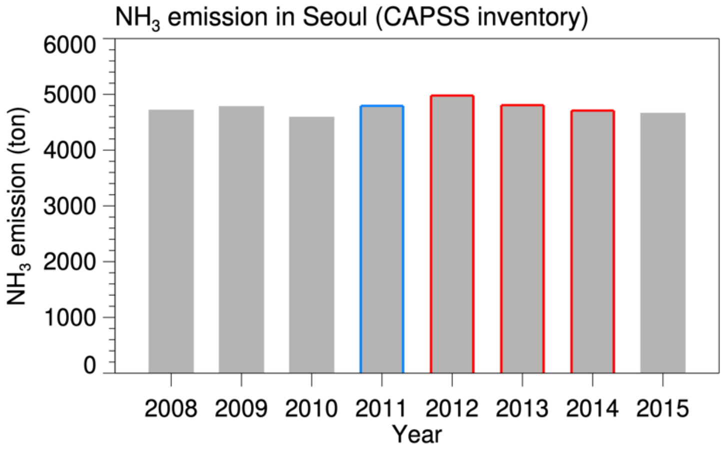


Figure S5: Estimated annual NH_3 emissions in Seoul for 2008–2015 from the Clean Air Policy Support System (CAPSS) inventory (NIER, 2018).

Lee, D.-G., Lee, Y.-M., Jang, K., Yoo, C., Kang, K., Lee, J.- H., Jung, S., Park, J., Lee, S.-B., Han, J., Hong, J., and Lee, S.: Korean national emissions inventory system and 2007 air pollutant emissions, Asian J. Atmos. Environ., 5, 278–291, https://doi.org/10.5572/ajae.2011.5.4.278, 2011.

NIER (National Institute of Environmental Research): National air pollutants emission 2015 (NIER-GP2017-210), NIER, Incheon, South Korea, available at: http://webbook.me.go.kr/DLi-File/NIER/09/023/5668670.pdf (last access: 21 October 2019), 2018 (in Korean).

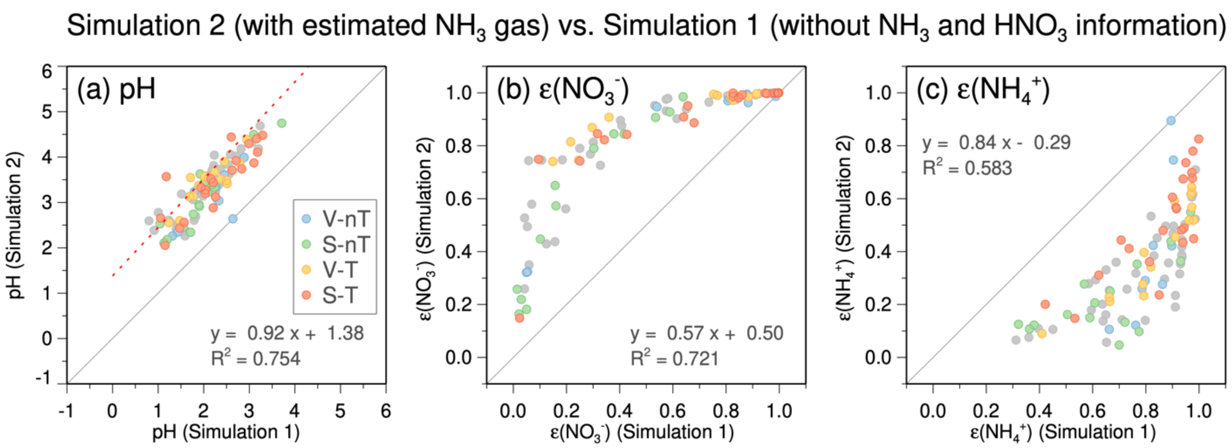
For HNO_3, the authors seem to assume that the NO_3/HNO_3 ratio does not depend on the sum of NO_3+HNO_3 concentrations. Please justify this assumption.

