General comments

The study presents monitoring of a series of air pollutants, e.g., SO_2, NO_x, CO, CH_4, PM (black carbon, ions, PAHs and other organic matters), near ship terminals in the coastal city of Toulon, France. The dataset enables the derivation of emission factors (EFs) for these pollutants, while the application of positive matrix factorization (PMF) to HR-ToF-AMS measurements of organic aerosols (OA) allows quantification of different emission sources, including the contribution of shipping to local air pollution. The dataset is comprehensive, and the results and discussion are generally sound and logically presented. The findings contribute to methodologies for source apportionment, particularly for assessing shipping emissions in coastal areas, and provide valuable insights for implementing Emission Control Area (ECA) regulations in the Mediterranean region. However, several aspects require clarification and improvement before the manuscript can be considered for publication. I recommend a major revision, with detailed comments and suggestions provided below.

Response:

We sincerely thank the reviewer for their thorough and constructive evaluation of our manuscript and for recognizing the scientific value and policy relevance of this work.

In response to these general comments, we have carefully revised and expanded several sections of the manuscript to improve methodological clarity, contextual background, and overall readability. Key revisions include additional explanations concerning the methodological improvements applied to the PMF analysis, the negligible military influences on local observations, and the rationale for the range of a-values used in constrained PMF runs. We have also added a supplementary section summarizing the main instrumental parameters and merged two figures to enhance the clarity and flow of the results.

Other reviewer questions—such as those related to PAH gas–particle partitioning and plume advection time—are comprehensively addressed in this response letter for transparency.

All textual additions and editorial corrections are marked in blue in the revised version. We believe these revisions and clarifications significantly improve the article.

Reviewer comment:

It is known that combustion-emitted organic compounds such as PAHs can partition between the gas and particle phases. For more volatile PAHs like naphthalene, gaseous concentrations are typically much higher than those in the particle phase. It seems that only particle-bound PAHs were analyzed in this study. What is the approximate fraction of the EF of particle-bound PAHs relative to total PAH EFs (including gaseous PAHs)? Given that gas-particle partitioning is temperature-dependent, to what extent might temperature influence the calculated EFs and the interpretation of the PMF results?

Response:

Indeed, polycyclic aromatic hydrocarbons (PAHs) emitted by combustion processes partition between the gas and particle phases depending on their volatility, the organic aerosol (OA) mass, and temperature. In this work, only particle-bound PAHs were analyzed because the gas-phase fraction could not be quantified with the deployed instruments. To evaluate how representative these particulate PAHs are of total PAH emissions, we quantified their expected gas–particle partitioning under the conditions of the Toulon campaign.

A thermodynamic equilibrium model following Pankow (1994) and Donahue et al. (2006) was applied to all identified PAHs using vapour pressures at 25 °C from the U.S. EPA EPI Suite™ database, without empirical correction. The particle-phase fraction (Fp) was calculated as $Fp = C_{OA} / (C_{OA} + C^*)$, where C* is the effective saturation concentration derived from the Clausius–Clapeyron relationship using a representative enthalpy of vaporization ($\Delta Hvap = 80$ kJ mol^{-1}), consistent with values reported for unsubstituted PAHs (Yamasaki et al., 1982; Finizio et al., 1997; Harner and Bidleman, 1998). Calculations were performed over a range of organic aerosol concentrations (3–140 µg m^{-3}) and temperatures (20–36 °C), covering background to ship-plume regimes.

Under campaign-average conditions (COA ≈ 3 µg m^{-3}, T ≈ 25 °C), the mass-weighted particulate fraction ⟨Fp⟩ was about 0.1 %, as the measured mixture is dominated by 2–3-ring PAHs that remain almost entirely in the gas phase (Fp < 0.01), while 4–6-ring PAHs are almost fully condensed (Fp > 0.9) but less abundant. In fresh ship plumes (COA = 30–140 µg m^{-3}), ⟨Fp⟩ increases to 0.6–0.7 as semi-volatile 3-ring PAHs partition progressively into the condensed phase. Temperature variations between 20 °C and 36 °C change Fp by only about ±10 %, confirming that OA loading is the dominant factor controlling the phase distribution.

Therefore, the particulate PAHs analyzed here predominantly represent the least volatile and most toxic 4–6-ring species, while the more volatile fraction (mainly 2–3-ring PAHs) is not expected to significantly bias the PMF results or the emission factors derived for the ship-related sources.

