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 #2:

This study systematically investigates the concentrations and sources of trace elements in atmospheric fine particles ($PM_{2.5}$) in coastal urban areas and offshore regions of northern China, focusing on the source characteristics and land-sea differences of trace elements in $PM_{2.5}$. It elaborates on the connections between land and sea, and analyzes the mutual influences of the atmospheric environment between coastal cities and offshore areas. The research results can provide data support and a scientific basis for ship emission control, land-sea coordinated pollution control, and marine ecological assessment. The content of this paper is detailed with sufficient data. However, some sections still have deficiencies in writing and format issues. It is recommended that the paper be published only after the following problems are resolved:

Comment 1:

(1) The structure of the abstract is inconsistent with the main text. The main text discussed $PM_{2.5}$ source apportionments and trace elements concentrations & sources, but the data in the abstract only includes percentages related to trace elements sources, lacking data on absolute concentrations. Trace elements over the ocean must originate from land (except V and Ni). Even if the concentration is low, the proportion of anthropogenic sources will inevitably appear large when only looking at percentages, so it cannot be used as the evidence for the severe conditions of trace elements over the ocean. Moreover,

the Bohai Sea and Yellow Sea are offshore seas, which are reasonably strongly affected by land, making it difficult to be a highlight. Therefore, I do not agree with the phrases "long-range pollutant transport" and "highlighting growing anthropogenic impacts" in the abstract. Furthermore, I do not understand what "highlighting growing anthropogenic impacts" specifically refers to—whether it is a temporal or spatial comparison.

Response:

We sincerely appreciate the reviewer's constructive feedback regarding the structure and content of our abstract. In the revision, we have thoroughly addressed the key points raised by the reviewer. To provide a solid quantitative basis, we have integrated absolute concentration data alongside source contribution percentages for representative elements at critical points in the text. All land-sea comparisons are now explicitly framed in terms of concentration values to ensure clarity. Furthermore, we have refined the phrasing regarding transport processes and anthropogenic influence to be more precise and better aligned with the evidence presented in the manuscript.

"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."

Comment 2:

(2) The conclusions also only contain data related to relative contributions, without absolute concentration data, which is inappropriate. Because if the concentration in the atmosphere is very low, studying relative contributions has little significance.

Response:

We thank the reviewer for this important point. In the revision, we have supplemented the Conclusions section with absolute concentration data alongside the relative contribution percentages for key elemental sources:

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 3:

(4) Are "the Circum-Bohai-Sea (CBS) region" and "the Bohai Rim" the same thing?

Response:

Thank you for raising this point. To avoid ambiguity, we have added a clarifying sentence in Sect. 3 (lines 172-175):

"In contrast, Zn, As, and Cd displayed slightly higher concentrations over the BS in summer than in

spring, suggesting anthropogenic emissions in the Circum-Bohai-Sea (CBS) region (a geographic area encompassing the land and coastal zones surrounding the BS in China, it includes, but is not limited to, the Bohai Rim) (Polissar et al., 2001).”

Comment 4:

(5) For the Section title “4.2 Variation in source contributions of $PM_{2.5}$ between coastal and marine environments”, this section mainly discusses land-sea differences, so "Difference" is more appropriate. However, since the section may also emphasize the connections between land and sea, would "Difference and linkage in source contributions of $PM_{2.5}$ between coastal and marine environments" be better?

Response:

Thank you. We agree with the reviewer's suggestion. The section title has been revised to:

“4.2 Difference and linkage in source contributions of $PM_{2.5}$ between coastal and marine environments”

Comment 5:

(6) The word “emissions” in the Section title “4.2.2 Summer biomass burning and coal combustion dominate marine emissions” is obviously incorrect. As a receptor model, PMF observes results rather than initial emissions; otherwise, there would be no need to study the impact of transport.

