Response to Reviewer #2

This paper focuses on the nitrate transboundary heavy pollution over East Asia in winter. They developed a technique that could differentiate the nitrogen or sulfur dominated air pollution based on a regional chemical transport model and surface observations. They also highlighted the importance of the transboundary air pollution dominated by nitrate, which may refine our understanding of the transboundary heavy PM2.5 pollution in winter over East Asia. Overall, this represents an important work to document the sources-transport-deposition of air pollutants in a hotspot region. I recommend it to be accepted but with revision, to allow the authors to address my concerns below. Also, they could provide, if possible further analysis from another episode to see how comparable/consistent their results could be, especially for type nitrate episode.

Dear Reviewer #2,

Thank you for taking the time to review our manuscript for *Atmospheric Chemistry and Physics*, and providing helpful comments. We agreed that more case studies are necessary to figure out the transboundary air pollution of nitrate. In this study, we have focused on an intensive observation period in January, and comprehensively analyzed two episodes. We would like to continue to apply model analysis to other episodes and report those results on another occasion.
We have revised our manuscript according to the reviewers' comments and suggestions. We believe that these revisions address all points raised by the reviewers. We also provide a point-by-point response below. The revisions are indicated in blue in the revised manuscript.

Sincerely,

Syuichi Itahashi

1) Page 2, Line 18: The conversion of gas to particle is not the only way producing nitrate in the air. Besides, coarse particles like Gobi desert surface soil also involved in the nitrate production during the transport [Atmos. Chem. Phys., 14, 11571-11585].

In this sentence, we have mentioned NO_3^- as fine mode. To clarify, we have revised the wording of 'NO_3^-' to 'NO_3^- in $PM_{2.5}$'.

The coarse particles of NO_3^- produced via the reaction with mineral dust are considered to be smaller in the winter case.

2) Page 3: It is better to introduce "why the observation period from January 7–17, 2015 was selected".

To capture the heavy transboundary air pollution in winter time, we have set an intensive observation for this period. This was introduced in the text (P3, L10-11).

3) Page 4, Line 12: The citation (Pan et al., 2016) is not identical throughout the text. It is better to use (Pan X. et al., 2016) here, to avoid mixing from another EST paper by Pan Y. et al., 2016.

Thank you for careful reading. We have modified these citations to indicate the appropriate references.

4) Page 4, Sect. 2.1.1, 2.1.2 and 2.1.3: All the measurements made have biases and in some cases they are significant. It was reported here that fine-mode aerosols were collected with a PTFE filter. It is well documented that positive artifacts of filter sampling are mainly caused by the adsorption of interference gases, such as acidic HNO3 gases, by the collected particles or the sampling filter [Atmospheric Environment 145, 293–298]. It is likely that nitrates have been overestimated due to the sampling filter itself, in addition to the difference in the cut-off diameter [Page 5, Line 1-4].

Because the gas-phase HNO_3 was collected with an annular denuder coated with NaCl before collection in a PTFE filter, the possibility of the adsorption of HNO_3, which would lead to overestimation of NO_3^-, is considered negligible. We have added an explanation of this (P5, L4-5).

5) Page 5, Line 1-4: Is the difference in the cut-off diameter was the only reason for the systematic differences between ACSA and D-F method? It was documented that ultraviolet spectrophotometric method will overestimate the concentration of nitrate. Please also add some details about the comparison here, as most of the readers cannot follow references in Japanese.

The difference in the cut-off diameter was considered to be the most important factor in differences between results from the ACSA and D-F methods. To support this assertion, we have revised our explanation (P5, L7-14), which is reproduced here.

"Comparing size-segregated SO_4^{2-} and NO_3^- data based on the D-F pack method with that from ACSA showed systematic differences. Linear regression analysis of fine-mode and coarse-mode SO_4^{2-} and NO_3^- showed good correlation, but the slope was not unity. Fine-mode aerosols were underestimated by the D-F pack relative to ACSA measurements, and coarse-mode aerosols were overestimated by the D-F pack relative to ACSA measurements. However, by summing the fine- and coarse-mode data, the slope between D-F pack and ACSA results was close to unity. The difference in the cut-off diameter of the D-F pack method was considered to be the most important factor in explaining differences between results from D-F pack and ACSA. More details of the comparison and validation of ACSA data are reported in Osada et al. (2016)."

