Response to Anonymous Referee #2

This paper discusses the results of a study of PM$_{2.5}$ bound inorganic - organic species and gaseous pollutants on the haze events in February 2014 at the outflow regions of Asian pollution. Meteorological factors and synoptic conditions are also discussed along with chemistry for the same context. These data of Asian outflow were collected at a site in highly industrialized region of Seoul and at a background site, Deokjeok Island, over the Yellow Sea. Paper contents important data and interesting discussions on the topic, hence I recommend for the publication in ACP. However, I have several comments/suggestions, especially at several places where statements are contradictory which should be addressed before making a final decision.

We thank the reviewer for the valuable comments and constructive suggestions. Following the reviewer's comments and suggestions, texts, figures, and tables in the original manuscript have been modified. In addition, we have conducted additional analyses, modified texts, figures, and tables, and added new figures (Figs. 2 and 5) and references in the revised manuscript. Each response to reviewer colored in blue and changes in the manuscript colored in red.

P1, L16-18: Not clear. It is an overall general statement for both the sites. Better to summarise according to individual site, as in the following sentences.

The sentence is an overall description for the haze in Seoul. To clarify it, we inserted "in Seoul" into the sentence.

Dominance of fine-mode particles (PM$_{2.5}$/PM$_{10}$ ~ 0.8), a large secondary inorganic fraction (76%), high OC/EC (> 7), and highly oxidized aerosols (oxygen-to-carbon ratio of ~0.6 and organic mass-to-carbon ratio of ~1.9) under relatively warm, humid, and stagnant conditions characterize the multi-day haze episode in Seoul

P4, L3-10: Do authors think that it is logically correct to measure PM$_{2.5}$ mass using low- volume sampler and compare PM$_{2.5}$ chemical measurement using high-volume sampler. Possible biases should be properly addressed here with references (e.g. MAPAN, 2013, Volume 28, Issue 3, pp 153–166).

We agree with the reviewer's comments. As summarized in Aggarwal et al. (2013), Lagler et al. (2011) reported underestimation of PM concentrations measured by high-volume air sampler. In addition, there also could be gas-phase artifacts in the OC measurement in this study, as the other reviewer pointed out. Considering both (i) difference between the high- and low- volume samplers and (ii) possible positive and negative artifacts of OC concentration, we added a new paragraph at the end of Sect. 2.1 as follows:

Note that the PM$_{2.5}$ sampling conducted in this study could result in artifacts of carbonaceous species. Firstly, we used the high-volume air sampler for carbon analyses, while the total mass and ion concentrations were obtained by the low-volume air sampler. Secondly, we did not employ preceding organic denuder and backup filters in the high-volume air sampler for correction of both positive artifacts (by adsorption of organic vapor) and negative artifacts (by volatilization of semi-volatile materials) of measured OC. Although the positive artifacts are thought to be larger than the negative artifacts (Chow et al., 2010; Kim et al., 2016), the high-volume air sampler tends to underestimate particle concentrations (Lagler et al., 2011; Aggarwal et al., 2013) and thus the measurement by the high-volume air sampler may partly reduce such positive artifacts as recently estimated by Kim et al. (2016). However, aging and oxidation properties and source characteristics of measured aerosols can still be altered by potential loss of the semi-volatile organic compounds. In this study, therefore, we used organic compounds more for qualitative comparisons between different places and periods rather than for quantitative analysis.

P4, L12-13: The readability/ sensitivity of microbalance should be mentioned here.

The precision of the microbalance we used was 1 µg. We added this information within the sentence as follows:

The mass concentrations of $PM_{2.5}$ and PM_{10} were measured by the Mettler MT5 microbalance (Mettler-Toledo, Greifensee, Switzerland) with a precision of 1 µg after 24 h standing of the Teflon filter sample in a desiccator.

P6, L13-16: Back trajectory analysis should also be discussed in support.