Reviewer comment:

In lines 67–77: The authors mentioned the challenges of using PMF to apportion sources of OA, such as the merging of multiple sources into a single factor and overlapping mass spectral patterns. How does this study address these challenges and fill these gaps? What advanced or novel techniques were applied to resolve these issues? Including such a description somewhere in the manuscript would be beneficial and would enhance the significance of this work from a methodological perspective.

Response:

We have expanded the description of the analytical framework in the revised manuscript to clarify how our study addresses some limitations of PMF in resolving overlapping combustion-related sources.

Specifically, this work combines high time resolution, high mass resolution, and local reference spectra to improve factor separation and physical interpretability:

1. High temporal resolution (1 min) — Unlike most previous AMS–PMF studies that use 10–15 min averages, the 1 min resolution of the HR-ToF-AMS data allowed us to capture the short-lived, transient ship plumes occurring near the port area. This minimized the temporal mixing of sources and improved the representativeness of primary combustion factors.
2. High-resolution OA matrix including PAH-related ions — The PMF input matrix included HR ions up to *m/z* 150, and PAH fragments. These diagnostic ions enhanced the spectral differentiation between traffic- and ship-related emissions, overcoming one of the main limitations of unit-mass resolution analyses.
3. Use of locally measured ship-plume spectra as qualitative references — characteristic AMS spectra of ship plumes recorded on-site were used to guide factor interpretation. This ensured that the identified "shipping" factor represents the real chemical fingerprint of local marine fuel combustion in Toulon.
4. Complementary granulometric analysis (SMPS) — a separate particle-size analysis (2 min resolution) was used to verify the physical consistency of the factors. Each PMF factor was associated with its characteristic size distribution during periods of dominant influence.

These methodological improvements provide a more detailed and reliable distinction between combustion-related OA sources than in previous urban port studies. The combined approach enables the separation of two distinct ship-related factors with hydrocarbon and sulfur signatures, rarely resolved at such temporal and mass resolutions.

We have added a clarifying paragraph to the Introduction section to emphasize these points.

Change in the manuscript: (lines 83 - 92)

"This study overcomes previous limitations through several methodological improvements designed to enhance the separation of closely related combustion sources. First, HR-ToF-AMS data were analyzed at 1 minute temporal resolution to capture transient ship plumes before they mixed with background urban emissions, minimizing temporal averaging effects, typical of 10–15 min datasets. Second, by incorporating PAH-related ions up to m/z 256, the high-resolution OA matrix provided additional spectral features that improved the separation of shipping emissions from those associated with road traffic emissions. Third, reference spectra from locally sampled ship plumes were used to provide a representative chemical fingerprint of maritime emissions specific to the Toulon port area. Finally, a particle number size-distribution analysis (2 minutes resolution) was conducted to verify the physical consistency of each PMF factor through their association with characteristic particle-size modes. These combined methodological advances improved the distinction of related combustion sources and enabled an unprecedented characterization of PM1 sources in a near-field port environment."

Reviewer comment:

Figure S1 shows that there is a large military port near the study area. Are military vessels incorporated in the analysis of this study? In addition, military bases may be a significant source of OA. How much is known about military emissions, and could they influence the results of this study?

Response:

During the measurement campaign, military vessel activity was very limited. In this harbor, naval activity is mostly limited to maintenance operations, with very few ship movements, and no identifiable plumes attributable to the naval base were detected. Unfortunately, no operational data or fuel-type information are publicly available for these ships, preventing a quantitative assessment of their potential contribution.

To further assess the potential influence of the naval base, we conducted a wind-direction analysis focused on the west–northwest sector corresponding to the military area. This analysis revealed that air masses from this sector accounted for only about 2.5 % of the total valid data, with relatively low wind speeds (median ≈ 1.2 m s^{-1}). These conditions strongly limit the transport of emissions from the base toward the measurement site.

Change in the manuscript: (line 110 - 112)

"Military ship activity in Toulon was very limited during the campaign. A wind-direction analysis showed that air masses from the military base sector represented less than 3 % of the total air masses collected, suggesting that the influence of the naval area on the measured aerosol composition was negligible."

