Review of

"Seasonal variations of high time-resolved chemical compositions, sources and evolution for atmospheric submicron aerosols in the megacity Beijing"

By Hu et al.

General comments

This study presents high time resolution chemical characterization of ambient submicron aerosols measured in Beijing between March 2012 and March 2013 using HR-ToF-AMS. Seasonal comparison of the chemical composition shows that organic aerosol (OA) and inorganic species (i.e. sulfate, nitrate, and ammonium) contributes equally towards total PM_1 mass. The chemical component composition and diurnal trend were impacted by atmospheric conditions of each season. Relationship between the atmospheric conditions to PM_1 composition need to be further discussed and/or clarified as outlined in the specific comments.

Additionally, sources of OA fraction in Beijing were identified using PMF. Primary OA (i.e. HOA and COA) and secondary OA sources were observed in all seasons, whereas BBOA and CCOA were only observed in autumn and winter, respectively. It is interesting that CCOA factor was resolved in winter dataset indicating significant contribution of coal combustion from domestic heating to ambient submicron aerosol. There seems to be an unresolved factor in winter dataset that could be a BBOA factor. Residual mass spectra should be added as supplementary information for evaluating the PMF solution.

Overall, this study falls within the scope of Atmospheric Chemistry and Physics journal. The results contribute to long-term and seasonal evaluation of air quality and can support air pollution prevention policy in Beijing. The manuscript is written pretty well with only some minor issues as outlined in the technical comments. I support publication of this manuscript after minor revisions.

Specific comments

1. PM_1 mass concentration is estimated as a sum of NR-PM_1 measured by AMS and BC measured by Aethalometer. However, cutoff size of the AMS's inlet (PM_1) is different from the Aethalometer ($PM_{2.5}$). How did you consider the cutoff size when summing the measurements? This information can be added into the experimental section.
2. Pg 6 Lns 9-11: What are considered in the certain atmospheric conditions? How do these conditions relate to the current study?
3. Pg 8 Lns 8-10: "Affected by different meteorological conditions, e.g., solar radiation, temperature, RH, boundary layer, and mountain-valley breeze in summer (Fig. S7), as well as different emission sources, the chemical compositions in PM_1 showed distinct diurnal patterns in four seasons." The beginning of sentence implies that the meteorological conditions specific for summer, whereas the ending suggests the distinctive diurnal patterns in four seasons. I think meteorological conditions in four seasons, not only summer, will affect the chemical composition and diurnal patterns in each season. This needs to be clarified.

4. Pg 8 Ln 19: “Flatter diurnal cycles of sulfate were observed in four seasons, …”. What does “flatter” here compare with? Does it compare with OA diurnal pattern? Also, add discussion about the diurnal patterns in spring and summer. Sulfate in spring showed small peaks around 13:00 and 20:00, whereas in summer, it peaked at evening only. What could possibly drive changes in sulfate diurnal patterns?
5. Pg 9 Lns 9-11: I think nitrate diurnal pattern in autumn is still significant; nitrate increased in the morning and then later in the evening. Also, what is the evidence of combined effect of sulfate and nitrate to ammonium diurnal pattern? Maybe you can correlate the diurnal variations and provide the coefficient of determination.
6. Pg 10 Ln 3: The size distribution of NH_4 is pretty similar to NO_3 in all four seasons. The size difference is not obvious in Fig. 4. To help comparison, you can consider increasing the size of the figure (panel for each season), or providing a summary table of size distribution in the SI section.
7. Pg 11 Lns 23-24: Provide reference(s) that show the role of emission reduction of gaseous precursors to SOA formation. For example: Pye, et al. Epoxide pathways improve model predictions of isoprene markers and reveal key role of acidity in aerosol formation. Environ. Sci. Technol. 2013, 47, 11056-11064.
8. Pg 14 Lns 18-20: Are you implying that there is a factor (BBOA) that is not resolved by PMF in the winter dataset? What may cause PMF can’t resolve BBOA factor in winter? Is the residual still showing important mass spectrum (e.g. *m/z* 60, 73) and time series features? Diagnostic plots of PMF winter dataset analysis (see Zhang et al. 2011) will be useful for readers to understand the analysis process. These diagnostic plots can be added in the SI section and referred in the main text. In addition to winter, diagnostics for other season should be provided in the SI section to help reader understand the PMF analysis process.
9. Pg 17 Lns 7-8: It is interesting that the LO- and MO-OOA fractions slightly increased around 100 $\mu g/m^3$ only. What influence the increase of OOA factors during particular OA mass concentration?
10. Pg 18 Lns 27-28: The VK diagram in winter does not show any correlation (r^2 = 0.02) between H/C and O/C. The slope is nearly zero (0.08; not broad). This suggests that hydroxylation and/or peroxidation processes were likely to occur in Beijing during winter. On the other hand, carboxylation process might be unlikely to occur since the slope is higher than -0.5. Please elaborate or clarify the discussion.

<u>Technical comments</u>

1. Pg 1 Ln 14: If PM_1 here is NR-PM_1+BC, it needs to be specified in the sentence.
2. Pg 2 Lns 26-27: Is SNA important only for the urban area or in general? Clarify the sentence and add reference.
3. Pg 5 Lns 7: ..., the last well calibrated…
4. Pg 5 Lns 8-9: Do you mean “the size distribution calibration”? Please clarify.
5. Pg 7 Lns 1-2: Do you mean “…PM_1 in winter was higher than previous studies in Beijing…”? Also please clarify what does “close periods” mean.
6. Pg 7 Ln 13: Figures S6 and S8 don’t display fire points as mentioned in the sentence.

7. Pg 9 Ln 27: …the internally mixed states…
8. Pg 11 Ln 8: The term “freshly secondary formation” is ambiguous. Consider “new SOA formation”.
9. Pg 12 Ln 26: Provide the coefficient of determination for any statement about correlation.
10. Pg 15 Lns 24-27: Insert respectively after on average. Breaking this sentence into two will be better as it is pretty long at the current state.
11. Pg 18 Ln 2: …, 1.52-1.63, …
12. Pg 18 Ln 18: What does “shallower” mean? Do you mean flatter slope?
13. Pg 20 Ln 7: …(i.e. lower H/C ratio, and higher O/C ratio and $\overline{\boldsymbol{OS_C}}$)….
14. Pg 20 Ln 28: What does “higher” compare to? Is it higher than “stable level”. What does stable level mean here?
15. Pg 21 Ln 28: Provide indicator (value) of the low aging degrees of air masses.
16. Fig 3: Need label (Hours of Day) for the X-axis.
17. Figs 5-8: Colors for MO-OOA and OOA are difficult to distinguish on print.
18. Figs 6-7: The legends for these figures are not consistent. OOA is missing from Fig. 7.
19. Fig. S13: … LV-OOA, MO-OOA…

References

Pye, H. O. T. Epoxide pathways improve model predictions of isoprene markers and reveal key role of acidity in aerosol formation. Environ. Sci. Technol., 47, 11056-11064, 2013.

Zhang, Q. Q. Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review, Analyt. Bioanalyt. Chem., 401, 3045-3067, 2011.