Assessing the Sources of Submicron Airborne Elements at two sites in the Fos-Marseille Basin through Rolling Positive Matrix Factorization

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We thank both referees for their insightful comments. Please find the detailed answers below. The referee comments are marked in *italic*, while the author comments are in **bold**. Extracts from the manuscript are shown "in quotation marks", while the revised parts from the manuscript are in red.

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Referee #1 comments: ***Note: referee #1 will be referred to here as RC1.***

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General comments

This manuscript investigates the sources of submicron airborne elements at an urban background site and an industrial site in the Fos-Marseille Basin using one-year high-time-resolution Xact measurements and rolling PMF. The study is well-designed, data-rich, and methodologically sound, with a clear novelty in applying the rolling PMF approach to long-term elemental XRF data. The dual-site setting enables the identification of regional and industrial contributions, and the major sources (secondary aerosols, shipping, biomass burning, steel industry, etc.) are reasonably interpreted. The manuscript is

generally suitable for publication in Aerosol Research after minor revision, as several key scientific clarifications, data validation, and presentation improvements are required to strengthen the robustness of source apportionment and readability.

Specific comments

1. *Line 195: Are there any references indicating the shortcomings of static PMF in capturing the seasonal variations in long-term data? If so, please suggest the relevant literature.*

Answer: We thank the reviewer for pointing out this omission. Some studies have indeed highlighted the limitations of conventional static PMF in capturing seasonal and short-term variations in aerosol sources when applied to long-term datasets. Relevant references have now been added to the manuscript, and the text has been revised accordingly.

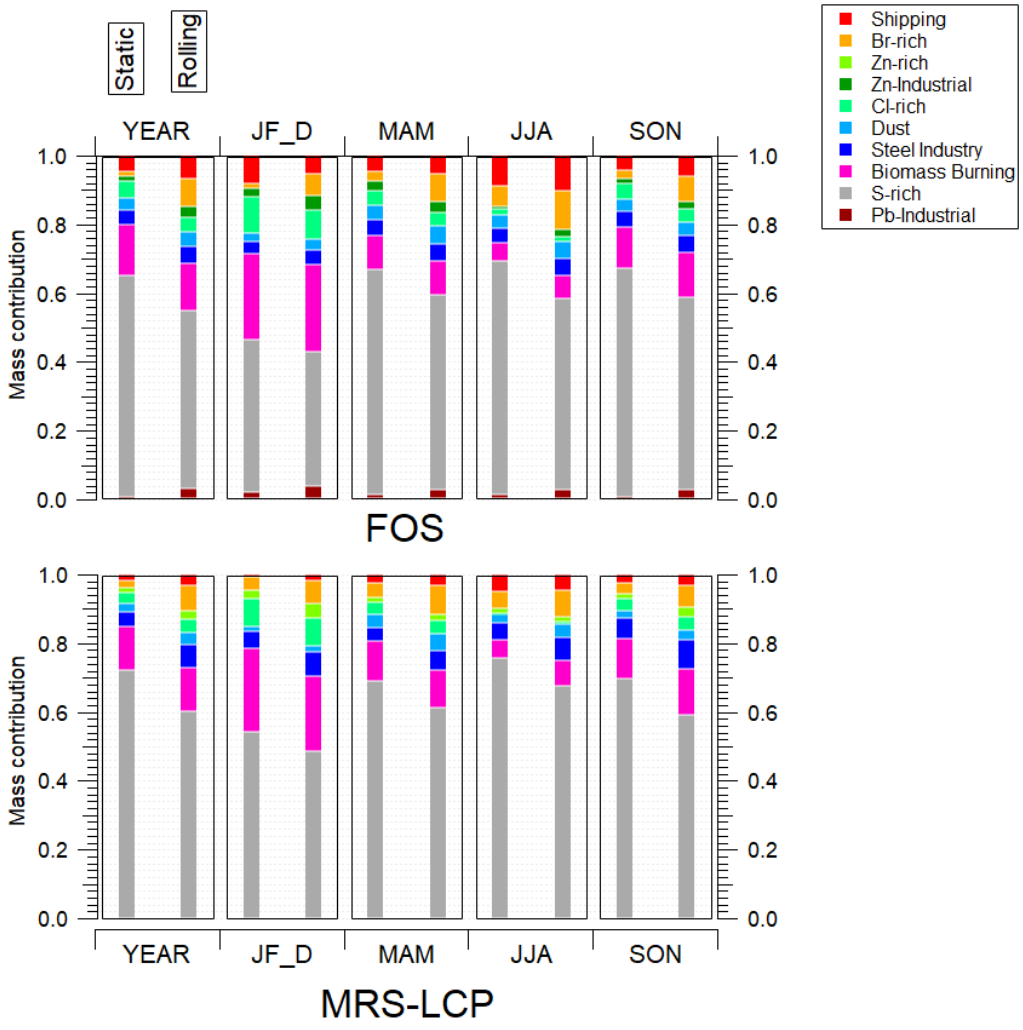
"For long-term datasets, covering several months to a full year, PMF factor profiles may exhibit seasonal variability that is not captured by the static PMF method. To address this, Parworth et al. (2015) introduced the Rolling PMF approach, which applies PMF in a rolling window to capture temporal variability in factors. This method allows for the identification of short-term source behaviour that would otherwise be averaged out in static analyses and has been shown to provide more environmentally interpretable results than conventional static PMF, especially in capturing short-term and seasonal atmospheric events (Lin et al., 2022; Guo et al., 2025)."

