Point by Point Response to Review Comments

[Paper #egusphere-2025-4005]

Elevated Anthropogenic Contributions to Trace Elements in Marine Aerosols Compared to Coastal Qingdao in Eastern China

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We sincerely thank the editor and all reviewers for their valuable feedback that we have used to improve the quality of our manuscript. We provide below a point-to-point response to reviewers' comments. The reviewer's comments are in regular **black**; the original (unrevised) text of the manuscript is in ***italicized black***; the response text is in **blue**; and the revisions in the manuscript are in ***red italics***.

Reviewer #1:

General comments:

This study addresses the emission sources of trace metals in $PM_{2.5}$ collected in Qingdao, the Bohai Sea, and the East China Sea. The content appears to fit within the scope of Atmospheric Chemistry and Physics. However, there are many major concerns that need to be addressed before this manuscript can be published. Across the manuscript, discussions on the key methods and findings of this study are very brief (see Major Concerns), while less important sections tend to be redundant. For instance, this manuscript addresses the factors controlling the metal solubility in aerosol particles. However, the discussion is somewhat speculative because no water-soluble metal concentrations were measured. Accordingly, the processes suggested to influence metal solubility may not necessarily represent the actual conditions of the samples analyzed. It would therefore be advisable either to include data on water-soluble metal concentrations and solubility, or to limit the discussion accordingly.

Response:

We thank the reviewer for this constructive comment. We acknowledge that our initial discussion on metal solubility was somewhat speculative. The manuscript was revised to limit the scope with a more cautious tone regarding this topic. We retain a focused subset and necessary part of this discussion, as sources characteristics (e.g., combustion, dust) are primary determinants of an element's solubility, and omitting this context would undermine the biogeochemical relevance of our findings.

The specific revisions we have made in the revision include the following:

In the Introduction: We have refined the phrasing and trimmed extraneous solubility-related content to better define the study's scope. Specifically, we now clarify that our discussion of solubility is framed from a source-property perspective, grounded in established literature, rather than making definitive claims about the precise solubility of the analyzed samples.

Lines 48-55: *"The total fraction of trace elements cannot be fully utilized by marine biota. In most cases, only the soluble fractions are more likely to be bioavailable (Shi et al., 2012), and the solubility is closely associated with their sources (Baker et al., 2006; Sholkovitz et al., 2012). For instance, while mineral dust is the principal source of Fe, numerous studies have demonstrated that Fe emitted from anthropogenic sources has a higher solubility (López-García et al., 2017; Sholkovitz et al., 2012; Sun et al., 2024). Model results also suggest that the combustion-derived Fe tended to account for over 20% of the Fe deposition near the Asian continent, and the efficiency of pyrogenic Fe in enhancing marine productivity exceeds that of lithogenic sources (Ito et al., 2021; Luo et al., 2008). Fe from the combustion source is typically present in finer particles (Buck et al., 2010; Ito and Feng, 2011)."*

Lines 60-65: *"Prior field cruise investigations have focused on the characteristics of total suspended particulates (TSP) and* PM_{10} *(*$D_p \leqslant 10\ \mu m$*) (Hsu et al., 2010; Li et al., 2025; Peng et al., 2025; Qiu, 2015; Shi et al., 2013; Wang et al., 2013; Yang et al., 2020). In contrast, trace elements in* $PM_{2.5}$ *have been scarcely explored. It has been revealed that trace elements in fine particles exhibit distinct potential environmental impacts with coarse particles (Li et al., 2018; Hsieh et al., 2022; Sakata et al., 2022; Zhang et al., 2022), highlighting the importance of targeting* $PM_{2.5}$*."*

Lines 66-74: *"Atmospheric processes during long-range transport from the continent to ocean can alter the physicochemical properties of aerosols, thereby influencing the bioavailability of nutrients in the particles upon deposition (Schroth et al., 2009; Sholkovitz et al., 2012; Wang et al., 2022; Wang et al., 2021; Luo et al., 2020; Xu et al., 2023; Zhang et al., 2024). Accurately identifying and apportioning the sources of fine particles and their trace elements, is crucial for quantifying this biogeochemical impact, especially given the differences observed across land-to-sea gradients. This study focuses on the characteristics and source apportionment of elements in* $PM_{2.5}$*, based on simultaneous observations in Qingdao and during BS and YS research cruises in the spring and summer of 2018 (Fig.1). The major purpose is to provide a more comprehensive understanding of the distribution and sources of trace elements in fine particles from coastal to marginal sea areas in eastern China."*

In Sect. 4.3.1: We have reframed the discussion to be more cautious. We state that our inferences are based on the well-documented physicochemical properties of particles from different sources (e.g., anthropogenic combustion typically yields more soluble Fe) and cite robust literature to support this statement. In addition, we have also moderated the tone of the discussion by using qualifying phrases. In the revised manuscript, the discussion is modified as follows, corresponding to these comments.

Lines 424-430: *"Notably, our source apportionment revealed a significant contribution of* *anthropogenic combustion to total Fe (Fig.6a). Such anthropogenic Fe was reported to typically exhibit higher solubility, in comparison with Fe from natural sources such as mineral dust (Ito et al., 2021; Sun et al., 2024). The greater solubility and consequent higher efficiency in enhancing productivity can be explained by the physicochemical properties of the particles. Combustion processes emit Fe in finer particles with a larger surface-area-to-volume ratio. Such particles are more susceptible to atmospheric acid processing, which efficiently converts insoluble Fe into soluble forms (Shi et al., 2012; Ito et al., 2021). In contrast, Fe in natural mineral dust is largely encapsulated within refractory aluminosilicate minerals, making Fe less available for solubilization."*

Reference:

"Hsieh, C. -C., Chen, H. -Y., & Ho, T. -Y.: The effect of aerosol size on Fe solubility and deposition flux: A case study in the East China Sea, Mar. Chem., 241, 104106, https://doi.org/10.1016/j.marchem.2022.104106, 2022."

I am also concerned about the interpretation of the correlation analysis. The use of phrases like "strong correlation" and "significant correlation" is misleading, as these terms should be reserved for cases where the correlation coefficient (r) is at least 0.6 or 0.7. However, the reported r values in this manuscript are frequently below 0.4. For instance, in Line 237, the correlation coefficient (r) is only 0.29, yet it is described as a "strong correlation. Since the section on PMF source apportionment is arguably the most important part of this work, such an overstatement of the results compromises its scientific integrity. I strongly recommend revising the language to more honestly and cautiously reflect the actual numerical data.

Response:

We sincerely thank the referee for pointing out this critical oversight. The use of statistical terminology was inappropriate and have thoroughly revised the entire manuscript to ensure all correlations are described accurately based on their coefficient values.

Sect. 4.1:

Lines 213-214: *"It correlated with NO_2 ($r = 0.45, p < 0.01$) and CO ($r = 0.39, p < 0.01$)."*

Lines 223-224: *"Factor 2 exhibited correlations with CO ($r = 0.54$, $p < 0.01$) and RH ($r = 0.36$, $p < 0.01$)."*

Lines 231-233: *"Diurnally, Factor 3 exhibited a moderate positive correlation with WS ($r = 0.43$, $p < 0.05$) in Qingdao in spring. Throughout the entire sampling campaign, it maintained a strong negative correlation with RH ($r = –0.72$, $p < 0.01$; Table S7) in Qingdao."*

Lines 240-242: *"During summertime, vehicular emissions correlated strongly and positively with NO_2 ($r = 0.78$, $p < 0.01$). Throughout the sampling campaign, the factor correlated positively with CO (r*

= 0.30, $p < 0.05$) and negatively with O_3 (r = –0.37, $p < 0.01$).”

Lines 244-246: *“Factor 5 was characterized by high concentrations of sea salt components, including Na^+, Mg^{2+} and Cl^-, and showed a positive correlation with WS (r = 0.35, $p < 0.01$) and a strong negative correlation with RH (r = –0.63, $p < 0.01$) (Sharma et al., 2016; Zhang et al., 2018).”*

Lines 263-264: *“It showed a positive correlation with SO_2 (r = 0.38, $p < 0.01$) (Table S7), further validating its association with ship emissions (Zhang et al., 2019b).”*

Lines 268-270: *“Its correlations with NO_2 (r = 0.50, $p < 0.01$) and SO_2 (r = 0.31, $p < 0.05$) underscored its industrial origins, although it is a minor contributor to total $PM_{2.5}$ (3.1% in Qingdao and 1.5% in the BS and YS areas, as shown in Table S7).”*

Lines 273-274: *“Furthermore, the factor exhibited a statistically significant correlation with SO_2 (r = 0.35, $p < 0.01$), a primary gaseous co-emission from coal combustion (Lin et al., 2022).”*

The manuscript also contains many other issues that I have outlined in the "Major Concerns" and "Specific Comments". Should the authors be able to make comprehensive and substantial revisions to address all of these points, I would be open to reconsidering its publication. However, if such major revisions are not feasible, the paper should be rejected. Therefore, I cannot recommend the current version for publication in ACP.

Overall Response:

We sincerely appreciate the reviewer’s detailed and constructive comments. In this revised manuscript, we have expanded the description of the sample collection protocols, analytical procedures, and data quality assurance and quality control (QA/QC) measures. We also include specific comparisons of blank samples levels with ambient atmospheric concentrations. Among all elements, only aluminum (Al) exhibited a relatively high blank fraction (43.4%) in marine samples. The blank fractions of other elements remained low; for instance, iron (Fe) blank fractions relative to average sample concentrations were 3.1% (at YS and BS) and 4.0% (at Qingdao).

To ensure more accurate source apportionment, we re-conducted Positive Matrix Factorization (PMF) analysis after excluding Al data. The revised results were broadly consistent with the original findings and remained statistically robust, with additional verification and detailed presentation of these results now included.

Regarding the use of relative proportions (rather absolute data) of PMF results in the abstract and discussion: This choice was made to avoid overloading the text with extensive elemental concentrations data while enhancing comprehensively across studies, particularly given that concentrations can vary substantially between different cruises, whereas relative proportions provide more objective basis for comparisons with numerical simulations and other research. We acknowledge the reviewer's concern that relative contribution alone may be misleading. Accordingly, in the Discussion section, we have added analyses of absolute contributions from key sources (e.g. Fe and Mn et al.,) to enhance readers' intuitive understanding of source impacts. Furthermore, we have expanded the discussion of coal combustion and ship emissions, incorporating additional evidence and contextual analysis to strength these sections.

All issues raised in both "Major concerns" and "Specific comments," have been carefully considered and thoroughly addressed based on our knowledge. We are fully committed to conducting comprehensive and substantive revisions to address each point, aiming to enhance the overall quality and suitability of our manuscript for publication in the journal.

Major comments:

Comment 1:

1. The methodology section is too brief. The following information is necessary to ensure the quality of the data obtained from the samples.

Sample duration: Please provide sampling duration for each aerosol collection or the total integrated volume should be provided. From the result and discussion section, it appears that sampling was conducted separately during the day and night, but it is unclear whether this applies only to Qingdao or also to the marine aerosol samples.

Response:

We thank the reviewer for this comment. We have now clarified the sampling duration information in the revised manuscript as follows:

For marine samples: We have added the sentence: *"Sampling durations varied from several hours to 28 hours in spring and from 18 to approximately 40 hours in summer to accumulate sufficient particle mass."* in Sect. 2.1, lines 86-87.

For Qingdao samples: We have clarified the sampling strategy by adding: *"At the coastal site, a day/night sampling strategy was primarily employed, and a few summer samples were collected over about 23-hour periods."* in Sect. 2.1, lines 93-94.

This revision makes it explicit that the day/night strategy was specific to the coastal (Qingdao) site, while marine sampling durations were variable and determined by the need to collect sufficient particle mass.

Selection of wind direction: For marine aerosol sampling, it is often insufficient to collect samples only while the vessel is underway to avoid contamination from the ship itself. It is therefore crucial to clarify whether sampling was restricted to specific wind directions (e.g., -90° to 90°, with 0° being the bow). If selection of wind-direction was not performed, the potential impact on the samples should be clearly explained. This is particularly important since one of the key findings of this study is the increasing influence of ship-derived aerosols in recent years.

Response:

We thank the reviewer for this comment. We have clarified this point in the revised Sect. 2.1 as follows: Lines 87-89: *"During the collection of marine aerosols, samples were exclusively collected while the ship was underway and the relative wind direction ranged between -60° and +60° (with 0° representing the bow) to avoid contamination from the vessel's own exhaust emissions."*

Filter blank: Please clarify the levels of trace metal blanks on the filters after cleaning and indicate the impact of the filter blanks on the measured samples. Given the short sampling time, the influence of filter blanks on the $PM_{2.5}$ and marine aerosol samples from Qingdao should be clearly stated.

Response:

We thank the reviewer's valuable insight regarding filter blanks. This concern has been comprehensively addressed through the following revisions:

In the main text (Sect. 2.2, lines 100-101), we have added a statement referring readers to the detailed QA/QC information: *"For quality assurance and control, blank filters were collected and processed, with detailed results and their impact assessment provided in Text S1a and Table S1."*

In the Supplementary Materials (SM), a new section (Text S1a) and table (Table S1) dedicated to quality control have been added, which include:

(i) Average blank concentrations and standard deviations for all trace elements.

(ii) Quantification of the typical blank fraction (%) relative to measured ambient samples.

(iii) A clear assessment indicating that blank fractions were below 10% for the majority of elements; for Fe specifically, contributions were 3.1% (marine samples) and 4.0% (Qingdao samples).

Table S1. *Average blank concentrations (μg L^{-1}), standard deviation (μg L^{-1}), and typical blank fractions (%) for trace elements in ICP-MS analytical solution.*

Element	*Average blank (μg L^{-1})*	*Standard deviation (μg L^{-1})*	*Typical blank fraction (%)**	
			Marine	*Qingdao*
Al	*52.7*	*3.1*	*43.4*	*11.8*
Fe	*6.0*	*8.0*	*3.1*	*4.0*
Mn	*0.1*	*0.1*	*3.8*	*1.1*
Ba	*0.1*	*0.1*	*3.8*	*4.6*
Zn	*2.3*	*2.6*	*17.2*	*10.1*
V	*0.6*	*0.3*	*11.2*	*9.7*
Pb	*0.0*	*0.1*	*0.7*	*0.6*
Ni	*0.2*	*0.3*	*-*	*9.4*
Cu	*0.3*	*0.3*	*4.3*	*12.8*
As	*0.0*	*0.0*	*0.4*	*-*
Cr	*0.0*	*0.0*	*4.6*	*4.6*
Cd	*0.0*	*0.0*	*16.0*	*9.7*
Co	*0.0*	*0.0*	*4.5*	*5.3*

*. *Typical blank fractions were estimated as (average blank concentration / typical sample concentration) × 100%. Typical sample concentrations were derived from the median values from marine and Qingdao samples, respectively. A dash (-) indicates concentrations below the detection limit for marine or Qingdao samples.*

SM: ***"Text S1:*** *Quality assurance and quality control*

(a) Trace elements

Assessment and implications of procedural blanks: *Blank filters were processed and analyzed following the identical protocol to that of the samples. Average blank concentrations and standard deviations for all trace elements are summarized in Table S1. The impact of blanks was evaluated by quantifying their typical percentage fraction to the measured sample concentrations. For most elements, the blank fractions were below 10%. Among these, seven elements exhibited particularly low blank levels (<5%), with Fe blanks notably evaluated at 3.1% (marine samples) and 4.0% (Qingdao samples). Although the blank fractions for Al were higher in marine samples, it is crucial to note that all reported data have undergone rigorously blank-correction. Furthermore, Al was not included as an input species in our PMF source apportionment. With these measures, uncertainties due to filter blanks have been minimized and are not expected to influence the results considerably."*

Furthermore, we noted a relatively high blank contribution of Al in marine aerosol samples. To ensure the robustness of the source apportionment, Al was excluded from PMF input species. Updates to resolved source profiles and contributions (generally minor in magnitude) are detailed below. For clarity, only changes that involve numerical adjustments without affecting the overall narrative are omitted here. All main text figures except Figure 1, along with related supplementary figures and tables, have been updated, but are not presented here. Details already addressed in responses to other reviewer comments are not reiterated here.

