Responses to Anonymous Referee #1

We thank the reviewer for the insightful and valuable comments. Our specific responses are addressed below and colored by blue. Changes made to the manuscript are in quotation marks.

General Comments: This measurement report titled "Characterization of severe spring haze episodes and influences of long-range transport in the Seoul metropolitan area in March 2019" submitted by Hwajin Kim, Qi Zhang, and Yele Sun reports on aerosol characteristics in Seoul Korea during haze events in early spring with comparisons to similar measurements taken simultaneously in Beijing China. The manuscript meets the requirements of a measurement report, i.e., it reports substantial new results from field measurements with conclusions of more limited scope than in research articles. The authors utilized measurements from the high resolution aerosol mass spectrometer (HR-AMS), meteorological measurements, other aerosol and gas phase measurements, and various analysis techniques to arrive at the main conclusion of the report, that long-range transport is a substantial (but not main) contributor to severe haze episodes in the Seoul metropolitan area. The overall quality of the manuscript is good, although some areas will need improvement. I recommend that the manuscript be published after making the following revisions.

Specific Comments:

Line 248: You mention a poor correlation between RH and nitrogen oxidation ratio (NOR), but you do not say what NOR (or later SOR) describe. You could say that NOR is the molar fraction of particle nitrate (NO3-) to particle nitrate plus gaseous NO2. Or, you could show an equation and cite a reference. It would also be nice for you to explain why we are looking at the correlation between RH and NOR. What is the typical trend for regional transport or local oxidation? What does good correlation between RH and NOR mean? Same questions for SOR.

Thanks for the suggestions. As reviewer suggested, we describe the NOR and SOR and also add the equations to calculate them. We are looking at the correlation of NOR and SOR with RH since RH can be a key factor to facilitate nitrate and sulfate formation, although many other factors (e.g., pH and T) may play a role as well. The correlations between RH and NOR (or SOR) thus suggest the possibility of the relevant reactions, not the exact evidence. With the suggestions of the reviewer, we rewrite the relevant section, which now reads;

"The relationships of nitrate and/or nitrogen oxidation ratio (NOR, molar fraction of NO3 in total N, i.e., NO3 + NO_2) and sulfate and/or sulfate oxidation ratio (SOR, molar fraction of SO_4 in total S, i.e., SO_4 + SO_2) with RH were often analyzed to understand the role of heterogeneous aqueous phase formation of secondary inorganic aerosols (Sun et al., 2013; Li et al., 2017; Xu et al., 2014). Both NO_3 and NOR showed an increasing trend with RH, but in a rather scattered relationship (i.e., r = 0.40). The correlation between RH and NOR is also positive but relatively weak (r = 0.48)). These results suggest that heterogeneous aqueous-phase processing likely contributed to some degree to the formation of inorganic nitrate and sulfate during this period (Fig. S9)."

In terms of the typical trend for regional transport or local oxidation, there are no specific numbers for each cases. For nitrate, generally, the concentration of its precursor (i.e., NO2) depends on local sources (although some are possibly from regional sources). Thus if NOR and NO3 enhanced, we can "suspect" an enhanced regional impact of nitrate. For sulfate, SO2 is mostly from regional sources and SO4 formation primarily occurs on a regional scale with some local contributions (mostly through aqueous phase reaction). Thus even if there is a significant regional impact, it is possible that SOR wouldn't enhance (since both sulfate and SO2 enhance). We've already discussed about it in section "3.3.3 Diurnal patterns of the PM1 composition during haze".

Line 257: What is your source for the assumption that PM1 represents approximately 80% of the PM2.5 mass?

Thanks, Mention the following reference to explain the assumptions.

Lim, S., Lee, M., Lee, G., Kim, S., Yoon, S., and Kang, K.: Ionic and carbonaceous compositions of PM10, PM2.5 and PM1.0 at Gosan ABC Superstation and their ratios as source signature, Atmospheric Chemistry and Physics, 12, 2007-2024, 10.5194/acp-12-2007-2012, 2012

Lines 293-294: You mention that nitrogen-to-carbon (N/C) ratio gradually increased overnight until 10:00 and indicated that both primary and secondary factors might influence the N/C ratio. Perhaps the increase of N/C ratio over the night is due to nighttime reactions of amines with nitrate radical, which has been observed in previous wintertime studies (Silva et al., 2008; Chen et al., 2016) and has been shown to increase during fog events (Chen et al., 2016). This might be worth mentioning in the manuscript.