2. *When comparing the static and Rolling PMF, only the variability of the factor profiles was analyzed, without comparing the differences in the quantitative source contribution concentrations between the two methods (such as the annual average contribution and seasonal contribution differences of each source). It is suggested to supplement the relevant quantitative comparisons to more comprehensively demonstrate the advantages of Rolling PMF.*

Answer: We thank RC1 for this valuable suggestion. To provide a more comprehensive comparison of factor contributions, as well as methodological and seasonal differences, we have added a new figure to the Supplementary Information (Fig. S13). This figure highlights clear methodological differences in contributions, with higher contributions from the Shipping, Br-rich, and Pb-industrial factors when using the rolling PMF approach, reflecting enhanced sulfur enrichment in these factors, as discussed lines 344-348. The main text and Supplementary Information have been revised accordingly to reflect these differences.

"Furthermore, most factors, except the S-rich factor, exhibit higher S enrichment in the rolling solution, concomitant with a reduced S contribution in the S-rich factor itself (Fig. S12). Such differences are particularly relevant given the wide range of potential sources contributing to secondary sulfate formation (e.g., various industrial activities, shipping), while the accurate attribution of the sulfate origins remains challenging (Chazeau et al., 2021; Su et al., 2025). The more homogeneous S apportionment leads to enhanced sulfur enrichment in the Shipping and Br-rich factors at both sites, as well as in the Pb-Industrial factor at FOS only, resulting in higher mass contributions of these factors in the rolling PMF solution across all seasons (Fig. S13). An exception is observed for the Shipping factor at FOS during winter, where a higher contribution is

obtained with the static approach. However, the rolling PMF contribution appears more environmentally interpretable, given the reduced sea-breeze advection during this period."



"**Figure S13: Factor mass contributions obtained using static (left bars) and rolling (right bars) PMF approaches, for FOS (top) and MRS-LCP (bottom), across different periods (bottom axis).**"

3. *Does the selection method for high BDL (below MDLs) element data affect the construction of the error matrix, thereby influencing the source apportionment results of PMF? Is it necessary to compare the PMF factor results after removing or retaining the high BDL elements?*

Answer: RC1 has raised an important point here. In this context, a cell-wise downweighing of the error matrix approach was used, meaning that the error matrix is adjusted for each sample and each element based on its signal-to-

noise ratio (SNR). Unlike OA-PMF applications, which typically handle a wide range of variables, Xact-PMF focuses on a more limited set of elements. It is therefore important to retain elements even when a large fraction of their data is BDL, as they may still carry relevant information. The cell-wise approach (line 233-235) allows for this by appropriately down-weighting low-SNR observations on a sample-specific basis.