We added new figures of backward trajectories for the haze and clean periods as Fig. 2 and modified L13–17 in p.6 as follows:

The wind direction during the overall analysis period was mostly westerly or west-northwesterly, except easterly winds on February 26. Considering negligible local emissions in and near the Deokjeok Island, the high $PM_{2.5}$ level in Deokjeok is most likely due to the regional transport from China, evidenced by the high $PM_{2.5}$ levels in the upwind Chinese cities (Fig. 1c) and backward trajectories during the haze period (Fig. 2a). On the other hand, the high $PM_{2.5}$ level in Deokjeok on February 26 seems to result from the easterly transport of pollutants from the SMA, as shown by backward trajectories passing through the SMA before reaching Deokjeok (Fig. 2b).
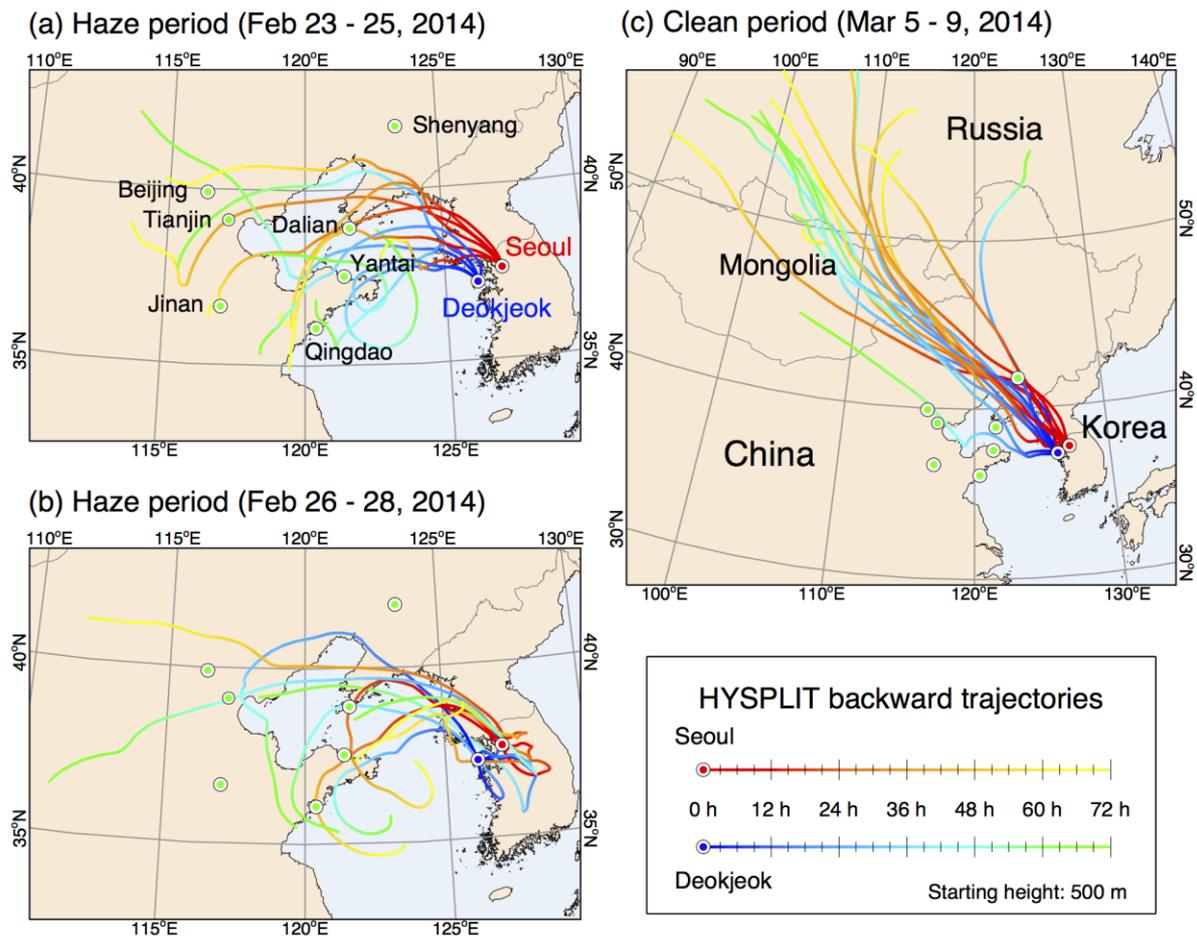

