PM$_1$ composition and source apportionment at two sites in Delhi, India across multiple seasons

Referee 2 comments in black. The response to the comments in orange.

The paper by Reyes-Villegas reports on measurements of aerosol composition and absorption at 2 sites in India (new Delhi and Old Delhi) where ground- based measurements were carried out in different seasons in 2018. Diurnal and seasonal trends in composition and organic aerosol types, resolved by positive matrix factorization, are reported. PM1 composition and concentration differences between the two sites in all seasons are minimal. Organic aerosols (OA) were the dominant component of PM1 in all seasons; higher concentrations of all species were measured in post-monsoon/winter, owing to changes in meteorological conditions. During pre-monsoon, oxygenated OA (LVOOA) was the dominant OA type with peaks appearing during the day, while in post-monsoon and winter periods, hydrocarbon-like OA (HOA) was the dominant aerosol type, with minimum concentrations during the day. Biomass burning OA, oxygenated primary OA, cooking OA, other oxygenated OA (SVOOA) were also identified although not consistently at all sites and all seasons (except for BBOA and COA).

The authors appreciate the value of the reviewer's comments and the improvements to the quality of the manuscript that have resulted from our responses.

Given this is not the first set of measurements in the area (see lines 94-105 for a list of comparable studies) and lack of new scientific insights presented here, I suggest the manuscript be considered as a "Measurement Report".

While AMS observations have previously been made in this region, these have been restricted to single sites and most restricted to a single season. Given the large size and inhomogeneity of sources within developing megacities such as Delhi, it is important that these are not assumed to be spatiotemporally representative. This is the first study to address this question and the systematic multi-dataset PMF analysis and critical comparison of the sites and seasons constitute more than a simply 'measurement' report.

When comparing the two sites, Old Delhi (OD) and New Delhi (ND), no remarkable difference on concentrations was observed; the C-PM$_1$ (C-PM$_1$ = BC + NR-PM$_1$) concentrations were OD (142 +/- 117 μg.m^{-3}) compared to ND (123 +/- 71 μg.m^{-3}). In some ways it was expected that we would observe a large difference between sites, due to their particular characteristics (OD being a more populated site with potentially more primary sources around and ND being a greener area with parks and business-like buildings in the surroundings). We found though, a large variation on C-PM$_1$ when looking at the seasonal analysis, for example, with C-PM$_1$ concentrations in monsoon to be lower than 60 μg.m^{-3}. The following paragraph has been added to conclusions: The fact that there is no remarkable difference on C-PM$_1$ concentrations between the two sites, suggests that, when aiming to control C-PM$_1$ high concentrations, the actions should be regionally orientated, for example as Delhi region, rather than considering controlling air pollution in OD or ND only.

Using PMF and Aethalometer model analysis, Traffic was shown to be the main primary aerosol source for both OA and BC, and as we mention in the conclusions, this indicates that in Delhi further control of primary traffic exhaust emissions would make a significant contribution to reducing PM$_1$ concentrations. Moreover, by controlling gas precursor emissions, OOA concentrations may also be reduced.

These findings are a novel advance, as is recognised by referee 1 and are a valuable addition to the literature. The manuscript provides scientific insight beyond that expected within a "Measurement

Report" and we contend that it should be published on ACP as a research article, after addressing the useful comments the referee has provided.
As such, I still have concerns about the analysis and data quality; some parts of the report also benefit from new reorganization and further clarifications.

Technical concerns:

- What was the sampling protocol/set up at different sites? Was there any cyclone used on the inlet? Was there any control on humidity? If not, how could changes in ambient RH diurnally and between seasons impact the measurements?
A cyclone and a drier were used in all the instruments. Text added to the manuscript: All set ups included a $PM_{2.5}$ cyclone to cut particle size and a drier to reduce humidity.

- Quantification of different AMSs and Figure S4: what is the difference between pre-flux and flux period? Why is the behavior of the comparisons so different between these periods when using the same CE correction factor (0.5 or CDCE)? For pre-flux period, slope with CE=0.5 and CDCE is very similar. It may be that the composition really dictates CE to be close to 0.5, but better justification/explanation needs to be provided as to why 0.5 is used for the whole study and not CDCE. Comparison is done on online PM1 and PM2.5 filter-based data. How/where are these filters collected? No information is provided, yet the measurements serve as the basis for justifying the selected value of the CE! What is the suspected contribution of 1-2.5 um particles to mass that justifies the comparison?