Sect. 2.4, lines 140-144: *"The 9-factor solution tended to resolve an additional factor; however, it exhibited relatively low BS mapping values (58%, 67%, and 73%) for several factors (Fig.S1b and Table S2). The 8-factor solution demonstrated the highest stability. The mapping percentages using the BS uncertainty method exceeded 80% for all factors (Table S3), surpassing the performances of the 7-factor and 9-factor solutions (Table S4 and S2)."*

Sect. 3, lines 161-163: *"The YS region recorded the lowest concentrations for most elements in both spring and summer. Conversely, Zn, As, and Cd exhibited elevated levels over the ocean in summer (Fig.S3b), highlighting the significant impact of transported primary anthropogenic emissions on marine aerosol composition."*

Lines 190-192: *"Only a few measurements in island were collected in summer (Yuan et al., 2023), and comparison with concentrations in this study showed no order-of-magnitude differences for most elements."*

Sect. 4.1, lines 265-268: *"It exhibited substantial loadings of heavy metals such as Zn, Cu, Cr, and Pb, which are tracers of waste incineration and industrial activities, including metallurgical smelting, oil mining, and the production of cement, plastic, pigment, chemical and building materials (Borai et al., 2002; Karar et al., 2006; Li et al., 2012; Tian et al., 2012; Wang et al., 2018)."*

Sect. 4.2.1, lines 290-292: *"Specifically, secondary nitrate was the predominant contributor at the coastal site, accounting for 41.6% (20.4 μg m^{-3}) of $PM_{2.5}$ mass. In contrast, its contribution was notably lower in the marine area (23.6%, 4.4 μg m^{-3}; Fig.5)."*

Lines 301-309: *"Sea salt, sulfate & BB, coal combustion, vehicular emissions and residual oil combustion showed higher contributions in the marine area, despite lower or comparable absolute concentrations to the coastal site (Fig.5). Sea salt contributions were 30.9% in the marine area, versus 13.0% at the coastal site, consistent with the fact of its marine origin. Furthermore, its temporal peaks at Qingdao closely resembled those of the dust factor (Fig.4a). It is hypothesized that during dust events, sea salt may mix with the transported dust, making the two factors difficult to distinguish and leading to the higher concentration of sea salt at Qingdao (6.4 μg m^{-3}) compared to those over the marine area (5.7 μg m^{-3}).*

On the one hand, increased RH in marine air favored the formation of sulfate and oxalate through liquid-phase reactions (Zhang et al., 2019a; Zhou et al., 2015), enhancing sulfate & BB contribution in the marine atmosphere (9.9%) compared to the coastal site (7.1%)."

Lines 316-318: *"Unlike the WI & IE factor, these four anthropogenic factors demonstrated that varying transport paths, particle size, and source proximity could affect land-sea distribution patterns of their contributions."*

Sect. 4.2.2, lines 330-336: *"This difference could be ascribed to the seasonal variations in pollutants transport direction, driven by the summer southeasterly winds, altering typical land to sea trajectories. Similarly, sea salt concentrations were higher at the coastal site (0.9 μg m*$^{-3}$*) compared to marine areas (0.6 μg m*$^{-3}$*), suggesting that summer southeasterly winds facilitate marine aerosol transfer inland, thereby influencing the air quality of coastal urban areas (Figs.S4c, d, and S8d). The coal combustion factor also showed a more pronounced contribution over the marine area (0.6 μg m*$^{-3}$*, 6.5%) than at the coastal site (0.4 μg m*$^{-3}$*, 1.3%). This variation was attributed to elevated concentrations of trace elements in marine aerosols during summer."*

Lines 390-392: *"The influence of dust and WI & IE sources decreased, whereas coal combustion, vehicular emissions (in spring) and sea salt exhibited enhanced contributions to elements over the marine area."*

Sect. 4.3.1, line 450: *"The source pattern of Cr shared some similarities with that of* Fe and Mn *in spring (Fig.6c)."*

Lines 452-455: *"WI & IE was the second-largest contributor to Cr in Qingdao during spring and the largest contributor during summer, qualitatively similar to the findings of* Yang et al. (2022) *for Beijing, although the industrial emissions contribution levels they reported (41%–77%) were substantially higher than those in our study (15.3% in spring, 27.3% in summer)."*

Sect. 4.3.2, lines 466-469: *"In Qingdao, WI & IE was an important source of Cu, consistent with observations in Beijing (Yang et al., 2022). Apart from the sea salt contributions, Zn originated from various anthropogenic sources including waste incineration, industrial emissions, coal combustion and secondary aerosol formation. In the marine area, coal combustion dominated Zn contributions, accounting for 31.5% and 52.5% of total Zn in spring and summer, respectively (Fig.6g)."*

Experimental conditions: It should be clarified whether the acid digestion of aerosols, especially the evaporation to dryness, was carried out in a clean room or under ambient air conditions. Given that metal concentrations in marine aerosols are low compared to continental aerosols, if the experiments were performed under ambient conditions, the potential impact of contamination during evaporation and drying should be addressed.

Response:

We thank the reviewer for raising this critical point regarding the experimental conditions of aerosol acid digestion. We acknowledge that the digestions were performed in a standard fume hood under ambient laboratory conditions. To directly address this concern and demonstrate rigorous contamination control, particularly critical for low-concentration marine aerosols, we have revised the manuscript to detail the measures implemented to ensure data integrity. The specific additions to Sect.

2.2 and Text S1a are follows:

Sect. 2.2, lines 105-106: *"After cooling to room temperature, the solutions were evaporated to near dryness at 180 °C using an electric heating plate (Text S1a)."*

Text S1a: *"**Digestion procedure and environmental control:** The acid digestion of aerosol samples, including the evaporation to dryness step, was conducted inside a standard fume hood under ambient laboratory conditions. The following stringent measures were implemented to assess and mitigate potential contamination, especially critical for the low metal concentrations in cases of marine aerosols: (i) All sample processing steps were performed in parallel with procedural blank filters. (ii) All labware underwent rigorous acid cleaning: rinsed six times with Milli-Q water (≥18.0 MΩ·cm), immersed in 20% HNO_3 bath for 24-hour, another six-time rinse with Milli-Q water, and finally dried in a clean bench. Filter samples were cut using a pre-cleaned ceramic knife and ceramic tweezers. (iii) All analytical results were blank-corrected using the procedural blanks. As evidenced by low blank levels for most elements, contamination introduced during the experimental process was effectively controlled and did not compromise data quality or the integrity of the scientific conclusions."*

These revisions clarify the experimental setup and validate that contamination risks were rigorously managed, ensuring the reliability of results for ambient aerosols.

OC and EC: Please provide more detailed information. I am sorry that I cannot get any information. If authors feel method section is too long, please provide details in Supplemental Information.

Response:

We thank the reviewer for this comment. As suggested, we provide a detailed description of the OC/EC analysis methodology in the Text S1c. The added text includes the instrumental principle, the thermal-optical protocol, the definition of the OC/EC split point, the detection limits, and quality assurance procedures:

Lines 117-118: *"**OC and EC:** 2.0 cm^2 section of samples and blank filters were analyzed by a Sunset OC/EC analyzer using NIOSH protocol (Wu et al., 2016). The data obtained were calibrated with a standard curve. Detailed information is described in Text S1c."*

Text S1c: *"**(c) Analysis of OC and EC***

The concentrations of OC and EC were measured using a Sunset OC/EC analyzer (RT-3131, Sunset Laboratory, OR, USA). A 2.0 cm^2 punch of each quartz filter sample was analyzed following the National Institute for Occupational Safety and Health (NIOSH) 5040 thermal-optical transmittance (TOT) protocol.

The analysis involved a two-stage heating process. Initially, the punch sample was heated in a pure helium (He) atmosphere through a series of temperature steps to volatilize and quantify OC. During *this stage, a portion of OC was pyrolyzed, forming pyrolyzed carbon (PC). Subsequently, the atmosphere was switched to a mixture of He and oxygen (He/O_2). In this oxidative environment, the sample was further heated, causing the remaining EC and the previously formed PC to combust. A critical correction for the PC formed during the He phase was applied. This was achieved by continuously monitoring the transmittance of a laser through the filter (Wu et al., 2016). The laser transmittance decreased as PC formed and recovered as PC and EC were combusted in the He/O_2 phase. The point at which the laser transmittance returns to its initial value is defined as the OC/EC split point. The carbon detected before this split point is defined as OC, and the carbon detected after is defined as EC. The carbonaceous gases produced in both stages were converted to carbon dioxide (CO_2) in a manganese dioxide (MnO_2) oxidation oven and then quantified by a flame ionization detector (FID) or a non-dispersive infrared (NDIR) detector.*

The method detection limit is approximately 0.2 μgC m^{-3} for filter analysis, with an analytical uncertainty (standard deviation) between 4% and 6%. Obtained data were calibrated using a standard curve, and routine quality assurance includes the analysis of calibration standards and blank filters."

Reference:

Wu, C., Huang, X. H. H., Ng, W., Griffith, S. M., and Yu, J. Z.: Inter-comparison of NIOSH and IMPROVE protocols for OC and EC determination: implications for inter-protocol data conversion, Atmos. Meas. Tech., 9, 4547-4560, https://doi.org/10.5194/amt-9-4547-2016, 2016.

PMF: It is stated that 81 samples obtained from both Qingdao and the ship-based marine observations were input together into the PMF analysis. If so, this would mean that samples collected on the same day at different sampling sites were included in the same model, which does not seem to align with the typical application of PMF. In particular, the emission sources and controlling factors for metal elements are expected to differ substantially between Qingdao and marine aerosols. In this case, including both types of samples could result in the outcomes being somewhat averaged, potentially failing to reflect the actual conditions at either Qingdao or the marine sites. If the input file indeed included both Qingdao and marine aerosol samples, the validity of the resulting source apportionment should be explicitly addressed.

By contrast, if PMF analyses were conducted separately for Qingdao and the marine aerosols (or for spring and summer), this should be clearly stated. In that case, the relatively small number of marine aerosol samples raises the question of whether the dataset is sufficiently large to support an 8-factor solution.

Considering that the PMF results form the core of this study, in either scenario, the current Methods description does not make it clear how the temporal variations in source contributions for the two sites (e.g., Figure S5) were obtained, nor does it provide information to evaluate the validity of these results.

Response:

We sincerely appreciate the reviewer's comments. As noted, we indeed combined 81 samples from both Qingdao and ship-based marine observations in a single PMF model. To address the reviewer's concerns, we provide the following clarifications and supplements:

(i) Rationale for integrating land and marine samples

A primary objective of this study is to characterize regional-scale aerosol sources and their cross-boundary transport between the coastal megacity (Qingdao) and adjacent marine environments (Bohai and Yellow Seas). Land-sea aerosol interaction (e.g., transport of land-based pollutants to marine areas and vice versa) is a key process in this contiguous regional atmospheric system. Merging samples from both environments allows us to resolve shared regional sources (e.g., long-range transported industrial emissions) and site-specific sources (e.g., local marine sources or urban emissions) within a unified framework, which aligns with our goal of understanding regional pollution dynamics.

(ii) Addressing concerns about divergent sources

We acknowledge the potential differences in emission sources between land and marine aerosols. However, PMF inherently handles such variability by resolving sources with location-specific contributions: for example, land-dominated sources (e.g., urban anthropogenic emissions) are assigned near-zero contributions to marine samples, while marine-specific sources (e.g., sea spray) show minimal contributions to Qingdao samples. This capability avoids "averaging" of source profiles and instead explicitly quantifies source activity across the regional domain. Prior studies have successfully combined samples from diverse urban, rural, and marine sites within a coherent regional framework to characterize cross-boundary source impacts (Dai et al., 2020; Sofowote et al., 2015a; Sofowote et al., 2015b).

(iii) Sample size and solution robustness

Regarding sample size: Separate PMF analyses for marine samples alone would have been constrained by the small sample size (n < 30), increasing uncertainty in factor resolution. By merging datasets, we ensured sufficient statistical power (n = 81) to support the 8-factor solution. To validate robustness, we conducted rigorous DISP and Bootstrap (BS) analyses: all 8 factors showed BS mapping rates > 80% with no factor swapping, confirming stable source profiles. We added a PMF QAQC section in the SM (Text S3) for details.

Sect. 2.4, line 146: *"Detailed information on the PMF performance, including time series analysis, can be found in Text S3."*

***"Text S3:** Detailed description of PMF analysis*

Source contribution time series: *The time series of individual PMF factor concentrations (e.g., Fig.4) were derived from the factor contributions output by the PMF model. A factor-specific scaling coefficient was calculated by comparing the factor contribution and absolute concentration. The complete absolute concentration time series for each factor was then generated by applying this coefficient to the entire factor contribution time series.*

PMF solution evaluation: *Multiple factors ranging from 6 to 10 were thoroughly evaluated to determine the optimal solution. The stability and reliability of the factor solutions were assessed using the displacement (DISP) and bootstrap (BS) uncertainty estimation methods (Norris et al., 2014). Ultimately, an 8-factor solution emerged as the most robust and interpretable. In contrast, the 7-factor solution failed to distinguish the industrial emissions from dust (Fig.S1a). The 9-factor solution tended to resolve an additional factor; however, it exhibited relatively low BS mapping values (58%, 67%, and 73%) for several factors (Fig.S1b and Table S2). The 8-factor solution demonstrated the highest stability. The mapping percentages using the BS uncertainty method exceeded 80% for all factors (Table S3), surpassing the performances of the 7-factor and 9-factor solutions (Tables S4 and S2). Moreover, the DISP analysis showed no occurrences of factor swapping and no reduction in the model fit statistic Q (both %dQ and the error code were 0), further validating the stability and interpretation of the 8-factor solution.*

Based on the established 8-factor PMF solution, a detailed evaluation of its performance in simulating Fe concentrations was conducted. The results showed that while the model performed well for most elements (e.g., Fig.S11b and c), the PMF-resolved total Fe in marine aerosols in summer (191.5 ng m^{-3}*) was substantially higher than the measured concentration (109.8 ng* m^{-3}*), indicating an overestimation in the absolute source concentrations for Fe in this specific scenario. Therefore, the reported concentrations by PMF for marine Fe in summer should be interpreted as upper-bound estimates. Crucially, the strong linear correlation (*$r^2 = 0.98$*,* $p < 0.01$*) between the PMF-simulated and measured Fe concentrations (*$r^2 = 0.76$*,* $p = 0.02$ *for summer marine samples; Fig.S11a) indicated that the overestimation was proportional. This high coherence in temporal trends strongly suggested that the relative source contributions for Fe remained robust."*

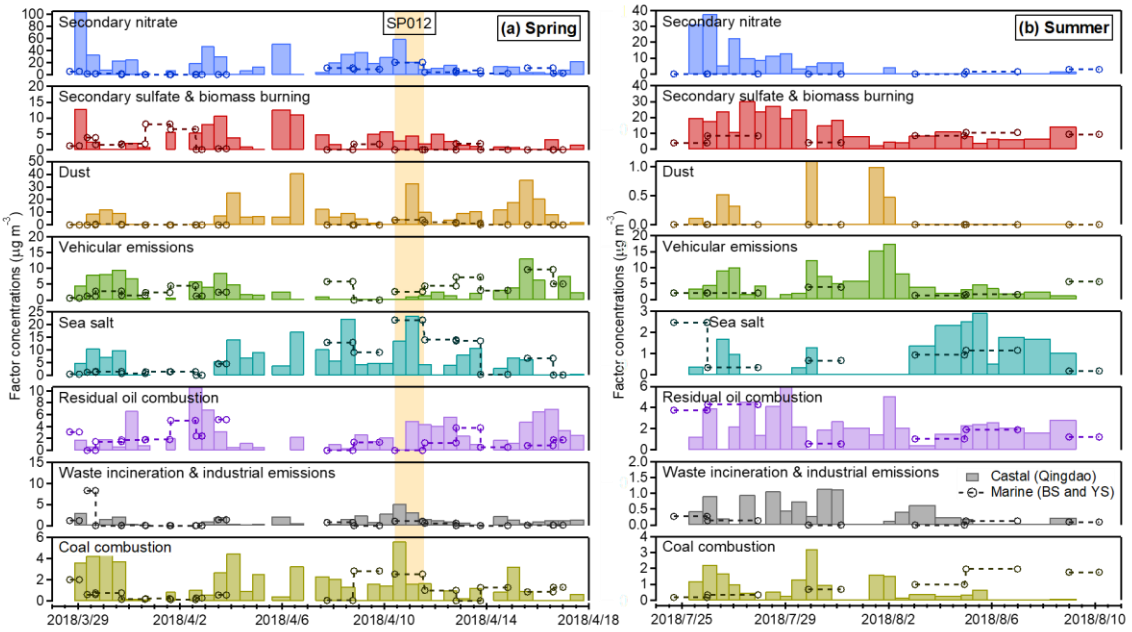


Figure 4: Time series of individual PMF factor concentrations for $PM_{2.5}$ in (a) spring and (b) summer. "SP012" marked in (a) shows the factor concentrations during the sampling period of sample SP012. The detailed procedure for converting the model's factor contribution output to concentrations is provided in Text S3.