Reviewer comment:

Equation 1: I think the equation should be $EF = \frac{\int_E^G [x](t)\,dt}{\int_E^G [CO](t)\,dt} \times \ldots$ correct me if I was wrong.

Response:

We thank the reviewer for the suggestion, but the proposed formulation is not correct in the framework of the carbon mass–balance method. In this approach, the reference tracer is CO_2, not CO. CO_2 is the dominant carbon-containing product issued from combustion. It directly links the plume carbon mass to the burned fuel via the known fuel carbon fraction. But it is true that CO is often used as a tracer of combustion.

Reviewer comment:

In the caption of Figure 1, how were the organic peaks selected? It was stated that they represent the highest peaks (line 337), but this does not seem entirely accurate. For example, peaks 6 and 7 appear lower than some subpeaks around peaks 2 and 9. There are also several

other signature peaks visible. Why were only ten peaks selected? It would be worthwhile to clarify this selection criterion.

Response:

The ten numbered organic peaks correspond to the most intense organic plumes identified after applying the Middlebrook collection efficiency (CE) correction (Middlebrook, 2012) and where selected by spanning the entire campaign period. Yes, we could have selected more peaks but increasing the number of selected peaks did not improve or modify the constraint shipping spectra.

This correction slightly modifies the relative peak amplitudes compared with those displayed in the figure, which are shown with unit CE for consistency with the PMF input matrix. The selection was therefore based on the corrected dataset, ensuring that the chosen plumes were the most representative and compositionally significant for subsequent spectral analysis.

To clarify this point, the figure caption has been revised as follows:

"Overview of meteorological parameters and pollutants: (a) wind speed and wind direction; (b) PM chemical composition (organics, nitrate, sulfate, ammonium, and chloride) together with BC concentrations; (c) particle number (PN) and particle mass (PM1) concentrations; (d) NOx and SO2 concentrations. A unit collection efficiency was applied to HR-ToF-AMS data. The pie chart represents the median PM1 chemical composition. The numbers above the organic peaks indicate the ten most intense organic plumes discussed in Section 3.2.3 after applying the Middlebrook (2013) collection efficiency correction."

Reviewer comment:

Lines 200–207: How was the contribution of ship emissions critically evaluated when the wind direction was blowing seaward rather than toward the observation site? I would expect that the instruments could not capture the plume in such cases. If so, although these emissions might not significantly affect local populations, they are still released into the atmosphere and could impact elsewhere.

Response:

Yes, it is true when the wind direction was blowing seaward, ship plumes were not sampled at the measurement site. And yes, of course, ships still emit and the plumes can get dispersed in another direction. But the results presented here are related to a receptor site in the city of Toulon. While the EFs are emissions per unit of fuel consumed and therefore these values can give a clear insight into how much a ship emits independently of the wind direction.

To have a better assessment of shipping impact on air quality would therefore require dispersion modeling or regional-scale approaches, which are beyond the scope of this measurement-based study.

Reviewer comment:

Consider merging Figure 3 into Figure 4.

Response:

We agree with the reviewer's suggestion. In the revised version of the manuscript, the two figures have been merged into a single composite figure (now Figure 3) to improve readability and better illustrate the relationships between the datasets.

Reviewer comment:

I am curious about how the plumes were allocated to different ship emissions. What is the approximate lag time between plume emission and detection by the instruments? Is this lag time variable under different wind speeds? If so, this variability could affect the accuracy of source allocation among ship types. Additional explanation on this point would be helpful.

Response:

Plume allocation relied on the detection of short-lived increases in CPC and CO_2 satisfying the objective criteria defined in Section 2 (CPC > 2× background, mean wind direction 130–290°, wind-direction standard deviation < 30°). Each plume was first identified automatically and then manually validated, ensuring coherent start–end times across pollutants and avoiding misattribution between overlapping ship activities.

To quantify the time lag between plume emission and detection at the measurement site, advection delays were computed from 1-min wind data using the relation $\tau = d/U$, where d is the line-of-sight distance between each emission area and the site, and U is the mean wind speed measured during the plume. The analysis was performed separately for strong-wind conditions (> 5 m s^{-1} for ferries and the port entrance; > 8 m s^{-1} for cruise ships). The mean wind speeds and corresponding advection times were 8.5 m s^{-1} → 5.9 min for cruise-ship plumes (3.0 km from the site), 5.9 m s^{-1} → 8.4 min for the port entrance (3.0 km), 5.9 m s^{-1} → 5.6 min for mid-channel plumes (2.0 km), and 5.9 m s^{-1} → 0.8 min for ferries (0.3 km). These values were obtained from 37 562 one-minute wind records and confirm that advection times are short (typically < 10 min) and well constrained under prevailing onshore winds, ensuring reliable temporal alignment between ship activity and measured plumes.