Response:

Thank you for the correction. The title has been revi*sed to* ***“4.2.2 Summer biomass burning and vehicular emissions dominate marine source contributions”*** *to accurately reflect the PMF-derived source contributions.*

Comment 6:

(7) Line 278: The caption of Figure 4 states that the calculation of concentration and contribution is volume-weighted. I don’t understand what this means, as time-weighting is usually adopted, which is unrelated to the sampling volume of the sampler. For example, different samplers have different sampling flow rates, and the sampling volumes will differ if different types of samplers are used during the same period. Using volume-weighting will lead to different results, which is obviously incorrect

because the concentration of chemical species in the atmosphere is not the sampling volume's business.

Response:

We thank the reviewer for the important clarification. It is a mistake of our using incorrect phrase. The term "volume-weighted" has been replaced with the correct "time-weighted" throughout the manuscript, including the caption of several figures.

"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 7:

(8) Lines 316-325: Why does the use of low-sulfur fuel increase the Ni/V ratio of the exhaust of oil combustion? Why can the increase in the Ni/V ratio represent the effectiveness of implementing DECA policy measures?

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., ≤ 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 8:

(9) Line 304: I don't consider the difference of 1.9% between 10.0% and 11.9% as a "moderate increase", because the experimental error may be larger than this. These two data can be regarded as almost the same, i.e., almost no change.

Response:

We agree with the reviewer that the difference is within the range of potential experimental uncertainty and does not constitute a substantial change. The description has been revised: (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 9:

(10) Line 333: I do not understand why Fe is closely related to the sulfur cycle. Can the authors further explain this?

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 10:

(11) It is commendable that the authors compared their observational results with previous relevant studies in China's offshore seas. However, it would be better if the observational results in China could be compared with those in other marine areas around the world. Because the trace element is a global issue, comparison with observations in other marine areas can reflect the uniqueness of China's sea areas, especially in Section 4.3 "Source contributions of individual elements", which is the most important part of this paper. But I am not sure whether relevant studies have been conducted abroad.

Response:

We thank the reviewer for this valuable suggestion. In the revision, we have added a new section (4.2.4) to compare our findings with studies conducted over the marginal seas of the Western Pacific, including the offshore eastern China Sea, around the Taiwan Island area, and the South China Sea. While this comparison is limited to the Western Pacific due to the aerosol types and source apportionment methodologies, it provides a key regional perspective. A broader global comparison, especially regarding individual elemental sources as suggested, remains an excellent direction for future work as more data from other ocean regions become accessible.