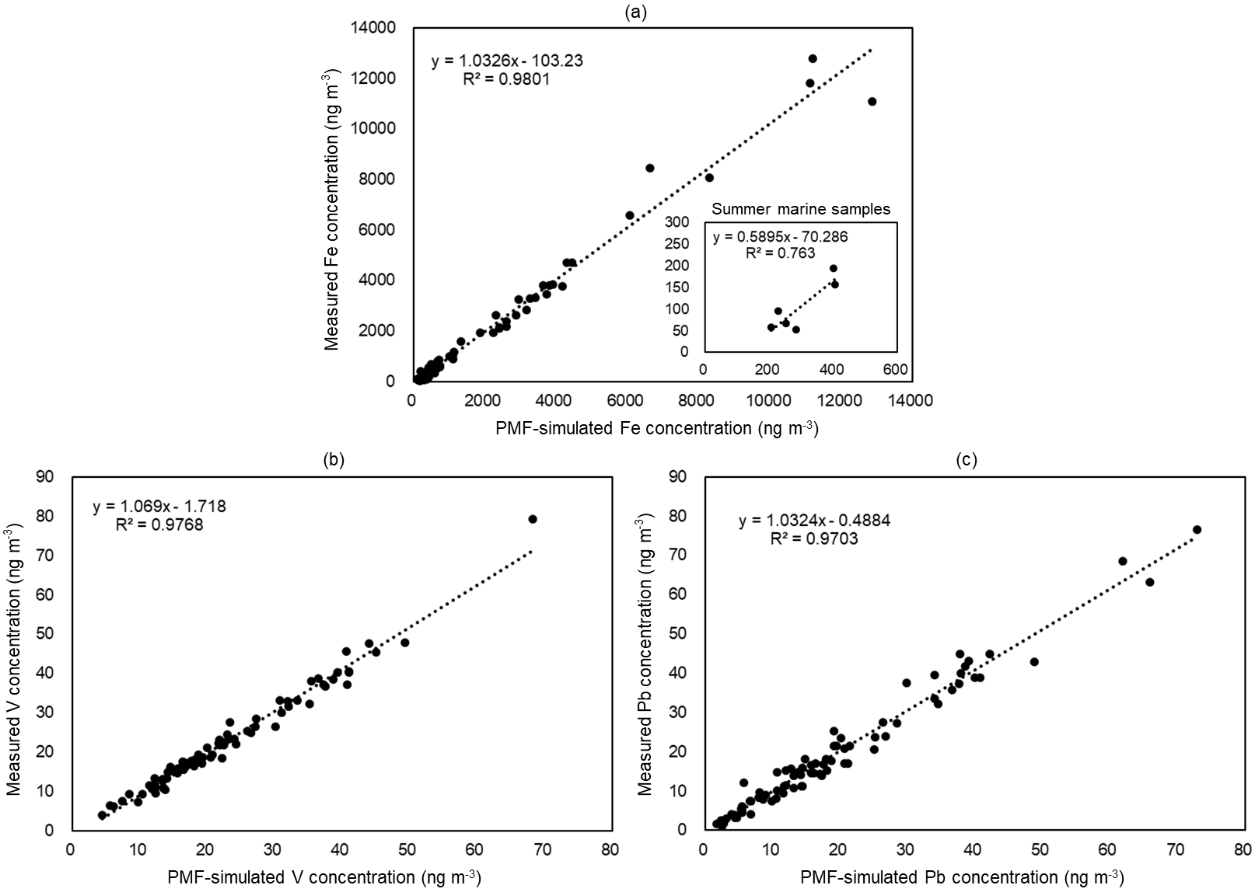


Figure S11. *Comparison of measured and PMF-simulated concentrations (ng m^{-3}): (a) Fe, (b) V, and* *(c) Pb.*

References:

Dai, Q., Hopke, P. K., Bi, X., and Feng, Y.: Improving apportionment of $PM_{2.5}$ using multisite PMF by constraining G-values with a priori information. Sci. Total Environ., 736, 139657. https://doi.org/10.1016/j.scitotenv.2020.139657, 2020.

Sofowote, U. M., Su, Y., Dabek-Zlotorzynska, E., Rastogi, A. K., Brook, J. and Hopke, P. K.: Sources and temporal variations of constrained PMF factors obtained from multiple-year receptor modeling of ambient $PM_{2.5}$ data from five speciation sites in Ontario, Canada. Atmos. Environ., 108, 140-150. https://doi.org/10.1016/j.atmosenv.2015.02.055, 2015a.

Sofowote, U. M., Su, Y., Dabek-Zlotorzynska, E., Rastogi, A. K., Brook, J. and Hopke, P. K.: Constraining the factor analytical solutions obtained from multiple-year receptor modeling of ambient $PM_{2.5}$ data from five speciation sites in Ontario, Canada. Atmos. Environ., 108, 151-157. https://doi.org/10.1016/j.atmosenv.2015.02.045, 2015b.

Comment 2:

2. In this manuscript, terms such as "coastal area," "offshore area," and "marine area" are frequently used to indicate aerosol sampling sites in Qingdao, the Bohai Sea (BS), and the Yellow Sea (YS). "Coastal" presumably refers to Qingdao. In the case of "offshore" and "marine", it was often unclear whether they referred exclusively to either the Bohai Sea or the Yellow Sea, or to both regions together. As a result, it took considerable effort to determine (and in many cases I could not determine) which area the terms "marine/offshore aerosol" referred to throughout the manuscript, which significantly reduced readability. Therefore, I strongly suggest that the sampling sites be explicitly specified as Qingdao, BS, and YS, in order to improve clarity.

Response:

We thank the reviewer for this critical comment regarding terminology clarity. We have thoroughly revised the manuscript to address this issue as follows (sentences, figures and tables that have already been presented in responses to other comments are not displayed here):

(i) Text revision: Throughout the main text, we have replaced ambiguous terms ("coastal area", "offshore area", "marine area") with explicit site specifications ("Qingdao", "BS", "YS") to ensure precise geographical referencing (the abstract is excluded). Due to the extensive nature of the revisions, they are not fully presented here.

Lines 135-137: *"In this study, the mass concentrations of 12 elements (V, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Cd, Ba and Pb), 9 water-soluble ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-} and $C_2O_4^{2-}$),* *and OC/EC from both Qingdao and cruise campaigns (81 samples) were input to the PMF analysis."*

Lines 210-211: *"This factor contributed a significant proportion of fine particles in both Qingdao and marine environments, accounting for 34.9% and 16.9% of $PM_{2.5}$ mass respectively (Fig.5b)."*

Lines 221-222: *"This factor accounted for 19.4% and 24.3% of the $PM_{2.5}$ mass in Qingdao and marine regions respectively."*

Lines 236-237: *"Factor 4 was identified as the vehicular emissions factor, characterized by significant apportionments for EC and OC, contributing 10.4% to the total Qingdao aerosol mass and 17.6% to the marine aerosols."*

Lines 259-260: *"Factor 6, the residual oil combustion factor, was characterized by high apportionments of V and Ni (Wu et al., 2020), contributing 6.6% and 9.0% to the total $PM_{2.5}$ mass in Qingdao and BS and YS areas, respectively."*

Lines 262-263: *"The contributions of Factor 6 highlighted the significant influence of shipping traffic on both the coastal city Qingdao and the BS and YS areas."*

Lines 292-295: *"Air masses arriving at Qingdao (spring clusters E, S, W and summer cluster L) contained higher concentrations of secondary components like NO_3^- and NH_4^+ (land-based species), which did not fully extend to marine areas (Fig.S4a and c, and Table S8). As NO_3^- and NH_4^+ are primarily associated with terrestrial sources, their influence is more significant in Qingdao."*

Lines 296-297: *"Dust, the second largest contributor in spring, accounted for 19.6% (9.7 µg m^{-3}) in Qingdao but sharply reduced to 2.7% (0.5 µg m^{-3}) over the BS and YS."*

Lines 310-312: *"The vehicular emissions, accounting for 17.9% in marine areas (Fig.5b), had nearly identical average concentrations in both Qingdao and marine environments (3.4 and 3.3 µg m^{-3}, respectively) (Fig.5a)."*

Lines 315-316: *"Residual oil combustion exhibited a lower average concentration in marine areas (1.7 µg m^{-3}) than Qingdao (2.9 µg m^{-3}), indicating the influence of ships and ports emissions on coastal urban areas."*

Lines 450-452: *"Marine aerosols exhibited a pronounced increase in coal combustion contributions (30.0% in spring and 49.1% in summer) compared to Qingdao particles, likely due to emissions from coastal power plants transported seaward."*

Lines 478-479: *"Similarly, coal combustion was identified as the primary source of As (34.6–75.0%), with its influence increasing over the BS and YS during spring (59.7%) and summer (75.0%) (Fig.6j)."*

Lines 492-494: *"Eight aerosol sources were identified in Qingdao and BS and YS regions, including secondary nitrate, the mixture of secondary sulfate and biomass burning, dust, vehicular emissions, sea salt, residual oil combustion (ship emissions), coal combustion, and the mixture of waste incineration and industrial pollutants."*

(ii) Figure revision: Relevant figures in the main text and Supplementary Materials have been updated, including titles, axis labels, and legends, to consistently use the specific site names (Qingdao, BS, YS). For example, see Fig.4 in Comment 1 in page R12 and Fig.5.

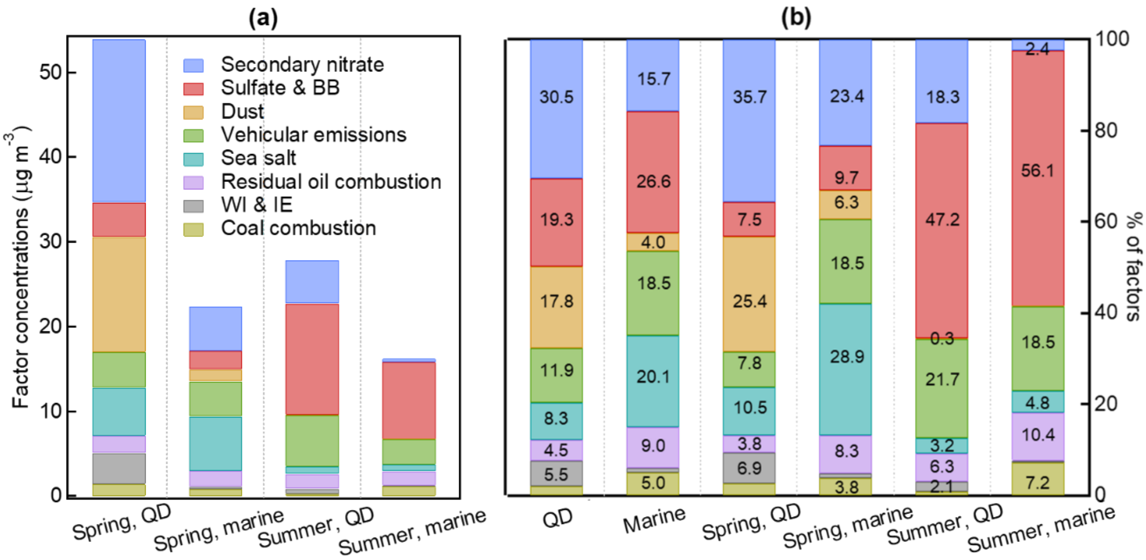


Figure 5: The averaged (a) concentrations and (b) relative percentage contributions of identified source factors to $PM_{2.5}$ as determined by PMF analysis. Sulfate & BB refers to sulfate & biomass burning. WI & IE denotes waste incineration & industrial emissions. "marine" refers to the BS and YS.

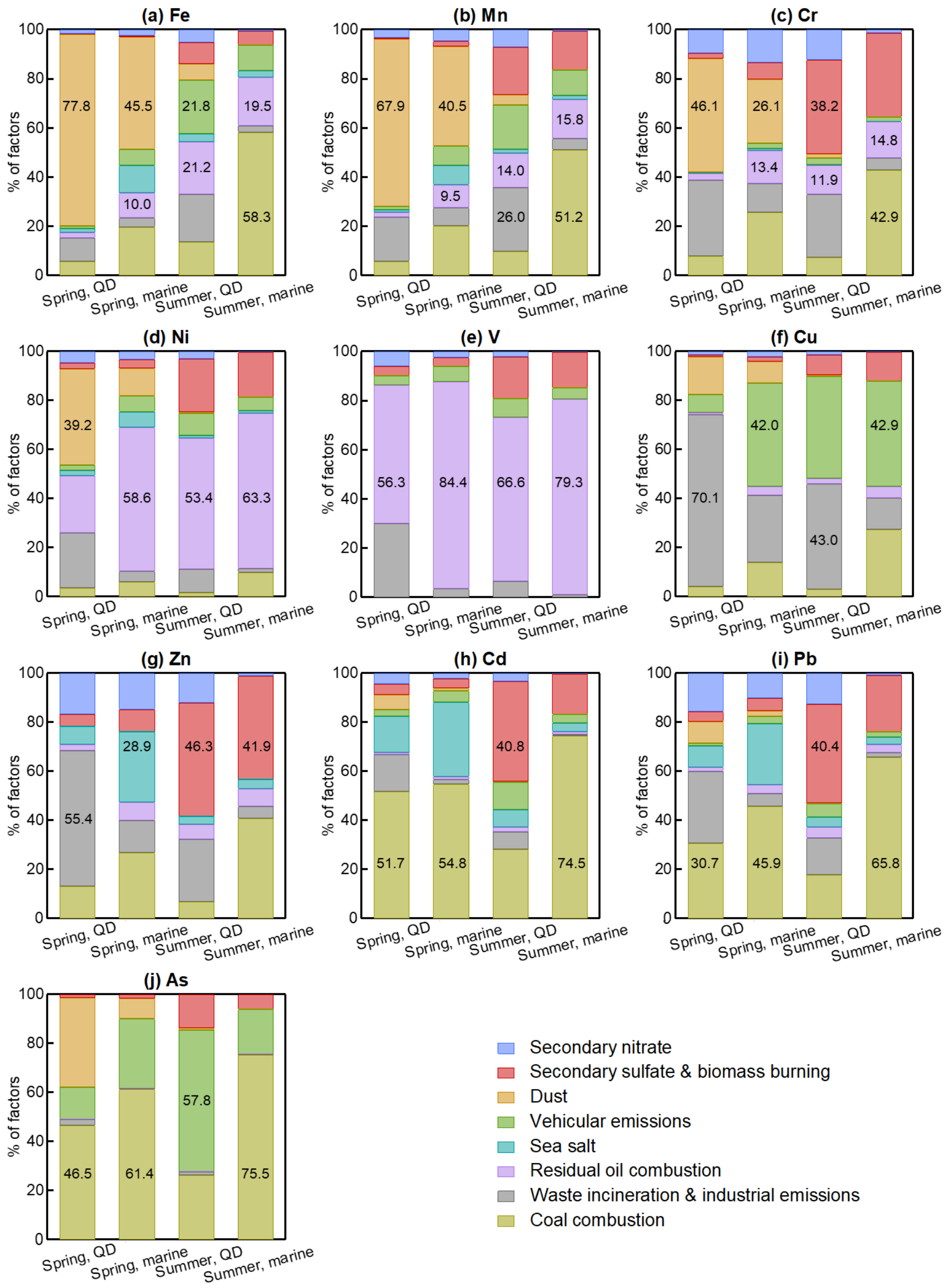


Figure 6: Percentage contributions of various source factors to individual elements based on PMF results. “marine” refers to the BS and YS.