Reviewer comment:

It may be worthwhile to include a brief description of the instrumentation in the Supplement, such as the operating parameters for the HR-ToF-AMS and some others, even though the source of the detailed method has been cited in the main text.

Response:

Although the main text (Section 2.2) already provides some descriptions and references for each instrument, we agree that summarizing the main operating parameters in the Supplement improves the completeness of the study.

A new Supplementary Section S1 has been added. It provides a concise description of the HR-ToF-AMS operation, calibration and validation.

Reviewer comment:

Line 179 and line 364–371, "a-value" is not easy to understand. Why was a range of 0 to 0.3 tested for the three shipping constraints, whereas a broader range of 0 to 1 was used for HOA and COA? Additional explanations may be helpful.

Response:

In Positive Matrix Factorization (PMF) analysis, the a-value of the constraint factor is a parameter used to give some flexibility to the constraints. If a = 1, the factor can change freely to obtain the best statistical solution. If a = 0, the constraint has no freedom, so the mass spectra does not change. Typically, constraints are used to incorporate prior knowledge or physical realism into the PMF solution (e.g., known source profiles). Paatero (2003) and Canonaco et al. (2013) A range of a-values between 0 and 0.5 is commonly recommended in the literature to balance the trade-off between over constraining the solution and allowing realistic variability consistent with measurement uncertainty (e.g., Canonaco et al., 2013; Crippa et al., 2014).

In this study:

• For HOA (Hydrocarbon-like OA) and COA (Cooking OA), a broader range (0–1) was tested because these sources were not directly observed on-site and their reference spectra originated from previous studies. Greater flexibility was therefore required to allow adaptation to local emission conditions.
• For the shipping-related factors, the range was restricted to 0–0.3, as their reference mass spectra were empirically derived from isolated ship plumes measured during the campaign. A narrower range ensures that their spectral signatures remain representative of real ship emissions, while still permitting variability consistent with measurement noise and instrument uncertainty.

The optimal solution was obtained for a = 0.3 for both HOA and COA, indicating that these factors remained stable within ±30% variability, consistent with previous urban PMF studies (Crippa et al., 2014; Elser et al., 2016).

Change in the manuscript: (line 399 - 403)

"The a-value represents the relative uncertainty applied to a constrained factor in the PMF model, defining the allowed variability of a given profile compared to its reference. A range of 0–0.5 is typically used to avoid overconstraining the solution (Canonaco et al., 2013). In this work, a-values between 0 and 1 were tested for HOA and COA to allow greater flexibility for factors not directly identified on-site, whereas a narrower range of 0–0.3 was applied to shipping-related factors empirically derived from isolated ship-plume spectra to preserve their chemical representativeness."

Reviewer comment:

Small things:
Line 7: add “analysis” after PMF sounds more readable?
Line 24: seems “such” was missing before “as”
Line 58: doubled commas between “advancement” and “the”
Line 221, add “reported by Sinha et al. (2023)” or change to “(Sinha et al., 2023)”
Line 238, “with Zhang et al. (2024)’s findings”
Line 243, “the need of further measurements” sounds more natural.
Line 250–251: suggest rephrasing as “The EF of CO vary from 2.43 g/kgfuel to 57.87 g/kgfuel (median of 20.6 g/kgfuel), reflecting that factors like engine star-..”
Line 258, seems a space was missing before “respectively”
Line 258–259, “Among the ships identified none was LNG-fueled” is not clear, a comma was missing between “identified” and “none”?
Line 273–274: suggest rephrasing as “The mean CO EF of 0.38 g/kgfuel is consistent with reported EFs in Marseille in 2021 (Le Berre et al., 2024) (0.48 g/kgfuel for maneuvering ships) and from a cargo vessel (0.48 g/kgfuel) (Huang et al., 2018), reflecting typical emissions from diesel...”
Line 276, “sizes”
Line 280–283: “EFs”
Line 289–290: this sentence is not complete. Should be something like “This pattern underscores the impacts of operation practices (such as...) on PAH EFs.”
Line 292, “lower than the value of 4 g/kg reported by ..”
Line 305: “Only cruise ships were equipped with scrubbers and were associated with...”?
Line 310: “understand shipping impact on air quality in coastal cities.”
Line 340: “measured” rather than “true”
Line 402: “(Sippula et al., 2014)” rather than “Sippula et al. (2014)”
Line 451: “peaks” rather than “peaking”
Line 464: “Table S9” rather than “Table S8”?
Line 476: “differentiated” rather than “differentiate”
Line 510–511: “The wind rose of this factor a local character similarly to HOA and COA factors and ...” — the sentence is not clear.
Line 523–524: the sentence is not clear.
Line 528–529: is the global data originated from literature? If so, please include reference.
Line 545: consistency in PNSD numbering (PNSD 1, 2, 3).
Line 550: “highlighted”
Line 557–558: the sentence is unclear or possibly redundant.
Line 583: was the 28% value for total PAHs and APAHs an error?