In general, the NO_3^- / HNO_3 ratio depends on temperature, aerosol liquid water (ALW), and pH. Among these three variables, temperature is an independent meteorological variable, and ALW is dependent on the sum of salts and relative humidity. Therefore, the NO_3^- / HNO_3 ratio obtained from the simulation with reconstructed NH_3 (Simulation 2 in Fig. 4 in the revised manuscript) can be changed solely by the potential changes in pH owing to the increase in total HNO_3 (from NO_3^- to NO_3^- + HNO_3). In the NH_3-rich condition like Seoul, the potential changes in pH can be small due to the buffering effect of NH_3 partitioning (Weber et al., 2016). Therefore, we can use the NO_3^- / HNO_3 ratio from Simulation 2 and the measured NO_3^- to estimate the total HNO_3. Fig. 4 shows comparisons of pH, $\varepsilon(NO_3^-)$, and $\varepsilon(NH_4^+)$ among three simulations (Simulation 1 with only ions, Simulation 2 with ions and reconstructed NH_3, and Simulation 3 with ions, reconstructed NH_3, and HNO_3 estimated by the NO_3^- / HNO_3 ratio from Simulation 2), and here we can see that the pH is largely changed by the introduction of NH_3 gas but is nearly not changed by the increase in total HNO_3.

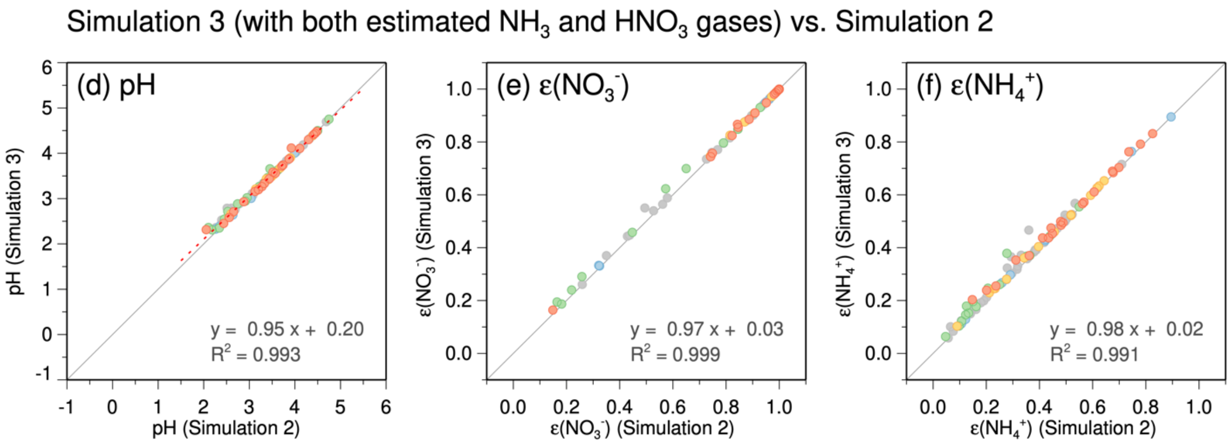
To justify the estimation of HNO_3 by using the NO_3^- / HNO_3 ratio, we added the following sentences to Line 119 on page 4 of the original version as follows:

Note that we regarded the HNO_3 / 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 HNO_3 / NO_3^- ratio is affected alone 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 [$\varepsilon(NO_3^-) = NO_3^- / (HNO_3 + NO_3^-)$], and ammonium partitioning ratio [$\varepsilon(NH_4^+) = NH_4^+ / (NH_3 + NH_4^+)$] from the ISORROPIA simulations with and without gas-phase HNO_3 information show negligible differences between each other (Figs. 4d–f), unlike the significant role of additional NH_3 information on increasing pH and $\varepsilon(NO_3^-)$ and decreasing $\varepsilon(NH_4^+)$ (Figs. 4a–c).

Also, we added Fig. 4 into the manuscript in the revised version.



Simulation 2 (with estimated NH_3 gas) vs. Simulation 1 (without NH_3 and HNO_3 information)



Simulation 3 (with both estimated NH_3 and HNO_3 gases) vs. Simulation 2

Figure 4: Comparisons of the predicted pH, nitrate partitioning ratio [$\varepsilon(NO_3^-) = NO_3^- / (HNO_3 + NO_3^-)$], and ammonium partitioning ratio [$\varepsilon(NH_4^+) = NH_4^+ / (NH_3 + NH_4^+)$] between (a–c) the simulation without gas-phase NH_3 and HNO_3 information (using NH_4^+ and NO_3^- as the total NH_3 and total HNO_3; Simulation 1) and the simulation with reconstructed NH_3 (using $NH_3 + NH_4^+$ as the total NH_3 but only NO_3^- as the total HNO_3; Simulation 2) and (d–f) the Simulation 2 and the simulation with both estimated gas-phase NH_3 and HNO_3 information (this study; Simulation 3). Filled circles in light blue, light green, light yellow, and light red colors represent daily data 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.