*“**Figure S3.** Temporal variations of meteorological parameters and selected species concentrations (μg m^{-3}) in (a) spring and (b) summer. “SP012” marked in (a) show the information about the sampling period for sample SP012. “Marine area” refers to the BS and YS.”*

*“**Figure S4.** To explore the influence of air mass history on variations in trace element abundances, the backward trajectories calculated by HYSPLIT model were classified into six categories in spring*

and three in summer at the coastal city site (Qingdao), using a systematic clustering method implemented in the software SPSS (Statistical Product and Service Solutions) Statistics v21. For the cruise missions, the trajectory endpoints corresponded to the cruise coordinates, thus the samples were manually classified into three categories in both seasons. Averaged 72 h backward trajectories of air masses arriving at 300 m altitudes and the averaged concentrations of trace elements and ions of individual clusters in spring at (a) the coastal site (Qingdao) and (b) marine areas (BS and YS) and in summer at (c) the coastal site and (d) marine areas. The black star indicates the coastal site, Qingdao. The solid black line indicates the cruise tracks. "YS-O" means "YS-ocean". Al and Fe use the left labels; other elements use the right labels."

(iii) Table revision: Table titles in the Supplementary Materials have been modified to explicitly identify the sampling sites (Qingdao, BS, YS).

*"**Table S8.** The information of averaged 72 h air mass backward trajectory clusters arriving at the coastal site (Qingdao) and marine area (BS and YS) in spring and summer."*

*"**Table S9.** Percentage contributions (%) of various source factors to individual elements based on PMF. "Marine" refers to the BS and YS areas, while "coastal" refers to Qingdao, hereinafter the same."*

Comment 3:

3. In the discussion of source contributions to $PM_{2.5}$, it is excellent that both relative contributions (percentages) and absolute contributions (atmospheric concentrations: µg/m^3) are presented. Unfortunately, the discussion for the source apportionment of metal elements in Sect. 4.3 seems to be based solely on relative contributions. When assessing the supply of metal elements to the ocean, the absolute deposition is more important than the relative contribution of anthropogenic emissions. For instance, while the contribution of coal combustion-derived Fe to $PM_{2.5}$ is higher in summer (60%) than in spring (about 20%) over the Yellow Sea, the Fe concentration itself is more than three times higher in spring than in summer (Fig. 2). Therefore, the deposition of coal combustion-derived Fe to the ocean surface is likely higher in spring or at least comparable to summer. In my view, the regional and seasonal variations in relative source contributions are considerably smaller than the variations observed in absolute concentrations. Thus, as demonstrated earlier for Fe emitted from coal combustion, similar cases are likely to occur in the discussions of other elements as well. Consequently, the current description could lead to significant misunderstandings about the seasonality of metal element inputs into the ocean from anthropogenic aerosols. I therefore strongly recommend that a discussion of absolute concentration be included.

Response:

We thank the reviewer for emphasizing the importance of absolute concentrations. We have expanded Sect. 4.3 with detailed discussion of absolute source concentrations and supplemented the Abstract with key absolute concentration data. Regarding the overestimation of marine Fe in summer, we have added a note of caution and, importantly, demonstrated via a scatter plot (Fig.S11) that the PMF model, despite the offset, captures the temporal trend of Fe concentrations with high fidelity (R^2 = 0.76). Additionally, we have included the PMF-simulated performance for V and Pb, representative anthropogenic elements, as reference.

Abstract: *"Long-range transport of trace elements (TEs) by aerosols plays a critical role in modulating marine biogeochemistry; yet, their source contributions and spatial variability across land-sea gradients remain poorly constrained. Here, we investigate TEs (e.g., Fe, Mn, Cr, V, Ni, Cu, Zn, As, Pb, Cd) in* $PM_{2.5}$ *aerosols collected from the coastal city of Qingdao (eastern China) and adjacent offshore regions (Bohai Sea and Yellow Sea) during spring and summer 2018, to quantify terrestrial vs. marine source contributions and unravel key drivers of their spatial patterns. All TEs exhibited higher concentrations in Qingdao than in offshore marine areas in spring, whereas Zn, Pb, As, and Cd (52.5–78.8% from coal combustion over the marine areas) reversed to higher concentrations in offshore marine areas than in Qingdao in summer, indicating intensified anthropogenic impact on the marine atmosphere. For traditional crustal TEs (Fe, Mn, Cr), terrestrial dust dominated in spring Qingdao (e.g., Fe: 62.3%, 148.6 ng* m^{-3}*), but dust contributions declined sharply in spring offshore marine areas (Fe: 16.8%, 52.3 ng* m^{-3}*). Instead, coal combustion emerged as the dominant source in summer offshore marine aerosols (Fe: 43.2%, 82.8 ng* m^{-3}*), exceeding its contribution to Qingdao (Fe: 14.45%, 45.46 ng* m^{-3}*). Ship emissions dominated sources of Ni and V (V: 81.2% in spring, 90.5% in summer) and contributed significantly to Fe, Mn, and Cr, particularly in summer offshore aerosols (e.g., Fe: 27.4%, 52.5 ng* m^{-3}*). Spring offshore marine aerosols showed elevated sea salt contributions to Fe, Mn, Zn, Cd, and Pb (18.5–33.6%), indicating extensive multi-source mixing (dust, sea salt, and anthropogenic sources); the biogeochemical implications of this mixing for element reactivity warrant further investigation. These findings highlight the dominant role of anthropogenic emissions (coal combustion and shipping) in shaping the TE composition of offshore aerosols over the Bohai and Yellow Seas. This work advances our understanding of land-sea interactions in atmospheric TE cycling and offers critical constraints for regional air quality and climate models."*

Sect. 4.3.1, lines 400-414: *"In spring, dust was the dominant source of Fe and Mn in Qingdao,* *contributing 81.6% and 78.6% to the total Fe and Mn, respectively (Fig.6a and b). However, marine aerosols exhibited significantly increased contributions from vehicular emissions (11.0% and 10.6% for Fe and Mn, respectively) and coal combustion (16.2% and 19.5%). Coal combustion contributed 92.4 ng m*$^{-3}$ *Fe and 4.0 ng m*$^{-3}$ *Mn to the marine atmosphere in spring, while dust contributed 145.2 ng m*$^{-3}$ *Fe and 4.8 ng m*$^{-3}$ *Mn (Fig.S10). In summer, coal combustion became the primary contributor to marine Fe and Mn (43.2% and 46.5%, respectively), exceeding Qingdao contributions by 3 times. The absolute concentration from coal combustion was 82.8 ng m*$^{-3}$ *for Fe and 3.6 ng m*$^{-3}$ *for Mn. It should be noted that the PMF-resolved total Fe concentration in marine aerosols during summer was higher than the measured value, indicating a proportional overestimation in absolute source contributions. However, the strong correlation between PMF-simulated and measured Fe concentrations confirms the robustness of the relative source apportionment. Detailed discussion on this discrepancy and its implications is provided in Text S3 and Fig.S11a. This shift highlights the long-range transport of fine anthropogenic particles to marine regions, enriching aerosols with pollution-derived elements. The comparison of source concentrations revealed that coal combustion was a substantial source of Fe to the marine aerosols in both seasons, with its importance increasing in summer. Nevertheless, in terms of absolute concentration, the spring contribution to Fe was slightly higher than that in summer. It is noteworthy that residual oil combustion was also a discernible source for Fe and Mn in summer (contributing 26.1%, 50.0 ng m*$^{-3}$ *and 24.4%, 1.9 ng m*$^{-3}$ *respectively in marine areas)."*

Text S3: *"Based on the established 8-factor PMF solution, a detailed evaluation of its performance in simulating Fe concentrations was conducted. The results showed that while the model performed well for most elements (e.g., Fig.S11b and c), the PMF-resolved total Fe in marine aerosols in summer (191.5 ng m*$^{-3}$*) was substantially higher than the measured concentration (109.8 ng m*$^{-3}$*), indicating an overestimation in the absolute source concentrations for Fe in this specific scenario. Therefore, the reported concentrations by PMF for marine Fe in summer should be interpreted as upper-bound estimates. Crucially, the strong linear correlation (*$r^2 = 0.98$, $p < 0.01$*) between the PMF-simulated and measured Fe concentrations (*$r^2 = 0.76$, $p = 0.02$ *for summer marine samples; Fig.S11a) indicated that the overestimation was proportional. This high coherence in temporal trends strongly suggested that the relative source contributions for Fe remained robust."*

Sect. 4.3.2, lines 459-466: *"Notably, Ni and V primarily originated from residual oil combustion, with contributions being markedly higher over the marine area (46.2–79.8%) compared to the coastal site (26.2–64.8%) (Fig.6d and e). However, the absolute concentrations of Ni and V from residual oil combustion were higher in the Qingdao atmosphere (Ni: 4.8–6.0 ng m*$^{-3}$*, V: 12.8–16.2 ng m*$^{-3}$*) than in* *the BS and YS atmosphere (Ni: 3.1–3.6 ng m^{-3}, V: 8.2–9.6 ng m^{-3}). This demonstrated that the emissions from residual oil combustion had a significant impact not only on the marine environment but, more notably, on the coastal urban air quality.*

Over the BS and YS, coal combustion (21.3–41.2%), vehicular emissions (26.5–29.2%) and WI & IE (13.9–35.3%) contributed more significantly to Cu (Fig.6f).”

Sect. 4.3.3, lines 472-478: *“Source apportionment revealed that coal combustion was the dominant contributor of Pb and Cd in BS and YS areas, particularly during summer, accounting for 71.6% of Pb and 78.8% of Cd (Fig.6h and i). The absolute concentrations revealed the land-to-sea transport: coal combustion contributed 4.6 ng m^{-3} of Pb to the marine atmosphere in summer, which was 1.8 times higher than its concentration in Qingdao (2.6 ng m^{-3}), clearly indicating the pervasive influence of terrestrial coal emissions across the sea. In Beijing, the predominant sources of Pb were coal combustion in spring and industrial emissions in summer (Yang et al., 2022), mirroring our coastal observations.”*

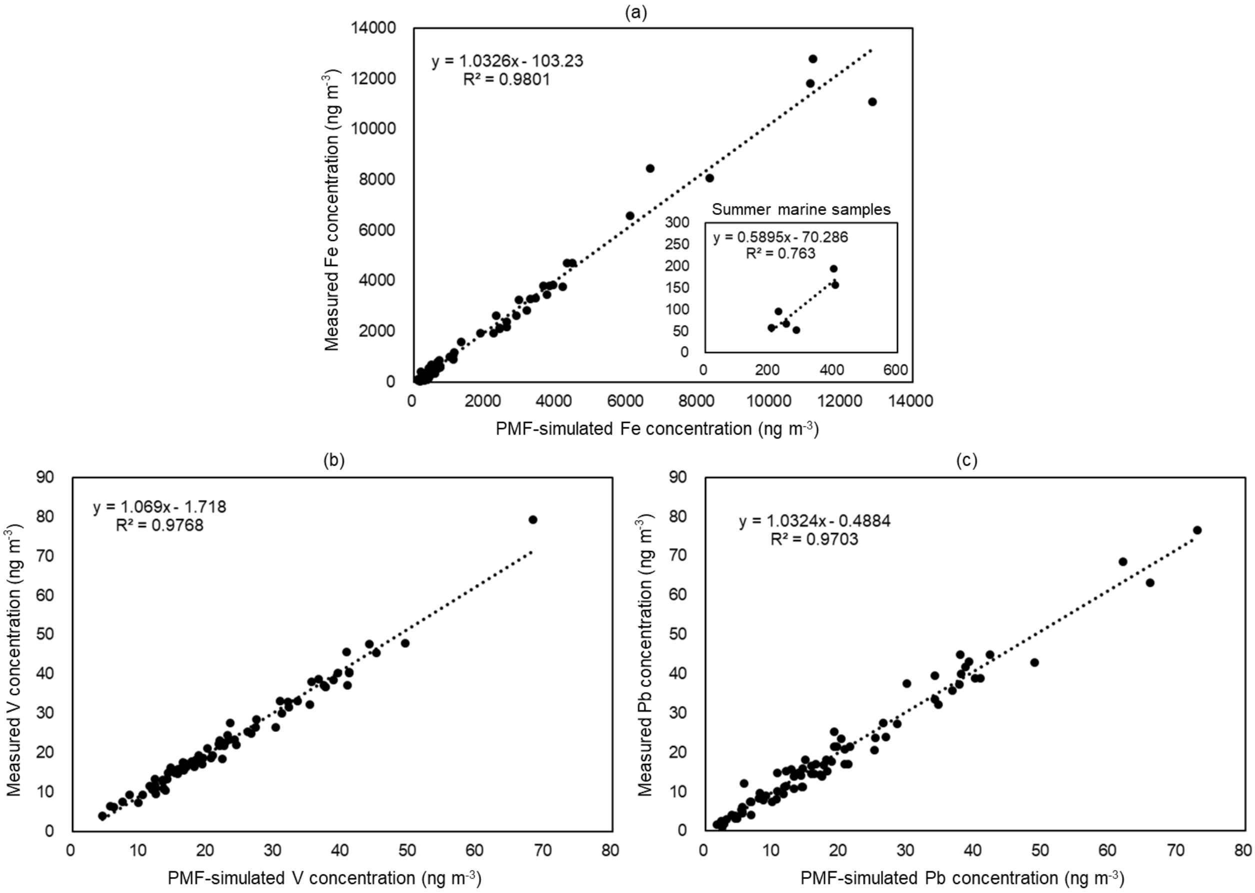


Figure S11. *Comparison of measured and PMF-simulated concentrations (ng m^{-3}): (a) Fe, (b) V, and (c) Pb.*

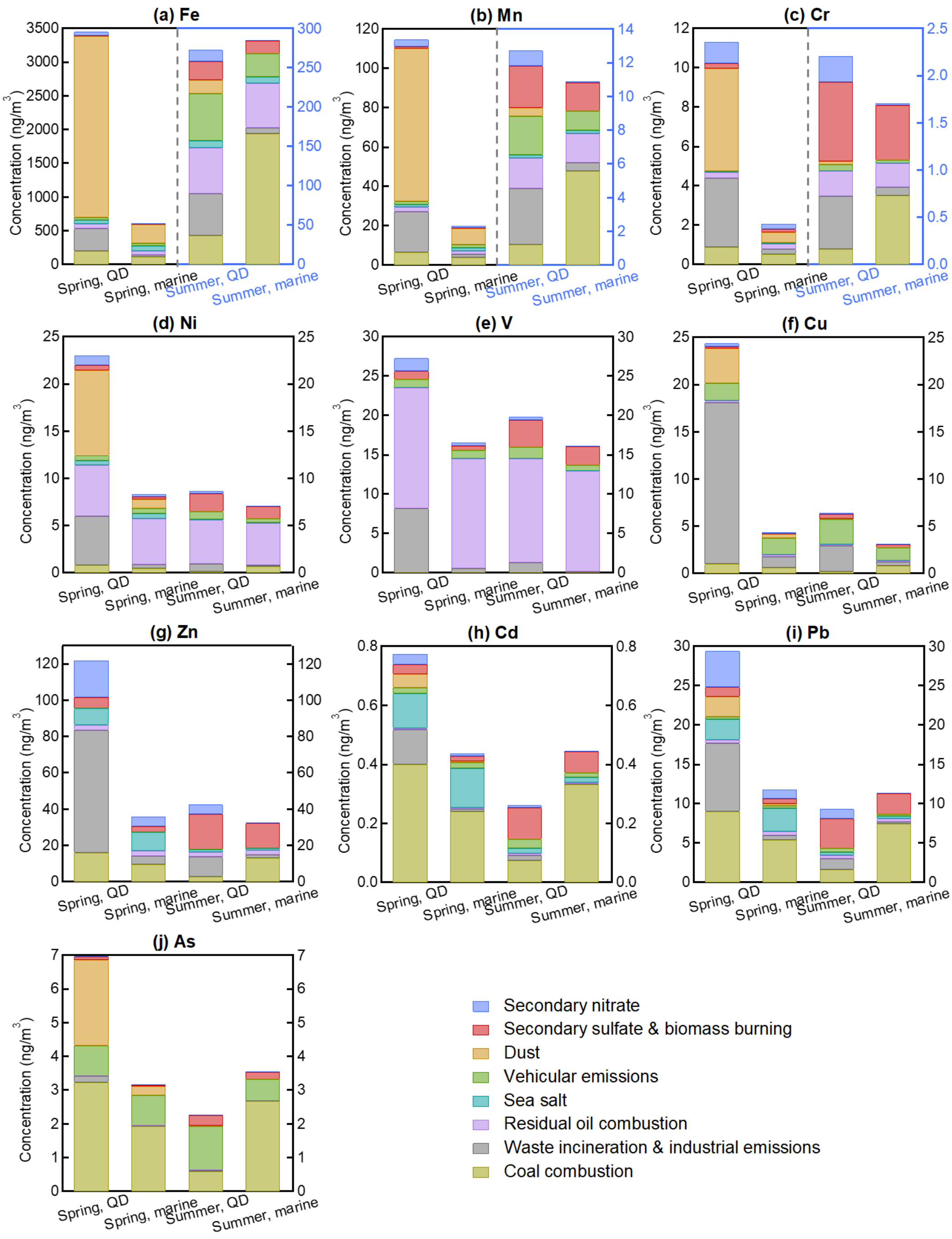


Figure S10. Concentrations of various source factors to individual elements based on PMF results. "marine" refers to the BS and YS. For Fe, Mn, and Cr, the left and right axes (spring vs. summer) use different scales, distinguished by color (right axis in blue).