However, to assess the sensitivity of the PMF results to high BDL fraction elements, we also compared solutions obtained with and without the elements showing the highest proportion of BDL values at each site, namely Mn, Cr, and Cd at MRS-LCP, and Mn, Cr, and Rb at FOS. No significant differences in factor composition were observed between the two approaches, except for the excluded elements, as shown on the figure below.

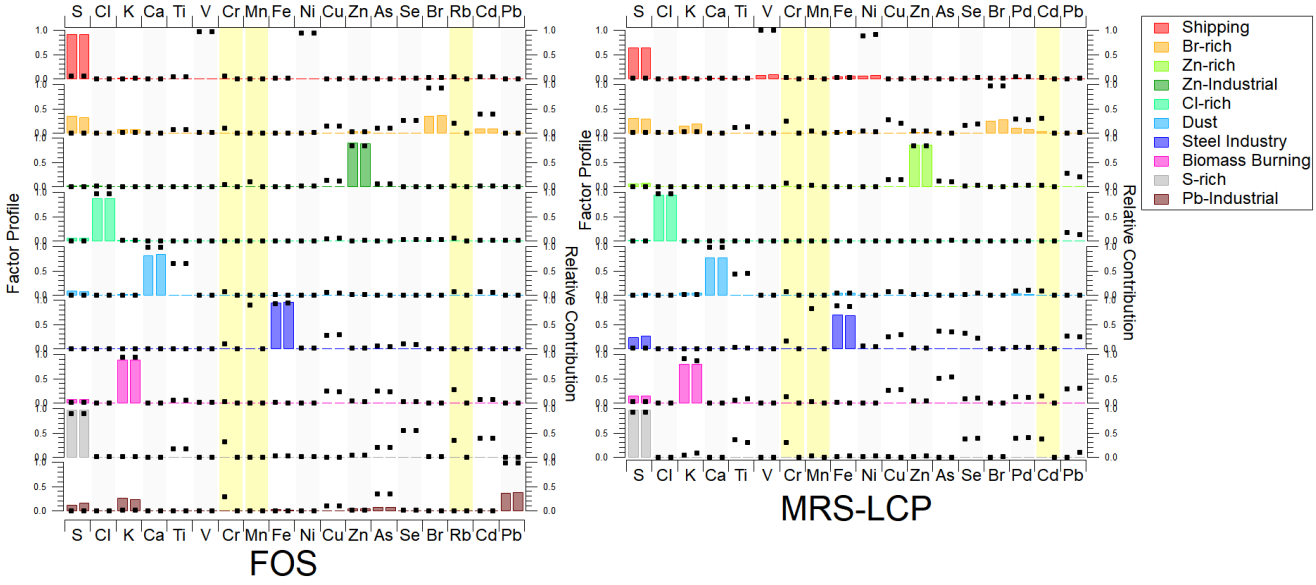


Figure for RC1: Factor profile composition for FOS (left) and MRS-LCP (right), with (left bars) and without (right bars) the elements showing the highest BDL fractions at each site (FOS: Mn, Cr, Rb; MRS-LCP: Mn, Cr, Cd). Yellow-highlighted columns indicate the corresponding elements with the highest BDL proportions.

Some clarification has been added in the main text (3.1) to justify the use of elements with high BDL fractions in this study.

"The use of a cell-wise downweighting of the error matrix, rather than classical variable-wise downweighting, allows for a more balanced integration of the variables in the model, while primarily considering data points above the detection limit."

4. *In Section 4.2, the analysis of each PMF factor reveals that the Zn-rich factor (MRS-LCP site) has excluded traffic and industrial sources, and it is hypothesized that solid fuel combustion is the main source. However, there is a lack*

of quantitative coupling analysis with biomass burning organic aerosols (BBOA), such as concentration correlation and ratio characteristics. It is recommended to supplement relevant statistical analysis to strengthen the basis for attributing the source of this factor.

