

Interactive comment on “Seasonal variations of high time-resolved chemical compositions, sources and evolution for atmospheric submicron aerosols in the megacity Beijing” by Wei Hu et al.

Anonymous Referee #2

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The manuscript investigates the seasonal variations of compositions, sources, and evolution for atmospheric aerosols in the megacity of Beijing. While field measurements have been carried out by other groups in this city, this work provides a more comprehensive exploration of organic aerosol composition and evolution. Generally, the paper is quite well written. The methodology and results are presented clearly. The measurements provide sufficiently new data that the manuscript may merit publication. However, the qualitative interpretation of the results may limit the application and impacts of this work. This calls for a more detailed data analysis, explaining the mechanisms behind the observations. I suggest the authors respond to the following suggestions before the paper is accepted to publication.

C1

Major Comment:

My main question is that as mentioned by the authors, the characteristics and evolution of aerosol pollution are multifactorial (e.g. meteorological conditions, regional transport, and local sources). These factors can have distinct patterns in different seasons, thus the formation, transformation and removal of pollutants are affected. The authors have provided nice discussions on the sources and evolution of ambient atmospheric aerosols under the influence of different meteorological conditions and sources. However, what would be the impacts of regional or long range transport on the composition, formation and evolution of atmospheric aerosols in different seasons in Beijing? For example, the authors mentioned that regional transport can play a role in the sulfate concentration in the winter season. While regional transport impacts have briefly discussed or mentioned in various sections or paragraphs, it would be nice to have a more coherent, quantitative discussion on the role of regional (or long range) transport in the concentration and evolution of different inorganic and organic components in different seasons.

Minor comments:

Abstract, “The evolution process of OA in different seasons was investigated with multiple metrics and tools. The average carbon oxidation states and other metrics show that the oxidation state of OA was the highest in summer, probably due to both strong photochemical and aqueous-phase oxidations.” Any evidence supports the contribution of aqueous-phase oxidation to OA? What is the relative contribution of photochemical vs. aqueous-phase oxidation to the concentration and evolution of OA?

Page 6, “In spring, summer and winter, SNA accounted for about 60% in PM1 due to the secondary aerosol formation through strong photochemical and aqueous-phase reactions.” Like OA, what is the relative contribution of photochemical vs. aqueous-phase oxidation to the concentration and evolution of SNA?

Page 6, “Wang et al. (2016) and Cheng et al. (2016) found that high levels of sulfate

C2

and fine PM can be explained by reactive aqueous oxidation of SO₂ by NO₂ under certain atmospheric conditions.” Please elaborate what the meaning of “certain atmospheric conditions”. How frequent these atmospheric conditions occur during the field campaign?

Page 6, “Compared with the previous results in Beijing (Fig. 1), PM₁ in summer was lower than before, which likely resulted from the more effective rainout (Fig. S7) and lower concentrations of gaseous precursors (Table 1).” What are the frequency of precipitation/rainout and the concentration of gaseous precursors reported in previous studies?

Page 7, “While, PM₁ ranged much more broadly, with the highest concentrations of over 200 or 300 $\mu\text{g m}^{-3}$, resulting from accumulated pollutants under extremely unfavorable meteorological conditions or strong primary emissions.” What is “the extremely unfavorable meteorological conditions”?

Page 7, “The proportions of nitrate increased more significantly, and the nitrate concentration increased rapidly under higher RH (Fig. 2; Pearson correlation coefficients $r=0.71, 0.34, 0.49$ and $0.79, p<0.01$). These results indicate that the aqueous reactions could contribute to nitrate remarkably in highly humid and static air.” What are the aqueous reactions referring to? Aerosol phase reactions, in-cloud reactions or both? Ambient RH is a good proxy for indicating the occurrence and importance of aqueous phase reactions. However, what the physical state of the ambient aerosols (e.g. aqueous or solid)? What is the aerosol water content inferred or predicted from the aerosol speciation data and meteorological conditions? Will the water content and physical state of the aerosols play a role in the aqueous phase reactions and nitrate formation? If the aqueous phase reactions involve in-cloud reactions, any data (e.g. cloud coverage) can be used to support the importance of in-cloud reactions to the formation of nitrate and organic compounds during the campaign?