During the revision of Table S10, we noticed a minor inaccuracy in the wording of Table S9 and have accordingly revised its caption:

"Note. Sulfate & BB represents sulfate & biomass burning. VE represents vehicular emissions. ROC represents residual oil combustion. WI & IE represents waste incineration & industrial emissions. CC represents coal combustion. A dash (-) indicates that the species is entirely absent from the factor

profile for that period, not that its concentration is rounded to zero, hereinafter the same.”

Table S10. *Concentrations (ng m^{-3}) of various source factors to individual elements based on PMF.*

Element	Season	location	Secondary nitrate	Sulfate & BB	Dust	VE	Sea salt	ROC	WI & IE	CC
Fe	Spring	Coastal	50.12	3.80	2832.00	63.72	212.82	98.67	38.36	170.19
		Marine	10.72	1.99	145.19	62.62	191.58	58.26	8.14	92.36
	Summer	Coastal	13.73	13.76	33.33	94.03	30.60	77.79	13.92	45.46
		Marine	1.11	5.49	-	31.90	18.75	50.02	1.48	82.77
Mn	Spring	Coastal	4.29	0.28	92.73	2.20	6.70	3.67	0.89	7.30
		Marine	0.92	0.14	4.75	2.16	6.03	2.17	0.19	3.96
	Summer	Coastal	1.17	1.00	1.09	3.24	0.96	2.89	0.32	1.95
		Marine	0.09	0.40	-	1.10	0.59	1.86	0.03	3.55
Cr	Spring	Coastal	0.80	0.17	6.88	0.10	0.17	0.37	1.74	1.15
		Marine	0.17	0.09	0.35	0.10	0.16	0.22	0.37	0.63
	Summer	Coastal	0.22	0.60	0.08	0.15	0.02	0.30	0.63	0.31
		Marine	0.02	0.24	-	0.05	0.02	0.19	0.07	0.56
Ni	Spring	Coastal	1.06	0.30	9.63	0.60	1.73	6.04	2.58	1.07
		Marine	0.23	0.16	0.49	0.59	1.56	3.57	0.55	0.58
	Summer	Coastal	0.29	1.10	0.11	0.89	0.25	4.76	0.96	0.29
		Marine	0.02	0.44	-	0.30	0.15	3.06	0.10	0.52
V	Spring	Coastal	2.37	0.74	0.31	1.21	2.23	16.23	4.23	-
		Marine	0.51	0.38	0.02	1.18	2.01	9.58	0.90	-
	Summer	Coastal	0.65	2.66	0.00	1.78	0.32	12.80	1.54	-
		Marine	0.05	1.06	-	0.60	0.20	8.23	0.16	-
Cu	Spring	Coastal	-	0.23	12.59	1.22	-	-	7.51	1.77
		Marine	-	0.12	0.64	1.20	-	-	1.59	0.96
	Summer	Coastal	-	0.82	0.15	1.80	-	-	2.73	0.47
		Marine	-	0.33	-	0.61	-	-	0.29	0.86
Zn	Spring	Coastal	14.36	2.90	24.79	-	7.83	5.16	46.12	21.82
		Marine	3.07	1.52	1.27	-	7.05	3.05	9.79	11.84
	Summer	Coastal	3.93	10.50	0.29	-	1.13	4.07	16.74	5.83
		Marine	0.32	4.19	-	-	0.69	2.62	1.78	10.61
Cd	Spring	Coastal	0.07	0.02	0.17	0.04	0.10	0.00	-	0.41
		Marine	0.01	0.01	0.01	0.04	0.09	0.00	-	0.22
	Summer	Coastal	0.02	0.05	0.00	0.06	0.01	0.00	-	0.11
		Marine	0.00	0.02	-	0.02	0.01	0.00	-	0.20
Pb	Spring	Coastal	5.41	0.43	7.02	0.92	2.24	0.62	3.19	9.53
		Marine	1.16	0.23	0.36	0.90	2.01	0.37	0.68	5.17
	Summer	Coastal	1.48	1.57	0.08	1.35	0.32	0.49	1.16	2.55
		Marine	0.12	0.63	-	0.46	0.20	0.31	0.12	4.64
As	Spring	Coastal	0.24	0.02	2.88	0.84	-	-	0.03	2.86
		Marine	0.05	0.01	0.15	0.83	-	-	0.01	1.55
	Summer	Coastal	0.07	0.08	0.03	1.25	-	-	0.01	0.76
		Marine	0.01	0.03	-	0.42	-	-	0.00	1.39

Note. Sulfate & BB represents sulfate & biomass burning. VE represents vehicular emissions. ROC represents residual oil combustion. WI & IE represents waste incineration & industrial emissions. CC represents coal combustion. Absolute source concentrations are reported with two decimal places to accurately represent low concentration values and to avoid reporting 0.0 ng m^{-3} for non-zero concentrations. This provides a more precise dataset for reference. The main text adheres to the one-

decimal-place convention for consistency in presentation.

Specific comments

Comment 4:

L20: Confirm whether Ni is truly from nearby sources. In the following text, it is stated that most Ni originates from heavy oil combustion.

Response:

We thank the reviewer for this insightful comment regarding the source of Ni. We have revised the manuscript to present a more precise and nuanced interpretation of Ni's origins. Ni is a multi-source element, and our PMF results reveal distinct spatial and seasonal variations in its dominant sources. Specifically, over land in spring, Ni inputs are jointly influenced by dust (41.9%) and anthropogenic sources (including heavy oil combustion, 26.2%). In contrast, over the spring ocean and during summer (both land and marine environments), Ni is unequivocally dominated by residual oil combustion, accounting for 46.2% (spring ocean) and 55.2%/66.6% (summer land/marine), respectively.

Additionally, the enrichment factor (EF) of Ni exhibits notable seasonality and land-sea differences, further supporting these source patterns. Over land, Ni EF values decreased to 1–10 in spring but increased to over 10 in summer. In marine environments, Ni EF was consistently higher than over land, with values of about 10 (spring) and 10–100 (summer), respectively. These EF variations—coupled with the PMF source apportionment results—collectively confirm that Ni sources are strongly modulated by seasonal and land-ocean gradients. The abstract now is rewrite.

"Abstract. *Long-range transport of trace elements (TEs) by aerosols plays a critical role in modulating marine biogeochemistry; yet, their source contributions and spatial variability across land-sea gradients remain poorly constrained. Here, we investigate TEs (e.g., Fe, Mn, Cr, V, Ni, Cu, Zn, As, Pb, Cd) in* $PM_{2.5}$ *aerosols collected from the coastal city of Qingdao (eastern China) and adjacent offshore regions (Bohai Sea and Yellow Sea) during spring and summer 2018, to quantify terrestrial vs. marine source contributions and unravel key drivers of their spatial patterns. All TEs exhibited higher concentrations in Qingdao than in offshore marine areas in spring, whereas Zn, Pb, As, and Cd (52.5–78.8% from coal combustion over the marine areas) reversed to higher concentrations in offshore marine areas than in Qingdao in summer, indicating intensified anthropogenic impact on the marine atmosphere. For traditional crustal TEs (Fe, Mn, Cr), terrestrial dust dominated in spring Qingdao (e.g., Fe: 62.3%, 148.6 ng* m^{-3}*), but dust contributions declined sharply in spring offshore marine areas*

(Fe: 16.8%, 52.3 ng m^{-3}). Instead, coal combustion emerged as the dominant source in summer offshore marine aerosols (Fe: 43.2%, 82.8 ng m^{-3}), exceeding its contribution to Qingdao (Fe: 14.45%, 45.46 ng m^{-3}). Ship emissions dominated sources of Ni and V (V: 81.2% in spring, 90.5% in summer) and contributed significantly to Fe, Mn, and Cr, particularly in summer offshore aerosols (e.g., Fe: 27.4%, 52.5 ng m^{-3}). Spring offshore marine aerosols showed elevated sea salt contributions to Fe, Mn, Zn, Cd, and Pb (18.5–33.6%), indicating extensive multi-source mixing (dust, sea salt, and anthropogenic sources); the biogeochemical implications of this mixing for element reactivity warrant further investigation. These findings highlight the dominant role of anthropogenic emissions (coal combustion and shipping) in shaping the TE composition of offshore aerosols over the Bohai and Yellow Seas. This work advances our understanding of land-sea interactions in atmospheric TE cycling and offers critical constraints for regional air quality and climate models."

In the Conclusion, we have removed Ni from the discussion of seasonal terrestrial-to-marine shifts to prevent overgeneralization. Our revised analysis clarifies that Ni primarily originates from ship emissions (residual oil combustion), with notable dust contributions (41.9%) in spring over Qingdao. This distinction is now addressed separately in the results section with supporting data.

Lines 508-515: *"Regarding the sources distribution, traditional crustal TEs (Fe, Mn, Cr), terrestrial dust dominated their spring levels in Qingdao (Fe: 81.6%, 2832.0 ng m^{-3} ; Mn: 78.6%, 92.7 ng m^{-3}; Cr: 60.4%, 6.9 ng m^{-3}), but contributions sharply decreased over marine areas (Fe: 25.4%, 145.2 ng m^{-3} ; Mn: 23.4%, 4.8 ng m^{-3}; Cr: 16.9%, 0.4 ng m^{-3}). Instead, coal combustion became the dominant source of these elements, particularly in summer marine areas (Fe: 43.2%, 82.8 ng m^{-3}; Mn: 46.5%, 3.6 ng m^{-3}; Cr: 49.1%, 0.6 ng m^{-3}). Ship emissions not only dominated the Ni and V sources (except spring Qingdao Ni, 41.9% sourced from dust), but also contributed substantially to Fe, Mn and Cr, particularly in summer (Fe: 24.1%, 77.8 ng m^{-3} in Qingdao and 26.1%, 50.0 ng m^{-3} marine; Mn: 22.9%, 2.9 ng m^{-3} in Qingdao and 24.4%, 1.9 ng m^{-3} marine)."*

Comment 5:

L24: In the abstract, vehicular emissions are described as important for As and Cu, but in the main text, vehicular emissions are reported to be important for OC/EC, Cu, and Zn. Please clarify which is correct.

Response:

We thank the reviewer for identifying this inconsistency. The abstract emphasizes the quantitative contribution of the vehicular emission factor to specific elements (As and Cu) based on our PMF results, reflecting their significant fractional contributions from this source. In the main text, the cited sentence served to justify the identification of this factor as vehicular emissions by describing its chemical source profile: EC and OC were the primary tracers (consistent with vehicular exhaust signatures), with Cu serving as supplementary evidence (e.g., from brake/tire wear or fuel additives). The original manuscript, "*The presence of Cu and Zn was likely due to additives in motor oil, fuel/lubricant combustion, brake linings and tire wear (Lee et al., 2006; Pant and Harrison, 2013)*", cited literature reporting both Cu and Zn. However, we only observed high loading for Cu. Zn in this sentence was also confusing, and has been removed. To resolve confusions, we have revised the text in Sect. 4.1 as follows:

(i) Removed Zn in the manuscript Sect. 4.1 (lines 238-240), explicitly focusing on Cu:

"The presence of Cu was likely due to additives in fuel/lubricant combustion, brake linings and tire wear (Gu et al., 2011; Lee et al., 2006; Pant and Harrison, 2013), further supporting this identification."

(ii) Retained and clarified the quantitative contribution of vehicular emissions to As in Sect. 4.3.3 (lines 480-482), aligning with the abstract:

"Furthermore, vehicular emissions also contributed significantly to As (12.3–56.6%), which can be attributed to the role of As as a recognized tracer for fossil fuel combustion (Chen et al., 2013)."

Comment 6:

L26–29: The abstract states that ship emissions had a significant impact on Fe and Mn, whereas the main text indicates that the impact was from coal combustion (in fact, the main text does not explicitly mention Fe from ship or heavy oil combustion).

Response:

We sincerely thank the referee for this critical observation. While the ship emissions (residual oil combustion) source was a discernible source for Fe and Mn, coal combustion was unequivocally the dominant anthropogenic source for these elements in marine aerosols, especially in summer.

In the Abstract: We have removed the phrase regarding ship emissions' impact on Fe/Mn and replaced it with the accurate statement.

"All TEs exhibited higher concentrations in Qingdao than in offshore marine areas in spring, whereas Zn, Pb, As, and Cd (52.5–78.8% from coal combustion over the marine areas) reversed to higher concentrations in offshore marine areas than in Qingdao in summer, indicating intensified anthropogenic impact on the marine atmosphere. For traditional crustal TEs (Fe, Mn, Cr), terrestrial dust dominated in spring Qingdao (e.g., Fe: 62.3%, 148.6 ng m^{-3}), but dust contributions declined

sharply in spring offshore marine areas (Fe: 16.8%, 52.3 ng m^{-3}). Instead, coal combustion emerged as the dominant source in summer offshore marine aerosols (Fe: 43.2%, 82.8 ng m^{-3}), exceeding its contribution to Qingdao (Fe: 14.45%, 45.46 ng m^{-3}). Ship emissions dominated sources of Ni and V (V: 81.2% in spring, 90.5% in summer) and contributed significantly to Fe, Mn, and Cr, particularly in summer offshore aerosols (e.g., Fe: 27.4%, 52.5 ng m^{-3})."

In the main text (Sect. 4.3.1, lines 413-423): We have added a sentence to clearly state the contribution from residual oil combustion while emphasizing the dominance of coal combustion: "It is noteworthy that residual oil combustion was also a discernible source for Fe and Mn in summer...," and have also incorporated the statement "Southeasterly winds transported ship-derived pollutants coastward…," which was relocated from the abstract. This revision provides a complete and accurate picture without overstating the role of residual oil combustion.

"It is noteworthy that residual oil combustion was also a discernible source for Fe and Mn in summer (contributing 26.1%, 50.0 ng m^{-3} and 24.4%, 1.9 ng m^{-3} respectively in marine areas). Southeasterly winds transported ship-derived pollutants coastward, markedly increasing the relative contributions of Fe (24.1%) and Mn (22.9%) in Qingdao compared to spring (2.8% and 3.1%, respectively). However, from the perspective of absolute concentration, the contributions of residual oil combustion to Fe and Mn in Qingdao remained lower in summer (77.8 and 2.9 ng m^{-3}, respectively) than in spring (98.7 and 3.7 ng m^{-3}).

These findings align with previous studies: Chen et al. (2024) reported dust as the predominant source of Fe (88%) in Qingdao during spring (Chen et al., 2024), while Zhang et al. (2024) observed substantial contributions from both dust (68.6%) and coal combustion (21.2%) in the YS, ECS, and Northwest Pacific. The findings regarding Mn in Beijing align with our analysis for Qingdao, where dust served as the primary source during spring, but shifted to industrial emissions in summer (Yang et al., 2022)."