Please see responses to reviewer 1.

- Aethalometer data and contribution of BB vs. traffic: it was not explained why AAE_{wB}=2 and AAE_{tr}=0.8 is selected. It seems the basis for selecting these factors is the match between the traces in Fig. S13 for the time period in the box, but it wasn't explained why is it expected to have equal absorption from wood burning and traffic at two different wavelengths during Diwali period to justify selecting the default AAEs? I also disagree that there was no change in the absorption calculations using different values of AAE; clearly the b_abs_470wb changes in other panels of this graph depending on the AAE value. Why was a different AAE_{tr} used for AE-33 ND-Winter period (Fig. S15)?

The following paragraph describing the aethalometer analysis has been added to the supplement material (line 199):

A sensitivity test was performed to determine α_{ff} = 0.8. and α_{bb} = 2.0, varying α_{ff} from 0.4 to 2 and α_{bb} from 1.4 to 2.6 and increments of 0.1. Figure S16 shows example plots of the performed analysis. An improvement was observed when using α_{ff} of 0.8 compared to 1.0, thus a value of 0.8 was derived (figures S16.a and S16.b). No significant changes were observed when testing different α_{bb} values (figures S16.c and S16.d), thus the default value of 2.0 was used (Fig. S16). A similar analysis was performed to select values for the subsequent Aethalometer model analyses.

