

We thank the reviewers for their comments. All comments are addressed below. Reviewers' comments are included in italics, our responses are included in blue, and updated manuscript text is included in red.

Reviewer 2

General Comments:

The manuscript by Bhandari et al. presents an innovative application of the PMF for long term and highly time resolved datasets. The fact that various sources influence a site at specific hours throughout the day, running PMF at different time of the day appears to be a logical approach, as it also allows for more MS variability. The application of this time-of-day PMF on a long term ACSM dataset (Delhi, winter and monsoon 2017) improved the source apportionment of OA, by further separating source-specific POA compared to results obtained with standard seasonal PMF. This paper is clearly written and relatively well structured. Some minor comments need to be addressed before being accepted.

Minor Comments:

1. *“Results from PMF analysis for all times of the day are presented in a companion paper (Bhandari et al., 2022).” I find that at least a brief overview of the different factors observed for all time-of-day results should be described in the supplement. Indeed, the change in POA factors from non sequential time-of-day, here 11am-15pm and 23pm-3am, is possible assuming dilution, atmospheric processing, or drastic change in air masses influencing the site. While, for time-of-day following one another (e.g. 11am-3pm and 3pm-7pm), I wonder if POA factors and their concentrations show a decrease before disappearing at a later timing (e.g after 7pm). Reconstructing the diurnal profiles of all POA and SOA of all time-of-day results compared to seasonal one could support the advantage of the new approach.*

Response: We agree with the reviewer that reconstructing the diurnal profiles of POA and SOA factors could show the continuities in time-of-day PMF factor concentrations and thus, the advantage of the new approach. In the companion publication, we generate diurnal profiles for reconstructed POA and OOA in the winter and monsoon seasons (Figs. 2–3, Figs. 4, 7 in Bhandari et al, 2022). We adapt the figures in the companion paper to present diurnal patterns for POA and OOA in the two seasons in the Supplement of this manuscript. In addition, we recently submitted the final response to the companion paper, and as such we expect the two papers to be published at a similar time. In line with the reviewer's suggestion, we have updated the text (Sect. 2.4):

“Results from PMF analysis for all times of the day are presented in a companion paper (Bhandari et al., 2022), and a brief summary of those results is also provided in the Supplement (Sect. S5).”

The text above was moved to Sect. 2.4 to address another reviewer's comment. We have also updated the Supplement (Sect. S5):

“Results from PMF analysis for all times of the day are presented in a companion paper (Bhandari et al., 2022). Here, we share a brief summary of those results, focusing on diurnal patterns of POA and OOA in seasonal PMF and time-of-day PMF. Figure S41a-b show the diurnal time series patterns of POA (HOA+BBOA+COA) and OOA (Local OOA + Regional OOA) factors for winter and monsoon of 2017. Clearly, POA concentrations exhibit larger variability than OOA concentrations in both seasons. Our results show that the time series (TS) concentrations of time-of-day PMF factors are broadly consistent with seasonal PMF factors. In winter, we separated BBOA or BBOA-like factors in all periods but did not separate cooking organic aerosol (Table S3 in Bhandari et al., 2022). We also separated HOA or HOA-like factors in all time-of-day periods in winter. In monsoon 2017, we separated HOA or HOA-like factors, and COA or COA-like factors in all time-of-day periods but did not separate biomass burning organic aerosol above detection limits (Tables 2, S3 in Bhandari et al., 2022). The behaviour of POA and OOA TS obtained by combining all time-of-day PMF results suggests strong similarities to seasonal PMF POA and OOA TS, respectively (W17 POA: slope ~ 0.83 , intercept ~ 1.6 , $R \sim 0.97$; W17 OOA: slope ~ 1.26 , intercept ~ -7.0 , $R \sim 0.88$; M17 POA: slope ~ 1.15 , intercept ~ 1.5 , $R \sim 0.97$; M17 OOA: slope ~ 0.91 , intercept ~ -0.5 , $R \sim 0.98$). In winter, we observe largest differences in POA TS diurnal concentrations midday where primary concentrations are higher in time-of-day PMF by $\geq 40\%$. Because of the low total OA concentrations in these periods, they likely have limited importance in seasonal PMF analysis with respect to determining the overall seasonal mass spectra and time series patterns, and thus conducting time-of-day PMF analysis results in factors exhibiting substantial deviations from seasonal analysis. In monsoon, seasonal PMF analysis underestimates POA concentrations throughout the day. Finally, we also observe that winter time-of-day PMF OOA time series patterns exhibit significantly lower diurnal variability than time-of-day PMF POA but stronger diurnal variability than seasonal PMF OOA. For the time-of-day PMF approach, winter peak OOA diurnal concentrations in the morning (0900–1000 hours) are ~ 2.7 times the diurnal minimum (which occurs in the evening, 1800–1900 hours); substantially greater than the ~ 2.2 observed for seasonal PMF winter OOA concentrations. This difference is driven by lower OOA concentrations midday (1100–1900 hours) and higher OOA concentrations at other hours. In monsoon, OOA concentrations show similar diurnal patterns between time-of-day PMF and seasonal PMF and OOA concentrations are almost always lower in time-of-day PMF. Clearly, time-of-day PMF captures different aspects of diurnal variability better than seasonal PMF, which is a major advantage of this new approach.”

