Response to Review Comments by Anonymous Referee #2 on "Short-term Source Apportionment of Fine Particulate Matter with Time-dependent Profiles Using SoFi: Exploring the Reliability of Rolling Positive Matrix Factorization (PMF) Applied to Bihourly Molecular and Elemental Tracer Data" by Q. Wang et al.

General Comments by Anonymous Referee #2:

The manuscript titled "Short-term Source Apportionment of Fine Particulate Matter with Time-dependent Profiles Using SoFi: Exploring the Reliability of Rolling Positive Matrix Factorization (PMF) Applied to Bihourly Molecular and Elemental Tracer Data" presents extensive datasets of real-time chemical characterization to employ both traditional and rolling Positive Matrix Factorization (PMF) techniques utilizing the SoFi software. The comparative analysis between traditional and rolling PMF methodologies is particularly intriguing, primarily in the context of effectively modeling primary sources, which exhibit relatively minor variabilities. Conversely, the study reveals substantial variations in the case of secondary factors. This result deserves more explanation and details regarding the relative differences. Furthermore, from what has been presented in the paper, the rolling PMF should always be based on source profiles from traditional PMF (Conclusion lines 300-302). This prompts the question of how to address scenarios where no source profiles are available, such as for newly emerging sources or in regions lacking local source profiles.
I recommend major revisions before considering the manuscript for acceptance:

Response to General Comments: We thank the reviewer for the comments. Below is our point-by-point response to each comment, marked in blue. The related text in the manuscript is copied here for reference, with newly added/revised text underlined. Changes made to the main text will also be marked in blue in the revised manuscript file.

(1) Regarding the substantial variations in secondary factors, please see our response to a similar comment by Reviewer #1. The response text is copied below for easy reference. The underlined text is newly added.
"Secondary nitrate, SOA_I and SOA_II showed large variations, with an average relative difference of 173%, 162%, and 75%, respectively. In the case of secondary nitrate factor, although the apportioned $PM_{2.5}$ contributions from individual source factors were comparable to the reference result, the resolved source profiles exhibited high time-dependent variabilities. We postulate this may be attributed to the sensitivity of nitrate formation to the reduction of NO_x and VOC precursors during the lockdown restriction (Yang et al., 2022). Previous laboratory studies indicated that reducing anthropogenic pollutants such as SO_2 and NO_x can also reduce the biogenic SOA formation via the anthropogenic–biogenic interaction (Zhang et al., 2019; Xu et al., 2015). This may to some extent explains the high

variabilities in source profiles of the two SOA factors. Additionally, the high variabilities may also arise from the uncertainties in the PMF analysis due to the limited data points available from the short-term time span (Wang et al., 2018). Therefore, in future studies, alternative approaches are needed to independently assess the contribution of secondary sources. Also, we recommend deploying higher time resolution measurement of the organic tracers. This will help ensure accurate source apportionment results for individual secondary sources, especially within the confines of a short-term time span."

References:

Wang, Q., Qiao, L., Zhou, M., Zhu, S., Griffith, S., Li, L., and Yu, J. Z.: Source Apportionment of PM2.5 Using Hourly Measurements of Elemental Tracers and Major Constituents in an Urban Environment: Investigation of Time-Resolution Influence, J. Geophys. Res. Atmos., 123, 5284–5300, https://doi.org/10.1029/2017JD027877, 2018.

Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., De Gouw, J., Baumann, K., Lee, S. H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proc. Natl. Acad. Sci. U. S. A., 112, 37–42, https://doi.org/10.1073/pnas.1417609112, 2015.

Zhang, Y. Q., Chen, D. H., Ding, X., Li, J., Zhang, T., Wang, J. Q., Cheng, Q., Jiang, H., Song, W., Ou, Y. B., Ye, P. L., Zhang, G., and Wang, X. M.: Impact of anthropogenic emissions on biogenic secondary organic aerosol: Observation in the Pearl River Delta, southern China, Atmos. Chem. Phys., 19, 14403–14415, https://doi.org/10.5194/acp-19-14403-2019, 2019.

(2) Regarding how to address scenarios where no source profiles are available, we'd like to note that the methodology presented here requires pre-existing monitoring compositional data at a locality that allows initial PMF analysis, which would generate a set of source profiles. For newly emerging sources, as long as we captured the event using the high time resolution measurement data, we can still build its local source profiles based on the measurement data. Then the source profiles can be documented and used later in the short-term source apportionment analysis for this location. We would like to emphasize that the purpose of such short-term source apportionment is to achieve the rapid source apportionment analysis for policy implication. This point is elaborated in the conclusion section and copied below:

"This suggests the potential for future work where rapid source apportionment can be achieved by utilizing a library of source profiles derived from existing measurement data. Short-term PMF analysis can be achieved by advancing the window frame to incorporate new measurement data (e.g., one day data), thereby obtaining source contributions for the most recent observations. This approach significantly reduces the time lag associated with receptor modelling source apportionment techniques. Such advancements hold important policy implications, as it enables prompt response during pollution episodes without the need to wait for the accumulation of sufficient data for conducting PMF analysis."