Comment 7:

L49–51: If 20% of d-Fe is anthropogenic Fe, this indicates that more than half of the d-Fe originates from mineral dust. In that case, if anthropogenic Fe is indeed more efficient than mineral-derived Fe in promoting primary production, it would be advisable to explain the reasons for this in the discussion.

Response:

Thank you for this valuable suggestion. We have revised the discussion in section 4.3.1 to explicitly address the comment, further clarifying the mechanistic explanation for anthropogenic Fe. The new text clarifies that the higher bioavailability of anthropogenic Fe stems from its finer particle size and greater susceptibility to atmospheric acid processing, compared to refractory mineral dust (Shi et al., 2012; Ito et al., 2021).

Lines 424-430: *"Notably, our source apportionment revealed a significant contribution of anthropogenic combustion to total Fe (Fig.6a). Such anthropogenic Fe was reported to typically exhibit higher solubility, in comparison with Fe from natural sources such as mineral dust (Ito et al., 2021; Sun et al., 2024). The greater solubility and consequent higher efficiency in enhancing productivity can be explained by the physicochemical properties of the particles. Combustion processes emit Fe in finer particles with a larger surface-area-to-volume ratio. Such particles are more susceptible to atmospheric acid processing, which efficiently converts insoluble Fe into soluble forms (Shi et al., 2012; Ito et al., 2021). In contrast, Fe in natural mineral dust is largely encapsulated within refractory aluminosilicate minerals, making Fe less available for solubilization."*

Comment 8:

L65–69: This study performed the source apportionment of total metals, not dissolved metals. Consequently, it is difficult to address whether atmospheric processes affect metal solubility or not. Therefore, it seems inconsistent to present such discussion as if it were directly linked to the objectives of this study.

Response:

Thank you. We have revised the introduction to clarify the scope. The revised text states clearly that this study focuses on the source apportionment of total elements, which is a critical step for the discussed biogeochemical impact.

Lines 66-74: *"Atmospheric processes during long-range transport from the continent to ocean can alter the physicochemical properties of aerosols, thereby influencing the bioavailability of nutrients in the particles upon deposition (Schroth et al., 2009; Sholkovitz et al., 2012; Wang et al., 2022; Wang et al., 2021; Luo et al., 2020; Xu et al., 2023; Zhang et al., 2024). Accurately identifying and apportioning the sources of fine particles and their trace elements, is crucial for quantifying this biogeochemical impact, especially given the differences observed across land-to-sea gradients. This study focuses on the characteristics and source apportionment of elements in* $PM_{2.5}$*, based on simultaneous observations in Qingdao and during BS and YS research cruises in the spring and summer of 2018 (Fig.1). The major purpose is to provide a more comprehensive understanding of the distribution and sources of trace elements in fine particles from coastal to marginal sea areas in eastern China."*

Comment 9:

L71: Typo: contributs → contributes.

Response:

We thank the reviewer for pointing out this typo. The sentence was modified in response to other comments (refer to responses to Comment 8).

Comment 10:

L83–84: Are the 18 and 9 samples the combined totals from the Bohai Sea (BS) and Yellow Sea (YS) in spring and summer, respectively? If that is the case, please specify the number of samples from each region.

Response:

We thank the reviewer for seeking this clarification. Yes, the numbers 18 and 9 refer to the total marine samples collected in spring and summer, respectively. In the revision, it was clarified in Sect. 2.1:

Lines 84-86: *"A total of 18 and 9 samples were collected in spring and summer over the marine areas, respectively. Specifically, these comprised 3 samples from the BS and 15 from the YS in spring, and 2 from the BS and 7 from the YS in summer."*

Comment 11:

L108–109: Please clarify the rationale for analyzing filter blanks every 10 samples.

Response:

We thank the reviewer for this comment. We have clarified the rationale in the manuscript and Supplementary Materials (Text S1b):

Lines 113-116: *"Water-soluble ionic species, including Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-} and $C_2O_4^{2-}$, were analyzed using a Dionex ICS-3000 ion chromatography. To monitor instrumental precision/accuracy and quantify background contamination over the analytical sequence, blank filter solutions and standard solutions were analyzed every 10 samples. See Text S1b for additional QA/QC details."*

Text S1: *"**(b) Water-soluble ions***

Standard solutions were analyzed after every 10 samples to monitor instrumental precision and accuracy. Blank filters were analyzed at the same frequency to quantify and subtract any contamination introduced during the sample extraction process."

Comment 12:

L145–146: Please elaborate the reasons for concluding that Zn is of anthropogenic origin. And what does it mean that anthropogenic zinc shows the highest concentration? Enrichment factor relative to average upper continental crust (EF = $(X/Al)_{aerosol}/(X/Al)_{crust}$, X is your target elements) is helpful to discuss source of metal elements in aerosol particles.

Response:

We thank the reviewer for the suggestion. We have included Enrichment Factor (EF) analysis in the revision. The method is described in the Supplementary Materials section (Text S2), and results are in Fig.S2. The high EF for Zn (>100) robustly confirms its dominant anthropogenic origin, as stated in the revised text. We have revised the sentence on Lines 151–155 to clarify that zinc (Zn) was the most abundant among the measured anthropogenic trace elements (e.g., Pb, Cd, As, Cu), not compared to crustal elements:

"In the coastal city, the dominant trace elements were Al and Fe, with average concentrations of 5573.5 ± 5641.1 and 3347.3 ± 3249.3 ng m^{-3} in spring and 572.9 ± 395.4 and 228.3 ± 211.7 ng m^{-3} in summer, followed by Mn in spring and Zn in summer, respectively (Fig.2c). Among the measured anthropogenic trace elements (e.g., Pb, Cu, As, Cd), Zn was the most abundant in both marine and coastal environments, with its anthropogenic origin confirmed by a high enrichment factor (Text S2 and Fig.S2) (Taylor, 1964)."

*"**Text S2:** Enrichment factor (EF) calculation*

The EF was calculated to assess the anthropogenic influence on trace elements using Al as a reference element (R). The calculation followed the equation:

$$EF = \frac{(C_X/C_R)_{aerosol}}{(C'_X/C'_R)_{crustal}} \qquad (1)$$

Where C_X is the concentration of element X in aerosols, C_R is the concentration of the reference element R in aerosols, and the denominator is the ratio of the content of element X to R in the Earth's crust. The crust values were taken from the upper continental crust composition reported by Taylor (1964)."

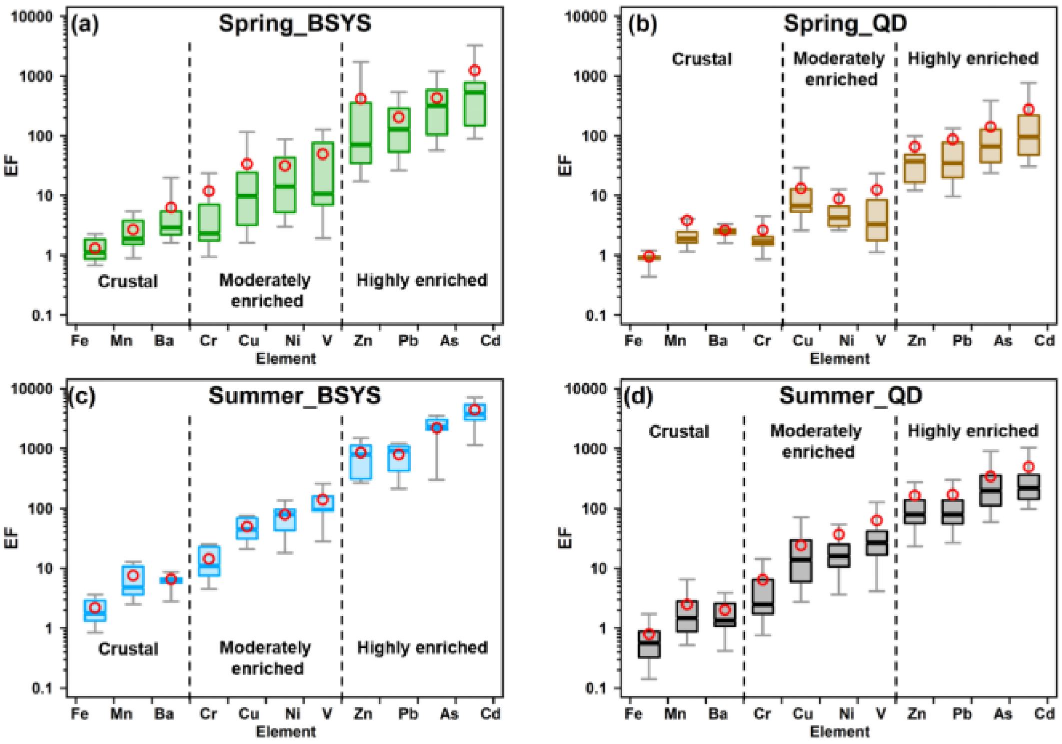


***Figure S2:** Elemental EFs in fine particles over (a) spring BS and YS, (b) spring QD, (c) summer BS and YS, and (d) summer QD. 25th and 75th percentile boxes; 10th and 90th percentile whiskers; the solid line is the median value, and the red circle is the mean value.*

Reference:

"Taylor, S. R.: Trace element abundances and the chondritic earth model, Geochim. Cosmochim. Ac., 28, 1989-1998, https://doi.org/10.1016/0016-7037(64)90142-5, 1964."

Comment 13:

L152–154: Figure 2 appears to plot the average metal concentrations of aerosols collected from each region. However, average values are highly sensitive to outliers with extremely high concentrations, particularly when the number of samples is small. Consequently, the higher mean concentrations of Zn observed in summer compared to spring at YS are likely influenced by samples such as SU005. Therefore, it is important to carefully consider whether SU005 should be included in the calculation of summer average concentrations (or consider plotting the median values instead of the mean) when comparing with spring samples.

Furthermore, this sample frequently appears in discussions of key aspects of this study. Omitting detailed information about SU005 in the manuscript would therefore be highly unhelpful, and its characteristics should be explicitly addressed within the discussion.

Response:

We sincerely thank the reviewer for this critical observation regarding the sensitivity of mean values to outliers in small sample sizes. We fully agree and have implemented the following revisions in the manuscript:

(i) Exclusion of influential outlier: The potentially influential sample SU005 was excluded from the dataset used for the PMF source apportionment analysis and from all subsequent calculations of average and median concentrations presented in this study.

(ii) Clarification of sample characteristics: We have added a detailed description of sample SU005 in the Sect. 3, characterizing it as a typical case of severe pollution under stagnant conditions, with air masses tracing back to industrial and coal-combustion regions. This highlights the impact of transported primary emissions. However, since this sample has been excluded from most analyses, related discussions have been trimmed accordingly. In addition, the annotation for sample SU005 has been removed from Fig.4, as shown on page R14.

Lines 161-169: *"Conversely, Zn, As, and Cd exhibited elevated levels over the ocean in summer (Fig.S3b), highlighting the significant impact of transported primary anthropogenic emissions on marine aerosol composition. Notably, a severe pollution event (sample SU005, 1-2 August 2018) under stagnant meteorological conditions (WS < 2 m s^{-1}) led to a pronounced concentration peak of these elements over marine areas. Back trajectory analysis indicates that the air masses originated from the industrial emissions and coal combustion-intensive regions of the BS and Liaodong Peninsula (Fig.S4d), further underscoring the significant impact of transported primary anthropogenic emissions on marine aerosol composition. Given the high sensitivity of the mean to such an extreme outlier, particularly with the limited sample size, this sample was excluded from both the calculation of average values and subsequent PMF analysis."*

(iii) Enhanced data visualization: Additionally, following the reviewer's suggestion, the original Fig. 2 has been supplemented by adding median values alongside the mean concentrations in the bar plots. The median, being robust to outliers, provides a complementary and more resistant measure of central tendency, enabling readers to better evaluate typical concentration levels.

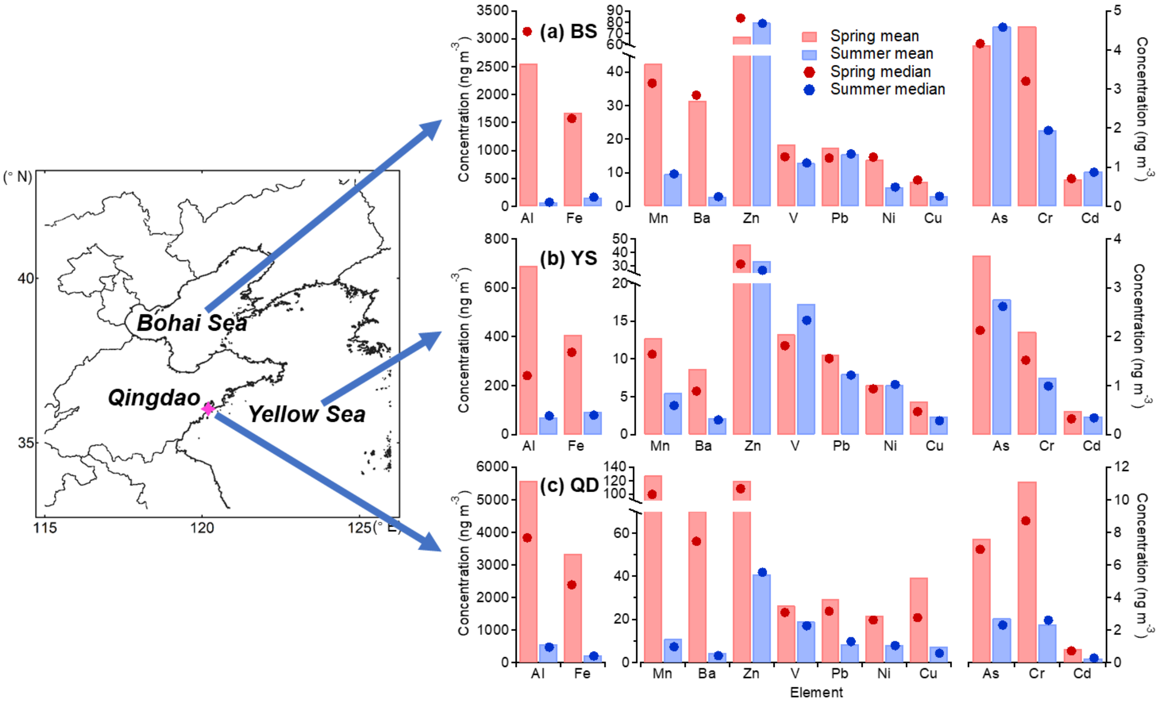


Figure 2: Concentrations of trace elements (ng m^{-3}) over the (a) BS, (b) YS, and (c) Qingdao during the campaigns in 2018. The bars represent the time-weighted (hereafter) average, and the circles represent the median.

Comment 14:

L158–159: V and Ni were employed as tracer elements for heavy oil combustion in L147–148; however, heavy oil combustion does not appear to be included here. Since this is also important for source apportionment using PMF, a consistent discussion is required.

Response:

We thank the reviewer for this observation. We have revised the sentence in Sect. 3 to include "residual oil combustion emissions" as a key consistent anthropogenic source for V, ensuring full consistency with their use as tracers earlier in the manuscript. Additionally, Ni exhibited some seasonal variation in spring due to the influence of dust, and corresponding modifications have been made in this regard. Lines 175-176: *"Conversely, V and Pb exhibited no discernible seasonal variations, likely due to the consistent anthropogenic emissions such as industrial and residual oil combustion emissions (Wu et al., 2017)."*

Comment 15:

L165–167: This discussion is highly speculative. If only the anthropogenic tracers (Zn, V, Ni, Cd, etc.) in YS aerosols showed lower concentrations in 2018 compared with 2011, the decrease could be attributed to emission regulations. However, the concentrations of mineral dust tracers, such as Fe and Al in the $PM_{2.5}$ samples collected in your study, are also significantly lower than in 2011. Therefore, rather than reflecting the effect of emission controls, the difference may simply indicate that less East Asian aerosols were transported to the Yellow Sea in 2018 than in 2011. If you wish to emphasize the impact of emission regulations, a more detailed discussion is required.