2. Table S2: how do you explain the differences in term of mass concentrations for OOA during W172303 even though similar factors are identified with both PMF type?

Response: We agree with the reviewer that similar factors are identified during W172303 using seasonal PMF analysis and time-of-day PMF analysis (Table 2). In addition, MS and TS

patterns of the respective factors are also very similar (Sect. 3.3). While a comparison of MS shows that the two techniques generate similar MS, we also note that they apportion substantially different mass contributions of an important m/z, m/z 44, in OOA MS (about 4% larger organic mass at m/z 44 in seasonal PMF OOA, Fig. S35). We also see differences in the POA MS (Fig. 7), but the difference in MS is much smaller (about 1% smaller organic mass at m/z 44 in seasonal PMF POA). This change between the apportionment of the two techniques means that for similar total apportioned concentrations at m/z 44 (which is fixed and based on the underlying data common to the two approaches), the time series concentrations for the time-of-day PMF OOA would end up larger, which is the case (Table 2). Nevertheless, we also show that the time series concentrations for W172303 OOA based on the two techniques are strongly correlated (Table 3; Pearson R of 0.98).

3. Page 7 line 215: You mentioned that focusing on the 11am-15pm time of day “we expect to see more oxidized aerosols”. Two SOA were identified regardless of the type of PMF applied. Is the ACSM mass resolution limiting further separation or could it be that some of the seasonal SOA are identified as oxidized POA in the time-of-day PMF (e.g oxidized BBOA)?

Response: Yes, conducting PMF on the midday period leads to the same two SOA factors identified regardless of the type of PMF applied. Additionally, changes in MS between the seasonal PMF and time-of-day PMF analysis result in mass moving from seasonal OOA to POA in the midday PMF windows (Table 2). Also, in line with the rapid photochemical processing midday, we observe more oxidized POA in time-of-day PMF than seasonal PMF (Figs. 7, 8). However, in both seasons, we observe strong correlations of these POA factor TS with primary tracers (Figs. S21, S23) and POA MS with reference POA MS profiles (Figs. S16, S19). We also conducted detailed uncertainty analysis to ascertain the validity of our PMF solutions (Sect. 2.5). Thus, the seasonal SOA likely have minimal influence on the identified oxidized POA factors, given the evidence of POA MS and TS signatures of these factors. Instead, we believe that time-of-day PMF analysis provides a more realistic set of MS and TS patterns than the seasonal PMF analysis, given that by design, time-of-day PMF analyses conducts PMF analysis for each period independent of the influence of the variability in the other periods. The deployment of higher mass-resolution instrumentation such as EESI-TOF allows separation of specific SOA factors, even in seasonal PMF analysis (Stefenelli et al., 2019). This observation suggests that the ACSM mass resolution might limit further separation. Also, in this work, no constraints were imposed on the presence of more detailed secondary organic aerosol factors, such as cooking SOA or traffic SOA. Future work could explore constraining the presence of these factors in ACSM-based PMF analysis.

4. Page 7 line 222: “Future work should investigate the optimal length of the time window to sufficiently represent the diurnal variations in mass spectral profiles while managing computational burden”. I also think that more explanations should be provided regarding your choice of using a 4 hours window and to focus on 11-15 and 23-03.

Response: We address the second part of the reviewer’s comment first. As shown in Table 1 and Fig. S1, and described in Sect. 2, the two periods allow differentiation between two

extremes in terms of reaction chemistry and meteorology. Midday periods typically have rapid photochemical processing and higher temperatures compared to nighttime periods. Additionally, they also differ in the influencing primary sources in those time periods; midday is expected to have a stronger influence of cooking, and nighttime of biomass burning. Additionally, as shown in the companion paper, these periods represent the two extremes in total NRPM1 concentrations (Tables 1–2, Bhandari et al., 2022).

