Response to the reviewer comment 1:

This manuscript describes analysis of soot particle aerosol mass spectrometer (SP-AMS) measurements conducted in Singapore during a ~2-month period. The manuscript systematically explores and demonstrates the application of PMF to the SP-AMS data. The analysis starts with a more traditional approach of using organic aerosol (and refractory BC, rBC) signals and then sequentially adds in metal signals and then inorganic signals, all from the SP-AMS spectrum. With the traditional approach, 4 meaningful source factors are resolved. With the addition of the metals, another 3 factors are resolved, an aged biomass burning and a fresher primary biomass burning factor, as well as an industrial and shipping related factor. Addition of the inorganic signals yield one more factor, a biomass burning-influenced OA factor associated with different inorganic fragments. Various additional formulations are used to provide support for the meaningfulness and robustness of the PMF separations, e.g. size diurnal cycles, size distributions, wind and back trajectory analyses, as is typically required for testing PMF results. Apportionment of the rBC among the factors and the contributions of the factors to overall composition are reported. The manuscript is primarily a methods demonstration, with a few relatively generalized observations of aerosol chemical and source processes.

The paper is well-organized and clearly written. It will make a valuable contribution to the body of literature of aerosol composition analytical methods. I liked the way the expansion/exploration of the additional PMF chemical inputs were discussed sequentially, building on the previous results. I also particularly found Fig 12 to be a valuable in putting these new and previous BBOA factor separations in context. I recommend publication in EGUsphere with a few minor suggested changes.

Response: We thank for the positive feedback from the reviewer on the significance of this work. Our responses to specific comments are in blue color below:

A few general comments. While I understand that the primary focus of this work is methods demonstration, it would seem useful to provide more of a general presentation of previous aerosol measurements conducted in this region for context. There are a few statements and references that are sprinkled in at points in the manuscript to compare to relevant observations. However, it was difficult as a reader not familiar with this region to get a sense of what is known about aerosol concentration, composition, and sources in this region. Also, during particularly the 1st half of the manuscript, there were a number of instances where the discussions and interpretations were a bit overreaching or protracted discussion of details that may not add any additional information. Those probably at unnecessarily length to an already fairly long manuscript and water down the more interesting and insightful information in this manuscript. See for example the detailed comments below on nitrate composition (P16, L25), diurnal cycles of O/C (P15, L8-11), and ions fragment size distributions (P17, L25-30). I encourage the authors to review the paper and trim any unnecessary text and discussions along those lines.

Response:

We agree with the reviewer's comment that the reader can benefit by including more information about the PM concentrations and their potential large sources in our sampling location. The co-located ACSM and aethalometer measurements can provide more details of $NR-PM_1$ and BC during the sampling period of this work, and the relevant discussion has been included in the revised manuscript. The details is provided under the response for the specific comments from both reviewers. As suggested by the reviewer, some of the discussions have been shortened or moved to supplementary information.

In addition, some minor modifications have been made in the last paragraph of the introduction to improve the description of the complexity of PM sources in the urban area of Singapore as shown below.

Page 4 Lines 14-21: Singapore is a highly developed coastal urban environment located at the end of the Malay Peninsula in Southeast Asia. Aside from typical engine emissions from local traffic and local cooking emissions (Budisulistiorini et al., 2018; Rivellini et al., 2020), Singapore has the world's second busiest shipping port (World Shipping Council, 2024) and fifth largest oil refining capacity (Lau et al., 2021), which can be potential large anthropogenic combustion sources of air pollutants. Furthermore, together with atmospheric processing during transport, air quality and concentrations of atmospheric PM in Singapore can be significantly influenced by SOA (Budisulistiorini et al., 2018; Rivellini et al., 2020) and transboundary haze due to regional/transported biomass burning emissions in Southeast Asia (Budisulistiorini et al., 2018; Heil and Goldammer, 2001; Kuwata, 2024).

Detailed Comments:

P7, L8-9. Incomplete sentence

Response:

The manuscript has been revised as shown below:

Page 7 Lines 10-11: Noting that mIE_{NO3} and mIE_{rBC} were determined when the LV was off and on, respectively. The TV was operated at 600 °C throughout the calibration.

P8, L20-21. Would be useful to explain the methodological reasoning for downweighting K^+ and upweighting Rb^+, V^+, and Ni^+. I.e. how does this improved separation, what happens if you keep them at their native S/N? Of if this was explored more systematically in the papers referenced, perhaps briefly state how it can help. These types of details/discussions could be quite useful for others conducting "combined" PMF" as indeed this manuscript is in large part a methods demonstration.