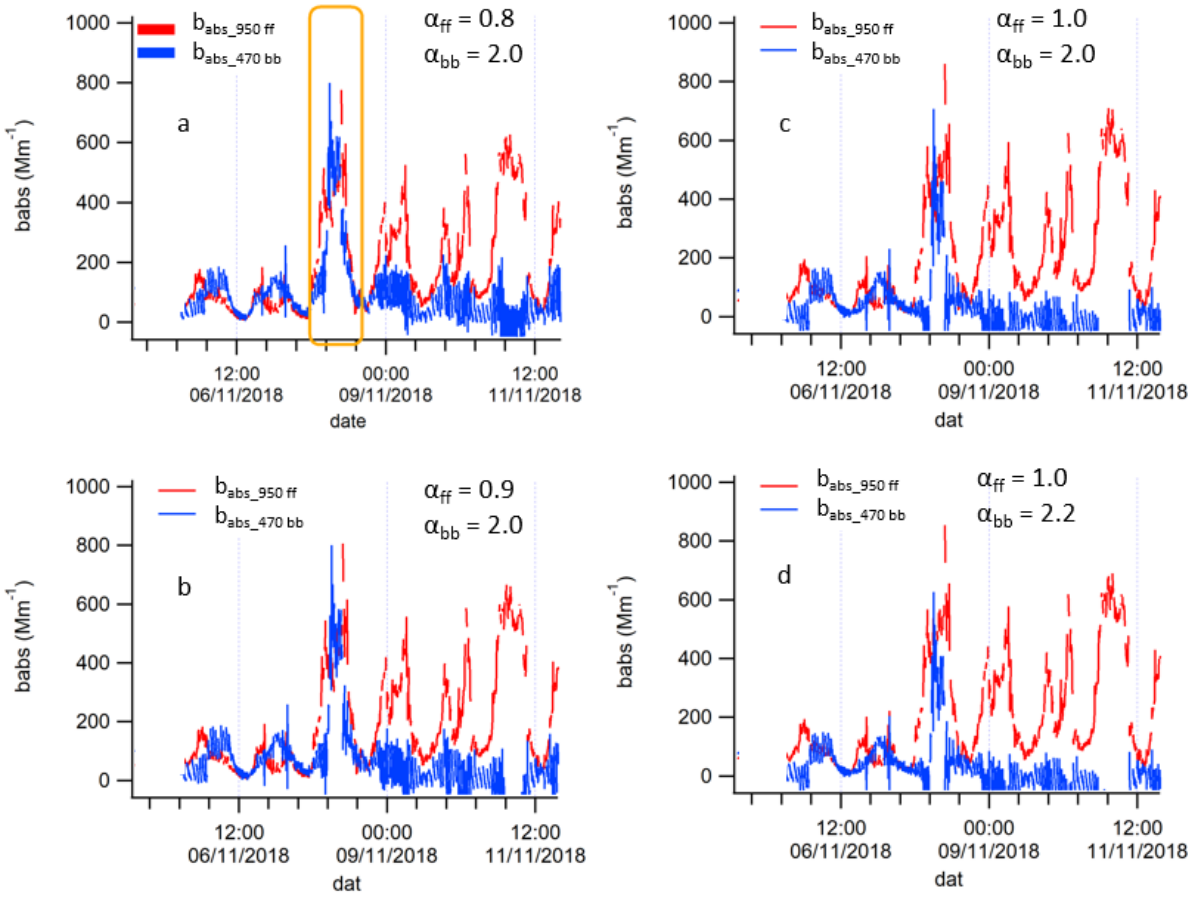

Figure S16. Sensitivity test to select αff = 0.8. The peak marked in panel (a) relates to the Diwali celebrations.

Additional edit. In section S4. Aethalometer analysis, the term b_{abs_950tr} (traffic) was replaced with $b_{abs\_950\ ff}$ (fossil fuel) and b_{abs_470wb} (wood burning) with babs_470 bb (biomass burning) to agree with what is presented in the manuscript.

In general, I'm also not sure the way aethalometer data are presented is useful. What would be more useful could be the fraction of absorption at 470 nm that is due to wb vs. traffic and not the absolute value of absorption due to wb at 470 nm.
We are using the Aethalometer model proposed by Sandradewi et al. (2008), which has been widely used to determine the contribution of wood burning and traffic to carbonaceous material using b_{abs_470wb} and b_{abs_950tr} respectively. We consider the Aethalometer analysis presented on this manuscript to do a efficient analysis on identifying traffic to be the main carbonaceous source in Delhi, India.

- References to PMF factors for oxygenated OA are given in terms of expected volatility (LV/SVOOA). Isn't it more accurate to call them based on their oxygenation level since the AMS doesn't measure volatility directly?
The terms MO-OOA instead of LVOOA and LO-OOA instead of SVOOA have been used in all the manuscript.

Factors show up in the last panel of Fig. 4 (SFOA and nHOA) that are not discussed anywhere in the paper.
In the last version of the manuscript, in the caption of figure 4, we mention that this dataset is analysed into detail by Cash et al. (2020)

Additional analysis is presented in table S4 where we mention that in order to compare the 7-factor solution selected by Cash et al. (2020) with our 5-factor solution we did the following calculation: **HOA** = HOA_ + NHOA and **BBOA** = SFOA + SVBBOA.

Is it common to look at Q/Qexp for different m/z's? I was under the impression that always an overall Q/Qexp is considered in PMF. What is the acceptable range of this ratio when considering individual m/z's? Values up to 300 are way too high for the overall Q/Qexp. It's concerning that some of the key fragments (43, 55, etc.) have such high values.

The Q/Qexp for different m/z's (for example figure S11) is additional information to look if there is a particular m/z showing a high value. The overall Q/Qexp are also presented in the supplement (for example figure S9). Figure S9 shows Q/Qexp values of around 5.52 for 4-factor solutions and values of around 5.2 for 5-factor solutions. The 6-factor solutions presented two factors with similar time series and mass spectra, characteristic of factor splitting. Hence, the 5-factor solution was chosen to be further analysed. This is explained in S3.

- Section 3.1 as written is very confusing. It's mentioned the highest conc. were seen in post-monsoon, but then two periods in post-monsoon are reported. If the point is to discuss the highest concentration, only one number/site/season should be reported. Overall I don't find this beginning paragraph of 3.1 useful as written. If the authors want to describe seasonality, I think the two sites need to be considered separately, so I suggest reorganizing this part.

This section has been edited in the manuscript comparing only post-monsoon and monsoon as periods with the highest and the lowest concentrations.

Aerosol measurements were taken in OD and ND over different seasons in 2018. The highest concentrations were observed in the post-monsoon season, where OA concentrations of 400 $\mu g.m^{-3}$ were found (Fig. S8). Lower aerosol concentrations were observed in the monsoon season, where OA reached between 80 – 200 $\mu g.m^{-3}$.