Response:

We thank the referee for this important comment. We agree that attributing the lower concentrations solely to emission controls was an overstatement. Especially the concurrent decline in both anthropogenic and crustal elements strongly suggests a contribution from interannual variations in large-scale aerosol transport. We have revised the text accordingly. The speculative link to emission policies has been replaced with a more balanced statement that acknowledges the observed decrease in overall aerosol burden and presents both interannual transport variability and emission controls as potential, co-existing factors.

Lines 181-186: *"We compared our results to other literature data on the concentrations of selected elements in various oceanic regions and typical megacities in China (Tables S5 and S6) (Qi and Zhou, 2021). Notably, elemental concentrations over the YS in this study were significantly lower than those observed during spring 2011 (Zhao et al., 2015). This decrease suggests a potential reduction in the overall aerosol burden transported to the YS in 2018. It could be a consequence of interannual variations in continental outflow and/or the effectiveness of emission control policies and environmental remediation measures, with the decline in anthropogenic tracers (e.g., Zn, V, Ni, As) providing specific support for the potential role of emission controls."*

Comment 16:

L175–181: The paragraph is difficult to follow and requires revision. Specifically, (i) what does the lower Fe concentration in Qingdao compared to other megacities imply? Does it indicate a smaller contribution from anthropogenic Fe? (ii) Please explicitly indicate the anthropogenic sources for Zn, Pb, and As. (iii) what does "sampling time" refer to? Does it mean the year when samples were collected, the time of day (e.g., daytime vs. nighttime), or the sampling duration? In any case, a more detailed discussion is necessary.

Response:

We thank the referee for these specific suggestions. Our initial intention was to provide a general comparison to demonstrate that our data are broadly comparable with previous studies. In the revision, we have expanded the discussion accordingly. The revisions have been implemented point by point as follows:

(i) Implications of lower Fe concentrations: We have added a sentence to explicitly interpret the seasonal pattern of crustal elements. It clarifies that the lower concentrations in summer indicate a "substantially weakened" input of crustal dust, directly addressing the question of what the lower Fe concentration in Qingdao imply.

(ii) Anthropogenic sources for Zn, Pb and As: We have incorporated the typical anthropogenic sources for these elements directly into the text. The revised sentence now specifies their association with "coal combustion, non-ferrous metal smelting, and various industrial processes," supported by relevant references, as requested.

(iii) Clarification of "sampling time": We have removed the ambiguous phrase and replaced it with a precise statement: "Notwithstanding the differences in sampling year and season." This eliminates any previous ambiguity.

Lines 193-202: *"In Qingdao, most crustal elements, such as Fe and Mn, exhibited higher concentrations in spring and lower concentrations in summer than the annual average concentrations reported in Beijing, Shanghai, and Guangzhou, the typical megacities in China (Table S6) (Chen et al., 2008; Yang et al., 2011). This pattern highlighted the pronounced seasonality of crustal influence in Qingdao, with spring being strongly impacted by dust events, while the input of crustal dust was substantially weakened in summer. Anthropogenic elements such as Zn, Pb, As, Cr, and Cd, which are typically associated with sources like coal combustion, non-ferrous metal smelting, and various industrial processes (Borai et al., 2002; Chen et al., 2013; Karar et al., 2006; Li et al., 2015; Li et al., 2020), were consistently at lower levels in Qingdao than in the three megacities, indicating a lower overall burden from these anthropogenic sources in Qingdao. Notwithstanding the differences in sampling year and season, V concentrations in Qingdao were 2–3 times higher than those in Shanghai (Chen et al., 2008), suggesting a more severe pollution from ship emissions or other residual oil combustions in Qingdao."*

Reference:

"Chen, J., Liu, G., Kang, Y., Wu, B., Sun, R. Y., Zhou, C. C., and Wu., D.: Atmospheric emissions of F, As, Se, Hg, and Sb from coal-fired power and heat generation in China, Chemosphere, 90, 1925-1932, http://doi.org/10.1016/j.chemosphere.2012.10.032, 2013."

Comment 17:

L188–190: It is likely that the correlation between Factor 1 and NO_2 or CO indicates that the normalized contribution of Factor 1 obtained from PMF correlates with NO_2 or CO. However, for readers who are not familiar with PMF, this is not easy to understand. A more detailed explanation is needed.

Response:

We thank the reviewer for this suggestion. We have added a clarifying sentence in Sect. 4.1, lines 212-214:

"To help validate the source of this factor, its time-series contribution was compared to ambient gas measurement data (Text S3, Fig.4, and Table S7). It correlated with NO_2 ($r = 0.45$, $p < 0.01$) and CO ($r = 0.39$, $p < 0.01$)."

Comment 18:

L204: Please correct Ca2+ to Ca^{2+}.

Response:

We thank the reviewer for pointing this out. It has been corrected in the revised manuscript, lines 227-228:

"Factor 3, identified as the dust factor, was characterized by high loadings of crustal species, including Ba, Fe, Mn and Ca^{2+} (Fig.3) (Amil et al., 2016; Gugamsetty et al., 2012; Mustaffa et al., 2014)."

Comment 19:

L204–205 What does the anthropogenic origin of Co in the dust factor indicate?

Response:

We thank the reviewer for raising this point. After a thorough re-examination of our data, we have revised our interpretation regarding Co in Factor 3. Our analysis suggests a strong crustal contribution in our study. Specifically, (i) the calculated enrichment factor (EF) for Co is close to 1, indicating a predominantly crustal source; (ii) Co exhibits strong correlations with crustal elements Al and Fe in our dataset; and (iii) our finding is supported by low EF values reported for Co in other regional studies (Wu et al., 2023). To reflect this more precise interpretation, we have revised the relevant sentence in the manuscript (lines 228-229) by removing the reference to an anthropogenic origin.

"A significant portion of Co was also apportioned to Factor 3, denoting its crustal origin (Wu et al., 2023)."

Reference:

"Wu, H. Y., Hsieh, C. C., Ho, T. Y.: Trace metal dissolution kinetics of East Asian size-fractionated aerosols in seawater: The effect of a model siderophore. Mar. Chem., 254, 104277. https://doi.org/10.1016/j.marchem.2023.104277. 2023."

Comment 20:

L205–207 While many studies employ elemental ratios with respect to Al for source estimation, what is the reason for using ratios relative to Ca in your study? In addition, Ca in the denominator means Ca^{2+}? Although Ca^{2+} was measured by ion chromatography after water extraction, is it certain that all Ca present in the aerosols is dissolved?

Response:

We thank the referee for this critical and correct observation. Using water-soluble Ca^{2+} to represent total Ca for calculating crustal mass ratios was not methodologically sound. We have therefore removed the entire sentence concerning the Fe/Ca and Mn/Ca ratios from the manuscript. We agree that the core identification of the dust factor should not rely on this flawed comparison. Instead, the identification of Factor 3 as a dust source is robustly supported by three lines of evidence: (i) its high loadings of established crustal tracers (Ba, Fe, Mn, and Ca^{2+}); (ii) The exact temporal coincidence of its peak contributions with independently documented Asian dust events; and (iii) its correlation with meteorological conditions (positive with wind speed, negative with relative humidity) characteristic of dust transport. All these points have been retained in the current manuscript.

Comment 21:

L213: Please correct PM2.5 to $PM_{2.5}$.

Response:

We thank the reviewer for pointing this out. It has been corrected in the revised manuscript, lines 234-235:

"Factor 3 accounted for 13.6% of the total $PM_{2.5}$ mass at coastal site and diminished to 1.7% within the marine environments (Fig.5b)."

Comment 22:

L215–216: At least to me, Cu and Zn do not appear to contribute to this factor.

Response:

We thank the referee for this comment. As part of our response to Comment 5, we have already removed any mention of Zn from the description of the vehicular emission factor (Factor 4), as it was not a prominent component. The revised text only discusses Cu, which had a meaningful loading of 15.1% in this factor, supporting its association with vehicular emissions. We have modified the specific source of Cu and added the reference, Gu et al. (2011), which mentions that the sources of Cu include tire wear and brake linings.

Lines 238-240: "The presence of *Cu* was likely due to additives in *fuel/lubricant combustion, brake* *linings and tire wear (Gu et al., 2011; Lee et al., 2006; Pant and Harrison, 2013), further supporting this identification."*

Comment 23:

L224–227: The text is extremely difficult to understand. The term "marine area" in the first sentence likely refers to either the Bohai Sea or the Yellow Sea. However, the time series trend of sea salt in marine area (probably represented by the dashed line and open circles in Figure S5) does not resemble that of the dust factor in either summer or spring. In contrast, for the coastal site (presumably Qingdao) shown in the bar graph, the time series trends of sea salt and dust appear to be similar in spring, but not in summer. However, spring is the season with the highest emissions of Asian dust throughout the year, and it is also the period when the influence of air masses from inland regions is strongest (Fig. 1). As a result, dust concentrations are elevated in spring. Nevertheless, it is difficult to understand why the time series trends of dust and sea spray would be similar and attributed to reverse transport from the marine area. If reverse transport is indeed the cause, a more convincing explanation should be provided.

Response:

We thank the reviewer for this critical observation. We have clarified that the marine regions refer to the BS and YS. We agree that the "reverse-transport" explanation was unclear and possibly misleading in the original manuscript. We made clear with a more straightforward interpretation: the concurrent peaks of sea salt and dust are likely due to their co-transport and mixing under the prevailing westerly/northwesterly winds, as stated in the revised text. Additionally, we have included the air mass back trajectories for the sample with the highest sea salt source concentration (SP012, Fig.S6), showing the passage of the airmass over the BS and YS before arriving at the sample collection sites.

Lines 248-258: *"Time series analysis indicated that Factor 5 had a prevalent influence over the BS and YS (Fig.4). Notably, the concurrent peak concentrations in the time series of Factor 5 and Factor 3 observed in Qingdao during spring, strongly suggested the mixing of sea salt and dust during atmospheric transport. This co-variation is consistent with the prevailing westerly/northwesterly winds (Fig.1) facilitate the transport of both continental dust and sea salt aerosols (generated over the BS and YS regions) to the coastal sampling site. To further support this transport mechanism, backward trajectories are presented in Fig.S6 for a representative marine sample (SP012, exhibiting the highest sea salt source concentration) and its corresponding Qingdao samples during the same period. These trajectories clearly illustrate that the air masses originated from the YS and approached Qingdao from the west prior to their arrival at the sampling site. Additionally, high wind speeds associated with dust events can also generate sea salt aerosols (Feng et al., 2017), which represents a primary driver of the* *observed similarity in the temporal profiles of dust and sea salt. On average, the sea salt factor contributed 9.9% to PM$_{2.5}$ mass at the Qingdao site and 22.1% in marine PM$_{2.5}$ samples."*

Reference:

"Feng, L., Shen, H., Zhu, Y., Gao, H., and Yao, X.: Insight into Generation and Evolution of Sea-Salt Aerosols from Field Measurements in Diversified Marine and Coastal Atmospheres, Sci. Rep., 7, 41260, https://doi.org/10.1038/srep41260, 2017."

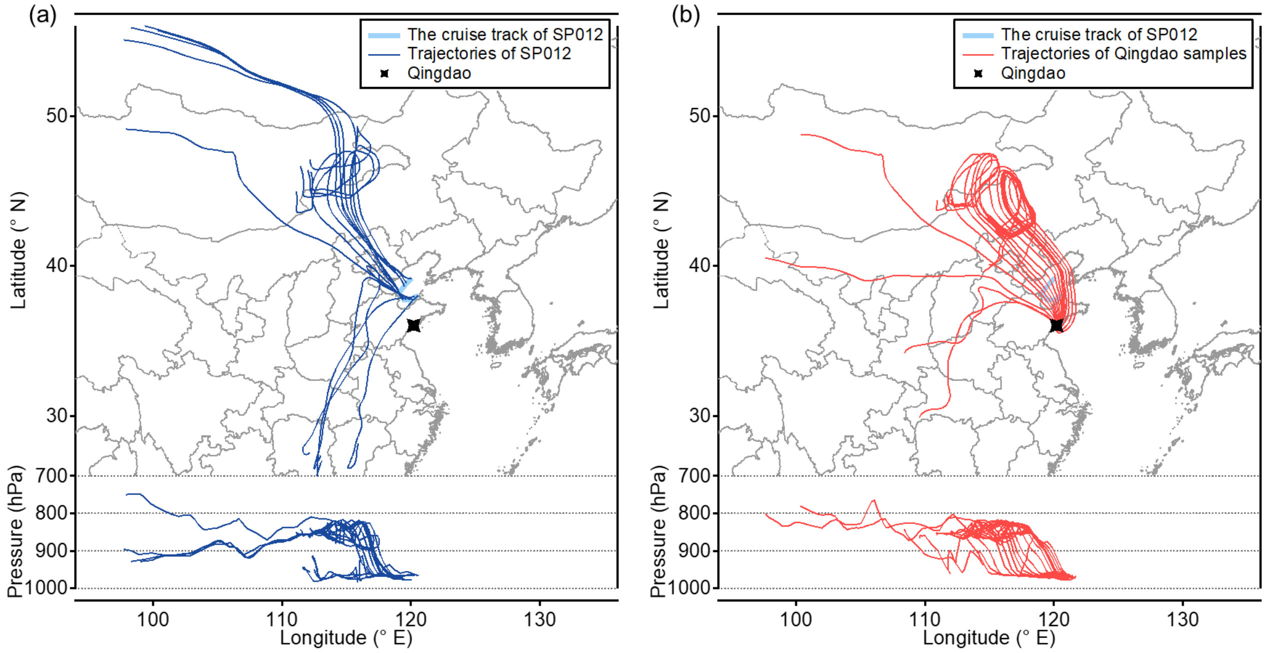


Figure S6. *72 h backward trajectories of air masses arriving 300 m altitude of (a) the marine sample SP012 and (b) its corresponding Qingdao samples.*

Comment 24:

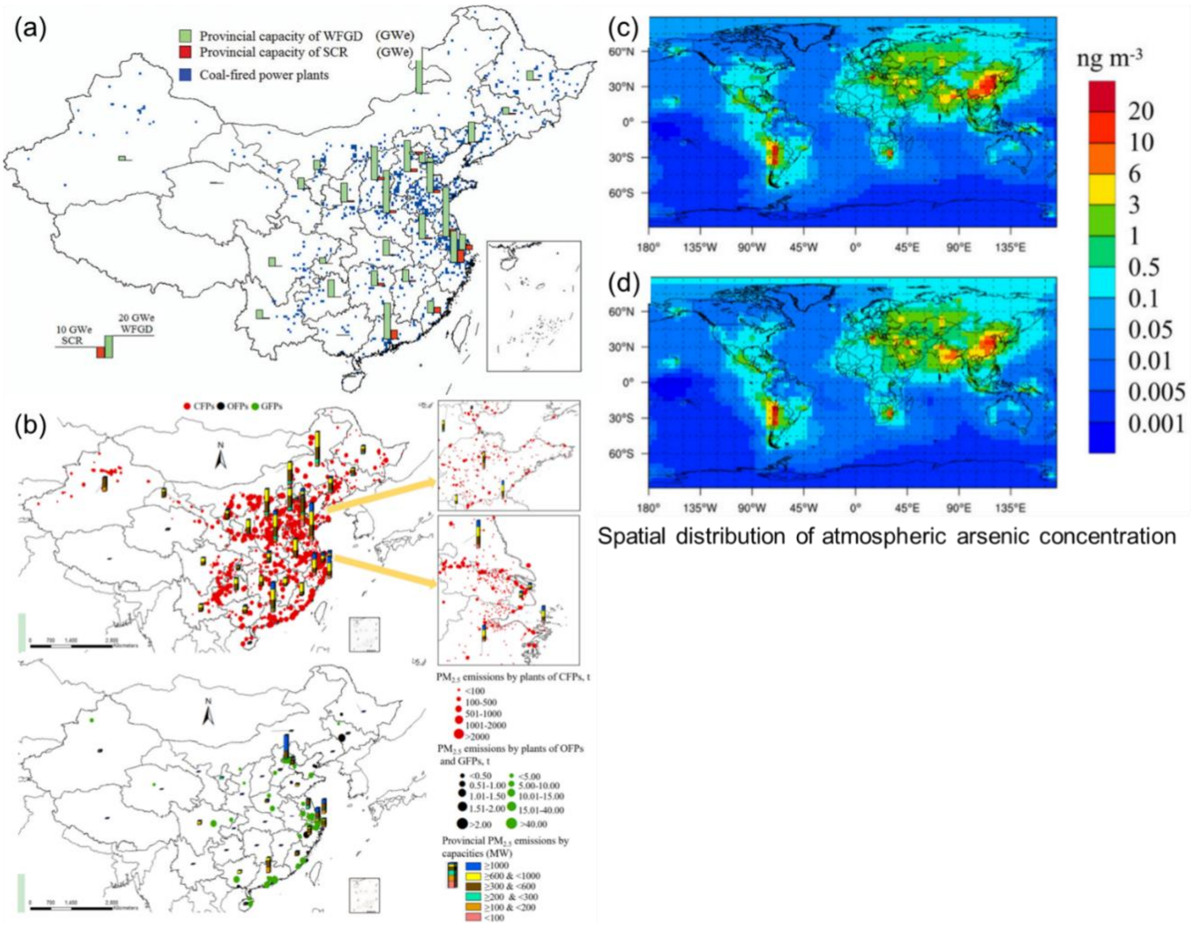
L:240–242: It seems that coal combustion plays an important role in the subsequent discussion; however, the explanation provided is rather brief. A more detailed discussion is warranted.