Response:

Downweight and upweight signals of AMS data for PMF analysis has been more systematically investigated by previous studies to improve the separation of factors (Adam Reff et al., 2012; Lee and Hopke, 2006; Paatero and Hopke, 2003). In general, OA fragments with signal-to-noise ratios (S/N) less than 0.2 are "bad" signals, and S/N between 0.2-2 are "weak" signals that require downweight or removal. A general description can be found for the PMF analysis of AMS data (https://cires1.colorado.edu/jimenez-group/wiki/index.php/ToF-AMS_Main), but the decision largely relies on specific data set and user judgment.

As described above, the general goal of signal adjustment is to generate comparable S/N values to a major fragment S/N (e.g., $C_2H_3O^+$ has an S/N ~25, C_3^+ has an S/N ~21). K^+ had a native S/N of ~130, which was too strong, leading to poor factor separation and requiring downweight. In contrast, Rb^+, V^+ and Ni^+ had S/N below 2 that required upweight to generate meaningful results. Figure R1 shows the comparison of 7-factor solutions using default S/N, adjusted S/N in $PMF_{metal-7}$, and over-adjusted S/N (i.e., S/Ns < 0.2), using metal ions as an example. Default S/N (Fig. R1a) led to a factor dominated by K^+ (> 99% signal contribution). Our $PMF_{metal-7}$ had a good factor separation as metal S/Ns were between 2-20. When the S/N were low (i.e., S/N < 0.2, Fig. R1c), the factor separation was not affected by the addition of metal ions.
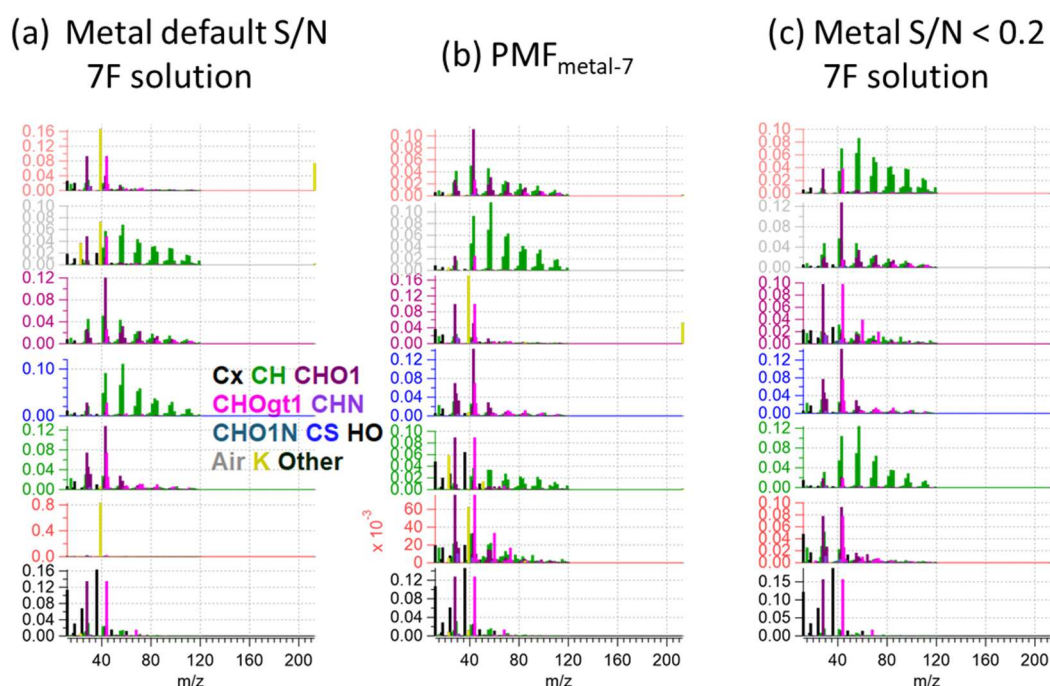

Figure R1. A 7-factor PMF solutions for metal ion with original and adjusted S/N.

The manuscript has been revised as shown below to highlight that the metals were downweighed or upweighted to generate comparable S/N ration to OA and rBC fragments in our PMF analysis.

Page 8 Lines 23-25: The signal of K^+ was downweighed by 10 times, whereas Rb^+, V^+, and Ni^+ were upweighted by 3 times to generate comparable signal-to-noise ratio (S/N) strengths to OA and rBC fragments.