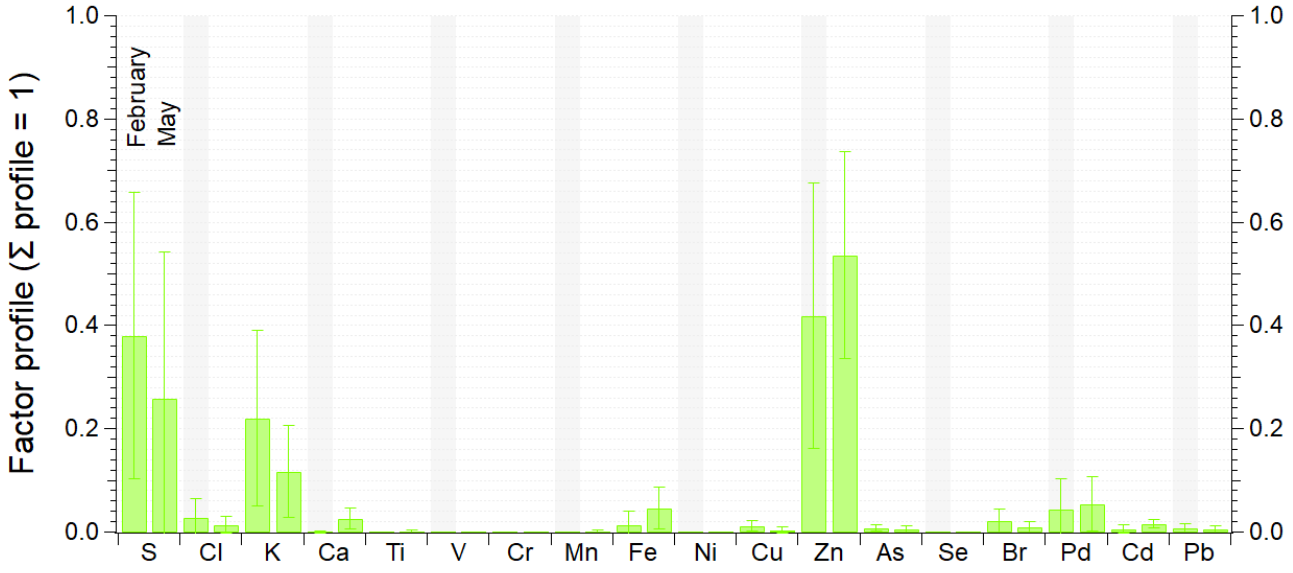
Answer: We thank the reviewer for this valuable suggestion. A comprehensive coupling analysis was explored to further assess the link between the Zn-rich factor and biomass burning sources at MRS-LCP (Fig. S25). However, correlation analyses between the Zn-rich factor and biomass burning tracers (BC_{SF}, Biomass Burning factor from Xact PMF, and BBOA factor from ToF-ACSM PMF) did not show significant associations, suggesting that biomass burning alone cannot explain this factor.

The attribution to combustion-related sources is therefore primarily supported by the enrichment in K and the north-eastern origin under land-breeze conditions, which are consistent with biomass burning influences. Nevertheless, the absence of strong correlations and the contribution to Pb concentrations indicate that this factor likely reflects a mixture of sources rather than a single dominant origin.

Furthermore, additional analyses were conducted to compare the evolution of the Zn-rich factor at different times of the year. Figure S32 has been added to illustrate changes in factor chemical composition between cold and warm periods (namely February and May), showing substantial variability that likely reflects the influence of different aerosol sources across seasons.

These limitations and the mixed-source interpretation have now been clarified in the revised manuscript.