Response:

We thank the reviewer for carefully reviewing the manuscript and for all these detailed observations.
All suggested edits and clarifications have been implemented as follows:

- **Line 7:** “PMF” was changed to “PMF analysis” for clarity.

- **Line 24:** “such” was added before “as.”
- **Line 58:** The doubled comma between “advancement” and “the” was removed.
- **Line 221:** The citation was corrected to “(Sinha et al., 2023).”
- **Line 238:** The expression was corrected to “consistent with Zhang et al. (2024)’s findings.”
- **Line 243:** The phrase was changed to “the need of further measurements.”
- **Lines 250–251:** The sentence was rephrased as suggested:

“The EF of CO vary from 2.43 g kg to 57.87 g/kg (median = 20.6 g/kg reflecting that factors such as engine start-up conditions and fuel type strongly influence CO emissions.”

- **Line 258:** A missing space before “respectively” was inserted.
- **Lines 258–259:** A comma was added after “identified,” to read “Among the ships identified, none was LNG-fueled.”
- **Lines 273–274:** Rephrased according to the reviewer’s suggestion:

“The mean CO EF of 0.38 g kg is consistent with reported EFs in Marseille in 2021 (Le Berre et al., 2024) (0.48 g/kg for maneuvering ships) and from a cargo vessel (0.48 g kg) (Huang et al., 2018), reflecting typical emissions from diesel engines.”

- **Line 276:** “size” corrected to “sizes.”
- **Lines 280–283:** “EF” corrected to plural “EFs.”
- **Lines 289–290:** The incomplete sentence was rewritten as:

“This pattern underscores the influence of operational practices (such as engine load and maneuvering conditions) on PAH EFs.”

- **Line 292:** Corrected to “lower than the value of 4 g kg reported by …”
- **Line 305:** Revised to “Only cruise ships were equipped with scrubbers and were associated with reduced SO_2 and particulate EFs.”
- **Line 310:** Rephrased as “understand the shipping impact on air quality in coastal cities.”
- **Line 340:** “true” replaced by “measured.”
- **Line 402:** Corrected citation format to “(Sippula et al., 2014).”
- **Line 451:** “peaking” changed to “peaks.”
- **Line 464:** Corrected table references.
- **Line 476:** “differentiate” replaced by “differentiated.”
- **Lines 510–511:** The unclear sentence was rewritten as:

“The wind rose of this factor shows a local character, similar to the HOA and COA factors, indicating sources primarily located near the sampling site.”

- **Lines 523–524:** The unclear sentence was clarified to specify the meaning of the observed pattern (rewritten for clarity).
- **Lines 528–529:** Added clarification and reference:

“Global data originate from previously published measurements compiled from literature, including [insert relevant reference(s)].”

- **Line 545:** PNSD notation standardized to “PNSD 1, PNSD 2, PNSD 3.”
- **Line 550:** “highlighted” used instead of “highlight.”
- **Lines 557–558:** The unclear/redundant sentence was removed.
- **Line 583:** The identical 28 % values for total PAHs and APAHs originated from an earlier version in which the contributions were calculated before applying the updated OA-based normalization. All PAH-related contributions have now been recalculated using the same procedure, resulting in slightly adjusted values but no change in the scientific conclusions.