Chen, C.; Chen, S.; Russell, L. M.; Liu, J.; Price, D. J.; Betha, R.; Sanchez, K.; Lee, A. K. Y.; Williams, L.; Collier, S. C.; Zhang, Q.; Kumar, A.; Kleeman, M.; Zhang, X.; Cappa, C. D. Organic aerosol particle chemical properties associated with residential burning and fog in wintertime San Joaquin Valley (Fresno) and with vehicle and firework emissions in summertime South Coast Air Basin (Fontana). J. Geophys. Res. - Atmos., 2018, 123, DOI:10.1029/2018JD028374

Silva, P. J.; Erupe, M. E.; Price, D.; Elias, J.; Malloy, Q. G. J.; Li, Q.; Warren, B.;Cocker III, D. R. Trimethylamine as precursor to secondary organic aerosol formation via nitrate radical reaction in the atmosphere. Environ. Sci. Technol. 2008, 42, 4689-4696. DOI:10.1021/es703016v

Good suggestions. Enhanced N/C ratio during night could be due to amines formed by nitrate radical reaction and/or fog processing. Although we do not have other evidence other than higher N/C ratio, we can suggest the possible night time reaction. Also RH during night was higher than during daytime. Now the relevant section reads;

"Or this enhanced N/C ratio overnight is possibly due to the night time reactions of amines with nitrate radical (Silva et al., 2008; Chen et al., 2016) which can be more increased during fog events (Chen et al., 2016). High night time RH during this study (Fig. 7) further suggest the possibility of night time reaction of nitrogen containing species. More investigations will be needed to confirm this night time processes in SMA."

Line 372: You say, “However, the mass spectrum of the LO-OOA2 is somewhat different from the less oxidized mass spectrum.” Do you mean the less oxidized mass spectrum determined by Sun et al., 2014? If so, place the reference at the end of the sentence.

It was meant that the LO-OOA2 is somewhat different from the mass spectrum of ROSA (sun et al., 2014). Relevant section has been clarified;

“However, the mass spectrum of the LO-OOA2 (Fig. 2n and o) is somewhat different from the mass spectrum of RSOA (Sun et al., 2014).”

Line 374: Which haze episode is being referred to in this sentence? Is it an average of all haze events? Please specify.

Yes, it was an average of all haze events. It has been specified as below;

“Compared to the clean period, the averaged RSOA (LO-OOA2+MO-OOA2) concentration during the three haze episodes had increased by a factor of ~8 (Figs. 2, 5, 6 and Table 2) ~”

Lines 411-412: You state, “Furthermore, we also observed that the evolution of the MO-OOA1 and SFOAs appeared to by intrinsically linked.” Upon first reading, it took me a while to realize that the following three sentences described how this was observed. I suggest making the following changes to the next sentence to clarify this better: Change “Overall, both diurnal patterns . . .” to “Overall, the diurnal patterns of both MO-OOA1 and SFOA . . .” in line 412.

Thanks. We make this clear in the paragraph and now reads;
“Overall, diurnal patterns of both MO-OOA1 and SFOA appeared similar during the high-loading period~”

Line 427: You report the range of aerosol concentration increases from low- to high loading periods of all aerosol components and OA sources as 1.7 – 8.6 and reference Table 2 and Figures 4 and S11. However, the upper range of 8.6 is not shown in any of the references. According to Table 2, the high value is 10.7. Please check these numbers.

Thanks, the numbers are from the value of RSOA (averaged value of LO-OOA2 + MO-OOA2). Since we didn’t use that value in both table and figure, the relevant section has been corrected;

“the average concentrations of all aerosol components and sources of the OA were 1.31 – 10.7 times higher during the high-loading periods than those during the low-loading periods (Table 2, Figs. 4 and S11). ”

Lines 436-438: In comparing the enhancement factors for the regional transport factors LO-OOA2 and MO-OOA2 with the local source factors HOA and COA, you state that the enhancements are considerably higher for the regional transport factors. This may be true for LO-OOA2 (10.7), but MO-OOA2 (5.4) is similar to HOA and COA (5.2 and 4.7, respectively). They are both higher, but only LO-OOA2 is considerably higher (in my opinion).

