

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.

I thank the authors for taking on board my comments, however I do not feel that they have addressed all of the comments I raised.

The issue regarding COA is still not resolved. As I was at pains to point out, similarity with previously published mass spectra does not in itself prove it is related to cooking as the peaks are common to various long-chain fatty acids that could have other sources. The discussion regarding correlation with tracers adds nothing; all this does is prove that the factor contributes the most variance to those markers but as they are not unique to cooking, this does not prove that cooking was responsible. I would disagree that the diurnal cycle is in any way consistent with previously reported urban studies and it is very misleading to say it undergoes an 'enhancement' at 19:00 when the peak is clearly later at 22:00. Furthermore, the slow decrease in signal over the subsequent hours is very inconsistent with previously published cooking profiles, which typically drop off within only an hour or two of the initial peak. As such, I still doubt that this can be associated with cooking and I request that the authors add the caveats I originally requested.

Thank you for the suggestions. As reviewer mentioned, diurnal pattern of COA does not clearly show the expected cooking activities and possibly due to the influences of other factors as others investigated in previous studies. However, it is also possible due to the complexity of organics in urban SMA. For example, small lunch time peak might be due to the intensive formation of secondary organic aerosols and the large and broad peak (start to enhance at 19:00 and peak is shown at 22:00) for dinner time might be influenced by decreased mixing height. And it is true that although representative mass spectra of COA is shown, it could possibly contain other sources. For these kind of unclear cases, other studies (Dall'Osto et al., 2013) discussed these "COA like/or COA influence" cases referring them as COA. We are thinking that it is still better to refer it as COA rather than COA-like since there's no significant difference to make the new organic source from the previous report. However as reviewer suggested, we need to address the possibilities that COA is contributed by other source. Thus, in order to clarify the facts, we discuss the possible influences from other sources on COA, so please reconsider referring the factor as COA. Now the section reads;

"As widely reported in other highly populated urban cities, COA was resolved in SMA as well, with the key tracers for identifying the presence of aerosols from cooking related activities, such as $C_3H_3O^+$ (m/z 55), $C_3H_5O^+$ (m/z 57), $C_5H_8O^+$ (m/z 84) and $C_6H_{10}O^+$ (m/z 98) (He et al., 2004; Adhikary et al., 2010; Mohr et al., 2009; Zhao et al., 2007; Ge et al., 2012; Sun et al., 2011; Young et al., 2016; Allan et al., 2010; Huang et al., 2010; Sun et al., 2013; Hayes et al., 2013; Mohr et al., 2012; Dall'Osto et al., 2013). All showed good correlation in time series with COA, e.g., $C_3H_3O^+$ ($r = 0.75$), $C_3H_5O^+$ ($r = 0.61$), $C_5H_8O^+$ ($r = 0.89$), $C_7H_{12}O^+$ ($r = 0.70$), and $C_6H_{10}O^+$ ($r = 0.99$) (Fig. S18 and Table S2) and COA was a major contributor to the signals of $C_5H_8O^+$, $C_6H_{10}O^+$, and $C_7H_{12}O^+$, accounting for 62%, 94%, and 67%, respectively, of their signals

(Fig. S16). Also, showed a mass spectrum almost identical to the COA spectrum determined in winter 2015 – 2016 at the same site (Fig. 8b and S15) (Kim et al., 2017). Finally, the ratios between f_{55} and f_{57} for OA in Seoul increased proportionally as the fractional contribution of COA to total OA increased (Fig. S19b), with a “V” shape indicated by the two edges defined by the COA and the HOA factors from several urban AMS data sets (Mohr et al., 2012). COA displayed a large enhancement at evening starting from ~ 19:00, i.e., dinner time, and a small lunch time peak at ~ 12:00, although this does not reflect the expected cooking activities clearly. The reasons for the small lunch time peak was attributed to strong secondary formation affecting to the peak of COA emissions. And the large and broad nighttime peaks are due to lower boundary layer height. Although all these observations confirm the identification of COA at SMA, COA factor is the least defined of all defined organic sources. First of all, diurnal profile of COA in our study does not show the clear cooking activities although possible explanations have been given. Secondly, fragmentation of oxygenated species such as fatty acids which were detected at significant amount in cooking aerosols could be observed from not only in cooking aerosols (He et al., 2004; Mohr et al., 2009; To et al., 2000; Zheng et al., 1997) but also in other sources such as plant wax, fossil fuel, soil and SOA (Wang et al., 2006; Zhao et al., 2014). This might suggest a possibility for COA to include a combination of other factors or to be a cooking-influenced OA factor as several other studies raised the similar issues (Dall’Osto et al., 2013; Mohr et al., 2009; Mohr et al., 2012).”

