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.

Manuscript information:

Paper: https://doi.org/10.5194/ar-2026-5

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

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Submitted to: Aerosol Research

Referee #2 comments: ***Note: referee #2 will be referred to here as RC2.***

Citation: https://doi.org/10.5194/ar-2026-5-RC2

General comments

Regarding the manuscript entitled "Assessing the Sources of Submicron Airborne Elements at two sites in the Fos-Marseille Basin through Rolling Positive Matrix Factorization," I find the study to be very well written and scientifically interesting. The manuscript focuses on a highly relevant and complex region, and the dual-site design provides valuable insight into the spatial variability of submicron elemental sources. In particular, the work is noteworthy because it applies a methodological approach that has not been implemented before on a year-long, high-time-resolution elemental dataset. Overall, the study makes a valuable contribution to the understanding of airborne particulate sources in this important coastal-industrial region and can be published after minor revisions.

Specific comments

1. *Lines 214–223: The selection of elements retained in the PMF input matrix deserves a more detailed discussion in relation to factor identification. Since several elements were kept despite very high fractions below detection limit, the authors should clarify how their inclusion affected the robustness and interpretability of the resolved factors, especially for industrial factors driven by low-abundance tracers.*

Answer: RC2 raises an important point, also addressed in response to RC1. The inclusion of elements with high BDL fractions was carefully evaluated in the PMF input matrix. As detailed in response to RC1, a cell-wise error matrix down-weighting approach was applied, in which each observation is weighted according to its signal-to-noise ratio (SNR). This ensures that low-SNR data points contribute less to the solution, while still allowing potentially informative signals to be retained.

To further assess the robustness of the results, sensitivity tests were performed by comparing PMF solutions obtained with and without elements exhibiting the highest BDL fraction elements at each site, namely Mn, Cr, and Cd at MRS-LCP, and Mn, Cr, and Rb at FOS. These tests showed no significant impact on factor profiles or interpretability, except for the excluded elements themselves (see response to RC1 and figure below). This indicates that the inclusion of these elements does not affect factor identification or stability.

Moreover, the main tracers driving the resolved factors (V, Br, Zn, Cl, Ca, Fe, K, S, and Pb) exhibit relatively low BDL fractions (< 73%; Tables S2 & S3), ensuring that the factor interpretation is primarily based on robust and well-constrained variables.