P8, L25-26. "Sulfate fragments were downweighed by a factor of 3 due to their relative strong intensities." For PMF, it's the S/N, not the signal that controls the influence on the factorization. I.e. if intensity (signal) is high but so is the uncertainty, it's not necessarily going to have a strong influence. This is a useful paper, that I think future practitioners will read, so import to be precise with language.

Response:

Following the previous metal S/N comment, we have modified the sentence for the case of sulfate as shown below.

Page 8 Lines 28-29: Sulfate fragments' intensities were downweighed by a factor of 3 due to their relative strong S/N.

P8, L29. "FPEAK" not "F peak"

Response:

This error has been corrected as suggested.

Fig. 2e pie chart. In the time series it appears that Cl is on average greater than SO4, however it is not visible in the pie chart, while SO4 is?

Response:

Chloride mass is ~0.03% of total aerosol mass. The time series of Cl^- mass was scaled up by a factor of 20. The legend of Figure 2e has been updated to present this information.

P11, L10-11: Here quantitatively comparing SP-AMS rBC to aethalometer. It would seem key to discuss the absorption coefficients applied to the AE33 data (to convert optical absorption to mass) for comparison to be most meaningful.

Response:

We agree that the mass absorption coefficient (MAC) is critical to calculate equivalent BC (eBC) concentrations measured by the aethalometer. As aethalometer is more robust compared to SP-AMS for BC measurement, the primary goal of our time series comparison is to demonstrate that rBC mass concentrations measured by the SP-AMS are reasonable and their temporal variations can be captured due to changes in BC source contribution.

It is important to point out that quantification of rBC using SP-AMS strongly depends on the degree of overlapping between LV and particle beam, which ultimately affects the RIE_{rBC} values and collection efficiency of rBC particles (Willis et al., 2016). The coating thickness of rBC particles, which varies significantly within atmospheric BC particle population, can affect the particle beam width and subsequently the rBC quantification. Therefore, using the SP-AMS-measured rBC concentrations to evaluate the accuracy of MAC values applied in the aethalometer may not be appropriate, and such instrument comparison is out of the scope of this work. In this study we use the default MAC value of 7.77 m^2/g to calculate eBC concentration (Drinovec et al., 2015).

The manuscript has been revised as shown below:

Page 11, Lines 11-15: The rBC concentrations measured by the SP-AMS was about 31% higher than the equivalent BC (eBC) concentrations measured by the aethalometer, a strong temporal correlation between the two measurements was observed, suggesting that the temporal variation of BC concentrations can be captured reasonably well by both instruments (R = 0.89, Fig. S4). Such strong correlation between the eBC and rBC concentrations was consistently observed at the same sampling location (Rivellini et al., 2020).

P15, L8-11: O/C values of 0.38-0.39 on average during the morning and evening rush hours is a lot higher than typically HOA O/C ratios (typically <0.1), at least for standard vaporizer AMS. Authors should reconsider this statement or provide context for differences for the SP-AMS (perhaps discussed in more detail later, but this would seem to stand out as written here as a dubious statement for most readers with some familiarity of AMS OA analyses).

Similarly, in P15, L17-19 the higher evening O/C (~0.43) are interpreted as "suggests that the OA coatings were largely contributed by oxidized organic species". Together these statements suggest that a shift from 0.38-0.39 to 0.43 indicates a shift from mostly HOA to mostly OOA coatings. That seems like a big exaggeration of what appears to be a fairly subtle shift between degrees of moderately oxidized composition. Or perhaps I'm misunderstanding the intention, in which case consider making the point more precisely.

Response:

As the reviewer pointed out, the fragmentation of OA by LV of SP-AMS can be different compared to the standard AMS as reported in our previous work regarding the impacts of LV scheme on the elemental analysis of OA coating on BC particles (Ma et al., 2021). Note that the O:C ratios of HOA factor identified in our PMF solutions ranged from 0.1 to 0.14, which are comparable to the typical HOA factor observed from TV scheme of standard AMS measurement. The relatively high O:C ratios during the morning rush hours compared to that of typical HOA could be due to the oxygenated soot functionality in the rBC-rich factor due to traffic emissions. The O:C ratios of LO-OOA and MO-OOA were about 0.5 and 1, respectively as shown in the PMF solutions.

We agree with the reviewer that we may over-interpret some of the results based on the O:C ratio alone in this section. As the PMF results reported in the later sections provide evidence to support our arguments, we have revised/shortened the manuscript as follows.

