Reply to comments of reviewer 2:

The authors conducted PM10 sampling (both day and night) at two different sites in Barcelona and performed chemical analysis to report molecular markers during two distinct seasons, which is commendable. I have a few concerns listed below:

1. Only 28 samples to run the source-apportionment analysis?

The total number of samples used in the source-apportionment analysis was 52, encompassing both sampling periods and both sites. As addressed in our response to another reviewer, we ensured the robustness of the results by performing the decomposition using different numbers of variables, which confirmed the stability and consistency of the identified sources. We clarified the number of samples in Line 111 and Line 183.

2. Description and logic behind using this apportionment method

We added an omitted section in the revised manuscript (2.6). In this section, we describe the fundamentals of the MCR-ALS approach (matrix decomposition under non-negativity constraints) and explain its advantages in comparison to other source apportionment methods, such as CMB, PCA, and PMF. References were added to the list. This section also explains our choice of MCR-ALS, as it has been successfully applied in previous studies on atmospheric particulate matter and organic aerosols (Line 182).

"Multivariate Curve Resolution—Alternating Least Square (MCR-ALS 2.0) was applied to the dataset (67 variables and 52 samples) using MATLAB (Jaumot et al., 2005, 2015; Tauler, 1995). The MCR-ALS method is based on the D = CST + E matrix equation to decompose the initial matrix D (normalized dataset) into a reduced number of components. The output gives: C (a matrix with sample scores for each component), ST (a matrix with compound loadings for each component; profiles) and E (a matrix with residual non-explained data) The decomposition was performed under non-negativity constraints, which provide physically interpretable results and are more realistic for environmental data. The number of components was selected based on the interpretability of their chemical profiles in terms of emission sources and atmospheric processes.

Compared with other source apportionment approaches, such as Chemical Mass Balance (CMB), Principal Component Analysis (PCA), or Positive Matrix Factorization (PMF), MCR-ALS offers several advantages. CMB requires predefined source profiles and cannot resolve unknown sources, while PCA enforces orthogonality, which limits environmental interpretability. Both MCR-ALS and PMF apply non-negativity constraints and yield comparable results, but they differ in their optimization algorithms and normalization procedures

(Tauler et al., 2009). Importantly, MCR-ALS does not impose orthogonality between components, allowing for overlapping explained variance that better reflects the reality of atmospheric sources, which are rarely independent. Previous studies have demonstrated the robustness of this method for source apportionment of air pollutants and organic aerosols (van Drooge et al., 2022; Jaén et al., 2021b, 2023)."

3. L105:... PM10 was collected at two background sampling stations were installed at two altitudes .. needs rephrasing

The sentence has been rephrased for clarity and grammatical accuracy in the revised manuscript (Line 103).

"In the present study, PM10 samples were collected at two background stations at different altitudes (Figure 1) to assess how interactions between specific meteorological conditions and multisource particle emissions influence the organic composition of airborne aerosols in the city. One station, located at 81 m asl, represents the urban background site at IDAEA (city site), while the other, at 415 m asl, is situated atop the Collserola hills overlooking the city (elevated site). The two sites are separated by a horizontal distance of 3.5 km."

4. L116: Any justification for different times chosen for sampling?

As mentioned in our response to another reviewer, the sampling campaigns were conducted using Coordinated Universal Time (UTC), which resulted in a one-hour difference in local time between the cold and warm seasons. To maintain consistency, we adopted a fixed UTC-based schedule, ensuring standardized 12-hour daytime and nighttime sampling periods across all campaigns.

Although this approach prioritized comparability and operational consistency, sunrise and sunset times were not perfectly aligned between seasons. We are aware that this timing difference may have influenced certain results, particularly for traffic-related components, since rush hours often coincide with the beginning and end of the sampling periods. Nonetheless, we consider this standardized 12-hour scheme the most robust and reproducible strategy for comparing daytime and nighttime samples across different seasons.

5. L157: 'This information' means 'Meteorological parameters'? Moreover, it can be understood that the met station was not the same as the air quality monitoring station. Please mention this limitation in the text.

Indeed, "this information" refers to the meteorological parameters. To improve clarity, the text has been revised. Regarding the distance between sampling and meteorological station locations the limitation has been explicitly mentioned in

the revised manuscript. However, it is important to note that these meteorological data were used only as complementary information and have no direct influence on the main study outputs. The paragraph was re-written to (Line 158):

"These stations were located near the elevated and city sampling sites. The elevated station was adjacent to the corresponding sampling site, while the city station was situated approximately 1.2 km away from the PM sampling site (Figure S1). This spatial separation may introduce slight differences between the recorded meteorological parameters and those directly affecting the sampled air masses. However, the station shares the same urban background classification as the sampling site and was considered representative of the meteorological conditions."

6. L218: missing space after unit.

It has been corrected in the text.

7. L294: provide the reason for such results.

A possible reason for the reduction of nitro-PAHs and an increase of oxy-PAH may be attributable to reductions in NO_2 emissions in the city of Barcelona over the past decade. We added this to the text (Line 314).

"Regarding nitro-PAHs, few studies report their PM concentrations in southern Europe. In fact, the only measurements in ambient air in Barcelona were those by Bayona et al. (1994), conducted at heavily trafficked sites. They reported considerably higher concentrations of 9-nitroanthracene and 2-nitrofluorene than those observed in the present study, a pattern also reflected in the parent PAHs. In contrast, the oxy-PAH ANQ, which was also measured in that study, was found at lower concentrations. Studies conducted in European cities during the early 2010s similarly reported higher nitro-PAH concentrations than those observed here, particularly in winter (Alam et al., 2015; Alves et al., 2017; Tomaz et al., 2016), whereas more recent studies on the Iberian Peninsula reported comparable levels (Lara et al., 2022). Although further measurements are necessary, reduction of nitro-PAHs concentrations may be attributable to reductions in NO_2 emissions over the past decade, resulting from the implementation of low-emission zones and cleaner vehicle engines, which have decreased atmospheric formation of nitro-PAHs while potentially enhancing oxy-PAH formation through reactions with O_3."

8. Section 3.3: Some information must also be provided on 'already well-established' apportionment methods such as PMF.

In Section 2.6, we provide a comparison with other source-apportionment methods, including CMB, PCA, and PMF. Additionally, in section 3.3 we included discussions of our main findings in the context of previous source-apportionment studies in Barcelona that applied PMF. This allows readers to better understand the consistency of our results with established methods.

9. L325-6: ‘methyl phenanthrenes’ or ‘methylphenanthrenes’?

The term has been unified throughout the manuscript to ‘methylphenanthrenes’ to align with the literature.

10. L430: ‘Vertical’ should be rephrased.

In order to avoid confusion, “Vertical” was substituted by “Altitudinal”.