

Dear ACP editor,

Thank you for considering our manuscript for *ACP*. We carefully considered the reviewers' comments. Based on the feedback, we have made edits to address their concerns and believe we have a much stronger paper as a result of the helpful comments. Responses to each reviewer's comment and associated edits are shown in blue text and follow below.

Reviewer(s)' Comments to Author:

Reviewer #1

Comments:

This manuscript analyzed the spatial distribution of IN and ON over the Greater Bay Area and found differences in ON composition between urban and marine aerosols. The results are important to estimate nitrogen deposition and its impacts on ecosystems in coastal areas. However, the following comments need to be addressed before publication:

Lines 107-108: This study collected the data of biogeochemical oceanographic measurements. For the discussion on ecosystem implications, I may suggest the authors to combine seawater Chl-a and analyze the potential impacts of aerosol ON input to marine ecosystems.

Response: We thank the reviewer for this thoughtful suggestion. We agree that chlorophyll-a (Chl-a) is an important indicator of phytoplankton biomass. However, a contemporaneous comparison with aerosol ON would unlikely provide a meaningful assessment of the biological response to atmospheric ON deposition during a moving-ship campaign, as the response would occur after a variable time lag.

Multiple previous studies documented delayed Chl-a responses following atmospheric input events. For example, Tan et al. (2011) reported phytoplankton blooms 1–21 d after dust passage in the southern Yellow Sea. Hu et al. (2026) found that regionally averaged Chl-a anomalies in the northern Chinese marginal seas became positive after approximately 2–3 d and peaked at lags of 5–8 d following strong dust events, while southern waters exhibited a more rapid response. Delayed responses have also been observed in the South China Sea (SCS): Wang et al. (2012) reported elevated Chl-a approximately 10 d after dust passage during the 2010 event in the oligotrophic northern SCS. These findings indicate that the timing of Chl-a responses varies among regions and events, and that contemporaneous measurements cannot be assumed to capture the biological response to atmospheric nutrient inputs.

Furthermore, Chl-a variability reflects physical and ecological processes in addition to atmospheric nutrient supply. In the central SCS, He et al. (2024) reported Chl-a enhancement during days 3–7 following a precipitation event in 2019, with wind-driven vertical mixing and upwelling contributing substantially to the response alongside nutrients supplied by precipitation. Aerosol-addition experiments using SCS waters also showed that biomass responses depended on aerosol loading and the hydrographic and trophic conditions of the receiving waters. Under low aerosol loading, biomass accumulation was less apparent, potentially because nutrient stimulation was counterbalanced by enhanced grazing (Guo et al., 2012).

In our campaign, aerosol samples integrated atmospheric composition over several-hour periods along the ship track. Seawater Chl-a was not included in the present aerosol analysis. Moreover, measurements collected as the vessel moved between locations would not track the subsequent biological response of the same water mass, and imposing a time lag across stations would confound temporal responses with spatial variability. We therefore limit our discussion to implications of the measured aerosol N composition and estimated PM_{2.5}-bound N dry deposition.

The revised manuscript (Sect. 2.1), lines 107–113, now reads:

“However, chlorophyll-*a* responses to atmospheric nutrient inputs typically lag behind deposition, with the timing depending on regional and environmental conditions (Tan et al., 2011; Wang et al., 2012). Concurrent aerosol and seawater measurements along a moving cruise track were therefore unlikely to capture these delayed responses within the same water mass. Accordingly, we did not assess the relationship between biological responses and aerosol N. Instead, we focus on nitrogen speciation and chemical composition of aerosols collected over the GBA coastal waters during the cruise.”

Lines 147-151: The ship-exhaust influenced samples exhibited higher TC concentrations than clean marine samples. How about the EC concentrations in the PM2.5 samples with and without ship-exhaust influence? Did you observe any other difference in aerosol components between clean samples vs ship-exhaust influenced samples?

Response: We thank the reviewer for this suggestion. We re-evaluated the 16 operationally flagged ship-influenced samples and the 75 retained marine samples using the finalized dataset.

As expected from the operational screening criterion, sample-mean NO_x was substantially higher in the operationally ship-influenced group than in the retained marine group (87.7 ± 66.1 versus 6.61 ± 7.81 ppb; mean $\pm$ SD). Because NO_x was used in the screening procedure, this contrast is reported descriptively and is not considered independent validation of the classification.

Independent carbonaceous measurements provided additional support for the distinction between the two groups. The mean EC concentration was approximately 3.5 times higher in the operationally ship-influenced samples than in the retained marine samples (2.09 ± 2.94 versus 0.60 ± 0.57 $\mu\text{g m}^{-3}$; two-sided Mann–Whitney $p=0.016$). Mean OC, TC calculated as OC + EC, and WSOC concentrations were also higher in the operationally ship-influenced group: 5.65 ± 4.58 versus 3.30 ± 2.33 $\mu\text{g m}^{-3}$ ($p=0.0035$), 7.74 ± 7.42 versus 3.90 ± 2.78 $\mu\text{g m}^{-3}$ ($p=0.0032$), and 3.52 ± 3.11 versus 2.36 ± 2.87 $\mu\text{g m}^{-3}$ ($p=0.0016$), respectively.