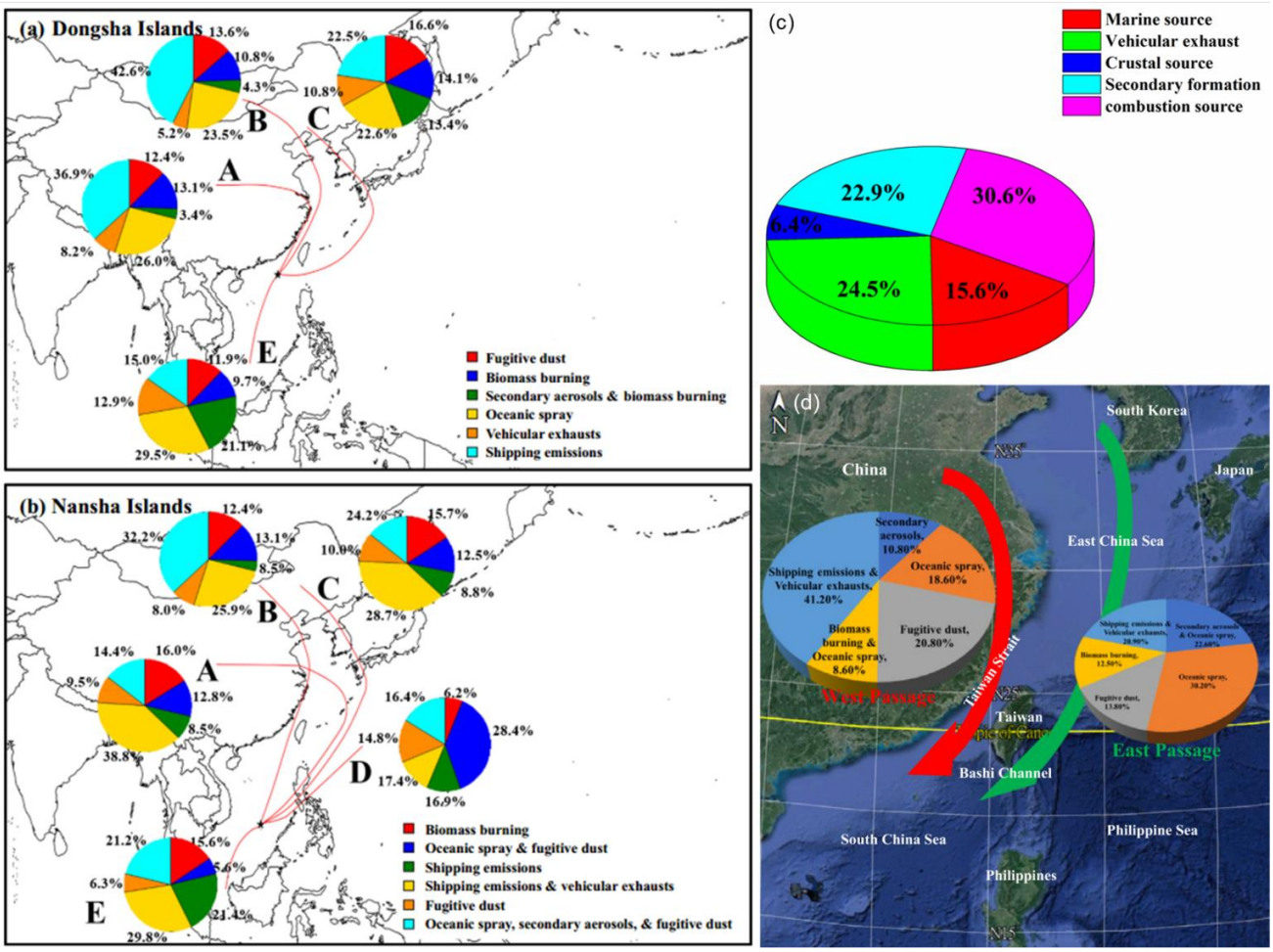
*"**4.2.4 Comparison with source apportionment studies in other marginal seas of the Western Pacific***

We compared the source apportionment results obtained over the BS and YS in this study with those from studies conducted over the offshore eastern China Sea (OECS), around the Taiwan Island (China), and over the South China Sea (SCS) (Sun et al., 2022; Yen et al., 2022a; Yen et al., 2022b). These sea areas all belong to the marginal seas of the Western Pacific, sharing the common influence of the East Asian monsoon and continental outflows, yet exhibiting differences in the types of pollution sources and their respective contributions.

Over the marginal seas of the Western Pacific, $PM_{2.5}$ sources were generally dominated by secondary

inorganic aerosols, dust (including crustal or fugitive dust as reported in other studies), sea salt (including marine source or oceanic spray), and specific anthropogenic emissions. Among these, secondary aerosols (dominated by nitrate and/or sulfate) and sea salt made particularly prominent contributions. In studies conducted over the OECS, secondary formation (22.9%) and combustion source (30.6%) were reported to make significant contributions (Sun et al., 2022; Fig.S9c), which is qualitatively similar to our findings. The notable contribution of sea salt in this work is also consistent with its important role reported in other sea areas, such as 18.6–30.2% around the Taiwan Island and 5.6–29.5% over the SCS (Yen et al., 2022a; Yen et al., 2022b; Fig.S9a, b, and d).

In terms of the apportionment results for specific anthropogenic sources, the $PM_{2.5}$ sources over the BS and YS exhibited a stronger continental signal, including the identification of more distinct factors for industrial processes and coal combustion. This characteristic was less pronounced over the more southerly sea areas, reflecting the profound impact of the industrial structure and coal-dominated energy mix of Northern China on the marine regions. Furthermore, vehicular emissions constituted a major and stable pollution source over the BS and YS, aligning with the high contribution (24.5%) reported in the OECS study (Sun et al., 2022). In contrast, studies conducted around the Taiwan Island and over the SCS commonly resolved a mixed factor combining ship and vehicular emissions, which was dominant (17.4–41.2%) (Yen et al., 2022a; Yen et al., 2022b). This suggested that over the BS and YS, traffic and shipping emissions were more readily separated, likely due to the differing coastal urban agglomerations and distinct emission patterns. The comparison revealed the regional commonalities of $PM_{2.5}$ sources in the Western Pacific marginal seas and their spatial divergence under the influence of local emissions."