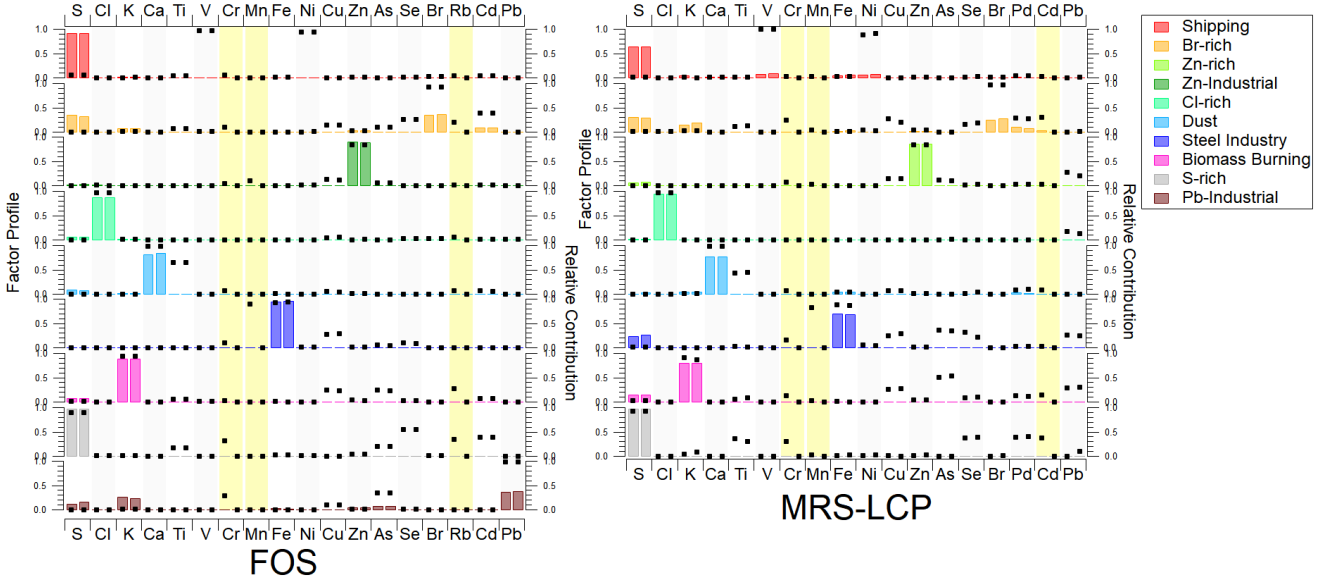


Figure for RC2: Factor profile composition for FOS (left) and MRS-LCP (right), with (left bars) and without (right bars) the elements showing the highest BDL fractions at each site (FOS: Mn, Cr, Rb; MRS-LCP: Mn, Cr, Cd). Yellow-highlighted columns indicate the corresponding elements with the highest 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."

2. *Lines 230–233: The exclusion of short-lived events may have important consequences for factor identification. Since episodic events such as Sirocco outbreaks, fireworks, or local construction emissions can carry distinct elemental fingerprints, removing them may simplify the factor structure but may also suppress potentially meaningful sources or alter mixed factors. This effect should be discussed more explicitly. Why have the authors not reintroduced these points at the end of the analysis and add extra factors?*

Answer:

We thank the referee for this comment regarding the exclusion of short-lived episodic events and their potential impact on factor identification. We agree that such events (e.g. fireworks, Sirocco outbreaks, or building work activities) can exhibit distinct elemental signatures and may contribute to aerosol variability.

Fireworks events were readily identified through their characteristic Bi signal. However, Bi was below detection limits for 99% of the dataset at both MRS-LCP and FOS (Tables S2 & S3), and therefore could not be reliably included in the PMF analysis or lead to a distinct factor, even when using a cell-wise downweighing approach.

Similarly, Si, which can be relevant for dust-related events such as Sirocco outbreaks, was also below detection limits for 99% of observations (Tables S2 & S3), reflecting its predominance in the coarse fraction, not efficiently captured in this PM_1 study.

Regarding Sirocco events, including potential Saharan dust intrusions, no distinct factor could be resolved, even when increasing the number of PMF factors or testing constrained solutions. This suggests that such episodic contributions are either weak in the PM_1 fraction or not sufficiently resolved by the available tracers in this dataset (no Si available).

To further investigate this point, we compared characteristic dust ratios (e.g., Ti/Ca, Ti/Fe, and Ca/Fe) from the literature (Gomes et al., 1990) with those derived from our dataset. The comparison of Ti/Ca and Ca/Fe ratios for periods influenced by Sirocco events, values reported by Gomes et al. (1990), and those from our Dust factor at

each site shows that the identified Sirocco events do not fall within the same Ti/Ca and Ca/Fe ranges as the resolved Dust factor. This indicates that different types of dust are captured at both sites.

However, the inability to resolve a distinct Saharan dust factor in our preliminary PMF analysis highlights the difficulty of distinguishing sources using Xact PMF when they rely on similar elemental tracers but differ mainly in their relative ratios, especially in the absence of a specific tracer such as Si.

Future work will benefit from the planned installation of a switching inlet at the Xact instrument, which will enable measurements of coarser particles and improve the characterization of episodic events such as Saharan dust outbreaks, where Si is expected to be more abundant.