Yes, as reviewer mentioned, both HOA and COA are also higher and it is possibly due to lower concentration during clean period since both showed the higher ratio of overall/low loading period, shown in Table 2. But higher ratios are also possible due to there are some effect of local accumulation which we also consider as a possible reason and mention about this in section 3.3.4. For the clarification, follow sentence has been added;

"Note that HOA and COA, which are locally emitted OA also showed the enhancement with a factor of 5.2, and 4.7, respectively, indicating that not only regional impacts but also local accumulation might impact on the haze episode. However, relatively higher ratio between overall- and low-loading periods (Table2) suggest that lower concentration during clean period also possibly enhance the ratio between high- and low-loading periods. Details on the haze evolution will be discussed in section 2."

Line 599: You state that, "The HOA, COA, and LO-OOA1 did not contribute to Pb."

However, figure 8 shows a significant contribution to Pb from LO-OOA1. Am I reading the figure correctly? It is difficult to tell because the text in the figure is very small and the figure itself is of low resolution (see my comments in the technical corrections section on figure resolution and readability) and the OOA colors are so similar.

Thank you for the comments. First, Figure is revised to make the text easier to read. According to linear regressions, the variability of Pb concentration is explained strongly by the variations of LO-OOA1. However, the linear correlation between Pb and LO-OOA1 was somewhat low (r = 0.24). In order to make this point clear, we have rewritten the relevant section;

"The contribution of the Pb sources analyzed using a linear decomposition algorithm further showed that the airborne Pb measured at SMA can be freshly emitted from burning sources and transported in aged air masses along with other unknown species. Figure 8 reveals that a major source mixed with Pb was the SFOA (40%). The other mass fractions of the Pb-associated OA sources were MO-OOA2 (22%), LO-OOA1 (17%), and LO-OOA2 (13%). In particular, the contributions of the MO-OOA2 and LO-OOA2 were greatly enhanced during the high-Pb period, which is also consistent with the haze periods, i.e., March 5-7, March 11-12 and March 19-21, thus further supporting that haze formation was indeed impacted by regional transport. Note that overall contribution of LO-OOA1 is higher than that of LO-OOA2 (Fig. 8e), suggesting that there could be another source of Pb in local scale in SMA. As discussed in previous, LO-OOA1 is the locally formed SOA mostly enhanced during the first haze episode, thus it showed the significant impacts on the Pb concentration during the first haze episodes together with MO-OOA2 and LO-OOA2. However, the fraction of LO-OOA1 is high during the low loading period as well resulting the third highest significance to Pb (Fig. 8e) although the correlation with Pb is low (r = 0.24). This might be because the variation of Pb, specially the high concentration of Pb is mostly caused by the regional transport related with MO-OOA2 (r=0.62) and LO-OOA2 (r=0.73) (Table 1). The HOA and COA rarely contribute to Pb. These results suggested that 40% of the Pb-containing

particles in the SMA originated from combustion sources of the OA, whereas the rest was associated with aged and transported sources of the OA (RSOA) and locally formed SOA. ”

Technical Corrections: There were a number of minor technical corrections in both the main text and supplement, as well as some important corrections for the figures and tables.

Thanks. We have looked through all main text and supplement and did the technical correction. Also figures and tables has been updated as suggested.

Main Text:
Line 20: Change “organic mass-to-carbon” to “organic mass to organic carbon”
Thanks, it has been corrected.

Line 33: Change “AMS” to “HR-AMS”
Thanks, it has been changed throughout the manuscript.

Line 38: Add a comma after “haze period” and place “was” between “local burning” and “also important”
Thanks, it has been corrected.

Line 60: Change “KORUR-AQ” to “KORUS-AQ”
Thanks, it has been corrected.
Line 110: Change “Fig. 1” to “Fig. 1a”
Thanks, it has been corrected.

Line 121: Change “9 h earlier than” to “9 h ahead of” and “1 h earlier than” to “1 h behind”
Thanks, it has been corrected.

Line 124: Change “AMS” to “HR-AMS”
Thanks, it has been changed throughout the manuscript.