We have modified the description about the impacts of OOA coating formation on the O:C ratios in this section.

Page 15, Lines 17-19: The higher O:C ratio and OS_c overnight suggests increasing contribution of oxidized organic species to the total OA coatings, which is consistent with greater influence from regional transport of aged aerosols with biomass burning influences overnight, as discussed above in Section 3.2.1.

We have moved the argument about the characteristics of traffic emissions (i.e., HOA) to the later section with the support from PMF results.

Page 17, Line 31 – Page 18, Line 1: Therefore, the observation of lower Org/BC, O:C and OS_c in Fig. 3 indicates that the rBC emitted from local traffic was mainly coated by POA and the thickness of such POA coatings was relatively thin for the majority of the rBC particles compared to those observed during the rest of the day.

P16, L1-7. The authors reference to the Cubison et al background value (0.3%) determined for a standard vaporizer AMS, but then discuss enhancement factors for oxygenated OA and levoglucason, as well as point to the f values in this data (Fig. 6). What are those enhancement factors referenced to? Cubison 0.3% or some revised LV-SP-AMS background? Can the authors report the typical background fC2H4O2+ for non-BB OA for the LV-SP-AMS, assuming that's what the factors are being reference to? Adding a horizontal line in Fig. 6d for background f's for LV SP-AMS might be useful as well.

Response:

We have revised the manuscript to deliver a clearer message on the calculation of $f_{C_2H_4O_2^+}$ background level based on the observations from Cubison et al. (2011) and Ma et al. (2021). A dashed line indicating potential $f_{C_2H_4O_2^+}$ background has been added to Fig. 6d along with a proper caption. The manuscript has been revised as shown below:

Page 15, Lines 2-4: Figure 6. Diurnal cycles of (a) V^+/Ni^+, (b) $K_3SO_4^+/K^+$, (c) $NH_4^+{}_{meas}$ / $NH_4^+{}_{pred}$, (d) $f_{C_2H_4O_2^+}$ and (e) NO^+/NO_2^+ measured by SP-AMS. The horizontal dashed line in panel (d) represents the background level of $f_{C_2H_4O_2^+}$ for non-BBOA reported by Cubison et al. (2011) with the correction factor for OA measured by LV scheme applied (Ma et al., 2021).

Page 15, Line 19 – Page 16, Line 9: To investigate the possible biomass burning influences on OA coatings, a mass contribution of a biomass burning tracer fragment to the total organic coating ($f_{C_2H_4O_2^+}$) was determined as shown in Fig. 6d. Cubison et al. (2011) reported that $f_{C_2H_4O_2^+} > 0.3\%$ obtained from standard AMS measurements

can be the indication of biomass burning influences. Ma et al. (2021) showed that $f_{C_2H_4O_2^+}$ can be enhanced by a factor of ~2.45 on average for oxygenated organic coating and 2.33 for levoglucosan vaporized by the LV scheme of SP-AMS. Therefore, the background level of $f_{C_2H_4O_2^+}$ was re-calculated using the correction factor of 2.33 as shown by the dashed horizontal line in Fig. 6d. Although the $f_{C_2H_4O_2^+}$ values of total OA were close to the background level, the higher values of $f_{C_2H_4O_2^+}$ and OS_c of OA coating materials between 2:00 and 8:00 LT suggests potential influences of biomass burning emissions on the chemical characteristics of rBC-containing particles during the night. The potential contribution of fresh and aged biomass burning emissions will be further discussed based on the PMF analysis (see Section 3.3).

P16, L25. "NO_3^- and Cl^- have elevated levels over midnight…" Does Fig. 6d really support elevated NO3? Nighttime NO3 doesn't seem higher than the average values and any diurnal cycles in the average look quite subtle. And given the variably/range (shown in swaths), those features barely seem significant. This appears to be another example of where the authors are reaching to draw conclusions/speculations from very subtle features.

Response:

As the nitrate and chloride concentrations were very low in this study, we have removed the argument about the nitrate and chloride elevated levels over midnight in the revised version to avoid over-interpretation. The current discussion focuses on the diurnal changes in NO^+/NO_2^+ ratio.

P17, L25-30: speculation on the m/z 43, 55, 57 peaks being $C_xH_y^+$ or $C_xH_yO_z^+$ peaks. Those peaks can be separated peaks using the HR PToF, assuming the .p files were saved. Otherwise, in this section, discussion of those ions doesn't seem to add any additional information. E.g. the distribution of m/z 44 and laboratory measurements are used to speculate what the composition of the m/z 43 is? So then, what does showing/discussing the measured m/z 43 distribution add?