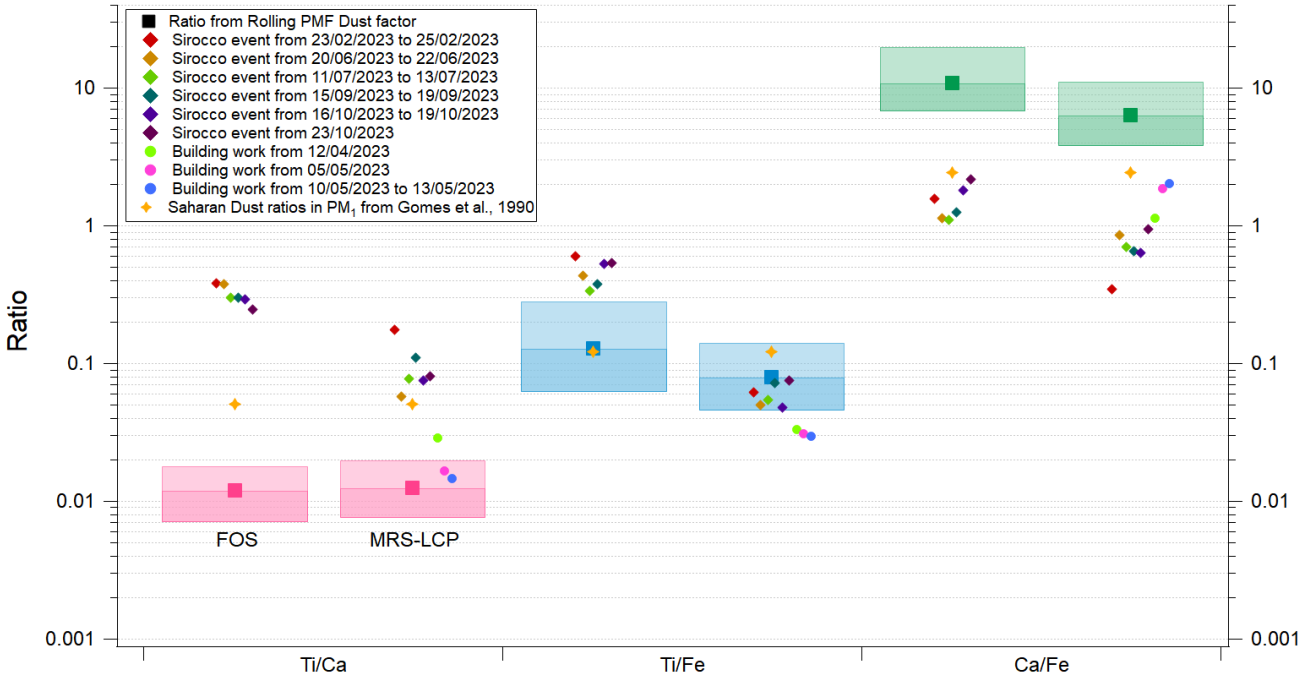


Figure for RC2: Characteristic dust ratios (e.g., Ti/Ca, Ti/Fe, and Ca/Fe) in PM_1 from both sites in this study and from the literature (Gomes et al., 1990, Saharan dust). Ratios derived from the Dust factor are compared with those calculated for specific periods strongly influenced by either Sirocco events or construction activities at each site. Markers indicate mean values, while error bars represent the standard deviation for the Dust factor at MRS-LCP and FOS. Ratios for episodic periods are calculated from average contributions during each identified event.

3. *Lines 254–264: The fact that the Shipping and Cl-rich factors could not always be identified in unconstrained seasonal runs raises an important question about factor stability. The manuscript would benefit from a clearer*

explanation of how confidently these factors can be considered physically distinct sources rather than partially resolved or constraint-dependent solutions.

Answer: we thank RC2 for this remark regarding the stability and physical robustness of the Shipping and Cl-rich factors.

We addressed this question through several sensitivity tests performed during preliminary PMF analyses.

Firstly, unconstrained PMF runs performed on the full year dataset consistently allowed the identification of both the Shipping and Cl-rich factors, supporting their year-long stability.

Secondly, removing either the Shipping or Cl-rich factor during specific seasonal runs (JF_D and JJA, respectively) resulted in the redistribution of their characteristic tracers (e.g., Cl for Cl-rich or V and Ni for Shipping) into other factors, without a clear geochemical interpretation. For example, resolving a 7-factor solution at MRS-LCP during summer led to an artificial enrichment of Cl in the Dust factor, which was not observed in other seasons when the Cl-rich factor is resolved as an independent source.

