

Referee comment on
“Seasonal characteristics of fine particulate matter (PM) based on
high resolution time-of-flight aerosol mass spectrometric (HR-ToF-AMS)
measurements at the HKUST Supersite in Hong Kong”

by Y. J. Li et al.

Anonymous referee #3

This manuscript reports results obtained during intensive field campaigns undertaken at Hong Kong during four different seasons. The authors deployed an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) to measure the concentration, chemical composition and size distribution of non-refractory submicron particles (NR-PM₁). The authors performed a source apportionment by positive matrix factorization (PMF) and discussed the properties of NR-PM₁ as a function of the air mass origin. This manuscript is well written and fits the scope of Atmospheric Chemistry and Physics. I recommend publication of the paper, after the authors have addressed the following comments.

General comments:

- 1) Size distributions: what is the relative contribution of ions from the CH, CHO₁, and CHO_{gt1} families to the total signals of Org43, Org44, and Org57? Do these contributions change with season? This information can help a lot when the authors discuss the size distributions of these *m/z*.
- 2) PMF analysis, figure S13: in my initial quick report, I had mentioned that there was obviously an issue in the PMF analysis of the summer dataset. Indeed, the HOA factor has a very high signal of CO₂⁺ (and thus of CO⁺, which is scaled to CO₂⁺), increasing the O/C ratio up to 0.25. In their responses to the reviewers, the authors said that this could be a result from highly oxidized organics in summer. I'm not convinced by this explanation, because if it was the case, we would also see other oxygenated fragments in the HOA profile. It is unlikely that photooxidation of organics induces an increase of CO₂⁺ (which is related to carboxylic acids) without inducing an increase of other oxygenated fragments related to intermediate oxidation (i.e., aldehydes, ketones). Therefore, I still believe that the CO₂⁺ signal has not been correctly apportioned into the different factors, and that a large portion of its signal in the HOA factor should not be there.
- 3) PMF analysis, factor profiles: it would be interesting if the authors include a discussion on the different factor profiles, especially on how these profiles change with season. For instance, we clearly see that the two OOA factors have a higher *f*_{CO₂⁺} and O/C ratio in summer, stressing the influence of photochemistry during that season. On the other hand, it seems that the profiles of HOA and COA are very similar during the four seasons (except HOA in summer, see above).
- 4) Back trajectory analysis: the main problem of this section is that the authors decided to perform a combined cluster analysis with data from the four field campaigns. This method introduces a bias when they compare the different air masses, because the frequencies of the clusters vary a lot with season, as shown in Table 1. For example, cluster 1 shows a very strong diurnal pattern for O/C ratio (Figure 8), because this cluster is mainly observed in summer and is highly influenced by photochemistry. On the other hand, cluster 5 shows a flat diurnal pattern for O/C ratio, because this cluster is observed only in autumn, when photochemistry is less intense. Therefore, it is a bit difficult to compare the different air masses, so I would suggest to perform a cluster analysis separately for each season.

Specific comments:

- 1) Page 20264, line 12: V- and W-modes correspond to the mode of operation of the mass spectrometer, while MS and PToF modes are related to the chopper cycle. This is not clear in the text, where V-, PToF- and W-modes are mentioned together (and without MS).
- 2) Page 20265, lines 12-14: I think the authors wanted to say “biomass burning aerosols as primary organic aerosols did *not* contribute significantly to the organics”.
- 3) Page 20268, line 26: the authors should be careful when they talk about ammonium nitrate and ammonium chloride, because they mention earlier that anions were not fully neutralized (section 2.3), so it is not sure that nitrate and chloride are under these forms. For nitrate, how does the scatterplot of NO^+ vs NO_2^+ look like (slope, correlation coefficient)? Is the slope close to that of ammonium nitrate during IE calibrations?
- 4) Figure 5: Concerning the slopes and y-intercepts of the Van Krevelen diagrams, I suggest to keep only those obtained with the orthogonal distance regression (ODR), and to remove the others.
- 5) Figures 5 and 8: please replace OSC by $\overline{\text{OS}}_c$ in the figure captions.
- 6) Figure 8: some information are hard to see in this figure. For each species (Org, SO_4 , Org44, and Org57), is it possible to include one panel with the size distributions of the four seasons, eventually with four different y-axes? It will be easier to see the variation of the modal diameters with the seasons.
- 7) Figure S1: it would be nice if the authors include a second map with a zoom on Hong Kong and the sampling site. We would have a better view on the location of local sources.
- 8) Supplementary material, page 2, line 8: I think that the reference DeCarlo et al. (2006) is more appropriate here than DeCarlo et al. (2004).
- 9) Figure S4: please color these scatterplots by time. It seems that in spring and winter, some periods are more acidic than others. I think it would be worth including a discussion on this in section 3.1.
- 10) Table S1: the authors mentioned earlier that they introduced a time dependent correction of the gas-phase CO_2^+ signal. I suggest that they include this information in the table.
- 11) Table S2: I would suggest to sort the data by sampling site characteristics (i.e., urban, suburban, rural/remote) instead of sampling date.
- 12) Figures S10 to S17: the signals in all the mass spectra are too broad, please reduce the line thickness.
- 13) Figure S22: please mention in the figure caption that the individual trajectories correspond to the 5-cluster solution with arrival height of 300 m.

References:

DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory, *Aerosol Sci. Technol.*, 38, 1185-1205, 10.1080/027868290903907, 2004.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, *Anal. Chem.*, 78, 8281-8289, 10.1021/ac061249n, 2006.