Figure 2: Backward trajectories from 500 m above sea level over the KIST site in Seoul (red) and the Deokjeok site (blue) at 09:00 and 21:00 local time (GMT+0900) during (a) the early stage of haze, (b) the late stage of haze, and (c) clean period.

P6, L17-18: Not clear.

To make the sentence clear, L17–18 in p.6 was modified as follows:

The high $PM_{2.5}$ levels in Seoul but the low $PM_{2.5}$ concentrations in Deokjeok on the following 3 days (Fig. 1b) as well as the stagnant backward trajectories (Fig. 2b) show that the prolonged haze period in Seoul did not only result from the transboundary transport of pollutant but could be also affected by local sources.

P6, L33: "compared and characterized in Table 4" should be "compared and summarised in Table 4"

Thanks for correction. We replaced "characterized" with "summarized."

P7, L3: Please mention (number) boundary layer height and wind speed here.

We inserted approximate values of boundary layer height (~400 m) and wind speed (~2 m s^{-1}) for the haze period into the sentence as the review suggested.

P7, L7-10: Backward trajectory should also be discussed here.

With the new figure set (Fig. 2), we modified the sentence as follows:

Therefore, the regional influences on the severe haze can be inferred from the high concentration of each chemical component (Table 1) as well as the backward trajectories from China (Figs. 2a–b) during the haze period in both Seoul and Deokjeok.

P7, L12-18: Section 3.2.2, this is in contrast to section 3.2.1 and following sections, e.g. P13, L10-12, and several other places (please see comments below).

In Sect. 3.2.1, we wrote that "regional influence" can be inferred from high concentrations of each chemical component in both Seoul and background and "local influence" can be inferred from the higher concentration of each chemical component in Seoul than those in background. In Sect. 3.2.2, we insisted that SO_2 in Seoul is affected by "regional transport" since SO_2 was high in both sites during the haze. On the other hand, NO_2 was significantly higher in Seoul than Deokjeok, and thus we insisted that NO_2 in Seoul is affected by "local emissions." In the sentences L10–13 on p.13, we insisted again that NO_2 and nitrate were higher in Seoul than Deokjeok and these species are related to "local emissions and production." We didn't find contrasting points among these three parts.

P8, L1-2: How about the contribution of marine aerosols, especially at Deokjeok? Mass concentration of $PM_{2.5}$ and PM_{10} should also consider while discussing $PM_{2.5}/PM_{10}$ ratios.

As shown by extremely low concentrations of Na^+ (~0.1 μg m^{-3}) in Deokjeok and Seoul during both haze and clean period (Table 1), marine aerosols seem to contribute little to observed $PM_{2.5}$ in this study. Sea salt estimated by known mass ratio of ions to Na^+ in seawater (0.25 for SO_4^{2-}, 0.037 for K^+, 0.038 for Ca^{2+}, and 0.12 for Mg^{2+}; Berg and Winchester, 1978) during the haze was ~0.4 μg m^{-3} in Seoul and ~0.5 μg m^{-3} in Deokjeok (Table S1). These values are negligible compared to the $PM_{2.5}$ mass concentrations of 116 μg m^{-3} in Seoul and 84 μg m^{-3} in Deokjeok.

Brief discussion about PM_{10} and $PM_{2.5}$ mass concentrations during the measurement period can be found in Sect. 3.1. PM_{10} was not much considered in this study because we focused on the fine mode particles, which occupied more than 80% of PM_{10} during the haze and thus induced the multi-day haze event.