Page 5, Line 13-14: It is easy to understand that the nitrate data from Goto Islands, Tsushima Island, and Tottori was not used due to volatilization. In addition to nitrate, ammonium was also affected by volatilization. So, why the data of ammonium was used?

We agree that ammonium particles can be somewhat affected by volatilization in the case of ammonium-nitrate formation, but ammonium can form ammonium-sulfate in preference, and the volatilization of ammonium-sulfate will not be considered. Therefore, we used ammonium concentration, which captures ammonium-sulfate. To note this point to the readers, we have mentioned the possibility of the volatilization of ammonium-nitrate (P5, L24-26).

Page 5, Line 5-22: How did PM2.5 measured by PM-712 compare to the Beta attenuation sampler? It is likely that PM2.5 have been overestimated, depending on temperature and relative humidity, and there could have been significant impacts.

PM-712 data were acquired at remote sites in Japan (Section 2.1.4), and beta attenuation sampler data were used at the observation sites in China (Section 2.1.5). We did not directly compare these results.

Page 5, Line 22: Change the title of 2.1.5 to 2.1.6.

We have revised the numbering.

Page 9, Line 10-12: Even that I agree with the results in this study, I am unsure how reproducible those results are on the regular basis, since the authors only study one episode for "type N" and "type S", respectively. Such an issue needs to be critically addressed.

Because of the limitation inherent in a short-term intensive observation campaign, we have discussed one episode of 'Type N' and one episode of 'Type S' in this study. We would like to

further analyze and demonstrate transboundary air pollution cases for both types; however, such analyses are beyond the scope of this study.

Page 9, Line 25-30: It is hard to believe the concentrations of ammonia are close to zero. As shown in Fig. 6, it seems the temporal variation of the NHx observation was mismatched with the ammonia simulation, especially for Type N. In a recent publication, enhanced values of NH3 were observed within the Asian summer monsoon upper troposphere, where it might contribute to the composition of the Asian tropopause aerosol layer [Atmos. Chem. Phys., 16, 14357-14369].

As an observation result, NH_3 showed nearly zero concentration for both types and in some cases (Fig. 6). As we have discussed in the text (P10, L15-19), NH_3 was fully converted to produce NH_4^+ in both types.

The reference mentioned here discussed the tropopause aerosol layer during the Asian summer monsoon, and this would not be closely related to our results, which concern the air quality in winter.

Page 10, Line 20-21: Why precipitation on Jan 15-16 was not captured in the model [Fig. 4]?

At 1500 LT, 15 January, precipitation at 2.5 mm/h was observed. For this precipitation event, the model underestimated the precipitation amount as 0.22 mm/h. Over north Kyushu island, the model simulated less than 1 mm/h of precipitation for this event. In general, the model simulation underestimated precipitation amounts, as we have reported in a previous study (Itahashi et al., 2014, Atmospheric Environment, 92: 171-177).

Page 11, Sect. 3.2: Although the long-term range transport of air pollutant was discussed here, the readers are still wondering the contribution of nitrate production during the process/pathway of transport, as well as the contribution from local sources surrounding the investigated sites.

First, nitrate production during transport from China to Fukuoka did not occurred in the examined winter cases, as we show in Figs. 11 and 12 for the trajectories and summarize in Fig. 13. In both types, high concentration of nitrate was directly transported from China, and the concentration level gradually decreased during transport (Fig. 13). We demonstrated that nitrate can be directly transported if sulfate production is not activated (Type N, Fig. 11), and nitrate concentration gradually decreased under the production of sulfate-ammonium (Type S, Fig. 12).

Second, as we discuss in Section 3.2, both types N and type S were dominated by the transboundary air pollution, and local contribution was not considered. Nitrate production involves nonlinearity with complex chemical mechanisms, but observation and model of black carbon also suggested little local contribution for both types.

Page 16: The aforementioned contributions are encouraged to be quantified in the conclusion and abstract to highlight the importance of nitrate long-range transport.

To address the comment, we have added a discussion of the direct transport of nitrate from China to Fukuoka (P15, L22-23).

Additionally, we have added a comment to the abstract about the high concentration of NO_3^- over China to emphasize the direct transport of NO_3^- from China to Japan.