The choice of the four-hour window was based on a preliminary PMF analysis conducted on monsoon that allowed us to identify the influence of cooking organic aerosol in the midday PMF run, based on the Robinson et al (2018) ratio of contributions at m/z 55:57 of 1.6 as a preliminary test for relative positioning of the HOA and COA profiles (COA factors with the ratio closer or greater than 1.6 (Bhandari et al., AAAR, 2019)). We started from 12-hour time windows and kept decreasing the window size until the ratio was significantly greater than expected for an HOA factor. We settled for a four-hour time window to limit computational burden and the number of PMF runs needed to cover all times of the day.

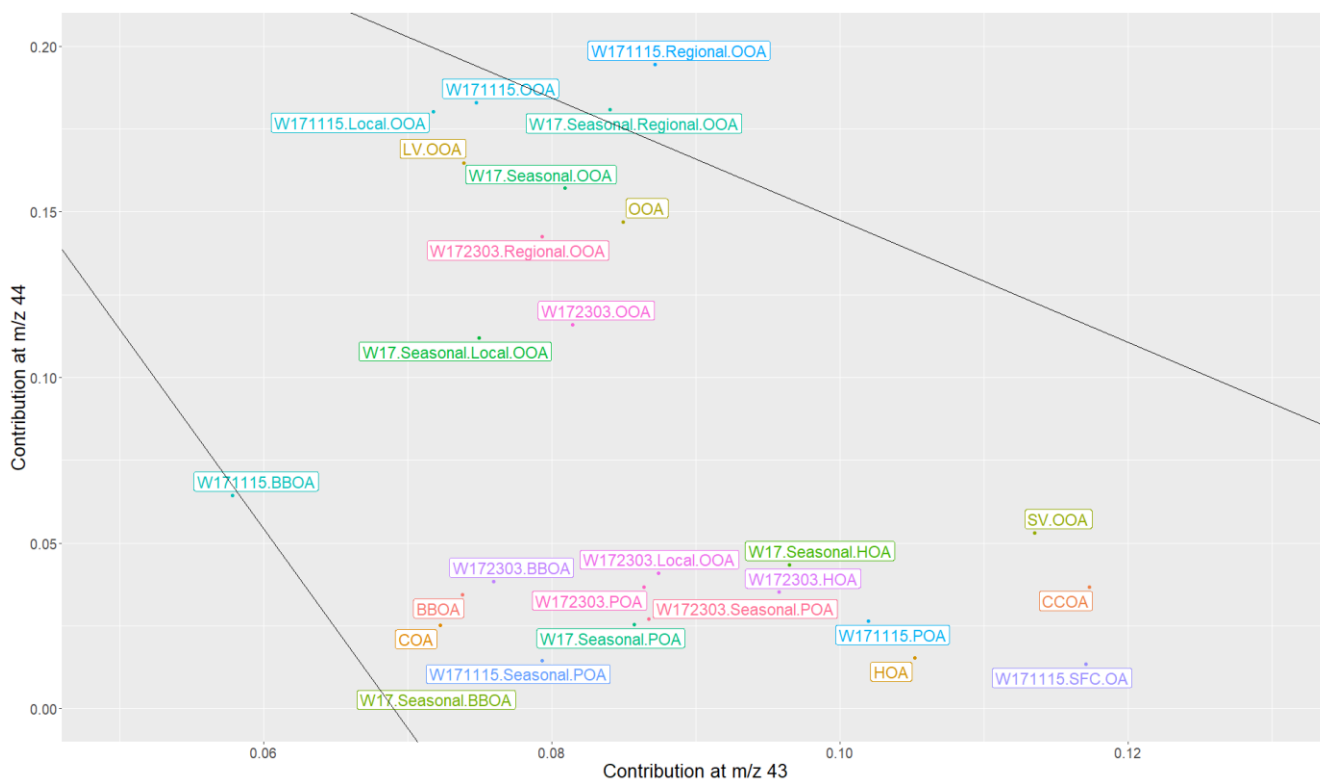
We have updated the manuscript by moving lines from Sect. 2.2 to Sect. 2.4 and have updated the text of these lines:

“Here, we used two alternative approaches for conducting PMF. In one approach, we apply PMF by splitting the data into six 4-hour time windows each day to illustrate the use of our time-of-day PMF method. The choice of the four-hour window was based on a preliminary PMF analysis conducted on monsoon that allowed us to identify the influence of cooking organic aerosol, based on the ratio of contributions at m/z 55:57 (Robinson et al, 2018). We started from 12 hour time windows and kept decreasing the window size until the ratio was substantially greater than 1.6, suggesting the presence of a COA factor in at least one such time window (in this case, it was M172303, Table 2). We also conduct seasonal PMF runs for winter and monsoon 2017 and time-of-day PMF runs for two periods (1100–1500 LT-local time and 1900–2300 LT) in the two seasons. Thus, we conduct four time-of-day PMF runs in total. The two time-of-day periods are selected to differentiate between influence of primary sources, changing MS due to reaction chemistry, and effect of meteorology (Table 1, Fig. S1). As shown in the companion paper, these periods represent the two extremes in total NRPM1 concentrations (Tables 1–2, Bhandari et al., 2022). Results from PMF analysis for all times of the day are presented in a companion paper (Bhandari et al., 2022), and a brief summary of those results is also provided in the Supplement (Sect. S5). In monsoon and winter, traffic is expected to be a dominant source at night due to low cooking-related emission and overlap with high night-time traffic on major traffic corridors (Mishra et al., 2019). At midday in monsoon, high temperatures and solar flux imply high photochemical processing of aerosols; therefore, we expect to see more oxidized aerosols (Table 1, Fig. S1). At winter night-time, biomass burning for heating is an expected source. We refer to the seasonal organic MS-based PMF analysis results as “seasonal PMF” and time-of-day organic MS-based PMF analysis results as “time-of-day PMF” results in the paper. To refer to PMF runs corresponding to specific time windows, we use the nomenclature “Season” + “Period” style in the format “STTTT” (Table 1). For example, W1115 corresponds to the 1100–1500 LT of Winter 2017.

Using data presented in this paper, we also compare the Q (and Q/Q_{exp}) values from the seasonal PMF runs corresponding to the periods of the time-of-day windows (Sect. 3.5). While this work addresses the diurnal variations in MS patterns, future work could investigate the optimal length of the time window to sufficiently represent the finer time variations (less than 4 hours) in mass spectral profiles while managing computational burden.”

6. Adding the F44 vs F43 diagram could help segregating the different type of OA.

Response: We show the triangle plot (Ng et al., 2010) for the different PMF factors presented in this paper in Figure S42. Broadly, we see that almost all factors lie within the plot. Also, broadly, the primary factors occupy the lower portion of the triangle plot ($0.05 < f_{43} < 0.12$, $f_{44} < 0.07$), and secondary factors occupy a narrow region of the plot in the top left ($f_{44} > 0.1$, $0.07 < f_{43} < 0.09$). We also observe that factors obtained in the time-of-day PMF analysis occupy a larger spread compared to those obtained in seasonal PMF analysis. For example, in time-of-day PMF POA factors, we observe a spread of about 5% in contributions at m/z 43. In contrast, the spread of seasonal PMF POA factors is less than 3%. Future work could utilize cluster analysis and other dimensionality reduction techniques on the distribution of f_{44} versus f_{43} in ambient data to identify sources (Isokääntä et al., 2020; Koss et al., 2020; Liang et al., 2021; Ma et al., 2022).



7. Figure 3 and later: keep consistent writing of the unit “ $\mu\text{g m}^{-3}$ ” in text/captions/figures (main text and SI).

Response: We have updated the text to reflect this change.

8. Lines 389-390: change “at” to “in the afternoon”.

Response: We have updated the following text (Sect. 3.2.1):

“These high contributions are likely a result of the highly oxidizing environment in the afternoon.”

9. I think that the different MS identified for the time-of-day PMF would add more value to the discussion and would be more useful in section 3.2.1 and 3.2.2 instead of having them in the SI.

Response: We agree with the reviewer that the obtained MS identified add value to the discussion and would be useful in the main manuscript. However, MS obtained for all PMF factors using the time-of-day PMF approach for all periods in winter and monsoon have been documented in the companion publication (Bhandari et al., 2022). As such, the main purpose of this manuscript is to document the development of a new approach to conducting PMF, the time-of-day PMF approach, and to validate the approach relative to the traditional seasonal PMF approach. We believe that the mass spectral comparisons shown in Figs. 7–8 , S31–S32, and S35-S38 document the most important MS identified in this work. We believe that the brief summary of results from the companion paper provided in the Supplement (Sect. S5), and the multiple references to the companion paper will encourage the readers to read the two manuscripts together to fully understand the scope of this work.

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