Line 125: Remove space between “HR-“ and “AMS”
Thanks, it has been corrected.

Line 136: Change “Fig. S1a” to “Fig. S1c”
Thanks, it has been corrected.

Lines 137-145: Change all five instances of “AMS” to “HR-AMS”
Thanks, it has been changed throughout the manuscript.

Line 139: Change “Figs. 1c and S1d” to “Figs. S1c and S1d”
Thanks, it has been corrected.

Line 141: Change both instances of “size distribution” with “concentration”
Thanks, it has been corrected.

Lines 168-170: Change both instances of “AMS” to “HR-AMS”
Thanks, it has been changed throughout the manuscript.

Line 188: Change “would be” to “is”
Thanks, it has been corrected.

Line 228: Add “ m” after “691”
Thanks, it has been corrected.

Line 228: What is the starting height for cluster 2? Add that value to the sentence.
The starting height for cluster 2 was the same with cluster 1.
The relevant sentence has been clarified;
“The average starting height for the back trajectories over the entire study period was approximately 225m for clusters 1, 2 and 691 m for cluster 3, respectively”

Line 228: Change “Fig. 1” to “Fig. 1d”
Thanks, it has been corrected.

Line 230: Add “(Fig. S19)” after “Beijing” at the end of the sentence.
Thanks, it has been added.

Line 232: Add “(Fig. S17)” after “species” at the end of the sentence.
Thanks, it has been added.

Line 240: Change “Ox” to “O3”. Note: Figure S8 in the SI is illegible, but the caption mentions an O3 time series.
Thanks, it has been changed and figure has been replaced with the updated one.

Line 249: Change “Fig. S8” to “Fig. S9”
Thanks, it has been changed.

Line 259: Change “AMS” to “HR-AMS”
Thanks, it has been changed throughout the manuscript.

Lines 260-262: Change sentence to say, “Using a global standard, 70% of the days (30 days) violated the WHO daily PM2.5 standard (25 ug/m3), thus indicating how significant the haze was during the measurement period.”
Thanks, it has been changed.

Line 278: Add a superscripted “-1” after “ppbv”
Thanks, it has been added.

Line 278: Rearrange parentheses to read, “The moderate correlation of the daytime (10:00~16:00) SOA/Ox ratio (r=0.60, 0.19 ug m-3 ppbv-1) suggests . . .”

Line 301: Change “Fig. 2” to “Fig. 2b”
Thanks, it has been changed.

Line 307: Vehicle emission control measures are not marked in Figure 5 as indicated.
The Figure 5 is to compare the time series of chemical species from SMA and Beijing during the haze period, thus it seems to be complex to mark the emission control measures, thus Fig. 5 has been erased from the text and only the period was mentioned in the text.

Line 322: Remove “s” from “winters”, and add “spring of” before “2016”. Also, winter of 2015 is not shown in either Fig. 2d or Fig. S14.
Thanks, it has been corrected.

Line 324: You say “during the 2016 winter”, do you mean “during the 2015 winter”?
That measurement has been done from 2015 Dec to 2016 Jan. For the clarification, the relevant sentence corrected to “2015~2016 winter (Kim et al., 2018)~”

Line 325: Change “Fig. S12” to “Fig. S15”
Thanks, it has been changed.

Line 371: Move “(Fig. 2g)” to just after “MO-OOA2” in line 370.
Thanks, it has been moved.

Line 373: Place “(Fig. 2n and o)” after “LO-OOA2”
Thanks, it has been moved.

Line 375: Change “Fig. 2n and o” to “Fig. 2p and q”
Thanks, it has been changed.

Line 376: Add “during the haze episode” after “RSOA concentration”
Thanks, it has been added.

Line 387: Add an “s” to the end of “fragment” and move the superscripted “+” to after the subscripted “2n+1” (and “2n-1”) in the parentheses.
Thanks, it has been corrected.

Lines 397-398: “Diurnal Patterns” should be placed third in the list (after “mass spectra” and “time variations”) because the diurnal patterns are shown in Figure 7 only.
Thanks, it has been corrected

Line 402: Place “the following” before “typical features.”
Thanks, it has been corrected

Line 404: Remove “the” before “photochemical production”
Thanks, it has been removed.