Introduction: It is imperative to clarify that the traditional PMF was conducted using the US EPA PMF, as indicated in your prior publication (Wang et al., 2022b). This should be explicitly mentioned unless this is not the case.

Response: The following underlined text are newly added and will be included in the revised manuscript:

"Due to the limited time resolution from offline filter-based sampling schedule, e.g., sampling duration of 24 h and sampling frequency of once every three or six days, PMF is often conducted using the Environmental Protection Agency-EPA PMF software (Norris et al., 2014) with data spanning one or multi years to meet the sample size requirement (e.g., Chow et al., 2022b; Scotto et al., 2021)."

"A thorough traditional source apportionment analysis conducted out using the EPA PMF software can be referenced in our previous study (Wang et al., 2022b). In this study, we specifically investigated the applicability of a short-term source apportionment strategy using the bihourly $PM_{2.5}$ chemical speciation data with the SoFi software and compared with those obtained through the traditional PMF".

Section 2.2: This section is lacking essential details regarding the specific species incorporated into the model, the total number of data utilized for traditional and rolling PMF, and the temporal resolution applied (e.g., 2-hour or 1-hour intervals). These specifics are fundamental for a comprehensive understanding of the methodology.

Response: The relevant information is provided below and will be added in this section in the revised manuscript:

"Figure 1 illustrates the flowchart outlining the source apportionment methodology employed in this study. Initially, a PMF run was conducted by EPA PMF software using campaign-wide bihourly data as input (referred to as PMF_{ref}) to derive the reference profiles for primary sources.…The results of the rolling PMF analysis were discussed and compared with the results obtained from PMF_{ref}. The 22 input species for both the PMF_{ref} and the short-term rolling PMF runs included sulfate, nitrate, ammonium, OC, EC, K, Ca, Mn, Fe, Cu, Zn, As, Ba, Pb and 8 organic species (hopanes, steranes, levoglucosan, mannosan, phthalic acid, α-pinT, β-caryT, and DHOPA). The specific input data utilized in individual PMF runs are shown in Table S1."

Table S1. Summary of the input data utilized in the reference run (PMF_{ref}), short-term PMF testing run and rolling PMF runs (PMF_{roll}) using the remaining data performed in this study.

	Run No.	Starting Time	Ending Time	Input sample size	Factor numbers
PMF_{ref} run		0:00 29 Dec. 2019	22:00 9 Feb. 2020	416	10
Short-term PMF run		0:00 29 Dec. 2019	16:00 15 Jan. 2020	190	9
PMF_{roll} with remaining dataset	1	0:00 30 Dec. 2019	22:00 22 Jan. 2020	195	9
	2	0:00 31 Dec. 2019	22:00 23 Jan. 2020	193	
	3*	0:00 1 Jan. 2020	22:00 24 Jan. 2020	193	10
	4	0:00 2 Jan. 2020	20:00 25 Jan. 2020	196	
	5	0:00 3 Jan. 2020	22:00 26 Jan. 2020	196	
	6	0:00 4 Jan. 2020	20:00 27 Jan. 2020	196	
	7	0:00 5 Jan. 2020	22:00 28 Jan. 2020	196	
	8	0:00 6 Jan. 2020	22:00 29 Jan. 2020	197	
	9	16:00 7 Jan. 2020	20:00 30 Jan. 2020	196	
	10	0:00 8 Jan. 2020	22:00 31 Jan. 2020	204	
	11	0:00 9 Jan. 2020	20:00 1 Feb. 2020	206	
	12	0:00 10 Jan. 2020	22:00 2 Feb. 2020	209	
	13	0:00 11 Jan. 2020	20:00 3 Feb. 2020	208	
	14	0:00 12 Jan. 2020	22:00 4 Feb. 2020	209	
	15	0:00 13 Jan. 2020	22:00 5 Feb. 2020	209	
	16	0:00 14 Jan. 2020	20:00 6 Feb. 2020	208	
	17	0:00 15 Jan. 2020	22:00 7 Feb. 2020	208	
	18	0:00 22 Jan. 2020	22:00 8 Feb. 2020	208	
	19	0:00 23 Jan. 2020	22:00 9 Feb. 2020	208	

*Run No. 3 was excluded due to very limited firework-influence data point in the input samples, leading to outlier results compared with other rolling PMF runs.

Line 128: The choice of an 18-day duration for data inclusion needs further justification. Is this duration adequate for achieving robust and optimal *a*-values?