Table S1: The average and standard deviation of PM$_{2.5}$ non-sea salt (nss-) ions and sea salt in Seoul and Deokjeok for the haze (February 23–28, 2014) and clean (March 5–9, 2014) periods.

Components	Seoul		Deokjeok	
	Haze	Clean	Haze	Clean
nss-SO$_4^{2-}$ (µg m^{-3})	34.9 ± 9.1	3.9 ± 1.4	29.2 ± 12.3	4.7 ± 2.6
NO$_3^-$ (µg m^{-3})	32.8 ± 8.4	4.6 ± 4.2	11.4 ± 8.5	2.8 ± 3.0
nss-Cl$^-$ (µg m^{-3})	0.9 ± 0.4	0.2 ± 0.2	0.4 ± 0.5	−0.1 ± 0.1
NH$_4^+$ (µg m^{-3})	21.6 ± 4.3	2.7 ± 1.6	14.4 ± 6.0	2.4 ± 1.8
nss-K$^+$ (µg m^{-3})	0.9 ± 0.2	0.2 ± 0.1	0.7 ± 0.3	0.2 ± 0.1
nss-Ca^{2+} (µg m^{-3})	0.3 ± 0.1	0.1 ± 0.0	0.2 ± 0.1	0.1 ± 0.0
nss-Mg^{2+} (µg m^{-3})	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.1
Sea salt (µg m^{-3})	0.4 ± 0.1	0.2 ± 0.1	0.5 ± 0.2	0.5 ± 0.3

P8, L15: For more clarity, it is better to also use nss-SO$_4^{2-}$ concentration in discussions.

Non-sea salt (nss-) ionic components were estimated by a simple calculation, which assumes that the sea salt contributes Na$^+$ in PM$_{2.5}$ alone (George et al., 2008), as follows:
$M_{nss-X} = M_X − (X/Na^+)_{SW} \times M_{Na}$
where, M_X is the total mass of a species X, $(X/Na^+)_{SW}$ is a mass ratio of X to Na$^+$ in seawater, M_{Na} is the mass of Na$^+$, and M_{nss-X} is the mass of the nss- component in M_X. The ratio of $(X/Na^+)_{SW}$ for each ion was mentioned above, and the nss-ion concnetrations were summarized in Table S1. Since the concentrations of nss-SO$_4^{2-}$ are nearly identical to SO$_4^{2-}$ as shown in Table S1, we used SO$_4^{2-}$ rather than nss-SO$_4^{2-}$ in this study.

P8, L20-21: OC/EC ratios in Deokjeok and Seoul are 7.4±1.7 and 7.3±1.1, respectively in haze period. Do authors think "The OC/EC ratio is higher in Deokjeok than in Seoul during both haze and clean periods." is a correct sentence if authors see the values in view of statistical significance? Similarly check such statements in other places as well.

We agreed with the reviewer's comment. In the revised version of manuscript, we estimated approximate primary OC (POC) and secondary OC (SOC) using simple EC tracer method (Castro et al., 1999) and added them on Table 1. For the analysis period, the minimum OC/EC ratios in Seoul and Deokjeok are respectively 2.88 and 2.18. We assumed that these values as the primary OC/EC ratios ([OC/EC]$_{pri}$) and calculated POC (= [OC/EC]$_{pri}$ × EC) and SOC (= OC – POC). Since the more secondary fraction in OC in Deokjeok compared to that in Seoul can be represented better by SOC/OC, we replaced OC/EC with SOC/OC in the text.