Page 8, “The peak concentration of OA in the evening in autumn was about two times

C3

higher than in spring and summer, consistent with the results in Oct.-Nov. 2011 (Sun et al., 2015), possibly because of the more intense cooking activities.” Please elaborate why there is more instance cooking activity in the evening in autumn, but not in other seasons?

Page 11, “LO-OOA dominated OA in summer (44%) due to the freshly secondary formation from strong photochemical oxidations; whereas, MO-OOA was dominant in OA in winter (33%), maybe because the air masses were more aged on heavy-polluted days.” Please elaborate why the air masses are more aged on the heavy-polluted days in winter, but not in other seasons?

Page 13, “Fewer cooking activities during and around the Chinese New Year holiday (7-19 Feb.; Fig. S17), as well as the lower evaporation rate of oil, led to the lower concentration and proportion of COA in winter.” This argument is interesting. How does the evaporate rate of oil depend on the temperature? What the contribution of this evaporation process to the total volatile organic compounds generated/originated from the cooking activities?

Page 16” In summer, OOA showed obvious diurnal variations: MO-OOA peaked in the morning and afternoon; LO-OOA showed two pronounced peaks at noon and at night, which was likely influenced by the photochemical oxidations and aqueous-phase formation from POA.” It is not clear why the formation of LO-OOA is likely influenced by the photochemical oxidations and aqueous-phase formation from POA. Any other processes that can be contributed to the formation and transformation of LO-OOA?

Page 16, “ the concentration and proportion of LO-OOA increased significantly in the afternoon (12:00-16:00), up to 7 $\mu\text{g m}^{-3}$ and 50%, respectively (Fig. 6b), suggesting that LO-OOA was a strong local/regional photochemical product despite the much higher PBL in the daytime (Hu et al., 2016a)” What is the contribution of regional transport to LO-OOA (and other components)?

Page 17, “In both autumn and winter, the fractions of OOA slightly increased around

C4

100 ug m⁻³, implying that POA probably transformed to SOA more effectively within this range." Please elaborate why the POA is more likely transformed to SOA under these conditions. What mechanisms or pathways?

Page 18, "In spring, summer and autumn, the slopes fell between -1 (the addition of carboxyl functional groups without fragmentation or carbonyl and hydroxyl in different carbons) and -0.5 (carboxyl functionalization with fragmentation)." In addition to overall oxidation pathways, what other information we could learn from the reported slopes between -1 and -0.5? Are these pathways consistent with the reactions we expected for the formation and chemical transformations of ambient aerosols in Beijing?

Page 19, "In winter, the scatterplot of H/C vs. O/C ratios in the VK Diagram showed "broader" slopes, hinting the more complex sources and evolution processes of OA. The scatterplot indicated that OA in winter mainly evolved between the hydroxylation or peroxidation reactions (slope = 0) and carboxyl groups addition with fragmentation (slope = -0.5)." Any hypothesis or explanation for the complex sources and evolution process of OA in the winter. Why these processes have not been observed or suggested in the other seasons?

Page 19, "compared with the oxidation states of SV-OOA, OOA and LV-OOA summarized by Canagaratna et al. (2015), the oxidation states of OOA in Beijing were generally higher than in other areas, especially for LO-OOA (Fig. 8). The oxidation states of MO-OOA in Beijing were only lower than those in very aged air masses in Ziyang in the basin (Hu et al., 2016b), over Mexico City (DeCarlo et al., 2010) and in Barcelona (Mohr et al., 2012). The oxidation states of LO-OOA were only slightly lower than those of MO-OOA in Beijing, and were comparable to those of MO-OOA in other urban areas (Fig. 8)." It is nice to compare the data with those collected at different locations. However, without explaining the causes/reasons for the differences would not be useful for the readers to understand the formation and evolution of atmospheric aerosols.

C5

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C6