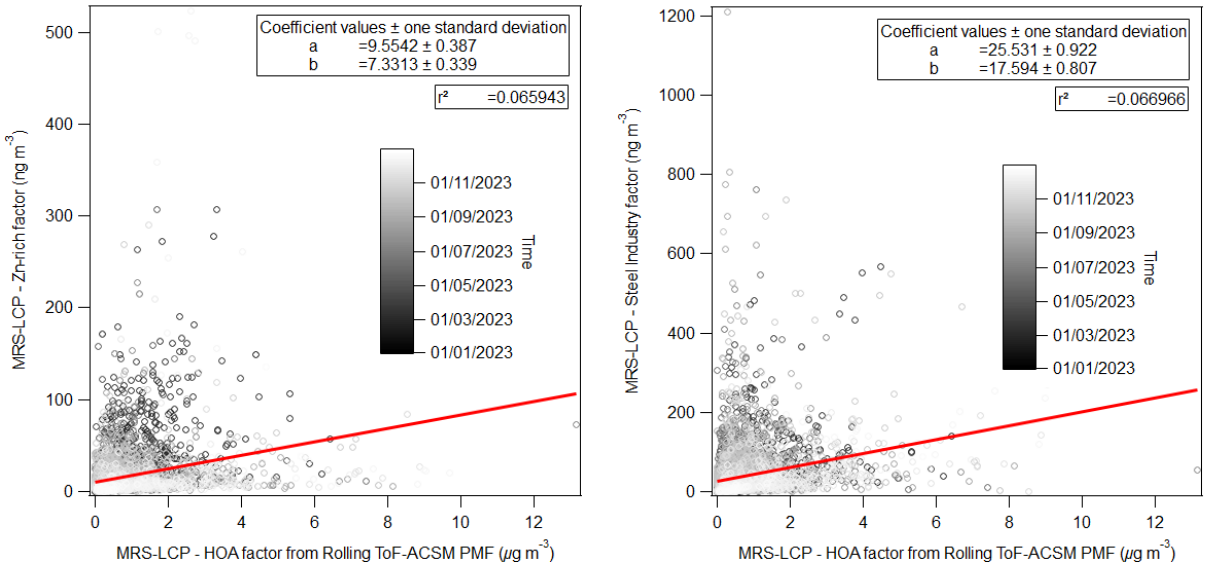
"Weak correlations with HOA and BC_{LF} ($R < 0.35$) further exclude road traffic emission as a major contributor (Fig. S25). Instead, the presence of K, similar to the Biomass Burning factor (4.2.2), together with its daily cycle (Fig. 6) and land-breeze transport, point to solid fuel combustion as a possible source. Nevertheless, its moderate seasonal variability (Fig. S22), its daily cycle (Fig. 6) and substantial contribution to Pb concentrations (34%) suggest little influence from waste incineration and indicate that this factor cannot be attributed to a single dominant source. Rather, it likely reflects a mixture of Zn-containing emissions, including combustion-related sources (e.g., biomass burning; Tissari et al., 2015), residual traffic emissions (Camman et al., 2024), and potentially waste-related activities (Enestam et al., 2011). Analysis of the factor chemical composition at different periods of the year (e.g., February and May) reveals marked seasonal variations in factor composition (Fig. S32), with higher enrichment in Fe and Ca in May, and increased contributions of K, S, Cl, and Br in February. This variability suggests changing source influences, with a stronger contribution from road dust and non-exhaust traffic emissions during warmer periods and enhanced contributions from combustion-related and secondary processes in winter (4.2.2, 4.2.7, 4.2.8). The northeastern sector origin (5°-90°) further supports the influence of locally transported and mixed aerosols, likely associated with nocturnal thermal breeze recirculation processes (Drobinski et al., 2007)."