With the brief description for estimation of POC and SOC, L18–22 on p.8 is now modified as follows:

Approximate primary OC (POC) and secondary OC (SOC) obtained by simple EC tracer method (Castro et al., 1999) using the minimum OC/EC values of 2.9 for Seoul and 2.2 for Deokjeok on March 9 as the primary OC/EC. As shown in Table 1, EC and thus POC concentrations in Seoul during both haze and clean periods are higher than those in Deokjeok, like CO. This shows that EC and POC in Seoul is largely contributed by local emissions while that in Deokjeok is mostly influenced by regional transport. Although OC concentration is higher in Seoul than that in Deokjeok, its secondary fraction (SOC/OC) is higher in Deokjeok than in Seoul during both haze and clean periods probably due to the secondary production during the long-range transport to the background, as discussed in Sect. 3.3.

P9, L4-16: Discussion is contradictory in context of sources discussed before this para and later in the text.

Since various diagnostic ratios of ambient organic compounds represent mixture of various source emissions, it is hard to avoid some contradiction and ambiguousness in their interpretation. In addition, there could be loss of semivolatile low molecular weight compounds during the measurement, strict interpretation of sources with reported diagnostic ratio could be inaccurate. Therefore, we here tried to compare the PAH ratios of different sites and different periods and to interpret them relatively. Following another reviewer's suggestion, we introduce a new figure (Fig. 5) and modified this paragraph (from the third sentence in the paragraph) as follows:

The average PAH ratios in Seoul and Deokjeok for the haze and clean periods are summarized in Fig. 5 with previously reported diagnostic ratios (Yunker et al., 2002; Pies et al., 2008; De La Torre-Roche et al., 2009; Akyüz and Çabuk, 2010; Oliveira et al., 2011). Interpretation of these PAH ratios all together seems ambiguous and contradictory due to mixing of various emission sources. However, relative comparisons of each ratio between different places and different periods reveal more pyrogenic sources such as fossil fuel combustion and vehicular emissions in Seoul than in Deokjeok (Figs. 5a–c), in the overall influence of coal combustion and/or biomass burning during the haze period (Figs. 5a–b, and 5d).

As wrote in this paragraph, more pyrogenic sources (fossil fuel combustion and vehicular emissions) in Seoul and overall influence of coal combustion and biomass burning during the haze were identified. As described in the next paragraph, levoglucosan shows higher concentration in both site during the haze, and this also indicate biomass burning during the haze.
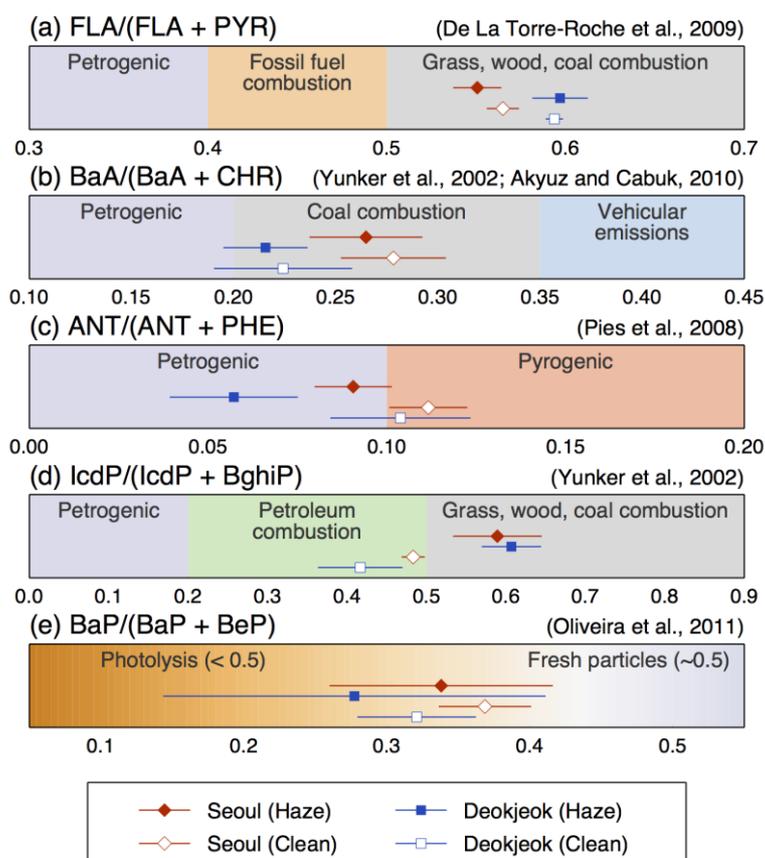

