

Interactive comment on “Characterization of carbonaceous aerosols in Singapore: insight from black carbon fragments and trace metal ions detected by a soot-particle aerosol mass spectrometer” by Laura-Hélène Rivellini et al.

Anonymous Referee #1

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The manuscript “Characterization of carbonaceous aerosols in Singapore: insight from black carbon fragments and trace metal ions detected by a soot-particle aerosol mass spectrometer” investigated the sources of carbonaceous aerosol in Singapore by using Positive Matrix Factorization. Besides utilizing the mass spectra of organics, they inserted the mass fragments of rBC and metals in the data matrix in order to improve the interpretation of the aerosol sources in urban area. The authors were able to resolve five sources/types of organic aerosols; hydrocarbon-like OA, oxygenated-HOA, cooking-related OA, less-oxidized oxygenated OA and more-oxidized oxygenated OA.

C1

This paper presents interesting results and novel data analysis methods. Paper is well-written and fluent, and in most parts also easy to understand. It utilizes nicely the whole high resolution mass spectra provided by the SP-AMS, and thoroughly validates the PMF results. However, the interpretation of the PMF factors is sometimes confusing. Additionally, there are shortcomings in the measurement methods, and the authors have drawn some conclusion based on rather weak evidences. Therefore I recommend publication of the manuscript only after the comments below are adequately addressed.

General comments

The quantitativity of the SP-AMS results is not considered adequately. Since there are several sources of uncertainty in the AMS measurement, e.g. CE, IE and RIE values, the validation of the SP-AMS needs to be done more accurately. Additionally, the weakness of this paper is that only the data from the SP-AMS is utilized. I assume there were also other instruments at the site (for PM, size distribution, BC etc.), or at the air quality monitoring stations nearby, that could be used for the validation/comparison of the SP-AMS data. Without auxiliary data, there accuracy of the given concentrations remains vague.

Regarding PMF, I don't understand why only few five metal ions were included in the PMF model even though the SP-AMS can detect quite a few metals. For example, Al, Ca, Cd, Cr, Cu, Fe, Mn, Zn and Sn could be included. I would assume that the inclusion of more metals would improve the interpretation of PMF results. I suggest adding more metals to the PMF analysis because I think that all the interesting information in the data set is not used so far.

In terms of metals, I disagree with the authors that all of the metals presented here can be used as tracers. I agree that Na can come from fuel but it can also originate from other sources in urban areas, for example from coal and biomass burning (e.g. Hsu et al. 2011). Similarly, Rb signal in AMS can originate from coal combustion (Irei et

C2

al., 2014). I suggest that the authors consider other sources of metals in urban areas (especially close to industrial areas), and revise their conclusion regarding metals.

Specific comments

1. Page 1, Abstract; lines 19-20; “local combustion sources” and “industrial emissions” need to be described in more detailed. What kind of combustion sources, just traffic? What industry there are in that area?
2. Page 4, line 27; “composition –dependent approach” CE values need to be shown in the paper and the uncertainty of the CE has to be evaluated carefully. Since the RIE for sulfate was not determined, the uncertainty analysis is very important.
3. Page 5, line 13; I don't understand why only few five metal ions were included in the PMF model. I suggest adding more metal ions.
4. Page 5, line 13-14; metals ions were included in Hz's into the PMF. How does that affect the results of the PMF?
5. Page 5, line 30; sulfate increase starting from ~10:00 can be explained by the active photochemistry. Could you add a diurnal plot showing solar radiation and sulfate in the same figure?
6. Page 5, line 30; NH₄ ratio and acidity; the discussion on acidity is somewhat unreliable because the RIE for sulfate was not measured. For example in Fig. S4a, it's hard to understand why all the points are below 1:1 line. To me, this seems to be due to the incorrect RIE for sulfate. Could you comment on that?
7. Page 7, line 5; industrial emission; be more specific what kind of emissions
8. Page 7, line 28; define POA, is it only HOA? Isn't COA also primary?
9. Page 7, line 38; “large combustion sources during nighttime” needs to be elaborated since it has such a large effect on diurnal cycle of HOA

C3

10. Page 9, lines 11-15; “organo-nitrate and nitrogen-containing fragments increased during the daytime in this field study.” Why there is not more discussion on these species if they were detected? What is their contribution to OA or LO-OOA? Add the ratio of N to C (and S:C) to Figure 3.
11. Page 11, line 5-; Na as a tracer for fossil fuel combustion. Revise this section by taking into account other sources of Na in urban areas (see general comments).
12. Page 11, Biomass burning tracers, I don't understand why the contribution of biomass burning has been investigated so extensively even though it does not show up in PMF and the metals are not very good tracers for it. Consider making Section 3.5.2. more compact.
13. Page 12, line 24-26; “Kasthuriarachchi et al. (2019) also found that MO-OOA was the major contributor to the observed nitrogen-containing organic fragments that could be largely generated by biomass burning emissions” is contradictory to page 9: “Kasthuriarachchi et al. (2019) reported that the concentrations of organo-nitrate and nitrogen-containing fragments (i.e., C_xH_yN₊ and C_xH_yNO_z⁺) increased during the daytime in this field study, suggesting that photo oxidation of VOCs under high-NO_x condition could be another potential pathway toward LO-OOA formation”. Please revise the sentence/sentences
14. Page 12, line 31-33 and Fig. S11, Fig. S11 is confusing. It is very difficult to see which trajectories really pass the two fires shown by the MODIS. Could you just select the trajectory for the peak concentrations of m/z 60? Where are the large urban areas in the map? Do the trajectories pass large cities as well? Is it possible that biomass burning emissions were mixed with urban emissions (that increased Rb and maybe also K)? Please add cities to the map. Why Fig. S11(b) and Fig S11(c) are not on the same scale? Now it is difficult to compare (b) and (c). Add lines between markers to m/z 60 and Rb in Fig. S11a.
15. Page 13, lines 21-23; “Furthermore, Na⁺ measured by the SP-AMS can potentially

C4

be useful for separating rBC from traffic and biomass burning combustion emissions, which required further investigation.” I suggest revising this sentence as the evidences provided by this study are not convincing enough. I think that there are multiple sources for Na in urban areas that should be taken into account.

16. Page 13, lines 36-37; “This observation suggest that, in the region, both K⁺ and Rb⁺ might be more appropriate tracers for the identification of aged biomass burning than m/z 60.” I suggest revising this sentence as Rb may also come from other sources.

Technical corrections:

1. Page 7, line 13; less-oxidized oxygenated OA (LO-OOA)
2. Supplemental material, could you add a figure showing the contribution of metals to each PMF factor? It would be interesting to see how metals divide between the factors.

References

Hsu, L. J., Alwahabi, Z. T., Nathan, G. J., Li, Y., Z. LI, S., Aldén, M.(2011). Sodium and Potassium Released from Burning Particles of Brown Coal and Pine Wood in a Laminar Premixed Methane Flame Using Quantitative Laser-Induced Breakdown Spectroscopy. *Applied spectroscopy*, 65, 684-91.

Irei, S., Shimono, A., Hikida, T., Kuramoto, K., Suzuki, Y., Takami, A. (2014). Qualitative Evaluation of m/z 85, 87, and 133 Signals in Organic Aerosol Mass Spectra of Fly Ash Produced by Coal Combustion. *Aerosol and Air Quality Research*, 14: 406–412.

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