Response:

We thank the reviewer for this valuable suggestion. In the revision, we have substantially improved the discussion of coal combustion's role through three key improvements: (i) restructuring the factor identification narrative to enhance logical flow, with more precise description of tracer elements and their statistical significance; (ii) clarifying the mass contribution analysis to contextualize its importance despite modest percentage values; and (iii) most importantly, incorporating new spatial analysis of coal combustion sources (Fig. S8) that strengthens evidence for regional transport as a key influencing mechanism. Revised text in lines 271-281:

"Factor 8 was identified as the coal combustion factor. This attribution was robustly supported by the

enrichment of well-documented coal combustion tracers of As, Cd and Pb, elements consistently linked to coal-fired emissions (Chang et al., 2018; Li et al., 2020; Rai et al., 2016; Zhang et al., 2011; Zhang et al., 2008). Furthermore, the factor exhibited a statistically significant correlation with SO_2 *(*$r = 0.35$*,* $p < 0.01$*), a primary gaseous co-emission from coal combustion (Lin et al., 2022). This coal combustion factor contributed modestly to the total* $PM_{2.5}$ *mass but showed notable spatial variability: 2.1% at coastal (Qingdao) site and 4.8% in marine* $PM_{2.5}$ *samples, with marine contributions exceedingly twice the coastal value. The spatial distributions of coal-fired power plants,* $PM_{2.5}$ *emissions by coal-fired power plants, and atmospheric As concentration in China collectively indicated that the coal combustion factor likely originated from transport (Fig.S7) (Tian et al., 2014; Wang et al., 2016; Zhang et al., 2020). In particular, the dense concentration of coal-fired power plants along the coastline serves as a persistent source of coal-burning aerosols over the sea. Furthermore, despite its limited contribution to* $PM_{2.5}$ *mass, its contribution to heavy metal concentrations is substantial, which will be discussed in detail in Sect. 4.3."*



Spatial distribution of atmospheric arsenic concentration

Figure S7. *(a) Geographical distribution of coal-fired power plants in China, 2010 (Tian et al., 2014). WFGD represents wet flue gas desulfurization. SCR represents selective catalytic reduction. (b) Spatial distribution of* $PM_{2.5}$ *emissions by coal-fired power plants in China, 2014 (Wang et al., 2016). CFPs, OFPs, and GFPs represent coal-fired power plants, oil-fired power plants, and natural gas-fired* *power plants, respectively. Spatial distribution of atmospheric arsenic (As) concentration from GEO-Chem in (c) 2005 and (d) 2015 (Zhang et al., 2020).*

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Comment 25:

L300 – 305: Although the differences from 10 years ago appear to be small (25.2%→30.7% for secondary nitrate, 25.7%→19.3% for secondary sulfate, and 10.0%→11.9% for vehicular emissions), are these changes statistically significant?

Response:

Thanks for the comments. Owing to the unavailability of the original dataset from the earlier study (Wu et al., 2017), only published mean values are accessible, a statistical significance test is not feasible. Accordingly, we have revised the relevant paragraph to: (i) Explicitly acknowledge this methodological limitation. (ii) Reframe the narrative from stating definitive "changes" to describing "observed differences" and "trends". (iii) Strengthen the contextual discussion by linking these trends more explicitly to known differential policy impacts. Revised text in lines 338-344:

"Comparative analysis of particulate matter source apportionment between the present study and earlier work (Wu et al., 2017) suggested evolving trends in source contributions over the past decade. Notably, statistical comparison is not feasible due to the lack of primary data from the earlier study. The observed differences showed an increase in the fraction of secondary nitrate (from 25.2% to 34.9%), a decrease in sulfate (& BB) (from 25.7% to 19.4%), and minimal change in vehicular emissions contribution (from 10.0% to 10.4%), accompanied by an elevation in the mass concentrations of Ni and V. These observed variations were consistent with the impacts of evolving environmental regulations and the transformation in the energy structure over the past decade."

Comment 26:

L309: Previous sections treated the coastal area similarly to urban areas. Why is it now referred to as a 'background' source, especially in a context where residual oil combustion is found to be low? This framing seems to be a rhetorical choice.

Response:

We thank the referee for pointing out this inconsistency in terminology. To ensure consistency and clarity, we have replaced "coastal background site" with the neutral and accurate term "coastal site" in the revised manuscript, line 348:

"In this study, residual oil combustion accounted for 6.6% at the coastal site and 11.1% over the marine area."

Comment 27:

L316–317: Please explain the reason why the transition to low-sulfur fuels led to an increase in the Ni/V ratio.

Response:

Thanks to the comments. The transition to low-sulfur fuels increases the Ni/V ratio of ship-emitted aerosols. This phenomenon was caused by the selective V removal during fuel desulfurization, as revealed by recent studies (including our cited references Zhang et al. (2019) and Yu et al. (2021)). To meet sulfur content regulations (e.g., $\leq$ 0.5%), residual fuels undergo desulfurization, which preferentially reduces V content, while leaving Ni content relatively stable (Yu et al., 2021) and resulting in high Ni/V ratio in the low-sulfur fuel. Since the elemental composition of ship-emitted particles closely reflects the fuel being burned, this shift in fuel composition directly causes the observed increase in the Ni/V ratio of ship-emitted aerosols, as confirmed by source apportionment results (Yu et al., 2021). We have revised our manuscript to include a brief explanation of this mechanism, as detailed below (lines 355-363):

"The transition to low-sulfur fuels led to a significant increase in the Ni/V ratio of emitted aerosols. This phenomenon was primarily caused by the desulfurization of fuels which removed V much more efficiently than Ni, thereby increasing the Ni/V ratio in the fuel itself, which is then reflected in the combustion emissions (Yu et al., 2021). In Shanghai, the Ni/V ratio in ship emitted particles derived from PMF increased from 0.34 to 0.45 between DECA 1.0 and DECA 2.0, reaching 2.14 in 2020 (Yu et al., 2021). In the present study, the Ni/V ratio for residual oil combustion aerosols resolved by PMF was 0.37, aligning with DECA 1.0 levels. Notably, Bie et al. (2021) reported a Ni/V ratio of 2.17 in 2019 near the Qingdao Port, confirming DECA policy effectiveness. The lower Ni/V ratio (0.37) in

our study suggested residual oil combustion pollutants in the study area may still include higher-sulfur fuel signatures, potentially from regional transport rather than strictly regulated local shipping."

Reference:

"Yu, G., Zhang, Y., Yang, F., He, B., Zhang, C., Zou, Z., Yang, X., Li, N., and Chen, J.: Dynamic Ni/V Ratio in the Ship-Emitted Particles Driven by Multiphase Fuel Oil Regulations in Coastal China, Environ. Sci. Technol., 55, 15031-15039, https://doi.org/10.1021/acs.est.1c02612, 2021."

Comment 28:

L333: sulfur cycle → carbon cycle?

Response:

Thanks for the comment. It is sulfur cycle, as suggested by the foundational work of Zhuang et al. (1992) cited therein. This coupling operates significantly through processes involving dimethyl sulfide (DMS). To clarify the specific link between iron and the sulfur cycles, we have revised the sentence (lines 394-397):

"As a limiting nutrient, Fe is closely coupled with sulfur cycles (e.g., via dimethyl sulfide production/processing) in both the atmosphere and ocean, triggering phytoplankton blooms, and enhancing carbon dioxide (CO_2) sequestration through the global carbon cycle (Shi et al., 2012; Zhuang et al., 1992)."

Comment 29:

L338–347: In the abstract, the importance of heavy oil combustion as a source of Fe in marine aerosols was mentioned; however, this does not seem to be the case here. Please clarify the content.

Response:

Thanks for the comments. In response to the previous comment (Comment 6), we have revised the abstract and main text to explicitly address the role of ship emissions. As detailed in Sect. 4.3.1, our source apportionment results identify residual oil combustion as a significant source, contributing 26.1% to Fe and 24.4% to Mn in marine aerosols during summer. The statement in the abstract is fully supported by the data and discussion in the main text. Specific revisions made to the Abstract are detailed in our response to Comment 6.

Sect. 4.3.1, lines 413-418: *"It is noteworthy that residual oil combustion was also a discernible source for Fe and Mn in summer (contributing 26.1%, 50.0 ng m^{-3} and 24.4%, 1.9 ng m^{-3} respectively in marine areas). Southeasterly winds transported ship-derived pollutants coastward, markedly increasing the relative contributions of Fe (24.1%) and Mn (22.9%) in Qingdao compared to spring*

(2.8% and 3.1%, respectively). However, from the perspective of absolute concentration, the contributions of residual oil combustion to Fe and Mn in Qingdao remained lower in summer (77.8 and 2.9 ng m^{-3}, respectively) than in spring (98.7 and 3.7 ng m^{-3}).

Comment 30:

L352–353: This discussion is highly speculative. Actually, internal mixing of mineral dust with sea spray aerosol has been reported by previous studies. However, the effect on fractional Fe solubility is usually not positive. For instance, Hsu et al. (2010) showed negative impact of sea salt on fractional solubility of Fe. Sakata et al. (2022) showed that organic carbon in sea spray has potential to suppress Fe precipitation under weakly-acidic conditions, but not further Fe dissolution from mineral dust. Furthermore, according to Wu et al. (2023), when attempting to extract Fe from aerosols collected in East Asia using seawater, the fractional Fe solubility decreased compared to ultrapure water extraction in the absence of organic matter, whereas in the presence of organic matter, the fractional Fe solubility was comparable to that obtained with ultrapure water extraction. Please elaborate how Fe dissolution is enhanced by internal mixing between mineral dust and sea spray aerosols.

Response:

We sincerely thank the reviewer's critical and insightful comments. We have carefully read these suggested references and related literature on the internal mixing of mineral dust and sea salt aerosols (SSA). Internal mixing between mineral dust and sea salt has been observed in various regions, including the marine atmospheres of East Asia, the Amazon basin, the eastern North Atlantic, the Southern Hemisphere ocean, and the Pacific Ocean, primarily through electron microscopic-based studies (Hus et al., 2010; Sakata et al., 2020 and references therein). Such mixing has been suggested to potentially affect trace element solubility, for instance by offsetting the effects of acid substances depending on interactions between dust and sea salt as well as reactions with pollutants. Additionally, such mixing is widely considered to form through cloud processes (Hsu et al., 2007 and references therein).

The study by Hsu et al. (2010) reported an inverse relationship between Fe solubility and the sea salt loading (as indicated by Na^{+}), though it was based on total suspended particle (TSP) analysis. Sakata et al. (2022) proposed that under moderately acidic conditions (3.0 < pH < 6.0), organic ligands (particularly humic-like substances, HULIS) can stabilize labile Fe in marine cloud water, rather than to further promote Fe dissolution from aerosol particles. Meanwhile, Wu et al. (2023) highlighted the critical role of organic compounds (e.g. DFB) in promoting and sustaining the release of Fe and other metals from dust particles into seawater over time. Therefore, we have revised the discussion to incorporate the following points:

i) several studies suggest a potentially negative effect of dust-SSA mixing on Fe dissolution, with pH being an important controlling factor; ii) the acidity of SSA is highly variable and strongly influenced by local environmental conditions; iii) the components in SSA e.g., organics may also influence the Fe solubility and the present data are not enough to evaluate the effects of organics especially HULIS on Fe dissolution.

Thus, we conclude that the net effect of dust-SSA internal mixing on Fe bioavailability remains uncertain and warrants future investigation. The revised text in lines 431-449:

"Furthermore, sea salt contributed *33.6%* to Fe and *29.7%* to Mn in marine aerosols during spring, suggesting mixing between crustal species or Fe/Mn from other sources with sea spray aerosols (SSAs) (Geng et al., 2014; Hilario et al., 2020). *Internal mixing between mineral dust and sea salt has been observed in various regions, such as the marine atmosphere of East Asia, the Amazon basin, the eastern North Atlantic, the Southern Hemisphere ocean, and the Pacific Ocean, through electron microscopic analyses (Andreae et al., 1986; Okada et al., 1990; Zhang et al., 2003; Zhang et al., 2006; Wagener et al., 2008; Hsu et al., 2010; Adachi et al., 2020; Knopf et al., 2022; Kwak et al., 2022). However, the net effect of this mixing on Fe bioavailability appeared complex and was not necessarily positive (Hsu et al., 2010; Sakata et al., 2022; Wu et al., 2023). Hsu et al. (2010) reported a negative correlation between sea salt and fractional Fe solubility, likely mediated via pH effects (Spokes & Jickells, 1996; Desboeufs et al., 1999). Proposed mechanisms include SSA buffering solution acidity to reduce particle solubility, and competing with dust particles for acid uptake, thereby inhibiting heterogeneous acid processing (Hsu et al., 2007). It should be noted, however, that Hsu et al. (2010) used TSP samples, whereas recent mesocosm experiments indicate that submicron SSA may rapidly acidify to pH 2.0 via evaporation, acidic gas uptake, and/or proton displacement from organics by* Na^+ *(Angle et al., 2021). Thus, the actual acidity of ambient submicron SSA may remain sufficiently high to promote dissolution. Moreover, organic constituents in SSAs (e.g. Humic-like Substances, HULIS) may primarily stabilize existing soluble Fe rather than enhance Fe dissolution, although Wu et al. (2023) demonstrated that strong organic ligands can significantly facilitate and sustain Fe release. Therefore, the overall impact of SSA mixing on Fe bioavailability likely depends on specific marine environmental conditions and requires future investigation."*

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Comment 31:

L406–407 Why internal mixing of mineral dust and sea spray is the synergistic interaction between mineral dust and anthropogenic matters.

Response:

Thanks for the comments. We have corrected this mischaracterization. Consequently, the conclusion frames this observation neutrally and accurately as “extensive multi-source mixing (dust-sea salt-anthropogenic) in aerosols,” and the speculative statement on facilitated dissolution has been replaced with a call for further research on its biogeochemical impact.

Sect. 4.3.3, lines 483-485: *“The time series suggested that the peaks in sea salt contributions coincided with the high concentrations of Pb, Cd and Zn (Figs.4a and S3a), supporting that sea salt particles acted as a carrier for these toxic anthropogenic elements during transport.”*

Sect. 5, lines 516-518: *“Springtime marine environments also showed elevated sea salt contributions to Fe, Mn, Zn, Cd, and Pb (18.5–33.6%), indicating extensive multi-source mixing (dust-sea salt-anthropogenic) in aerosols. The biogeochemical impact of this complex mixing on the reactivity of elements warrants further investigation.”*

Comment 32:

Figure S5. This figure is frequently mentioned in the text. Could you please move it into the main body of the paper?

Response:

We thank the reviewer for this suggestion. Fig.S5 has been moved to the main text (Fig.4) as requested. Please see our response to Comment 1 for specific details about this modification.

Sect. 4.1, lines 206-208: *"Eight factors were identified by PMF. The resolved factor profiles and time series are presented in Fig.3 and Fig.4 respectively. The mean concentrations and the relative contributions of each factor are displayed in Fig.5."*

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