Response:

We agree with the reviewer that the size distribution may not provide much new information, and they have been modified and moved to SI to reduce the main text length.

Sect 3.3.1 POA from fossil fuel combustion. This is interesting. Can the authors discuss why they think the rBC-rich and HOA factors were separated with PMF (case base-4) and what information that separation can provide? It is noted that both factor sources presumably come from combustion, and the diurnal cycles, NWR and PSCF plots are very similar. But clearly, there must be some significant difference in the time series from some changes in atmospheric sources/processes, instrumental drifts, etc.

Response:

There are two major differences between the temporal variations of HOA and rBC-rich factors. Firstly, the diurnal profiles of the rBC-rich factor peaked one hour earlier than the HOA factor in the morning rush hours. Secondly, although the NWR analysis shows high concentrations of both HOA and rBC-rich factors at the hotspot observed from the south due to the shipping and/or industrial emissions, the HOA concentrations exhibited a stronger enhancement at this hotspot than the rBC-rich factors.

Interpretation of the physical meaning of HOA and rBC-rich factors remains challenging. However, Dallmann et al. (2014) measured the rBC and OA concentrations in the emission plumes of on-road diesel trucks and gasoline cars as well as their ambient concentrations during the period with different diesel trucks traffic volume. Their results demonstrate that diesel truck emissions have a higher rBC content than that of gasoline vehicles, but the OA mass spectral features are similar between them. Therefore, the rBC-rich factor peaked one hour earlier than the HOA factor could be due to a relatively high contribution of heavy duty diesel trucks to the total traffic volume in the early morning in Singapore (Fwa et al., 1996).

The manuscript has been revised with such additional information to enhance the quality of our discussion.

Page 18, Lines, 6-15: Nevertheless, there are two major differences between the temporal variations of HOA$_{base-4}$ and rBC-rich$_{base-4}$ worth highlighting. Firstly, the diurnal profile of rBC-rich$_{base-4}$ peaked one hour earlier than that

of HOA$_{base-4}$ during morning rush hours. This could be due to the relatively high contribution of heavy-duty diesel trucks to the total traffic volume in the early morning of Singapore (Fwa et al., 1996). This speculation is well-aligned with an on-road investigation using SP-AMS that heavy-duty diesel trucks emit much higher rBC content than gasoline vehicles, but the OA mass spectral features in emission plumes are similar between them (Dallmann et al., 2014). Secondly, outside of the rush hours, both factors started increasing at ~12:00 LT and peaked at 17:00-18:00 LT that coincided with prevailing wind blown from the industrial and shipping region from the south direction. The NWR plots shows high concentrations of both HOA and rBC-rich factors at the hotspot observed from the south when the wind speed was greater than 8 m/s, but the HOA$_{base-4}$ concentrations exhibited a stronger enhancement at this hotspot than the rBC-rich$_{base-4}$ factors. Although most of the previous studies assigned their HOA and rBC-rich factors as local traffic-related OA (Carbone et al., 2019; Gentner et al., 2017; Malmborg et al., 2017), our results suggest that rBC-rich$_{base-4}$ and HOA$_{base-4}$ can be emitted from multiple combustion sources in this work. Nevertheless, the PMF$_{base}$ could not further resolve the contributions of traffic and shipping/industrial emissions to these two primary OA factors.

Fig. 8: should "Cother" be "C Other" in MO-OOA legend?

Response:

As the "Cother" in the original manuscript represented the metal signals, we have re-labeled "Cother" in all of our PMF analysis plots with "Metal".

Figure S6. "The NWR plots of factors identified by PMFbase-4." Would be helpful to point out the differences for these vs the plots in Fig. 8 (different WS resolutions, etc) in the caption.

Response:

The manuscript has been revised as shown below:

SI Page 15: Figure S7. The NWR plots of factors identified by PMF$_{base-4}$ with different wind speed ranges (< 3 m/s) and resolution than Fig. 8 (now Fig. 7).

Fig 11: Yellow metals bar color missing from legend

Response:

We have corrected and updated all the labels.

P29, L6: Should be Fig 9, not Fig 7

Response:

Figure number has been corrected.

P34, L4: Need "an" before "aged" or make "component" and verb made plural.

Response:

This grammatical error has been corrected as suggested.

P34, L13: hands shouldn't be plural

Response:

This grammatical error has been corrected as suggested.

Reference

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