In contrast, bulk IN, ON, and TN did not differ significantly between the two groups ($p=0.217$, 0.276 , and 0.929 , respectively). The mean ON/TN ratio was higher in the operationally ship-influenced group, but the difference was not statistically significant ($43.5 \pm 23.0\%$ versus $31.7 \pm 13.2\%$; $p=0.066$) due to large variations.

Among the major water-soluble ions, Na⁺ and Mg²⁺ concentrations were higher in the operationally ship-influenced group, with unadjusted p values of 0.0051 and 0.020 , respectively. The other six ions did not differ significantly between the two groups. Because Na⁺ and Mg²⁺ are major components of sea salt and may vary with sampling location and meteorological conditions, we do not interpret their differences as source-specific evidence of ship emissions.

We have added a new section (**Section S1**) and **Table S1** to the Supplementary Information presenting the complete comparison. Concentrations are reported as mean $\pm$ standard deviation to maintain consistency with the concentration summaries in the main manuscript. Because several variables showed skewed distributions and high-concentration observations, group differences were evaluated using two-sided Mann–Whitney U tests. The EC comparison directly addresses the reviewer’s question, whereas the remaining component-wise comparisons are treated as exploratory and their unadjusted p values are interpreted cautiously.

Overall, the results show that the operationally ship-influenced samples were most consistently distinguished by their higher carbonaceous aerosol concentrations, particularly EC and TC. We now refer to the two groups as “operationally ship-influenced” and “retained marine” and explicitly acknowledge that the operational screening identifies samples with evident fresh ship-plume influence but cannot exclude smaller contributions from diluted or aged ship emissions in the retained marine samples.

The revised manuscript (Sect. 2.2), lines 153–162, now reads:

“This criterion identified 16 of the 91 filters, leaving 75 samples for concentration analyses. Hereafter, “marine samples” refers to these 75 retained filters but does not imply complete absence of ship-emission influence. Independent carbonaceous measurements supported this operational separation: mean elemental carbon (EC) concentrations were significantly higher in the ship-influenced group than in the retained marine group (2.09 ± 2.94 versus $0.60 \pm 0.57 \mu\text{g m}^{-3}$; two-sided Mann–Whitney $p = 0.016$), as were organic carbon (OC), total carbon (TC) and water-soluble organic carbon (WSOC) concentrations (Sect. S1; Table S1; Fig. S7). This screening identifies evident fresh ship-plume influence but may not exclude contributions from diluted, aged or regionally transported ship emissions in the retained marine samples.”

Lines 252-253: Please describe how to calculate the offshore distance? Some sampling locations are very close to the shore and surrounded by the continent on three sides?

Response: We thank the reviewer for pointing out that the original definition and calculation of offshore distance were insufficiently described. The original estimates were obtained as the minimum great-circle distance from each representative sampling position to a finite set of manually selected coastal reference points. Although additional reference points were subsequently included, this approach did not calculate the minimum distance to a continuous coastline and could misrepresent coastal proximity in the complex geometry of bays and estuaries.

We have therefore replaced the original distance estimates with a reproducible GIS-based calculation. The revised primary metric is the shortest distance from each filter’s representative position to the continental mainland coastline, using the full-resolution Level-1 land–ocean boundaries of GSHHG v2.3.7 (Wessel and Smith, 1996). Each representative position is the arithmetic midpoint of the recorded sampling-start and sampling-end longitude and latitude. Sampling positions and coastline geometries were transformed from WGS84 to a local azimuthal equidistant projection centered at 113.7° E , 22.2° N , and the minimum point-to-coastline distance was calculated in this projected coordinate system. The revised distances range from 2.00 to 53.89 km.

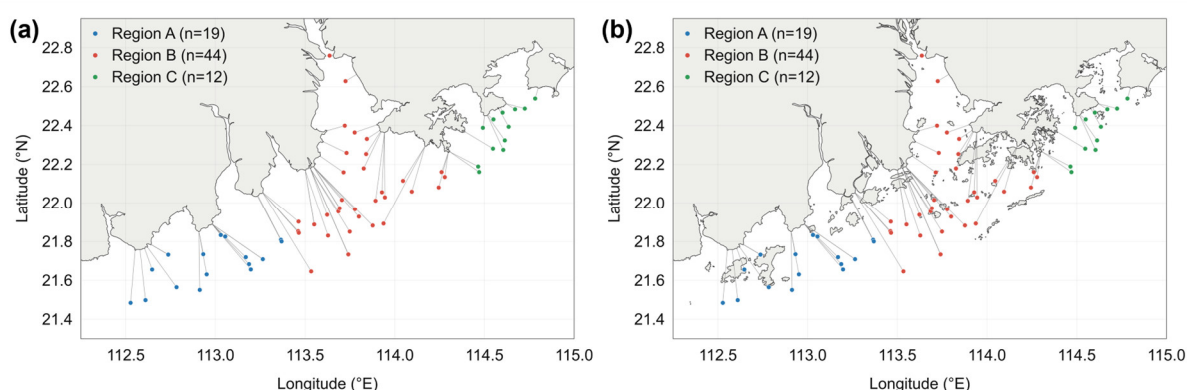
No predefined offshore direction is imposed: all mainland coastline segments within the study domain are considered, and the nearest segment is selected. Thus, a sampling position surrounded by the mainland on several sides is assigned the distance to the closest mainland shore, rather than to a selected coastal reference point.