Finally, from a geochemical point-of-view, continuous shipping activity at both Fos-sur-Mer and the Marseille harbour, combined with persistent sea-breeze-driven transport of port emissions, supports the expectation that Shipping-related emissions are present throughout the year, albeit with seasonal modulation (e.g., reduced sea-breeze advection during winter). This is further supported by the continued observation of specific environmental patterns of these factors during their "less favourable" season. For instance, we can observe a distinct 2 spikes Shipping diurnal pattern at MRS-LCP in winter (see figure below), similar to year-round observations (see figure below).

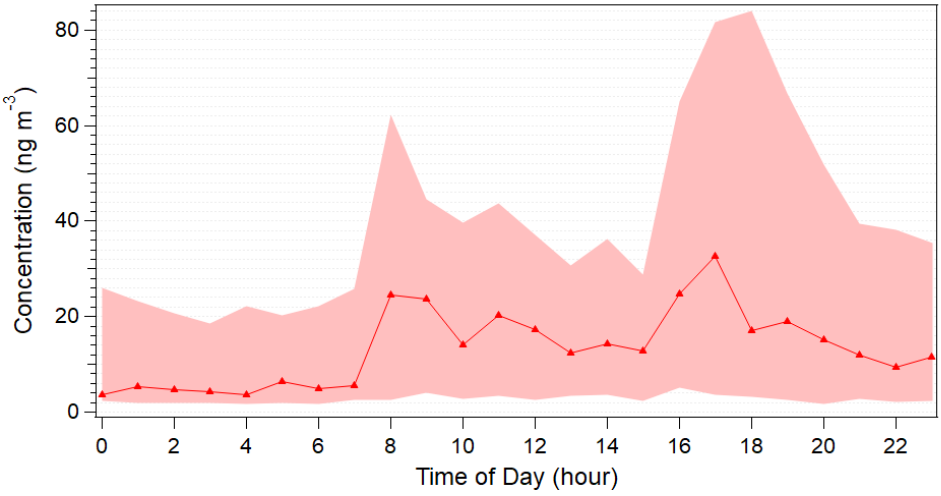


Figure for RC2: Typical Shipping diurnal cycle showing two daily peaks corresponding to Marseille harbour passenger ship activity, with morning arrivals and evening departures of ferries. Lines and markers indicate the

median, while shaded areas represent the interquartile range. Shipping factor obtained with static PMF analysis during winter period (JF_D).

These elements have been clarified in the revised manuscript.

"For instance, the Shipping factor was not retrieved during winter at both sites (Tables S5 & S6), probably due to reduced sea breeze advection of shipping plumes (Chazeau et al., 2021). Similarly, during JJA the Cl-rich factor was partly mixed with Dust in unconstrained runs (Tables S5 & S6). Although Dust may contain some residual Cl (Visser et al., 2015b), this is not consistent with the other seasons PMF results. On the other hand, the Shipping factor constrained during the winter season exhibits the same diurnal pattern, characteristic of passenger ship activity (Fig. S21, 4.2.1), as observed in summer, confirming the year-round environmental consistency of this factor."

4. *Lines 265–269: The decision to retain a Biomass Burning factor throughout the year is understandable, but the manuscript should discuss more carefully whether this reflects a true year-round source or whether, during summer, potassium may partly be redistributed from other sources into this factor. This is especially important for factor identification in periods when independent biomass-burning tracers are weaker.*

Answer: We thank RC2 for this remark. We agree that potassium may be partly redistributed from other sources during this period, particularly from K-enriched factors such as Pb-Industrial at FOS or Zn-rich at MRS-LCP. As shown in (Figs. S23-S24), during JJA, Biomass Burning factor has a local origin at MRS-LCP suggesting apportionment of K from various sources, whereas at FOS it shows a distinct S-E origin, associated with Pb-industrial activity (4.2.3).