*"**Figure S9.** (a) Source contribution resolved from the PMF analysis of $PM_{2.5}$ at (a) the Dongsha Islands and (b) the Nansha Islands for the transport route-based cluster analysis (A: Central China; B: North China; C: Korea, Japan, and Northeast China; D: the Philippines and the West Pacific Ocean; E: the South China Sea) (Yen et al., 2022b). (c) The contribution of different sources in $PM_{2.5}$ in the Eastern China Sea (Sun et al., 2022). (d) Source apportionment of marine fine particles at two islands through the west and east passages of the Taiwan Island (Yen et al., 2022a)."*

References:

"Sun. H., Sun, J., Zhu, C., Yu, L., Lou, Y., Li, R., and Lin, Z.: Chemical characterizations and sources of PM2.5 over the offshore Eastern China sea: Water soluble ions, stable isotopic compositions, and metal elements. Atmos. Pollut. Res., 13, 101410. https://doi.org/10.1016/j.apr.2022.101410, 2022.

Yen, P. -H., Yuan, C. -S., Ceng, J. -H., Chiang, K. -C., Tseng, Y. -L., Soong, K. -Y., and Jeng, M. -S.: Inter-comparison of chemical fingerprint and source apportionment of marine fine particles at two islands through the west and east passages of the Taiwan Island. Sci. Total Environ., 851, 158313. http://dx.doi.org/10.1016/j.scitotenv.2022.158313, 2022.

Yen, P. -H., Yuan, C. -S., Wu, C. -H., Yeh, M. -J., Tseng, Y. -L., Soong, K. -Y.: Transport route-based cluster analysis of chemical fingerprints and source origins of marine fine particles (PM2.5) in South China Sea. Sci. Total Environ., 806, 150591. https://doi.org/10.1016/j.scitotenv.2021.150591, 2022."

Comment 11:

(12) Format issues:

Line 65：Please correct "occurs" to "occur"

Line 71：Please correct "contributs" to "contributes"

Line 88：Please correct "a approximately" to "an approximate"

Line 204: Please correct "Ca2+" to "Ca^{2+}"

Line 213: Please correct "PM2.5" to "$PM_{2.5}$"

Line 261: There are two spaces between "WI & IE" and "to", please delete one

Line 271：Remove the space after the word "particles".

Line 387：Please correct "in $PM_{2.5}$ sources" to "of $PM_{2.5}$ sources"

In the caption of Figure S3, "μg/m^3" should be uniformly formatted as "μg m^{-3}"

Response:

Thank you for your careful review. All the formatting and typographical errors noted have been corrected in the revised manuscript. Terms mentioned have been removed in revisions made per other comments. These modifications are not displayed here but have been appropriately implemented.

Lines 72-74: *"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."*

Lines 90-92: *"The sampling site was located at the Baguanshan Atmospheric Research Observatory (BARO, 36.03° N, 120.20° E; 74 m above sea level) in the Shinan District Qingdao (Fig.1), with an approximately 600 m straight-line distance from the coastline (Li et al., 2024; Yang et al., 2024)."*

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)."*

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)."*

Lines 312-313: *"Characterized by small EC-rich particles, these vehicular emissions can be easily transported to remote areas (Gu et al., 2011; Vu et al., 2015)."*

Lines 490-492: *"This study investigated the spatial and seasonal distributions of $PM_{2.5}$ sources and associated trace elements in Qingdao and its adjacent offshore areas of the BS and YS during spring and summer 2018, delving into land-sea contrasts and the influence of anthropogenic activities on the marine air."*

*"**Figure S3.** Temporal variations of meteorological parameters and selected species concentrations ($\mu g\ m^{-3}$) 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."*