"**Figure S32: Zn-rich factor composition at different times of the year (February, left bars; May, right bars) at MRS-LCP. Colored bars represent the average rolling factor composition for each month, and error bars indicate the standard deviation.**"

5. *It is suggested to compare the correlation between the HOA factors of TOF-ACSM OA PMF and the Steel Industry and Zn-rich factors at MRS-LCP, in order to further determine whether road transport may contribute to the Steel Industry and Zn-rich factors at MRS-LCP.*

Answer: We thank RC1 for this remark. Pearson correlation coefficients were calculated between all external datasets and the rolling PMF Xact factors at each site (Figs. S25 & S27). The analysis at MRS-LCP did not show any preferential association between either the Steel Industry or Zn-rich factors and traffic-related emission tracers (HOA, NO_X, BC_{SF}). Linear correlation plots between HOA (from rolling TOF-ACSM PMF) and the Zn-rich and Steel Industry factors at MRS-LCP are shown below.



Figures for RC1: Linear correlations between the HOA factor from rolling ToF-ACSM PMF and the Zn-rich factor (left) and Steel Industry factor (right) at MRS-LCP in 2023.

Eventually, no clear link between Fe- and Zn-enriched emissions and road transport aerosols could be established in this study, possibly due to the focus on the PM_1 fraction, whereas most non-exhaust metal emissions are associated with the coarse fraction. Future analyses using an extended dataset with larger particle size fractions, enabled by a change in the Xact inlet configuration, could help better characterize coarse aerosols, particularly non-exhaust traffic emissions, at the MRS-LCP station.

6. *The Cl-rich factor from Xact and Cl- from ACSM represent the same submicron particulate chlorine. A correlation analysis is suggested to validate the factor.*

Answer: RC1 raises an important point regarding the comparison between the Cl-rich factor resolved by Xact PMF and chloride measured by the ToF-ACSM. The relationship between elemental Cl measured by the Xact and chloride (Chl^-) measured by the ToF-ACSM was investigated in the Supplementary Information (S6). The comparison shows a moderate correlation between Xact Cl (including the Cl-rich factor) and ToF-ACSM chloride (R^2 = 0.44; Fig. S36). This relatively weak correlation is consistent with previous studies and may be attributed to the predominantly refractory nature of chloride salts, which are inefficiently detected by the ToF-ACSM due to partial particle bounce on the vaporizer (Ovadnevaite et al., 2012; Tobler et al., 2020; Sustrena et al., 2024). Additional discrepancies may also arise from potential misclassification of organochlorine fragments (Wang and Ruiz, 2017).

7. *The extremely high contribution of the S-rich factor (>50%) is reasonable given strong photochemical sulfate formation in this photochemically active, industrial, and coastal Mediterranean basin, but the authors should further quantify SO_2/sulfate sources (shipping, industry, etc.) to improve interpretation.*

Answer: RC1 raises an important point regarding the high contribution of the S-rich factor. We agree that this reflects strong photochemical sulfate formation in the industrial and coastal Mediterranean basin. We have expanded the discussion in the manuscript to further clarify sulfate sources and their interpretation.

In particular, previous studies at MRS-LCP have shown that sulfate sources in the area are mainly associated with SO_2 oxidation from both industrial activities and shipping emissions, including contributions from local and regional sources across the Mediterranean basin. However, shipping emissions in the region have been significantly reduced following the implementation of recent IMO regulations, which may have affected the relative contribution of S-enriched sources observed in this study. The manuscript has been revised to clarify this point.

"The S-rich aerosols are typically attributed to oxidation of SO_2 to sulfate (SO_4^{2-}) or to direct sulfate emission (Visser et al., 2015b; Rai et al., 2020a, 2020b; Rai et al., 2021; Manousakas et al., 2022, 2025), originating from both local industrial and port activities as well as regional shipping emissions across the Mediterranean basin (Chazeau et al., 2021)."

"Previous work at MRS-LCP reported elevated sulfate levels from major shipping routes, highlighting the continued importance of shipping emissions in sulfate production (Chazeau et al., 2021), even after SO_2 reductions (4.2.1). The implementation of IMO regulations has led to a substantial decrease in SO_2 emissions from shipping (up to ~77%; IMO), limiting its use as a direct tracer of shipping activity compared to earlier studies at this site (Chazeau et al., 2022). However, the potential use of scrubbers may still result in direct sulfate emissions from ships (Kuittinen et al., 2024), thereby partially maintaining the shipping contribution to sulfate. Overall, while shipping-related SO_2 emissions have likely decreased, industrial activity and regional transport of aged marine emissions over the Mediterranean remain important contributors to sulfate observed at MRS-LCP."