Figure 5: Various PAH ratios of (a) FLA/(FLA + PYR), (b) BaA/(BaA + CHR), (c) ANT/(ANT + PHE), (d) IcdP/(IcdP + BghiP), and (e) BaP/(BaP + BeP) in Seoul (red diamonds) and Deokjeok (blud squares) during the haze (filled symbols) and clean (opened symbols) periods. Horizontal bars indicate standard deviation.

P9, L18: "total sugar" should be "total sugar identified"

Thanks, we corrected it as following the reviewer's suggestion.

P9, L31: Reference is needed.

The original sentence was modified and moved into the paragraph with references, as the third and fourth sentences of the paragraph as follows:

Whereas short-chain (light) *n*-alkanes are mostly associated with incomplete combustion or vehicle exhaust (Gentner et al., 2017), biosynthetic processes result in long-chain high molecular weight (C_{27}–C_{33}) *n*-alkanes with distinctive odd-to-even carbon number preference (Simoneit, 1991; Rogge et al., 1993). Note that *n*-alkanes in this study reflect less anthropogenic sources because we analyzed only high molecular weight *n*-alkanes (C_{20}–C_{36}).

P9, L33; P10, L1-2: Again contradictory statements (as pointed out above).

The sentence from L33 on p.9 to L2 on p.10 is modified as follows:

However, Seoul is more affected by fossil fuel combustion and vehicular emissions compared to Deokjeok and seems to also have local biomass burning and biogenic emission sources.

P10, L10: "OC/EC ratio" same comment as in P8, L20-21.

We replaced "OC/EC ratio" with "SOC/OC" in the revised version.

P10, Section 3.3.2: Result suggests that particles are fresh in Seoul and comparatively aged in Deokjeok. An analysis of fresh and aged $PM_{2.5}$, PM_{10} should be incorporated.

In general, aging and oxidation properties of OA is widely analyzed by its atomic oxygen-to-carbon ratios (O/C) and organic mass (OM)-to-OC ratios (OM/OC) (e.g.; Aiken et al., 2008; Jimenez et al., 2009). In the revised version, we newly estimated total OM from the identified OM (*n*-alkanes, PAHs, mono- and dicarboxylic acids, and sugars) and obtained OM/OC as well as O/C. We added average concentrations of OM with average values of OM/OC and O/C in Table 2 and inserted following sentences into the first paragraph of Sect. 3.3:

To explore the oxidation and aging properties of OA, atomic oxygen-to-carbon ratios (O/C) and organic mass-to-carbon ratios (OM/OC) of SOA have been widely used (Aiken et al., 2008; Jimenez et al., 2009). The organic mass (OM) identified in current study is ~5% of total OM estimated by OM/OC of the identified OM.

Also, we added following paragraph, discussing aging properties of observed particles in Seoul with OM/OC and O/C of identified OM, into Sect. 3.3.2 as its first paragraph:

Average OM/OC and O/C in Seoul were 1.92 and 0.59 for the haze period and 1.83 and 0.52 for the clean period (Table 2). Although these values may be overestimated because of possible loss of semivolatile compounds arising from the measurement and analysis addressed in Sects. 2.1 and 2.2, the higher values of OM/OC and O/C during the haze indicate OA was more oxygenated. Considering the higher OM/OC and OC in Deokjeok of 2.00 and 0.65 for the haze period (Table 2) together with the backward trajectories from China during the haze (Fig. 2), haze particles were already aged before arriving at Seoul and mixed with fresh compounds in Seoul.