Line 408: According to Figure 2q (MO-OOA1 factor time series) there is a large concentration spike on March 22, not March 23 as indicated in the text. Please check these dates. Similar comment for line 415.
Thanks, it has been corrected.

Line 428: Remove ", respectively" from the parentheses.
Thanks, it has been removed.

Line 437: Remove the "s" from the end of "enhancements"
Thanks, it has been removed.

Line 438: Change "(Figs. 4 and S11, respectively)" to "(5.2 and 4.7, respectively) (Figs. 4 and S11)"
Thanks, it has been changed.

Line 440: Change "Fig. S8" to "Fig. S9"
Thanks, it has been changed.

Line 458: Remove the "s" from "Figs. 4" and remove ", respectively" from the parentheses
Thanks, it has been removed.

Line 484: Replace "high" with "large"
Thanks, it has been replaced.

Lines 506-507: The dates mentioned in this sentence do not seem to match the dates in the axis of figure 6. Please check / correct these dates.
Thanks, it has been corrected. Now the sentence read;
"The PM concentration in Beijing started to increase on March 18 when no haze was observed in the SMA (S1), while the SMA haze started to intensify starting on March 19 12:00 (S2)."

Line 526: Replace "selected based on" with "highlighted in"
Thanks, it has been replaced.

Line 539: Remove "the" before "RH"
Thanks, it has been removed.

Line 543: Remove ", respectively" from the parentheses
Thanks, it has been removed.

Line 553: Change "Fig. 7b" to "Fig. 7". Note: there are no alphabet labels in figure 7.
Thanks, it has been changed.

Line 554: Place "(Fig. S10)" after "SO4 formation" at the end of the sentence.
Thanks, it has been changed.

Lines 558-560: These two sentences are redundant. I suggest removing the second sentence.

Thanks, it has been removed.

Line 585: Change “5-7 March, 11-13” to “March 5-7,”
Thanks, it has been changed.

Line 596: Add the percent contributions to Pb of MO-OOA2 and LO-OOA2 in parentheses just after they are mentioned.
Thanks, it has been added.

Line 612: Add an “s” to the end of “event” and replace “was strongly” with “were strongly”
Thanks, it has been added and replaced.

Line 616: Replace “decreased” with “shifted”
Thanks, it has been replaced.

Line 617: Change “AMS” to “HR-AMS”
Thanks, it has been changed.

Lines 621-622: Replace “has investigated” with “have been investigated”; change “AMS” to “HR-AMS”; change “2015 Dec.” to “December 2015”; replace “transport” with “transported”; and replace “features” with “NO3”.
Thanks, it has been all changed.

Lines 624-625: Rearrange sentence to read, “Due to the current emission control policies in China, SO4 and SO2 did not considerably change during the haze period compared to the low loading period.”
Thanks, it has been rearranged.

Tables and Figures: A general comment about figures. All figures in the manuscript, including the supplement, NEED to be of a high resolution (DPI 300 or greater). All font NEEDS to be large enough to be read easily (e.g., Time New Roman 10 or greater). Some of the figures in your main text (notably Figure 8 and the pie charts in other figures) were too low resolution with small text. Almost all of the figures in the supplement were too blurry (with text too small), which rendered them illegible (e.g., Figs S8 and S17). IMPORTANT: The main and supplement figures will need to be corrected before the paper is published.
Thanks for the suggestions. In the current revised version, all the figures of resolution is highly enhanced. Also font size was increased.

Table 1: Replace “K (AMS)” with “K (HR-AMS)”
Thanks, it has been changed.

Figure 1: Add “HYSPLIT” before “clusters” in section (d) of the caption.
Thanks, it has been changed.

Figure 4: In section (b) of caption, add a "," after "PM1" and place ", ratios," between "meteorological parameters" and "and tracers". Also, what do the dotted lines mean in 4b?
Thanks, it has been changed. Also the dotted lines are for the guiding eye. Follow sentence has been added in figure caption;
"The dotted lines in Fig. 1(b) are guide for the eye."

Figure 5: In the legend, change "BBOA" to "SFOA"
Thanks, it has been changed.

Figure 6: In the legend, change "BBOA" to "SFOA"
Thanks, it has been changed.