I feel that the authors misunderstood my comment about the f_{SO_4} ; using temperature data alone, it should be possible to estimate the OH concentration based on established rate constants for the $SO_2 + OH$ pathway to H_2SO_4 production. By comparing the inferred OH concentrations to previously reported urban concentrations, one could easily check whether this narrative is plausible.

Thank you for clarifying the comments. As reviewer suggested, we calculated the temperature dependent reaction rate constant, k ($8.75-9.24 \times 10^{-13} \text{cm}^3 \text{s}^{-1}$) for $SO_2 + OH + M \rightarrow H_2SO_4$ (Burkholder et al., 2015). With this established rate constant, corresponded daytime (11:00-18:00) OH concentration was calculated to be 1.2×10^6 which is in the range of the concentrations in other urban cities such as Tokyo (Miyazaki et al., 2006) and China (Rao et al., 2016). Using k and OH concentration, the life time of SO_2 during daytime (11:00-18:00) was calculated to be ~11 days. This doesn’t look like that the photochemical reaction of $SO_2 + OH$ is important for controlling SO_4^{2-} concentration and consistent with the fact that a major source of SO_4^{2-} observed in SMA is regional transport from the southwest and almost no enhancement diurnal profile of sulfate during daytime. However, a gradual increase of f_{SO_4} can be observed during daytime, at least partly due to the gas phase oxidation of SO_2 , though daytime sulfate formation could happen due to mechanisms other than $SO_2 + OH$. So we have revised the text so it now reads:

“Also, f_{SO_4} increased gradually from 11:00 till 6:00 of the next day. For the daytime increase from 11:00 to 18:00, the life time of SO_2 was calculated to be ~11 days, using the temperature dependent daytime reaction rate constant, k ($8.75-9.24 \times 10^{-13} \text{cm}^3 \text{s}^{-1}$) for $SO_2 + OH + M \rightarrow H_2SO_4$ (Burkholder et al., 2015) and corresponded OH concentration (1.2×10^6 molecules cm^{-3}) which is

in the range of other urban cities such as Tokyo (Miyazaki et al., 2006) and Beijing (Rao et al., 2016). This suggests that the localized photochemical reaction of $\text{SO}_2 + \text{OH}$ is not the major process for controlling SO_4^{2-} concentration during this period. However, observed gradual increase of f_{SO_4} could be at least partly due to the gas phase oxidation of SO_2 .”

It is simply not correct to infer that particles are pH neutral based on an observation of ion balance (as reported in S10) because given how strong the solution strengths are, only very small deviations from this can vastly alter the pH in haze droplets. Estimating aerosol pH requires explicit knowledge of the particle and gas phase ion concentrations, the water content of the particles and the invocation of a thermodynamic model such as e-AIM. Also, while the particles may begin as neutral, any formation of H_2SO_4 will immediately suppress the pH, so the NO_2 and O_3 pathways may potentially become self-limiting in haze particles unless there is an abundance of gas phase NH_3 to compensate. The text should be modified to reflect these details.

Thanks for the comments. We agree that pH cannot be simply derived by the particle neutralization. Since we did not measure/or calculated the pH of aerosol in this study, we have to be cautious to discuss these pH dependent reactions. As reviewer suggested, we discuss these details in our discussions. Now the text read:

“Possible oxidants during night are NO_2 and O_3 , although SO_2 oxidation by O_3 and NO_2 are both pH-dependent and the reaction rates increase with pH (Seinfeld and Pandis, 2006). NH_3 concentration in SMA is likely high since aerosol particles in this region are bulk neutralized (Fig. S10), suggesting that oxidation by both O_3 and NO_2 could occur actively. Furthermore NO_2 has been investigated as an important oxidant in aerosol water under hazy conditions (Cheng et al., 2016). However it is still open to other possible oxidation pathways since any formation of H_2SO_4 will immediately suppress the pH although particles may begin as neutral. Thus the NO_2 and O_3 pathways may potentially become self-limiting in haze particles unless there is an abundance of gas phase NH_3 to compensate.”

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