- L 289: a reference to Chloride deposition is presented here without any discussion of how deposition rate is inferred. Mere reduction in chloride does not mean it's being deposited. Either elaborate or remove this sentence.

We are grateful to the referee for pointing this out, our wording should have referred to concentrations rather than deposition. The line has been edited as follows: This is also consistent with the decrease on Cl^- concentrations before $NO3^-$ concentrations increase in the morning.

Moreover, the following line was added at the end of section 4.1: A more detailed analysis on the Cl^- processes is performed by Gunthe et al. (2021), where the ACSM Winter data is part of the analysed datasets.

- L 363: Aerosol sulfate does not evaporate with typical diurnal changes in temperature whereas ammonium chloride or nitrate do. If oPOA is behaving more like sulfate, I wouldn't call it semi-volatile. Based on the diurnal profiles, I also don't think oPOA has a similar diurnal profile to sulfate! It's more like chloride and nitrate, in which case it's justified to call it semivolatile.

The paragraph has been edited as follows: One additional factor (oPOA) had a particular diurnal trend, similar to Cl^-, and a mass spectral signature similar to OOA. However, from examination of the polar plots (Fig.S20), oPOA appears to have similar source sectors to SO_4^{2}. This suggests oPOA may be semi-

volatile and driven by changes in T and RH, like Cl-, whilst having different sources, undetermined at this time.

Other concerns:

- Sometime chloride is referred to as Cl and sometimes Cl-. Please use the latter and consistently.
The changes have been done as suggested.

- Sometimes numbers in molecular formulas are not subscripted; please correct.
All molecular formulas have been subscripted.

- This sentence doesn't full make sense: "Comparing these concentrations with the PostM_OD_H2 dataset, HOA concentrations of 30 ug/m3 were identified". Please rephrase.

The paragraph has been rephrased as follows: HOA is the factor with the highest concentration with 6.0 – 55.0 µg.m^{-3} for Pre-monsoon and Post-monsoon, respectively, in the PostM_OD_H2 dataset (Table S4), HOA concentrations of 30 µg.m^{-3} were identified. These HOA concentrations represent a relative contribution to OA sources of 20 to 50%.

- Figure S6: data gaps show up with a flat line; please remove those.

Figure S6 (now figure S8) has been updated.

- References to figures in SI (PMF section and those after) are not correct; Please correct.
The references to figures have been corrected.

- Fig. S17. Figure caption doesn't match all the panels that are plotted.

Figure 17 (now figure S20) has been updated as follows: Figure S20. Polar plots of various aerosols. Median concentrations [µg.m-3].

Cash, J. M., Langford, B., Di Marco, C., Mullinger, N., Allan, J., Reyes-Villegas, E., Joshi, R., Heal, M. R., Acton, W. J. F., Hewitt, N., Misztal, P., Drysdale, W., Mandal, T. K., Shivani, Gadi, R., and Nemitz, E.: Seasonal analysis of submicron aerosol in Old Delhi using high resolution aerosol mass spectrometry: Chemical characterisation, source apportionment and new marker identification, Atmos. Chem. Phys. Discuss., 2020, 1-42, 10.5194/acp-2020-1009, 2020.
Gunthe, S. S., Liu, P., Panda, U., Raj, S. S., Sharma, A., Darbyshire, E., Reyes-Villegas, E., Allan, J., Chen, Y., Wang, X., Song, S., Pöhlker, M. L., Shi, L., Wang, Y., Kommula, S. M., Liu, T., Ravikrishna, R., McFiggans, G., Mickley, L. J., Martin, S. T., Pöschl, U., Andreae, M. O., and Coe, H.: Enhanced aerosol particle growth sustained by high continental chlorine emission in India, Nat Geosci, 14, 77-84, 10.1038/s41561-020-00677-x, 2021.
Sandradewi, J., Prévôt, A. S. H., Szidat, S., Perron, N., Alfarra, M. R., Lanz, V. A., Weingartner, E., and Baltensperger, U. R. S.: Using aerosol light abosrption measurements for the quantitative determination of wood burning and traffic emission contribution to particulate matter, Environmental Science and Technology, 42, 3316-3323, 10.1021/es702253m, 2008.