Since we focused more on $PM_{2.5}$ rather than PM_{10}, various chemical analyses for PM_{10} sample were not conducted, and thus additional analyses based on PM_{10} data are not possible. Considering the high

PM$_{2.5}$/PM$_{10}$ ratios during the haze period (> 0.8), however, the aging properties of PM$_{10}$ in Seoul and Deokjeok are probably similar to that of PM$_{2.5}$.

P11, L5-8: How about boundary layer height?

Obviously the stable and stagnant environment during the haze (low winds and shallow boundary layer) could help the secondary formation of aerosols. We added correlations of SOR with wind speed and boundary layer height in L4–9 on p.11 as follows:

Along with the stable and stagnant environment, the warm and humid air conditions during the haze period (Fig. 6e) could be also conducive to both gas-phase and aqueous-phase oxidation of SO$_2$ (Liang and Jacobson, 1999; Seinfeld and Pandis, 2006). SOR shows significant correlations with temperature ($r = 0.72$) or RH ($r = 0.59$) as well as wind speed ($r = -0.64$) and BLH ($r = -0.88$).

P11, L10-22: I suggest to check and discuss the relation of RH, NO$_2$ with sulfate formation apart from photochemical formation.

Recent measurement study on the Chinese haze suggested that the aqueous SO$_2$ oxidation by NO$_2$ is a key process of sulfate formation in high RH and high SO$_2$, NO$_x$, and NH$_3$ condition, and this process promotes to nitrate and OM formation on aqueous particle (Wang et al., 2016). If we considered only Seoul, the aqueous SO$_2$ oxidation by NO$_2$ seems to be plausible because correlations of SO$_4^{2-}$ with RH ($r = 0.47$), SO$_2$ ($r = 0.87$), NO$_2$ ($r = 0.81$), and NO$_3^-$ ($r = 0.96$) in Seoul were high enough. However, in fact, the high SO$_4^{2-}$ in Seoul during the haze mostly came from the regional transport rather than the local formation, as shown by the high SO$_4^{2-}$ but extremely low NO$_2$ in Deokjeok during the same period (Fig. 6a and Table 1). If we made a crude assumption that SO$_4^{2-}$ concentration differences between Seoul and Deokjeok represents locally produced SO$_4^{2-}$, much lower correlations of it with SO$_2$ ($r = 0.35$), NO$_2$ ($r = 0.42$), and NO$_3^-$ ($r = 0.58$) in Seoul, and comparable correlation of it with RH ($r = 0.51$) in Seoul do not quite support a role of such aqueous SO$_2$ oxidation by NO$_2$ in Seoul.

P12, L1-2: I suggest to check and discuss primary and secondary OC contribution in haze and clean days at both the site to ustify this statement.

Although the POC and SOC values estimated by the EC tracer method are very crude, the local influence of POC on the high OM concentrations in Seoul during the haze can be inferred from the higher POC concentration with high POC/OC proportion in Seoul (5.7 µg m^{-3}, 40% of OC) than those in Deokjeok (2.5 µg m^{-3}, 31% of OC). Note that proportions of POC in OC in Seoul and Deokjeok are much higher during the clean period (81% in Seoul and 53% in Deokjeok) without regional transport of primary pollutants from China.

Thus, we modified L1–2 on p.12 as follows:

And this clearly indicate local influence of primary organic compounds on the high OM concentrations in Seoul during the prolonged haze, as also shown by the higher proportion of POC in OC as well as the higher concentration of POC in Seoul (5.7 µg m^{-3}, 40% of OC,), compared with those in Deokjeok (2.5 µg m^{-3}, 31% of OC) (Table 1).

P13, L10-12: Not clear.

To make it clear, the sentence is modified as follows:

The high concentrations of SO$_2$, sulfate, nitrate, CO, and OM in both Seoul and Deokjeok on these two days (Figs. 6a, 6c–d, and 7a) indicate quick transport of PM$_{2.5}$ components from China.

References

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