2. The reconstructed concentrations certainly introduce uncertainty, which the authors recognize. For example, they comment (lines 122-123): "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 may be small enough." They follow this comment by a discussion on why the impact may be small enough. In my opinion, there is too much uncertainty here (in the data and the language, e.g. "may" and "would"), and I suggest that the authors conduct a sensitivity analysis on how uncertainty in the reconstructed concentrations of NH_3 and HNO_3 affects their conclusions.

As the reviewer suggested, we conducted sensitivity tests to examine how various NH_3 levels can affect and change the results, particularly pH and inorganic partitioning ratios [$\varepsilon(NO_3^-)$ and $\varepsilon(NH_4^+)$]. 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 the reconstructed NH_3 data contains two types of error that are (i) from the day-to-day estimation by the multiple regression model (Text S1 and Table S1) and (ii) from the average concentration of NH_3 in Seoul. 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 [e.g., R^2 values of 0.779 for pH, 0.984 for $\varepsilon(NO_3^-)$, and 0.575 for $\varepsilon(NH_4^+)$ in 10 ppb]. If the fixed NH_3 level was not 0 ppb, correlations with 5, 10, 20, and 40 ppb are not significantly different. Therefore, the potential errors in pH and partitioning ratios raised 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. This can be already expected from the buffering effect of NH_3–NH_4^+

partitioning on pH, and thus the potential errors from the estimation of NH_3 do not change our conclusion.

Based on the sensitivity test, we removed words representing uncertainty from this section, and 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.

Also, we added Fig. 5 into the manuscript in the revised version.