However, several elements support the interpretation that the Biomass Burning factor still reflects a meaningful source contribution during summer. First, although weaker than during the whole year (R^2 = 0.60 at MRS-LCP and R^2 = 0.64 at FOS), the correlation with the independent biomass-burning tracer BC_{SF} remains visible during summer (R^2 = 0.21 at MRS-LCP and R^2 = 0.10 at FOS; figure below), suggesting that the factor is not solely driven by redistribution of K from other sources.

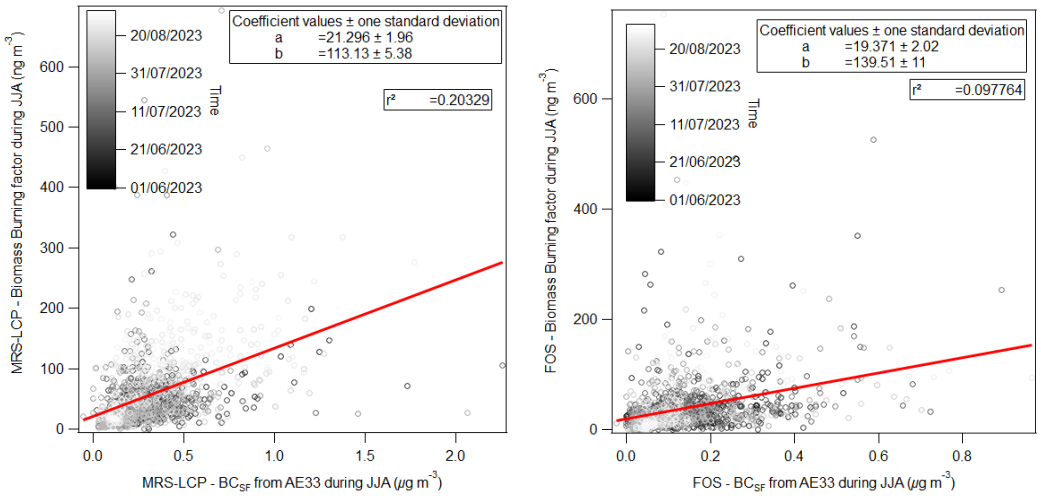


Figure for RC2: linear correlation between Biomass Burning factor and BC_{SF} during summer (JJA) at MRS-LCP (left) and FOS (right).

Second, its mass contribution remains higher in summer (> 7% in JJA; Fig. S22) than that of other K enriched factors potentially linked to combustion year-long (Pb-Industrial at FOS, and Zn-rich at MRS-LCP), without any drop in these factors' contribution during summer (Fig. S22). This suggests that the Biomass Burning factor represents a different source of K.

This has been clarified in the revised manuscript.