Additional response:

We would also like to draw the reviewers' attention to the addition of a clarification regarding our shipping factor. This update is based on the recent publication of our work (Brezins et al., 2026a, "Evolution of the V/Ni Ratio in Response to IMO Regulation-Induced Fuel Shifts and Scrubber Use", https://doi.org/10.1021/acs.estlett.5c01199), which provides further insight into the comparison of the two shipping factors observed at FOS and MRS-LCP, respectively.

"Consistent with recent IMO regulations and desulfurized fuel increased use (Yu et al., 2021; Fossum et al., 2024), V/Ni ratios have decreased compared to pre-IMO values (1.2 ± 0.2 at MRS-LCP, 1.6 ± 0.3 at FOS vs. approximately 2 in summer 2018; Camman et al., 2024). The slightly higher ratio observed at FOS may reflect a stronger industrial influence or the continued use of heavy fuel oil in combination with scrubbers on tankers and cargo vessels (Brezins et al., 2026a)."

Technical corrections

1. *Line 114 and 119: Please ensure the consistency of punctuation and formatting in the writing of latitude and longitude values (43°27'32.092''N;120 4°56'4.412''E).*

Answer: We thank RC1 for pointing out this inconsistency. The punctuation and formatting of latitude and longitude values have been revised accordingly.

"The first one, the Marseille-Longchamp Observatory supersite (MRS-LCP), is located in the center of Marseille, in Longchamp Park near the Marseille Observatory (43°18'18.84'' N; 5°23'40.89'' E; 71 m a.s.l.)."

2. *Is the "X" in Table 1 indicating that the instrument was equipped at this site?*

Answer: Yes, "X" indicates that the instrument was deployed at the corresponding site. We have clarified this in the Table 1 caption to improve readability.

"Table 1: Overview of the instruments deployed during the field campaign at MRS-LCP and FOS monitoring stations. "X" indicates that the instrument was equipped at this site."

3. *Line 157-158: Excessive commas in the "The lack of quantitative assessment … on marine aerosols," and the citation format of the literature needs to be adjusted in "(e.g. fresh and aged sea salt, Pey et al., 2013a)".*

Answer: We thank the reviewer for pointing out this issue. The sentence and citation format have been revised accordingly.

"The lack of quantitative assessment of Na and Mg causes strong limitations for coastal sites like ours where these elements provide key information on marine aerosols (e.g. fresh and aged sea salt; Pey et al., 2013a)."

4. *Line 214: Fig. S3 & S4 should be corrected to Figs. S3 & S4. All similar situations in the text should be uniformly revised.*

Answer: We apologize for this error. The manuscript has been corrected accordingly, and all references to figures have been made consistent throughout the text (with the added "s" highlighted in red in the revised manuscript).

5. *Line 311: "eg." should be "e.g.".*

Answer: The text has been revised accordingly.

"Unlike the seasonal static approach, rolling PMF operates on the full annual dataset; reference profiles were thus selected from the periods in which each factor was most robustly resolved (e.g. summer for Shipping and winter for Cl-rich, Tables S5 & S6)."

6. *In the sentence "$PM_{2.5}$ in Sylvestre et al., 2017 versus PM_1 in the present study", "Sylvestre et al., 2017" should be "Sylvestre et al. (2017)".*

Answer: The text has been revised accordingly.

"However, the Mn/Fe ratios observed here (FOS: 0.012; MRS-LCP: 0.006) are lower than those reported by Sylvestre et al. (2017) (0.056). This discrepancy likely reflects differences in particle size fraction ($PM_{2.5}$ in Sylvestre et al. (2017) versus PM_1 in the present study), as well as potential mixing of this factor with other Mn- and Fe-containing sources at MRS-LCP."