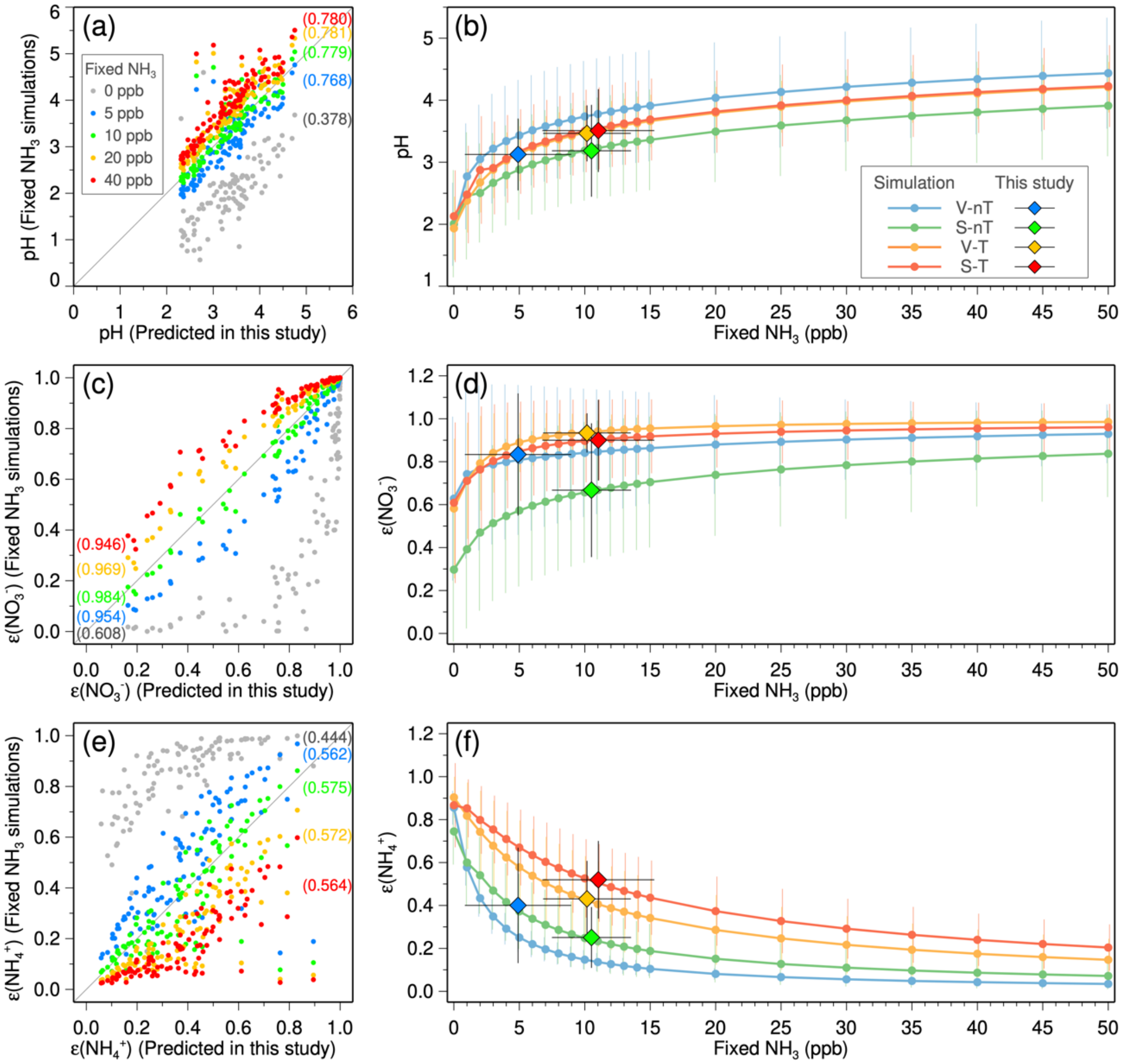


Figure 5: Sensitivity of (a–b) predicted pH, (c–d) nitrate partitioning ratio [$\varepsilon(NO_3^-) = NO_3^- / (HNO_3 + NO_3^-)$], and (e–f) ammonium partitioning ratio [$\varepsilon(NH_4^+) = NH_4^+ / (NH_3 + NH_4^+)$] to gas-phase ammonia ($NH_3$) concentrations. (a, c, and e) Comparisons between the 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.

Minor and technical comments:

Line 12: replace 'stagnant' with 'stagnation'

Thanks for the correction. It was now corrected.

Line 17: replace 'group' with 'grouped' or otherwise revise as this is unclear

We revised the sentence as follows:

$PM_{2.5}$ 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 and aerosol liquid water (ALW) compared to that measured under the non-transport condition.

Lines 32-35: the sentence is unclear, especially the second half (. . . " and also a situation. . ."). Please revise (splitting into two sentences would probably help).

As the reviewer suggested, we split the sentence into two as follows:

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).

Line 86: "The OM identified in this study is ～5% of the total OM." I think I know what you mean, but this sentence is confusing to me. Perhaps rephrase as "The organic compounds identified in this study constitute ～5% of the total OM."

The sentence was now revised as suggested by the reviewer.

Line 255: replace 'the more increase' with 'the higher increase'?

'the more increase' is now replaced with 'the higher increase.'

Lines 291-292: "Interestingly, SOR increase by temperature (and also irradiance) is not significant as much as inorganic ALW (Figs. 8c) despite. . ." please revise this phrase as it is not clear.

We revise the sentence as follows:

Interestingly, the increasing SOR by temperature (and also irradiance) is not significant as much as that by inorganic ALW (Figs. 8c) despite the high-temperature and strong-irradiance conditions conducive to photochemical oxidation of SO_2 in summer.

Lines 293-295: "This implies that the observed high SO_4 in the S-T group was induced by the aqueous-phase oxidation of SO_2 in the transported wet particles rather than the photochemical gas-phase oxidation." It seems appropriate to point out here that gas-phase oxidation likely also played a role (i.e. the data do not rule out gas-phase oxidation as a source of sulfate).

As the reviewer suggested, we modified the sentence not to rule out gas-phase oxidation as follows:

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.

There are several instances where the article "the" is overused. As an example, last sentence in the abstract: "This study reveals the synergistic effect of remote and local sources on the 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 the numerical air quality models". I would suggest removing "the" in front of 'urban', 'numerical air quality models'. This seems more consistent with common usage and would also further help to suggest applicability of the conclusions to other areas. I suggest the authors review the whole manuscript for use of "the".

Thank you for comments. We removed several "the" in the revised version of manuscript following the reviewer's suggestion.