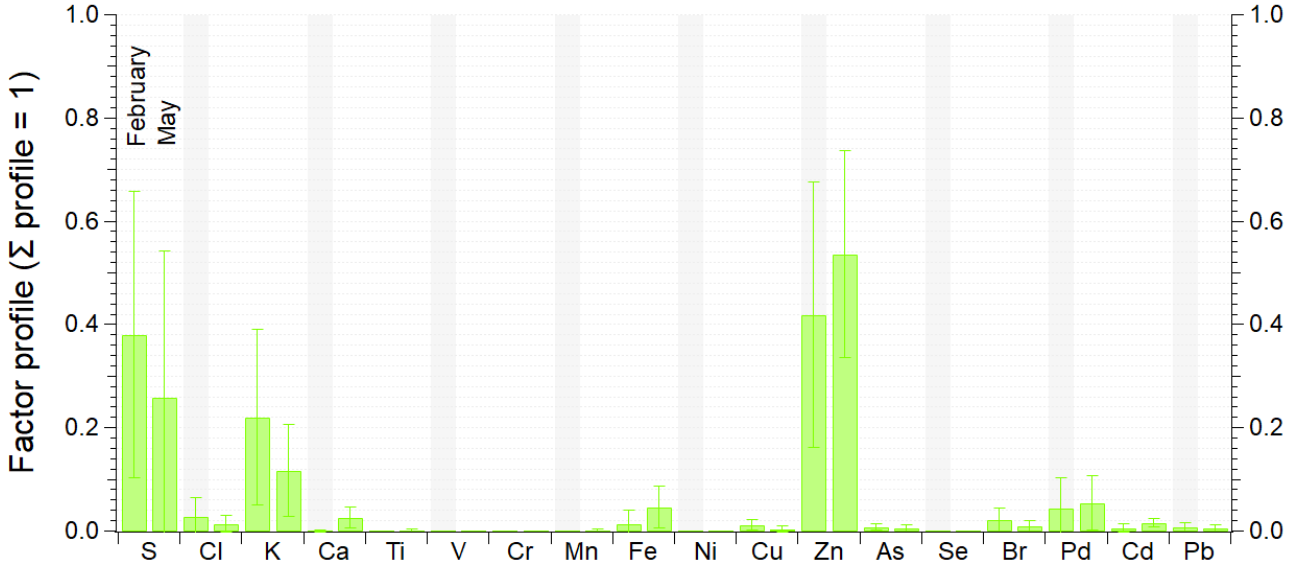
"Unlike the OA rolling PMF, where BBOA is resolved only from September to May, the Xact rolling PMF retained a Biomass Burning factor throughout the year. This choice reflects the expectation of year-round biomass burning emissions (e.g., wildfires, crop burning, barbecue) and avoids unrealistic redistribution of K into other factors. The relevance of this approach is supported by the year-round presence of BC_{SF} and its consistent albeit low correlation with the final Biomass Burning factor during summer (R^2 = 0.21 at MRS-LCP and R^2 = 0.10 at FOS), as well as still elevated Biomass Burning contribution (Fig. S22)."

Nevertheless, we acknowledge that the interpretation of this factor during summer is less robust due to the reduced strength of independent biomass-burning tracers and the potential influence of mixed sources. This limitation has been clarified in the revised manuscript.

"NWR analyses showed a clear land-breeze influence during winter, from the 5°-90° sector at both sites, consistent with biomass burning emissions transported by nocturnal land breeze (Figs. S23-S24). At FOS, an additional contribution was observed from the southeast (125°-145°), possibly linked to mixing with industrial combustion sources in the Port-de-Bouc area. During summer (JJA), the factor's geographical origin at MRS-LCP suggests a stronger influence of local sources, whereas at FOS it exhibits a distinct southeast origin associated with Pb-industrial activity (4.2.3), which may indicate partial redistribution of K from other sources during this period (Figs. S23-S24)."

5. *Lines 355–356: The observation that the Zn-rich factor may reflect multiple sources is important, but the discussion should go further. If this factor is not chemically homogeneous, the authors should clarify whether it should really be interpreted as a single source, or rather as a mixed factor grouping several Zn-containing emissions.*

Answer: RC2 raises an important point, which was also raised by RC1. We agree that the Zn-rich factor does not represent a chemically homogeneous source. As shown in Fig. S25, this factor does not exhibit a clear preferential association with any specific tracer, supporting the hypothesis of a mixed origin. Its composition, combined with its north-eastern origin and morning peaks, suggests the influence of multiple Zn-containing sources transported under nocturnal land-breeze conditions. These may include combustion-related emissions (e.g., biomass burning), residual traffic emissions, and potentially waste-related activities. This interpretation is further supported by the comparison of the rolling Zn-rich factor composition at different times of the year (new Fig. S32).



"**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.**"

We have therefore revised the manuscript to clarify that this factor should not be interpreted as a single source, but rather as a mixed factor grouping several Zn-containing emissions.

"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 time of the year (e.g., February and May) reveals marked seasonal variations in factor composition (Fig. S32), with higher enrichment in Fe, Ca, and Pd 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 regionally transported and mixed aerosols, likely associated with nocturnal thermal breeze recirculation processes (Drobinski et al., 2007).”

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).”