Response: The justification of the selection of the duration of the data are provided in Text S2, where bootstrap error estimation and factor profile mixing were examined. Compared with the shorter time window, the 18 d results showed less factor mixing. The result also passed the bootstrap error estimation. We will refine the text in the revised manuscript to improve the clarity:

"The short-term source apportionment analysis was conducted using data from the first sampling period, spanning 18 days from 29 Dec. 2019 to 15 Jan. 2020. The selection of the window length may vary depending on the specific data sets under study. The determination of the window length for our observational data set is shown in Text S2, where 4 d, 7 d, 10 d, 14 d and 18 d were initially evaluated."

Line 147: The difference in the correlation is clear for K and levoglucosan but what about K and Pb? They're still well correlated even in the CNY period?

Response: The good correlation between K and Pb may indicate the reginal feature of the two sources (i.e., biomass burning and coal combustion) at our observational site. Firework emissions emit extra amount of K compared with coal combustion, which leads to the elevated slope of K vs. Pb during the CNY period in Figure 2b.

Line 150: A discrepancy is noted between the number of factors reported in the paper by Wang et al., 2022b (14 factors) and the present manuscript (10 factors). The differences in PMF methodologies should be thoroughly explained and supported with additional details, either integrated into the main text or provided as supplementary information. Additionally, the manuscript should incorporate validation results for traditional PMF, including Bootstrap analysis, DISP analysis, reconstruction of species, Q/Qexp... .

Response: We will provide following additional details about the PMF_{ref} runs in the revised manuscript: "Source apportionment results over entire sampling period (i.e., PMF_{ref}) supplies an overview about the emission sources at this site. A thorough source apportionment result for this site can be found in our previous paper (Wang et al., 2022b), where 14 factors were resolved using a more comprehensive input species over the entire sampling period. Among these factors, the PAH-rich factor, cooking emission, and one SOA factor are negligible $PM_{2.5}$ contributors (<1%). The contribution of the residual oil combustion factor to $PM_{2.5}$ is also minor (<3%). Additionally, the detection frequency of V, a tracer for the residual oil combustion factor, was lower than 50% for the short-term input time window. Thus, these four factors were not incorporated in this study, and we focus on the 10 major factors resolved in our PMF_{ref} run. Using the data points falling in the short-term PMF runs, the 10-factor solution is more robust. The robustness of the PMF_{ref} result was tested by the bootstrap and displacement error estimation method embedded in EPA PMF 5.0 software (Norris et al., 2014). All bootstrap factors mapped to the base factors in >95% of the runs. No factor swaps and no decrease of *Q* were observed in the displacement result. The PMF-modelled reconstructed $PM_{2.5}$ mass is close to the measured one, with slope of 1.01 and R_p of 0.99. The model performance for individual species were also good, with slope ranged from 0.59-1.08 and R_p of 0.82-1.00."

Section 3.2: What is the reason behind not adding an *a*-value to the secondary sources?

Response: The reasons are multi-fold. First, compared with the primary sources, the secondary sources often do not represent specific emissions. Instead, they typically result from a complex interplay of multiple aging processes that occur over the measurement period. Second, the processes are often heavily influenced by environmental conditions at a given locality, including factors such as relative humidity and photoactivity. Thus, the potential variabilities of secondary sources would be larger, resulting in higher uncertainties for estimating secondary sources. The secondary sources are left unconstrained as well in previous studies (Chen et al., 2022; Canonaco et al., 2013).

The revised text is copied here for reference, and will be incorporated in the revised manuscript:

"Compared with primary sources, the secondary sources often do not represent specific emissions. Instead, they typically result from a complex interplay of multiple aging processes that occur over the observational period and are susceptible to environmental conditions such as relative humidity and photoactivity, etc. Thus, the four secondary factors were not constrained in the short-term PMF run using the *a*-value approach, consistent with the common strategy in previous studies (Chen et al., 2022; Canonaco et al., 2021)."

Section 3.4: The variabilities observed in secondary profiles demand a more in-depth exploration. Possible explanations, including the potential impact of poorly resolved profiles in traditional PMF, should be examined and discussed in greater detail.

Response: We agree that the high variabilities of the secondary sources need more in-depth exploration. Reviewer #1 raises the same comment. Please see the detailed response text at the beginning of this document where we address the general comments by the reviewer.

In the SoFi software, what are the validation methods in order to ensure that you have good results?

Response: Currently, the bootstrap resampling strategy is not available in the standard-unlimited version of SoFi. In order to get a robust solution, we increased the number of PMF calls to 100 to ensure the minimum Q value obtained. Among the 100 runs, the obtained Q values are quite stable.

The following text will be added in the revised manuscript:

"100 PMF calls were performed and the variability of the Q/Q_{exp} was examined. The ratio Q/Q_{exp} , where $Q_{exp} \approx n \times m- p \times (n + m)$, indicates the overall fitting of all input species and is reciprocally associated with the fitting (Norris et al., 2014). Among the 100 runs, the variation of the Q/Q_{exp} are consistently minimum, with a coefficient of variation of <1%. The one with the lowest Q/Q_{exp} was chosen for further analysis."