Figure 7: In the last sentence of the caption, add "the dashed line indicates the" before "high-loading periods".
Thanks, it has been added.

Figure 8: In section (e) of the caption, replace "components" with "factors"
Thanks, it has been changed.

Supplement:

Line 57: Add a space between "Expected" and "(deLeater"
Thanks, it has been corrected.

Line 58: Replace "(Figs. Sx and x)" with the figures you meant to reference.
Thanks, it has been removed.
Table 3: Replace "Natual" with "Natural" in table heading.
Thanks, it has been corrected.

Line 120: Replace "HRAMS" with "HR-AMS"
Thanks, it has been corrected.

Line 122: Remove "s" from end of "individuals"
Thanks, it has been corrected.

Figure S3: What do A, B, and C correspond to in the caption? The colors don't match the description in the caption.
A, B and C correspond to (a) m/z 206, (b) m/z 207 and (c) m/z 208 for $^{206}Pb^{+}$,$^{207}Pb^{+}$ and $^{208}Pb^{+}$.
More descriptions has been added to Figure captions and color description also has been corrected.

Line 127: Change "Figure S3" to "Figure S4"
Thanks, it has been corrected.

Line 128: Replace "HRAMS" with "HR-AMS"
Thanks, it has been corrected.

Line 130: Remove “s” from end of “individuals”
Thanks, it has been corrected.

Figure S4: Same issues as figure S3.
A, B and C correspond to (a) m/z 103, (b) m/z 103.5 and (c) m/z 104 for $^{208}Pb^{++}$, $^{207}Pb^{++}$ and $^{206}Pb^{++}$. More descriptions has been added to Figure captions and color description also has been corrected.

Figure S5: Replace “(red), closed” with “(red) and closed”; replace “(terquid)” with “(turquoise)”; bold the “(c)”.
Thanks, it has been corrected.

Figure S9: Replace “NOR” with “nitrogen oxidation ratio (NOR)”
Thanks, it has been corrected.

Figure S10: Replace “SOR” with “sulfur oxidation ratio (SOR)”
Thanks, it has been corrected.

Figure S11: Add label to figure with the names of the different pie chart components.
Thanks, the legend has been corrected.

Line 311: Replace “colored by the time of the day” with “colored by date”
Thanks, it has been replaced

Lines 315-316: In several places, the subtraction sign “-“ was accidentally subscripted. Need to remove subscripting.
Thanks, it has been corrected.

Line 317: Remove “the” before “comparison”
Thanks, it has been removed.

Line 354: Remove the “8” and replace “families” with “family”
Thanks, it has been removed.

Figure S17: Illegible figure. Cannot read the axes. Increase font size and improve figure resolution.
Thanks, it has been replaced with new updated figure.

Figure S19: Add more description to the caption. What are the different lines in the figure?

We add detailed figure caption;

Forward trajectory from Beijing measurement site. Each vertical and horizontal blue dotted line indicate longitude and latitude, respectively. Each black point indicate the endpoint of air parcel movement during 12 h.

Figure S20: Label images with the EP#s and S#s.
Thanks, the image has been labled and relevant figure caption has been added;
“Corresponded haze episode and stages are labeled left top of the figure”

Line 417: Change “Figure 21” to “Figure S21”
Thanks, it has been corrected.

Figure S21: the [NO2] times solar radiation data is not shown in the figure, but it is mentioned in the caption. Also, add “rad” to the legend.
Thanks the figure captions has been corrected and now reads;
“Figure 21. One-hour averaged diurnal profiles for nitrate and various parameters and proxies for formation pathways in (a-c) entire period (d-f) low loading period and (g-i) high loading period during 2019 spring. One-hour averaged diurnal profiles of NO_2, NO_3, NOR (nitrate oxidation ratio) are shown in top row; $[NO_2][O_3]$ as a proxy for nighttime formation of HNO3, RH and one-hour averaged O_3 are shown in middle row; and KAN as the equilibrium constant for gas-to-particle partitioning for ammonium nitrate and solar radiation are shown at the bottom row.”

Figure S22: Replace “nitrate” with “sulfate” in the caption, and subscript the 2 and 4 in “H2SO4”
Thanks, it has been changed.