We now use the term “distance to the continental mainland coastline” to distinguish this metric from distance to any shoreline. Islands are excluded from the primary calculation, so the metric does not capture proximity to island-based sources or represent air-mass travel distance. We have added a new section (**Section S3**) and **Figure S4 (reproduced below as Figure R1)** to document the coastline dataset, representative-coordinate convention, calculation procedure and individual-filter distances.

The revised manuscript (Sect. 3.1), lines 298–300, now reads:

“Offshore distance was calculated as the shortest distance from each sample’s representative position, defined as the midpoint of its sampling-start and sampling-end coordinates, to the mainland coastline, excluding islands (Sect. S3; Fig. S4).”

The figure is now included in Section S3:



(New Figure S4) Figure R1. Marine sampling locations and shortest distances to the mainland coastline. **(a)** Map showing only the continental mainland coastline. **(b)** The same map with islands included for geographic context. Blue, red and green markers represent the sampling positions of retained marine filters in regions A ($n = 19$), B ($n = 44$) and C ($n = 12$), respectively. Grey line segments connect each representative sampling position to its nearest point on the continental mainland coastline. Sampling positions and connecting segments are identical in both panels; islands are excluded from the distance calculation.

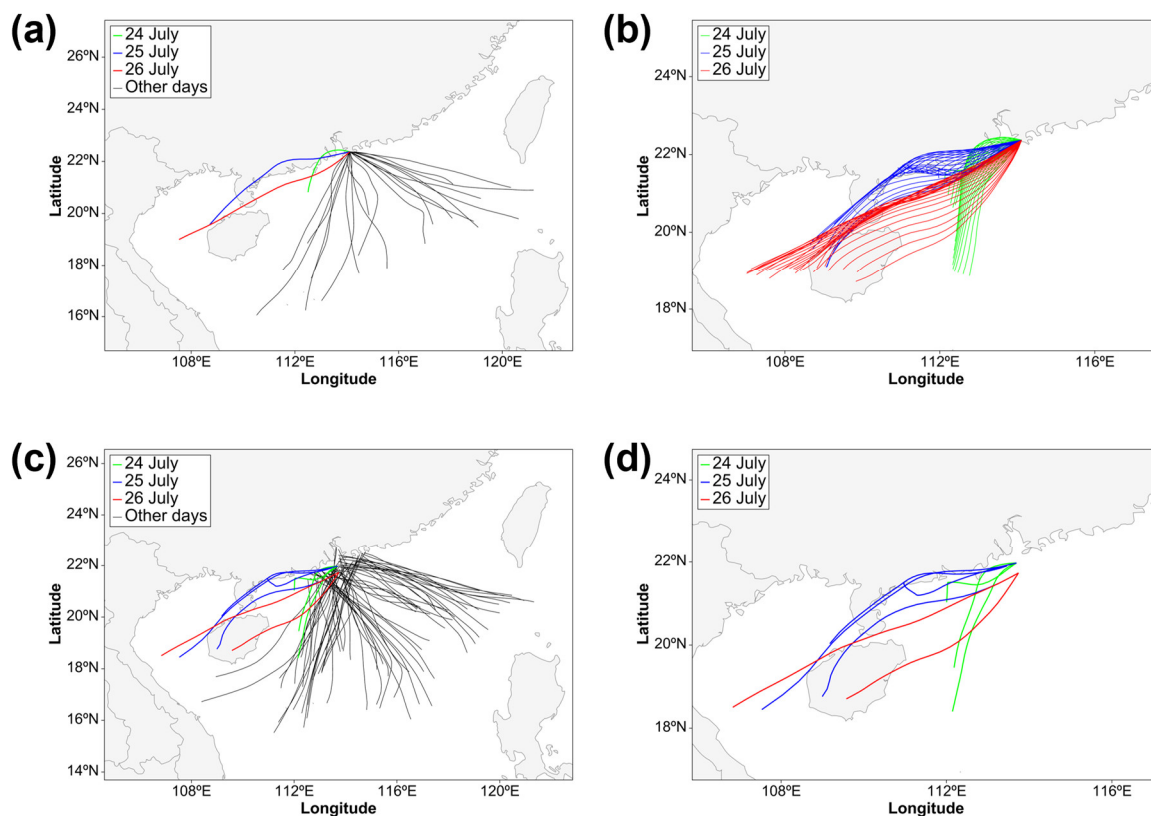
Lines 266-269: I may suggest adding the back trajectories of air masses to address the influence of anthropogenic pollutants on the sampling location.

Response: We have added 24 h backward-trajectory analyses for both the Tsuen Wan urban site and the moving marine sampling locations (revised Figure 4). The trajectories show frequent transport over the South China Sea and changes in pathways during 24–26 July. We discuss these transport changes together with the concurrent sulfate–ammonium enhancement in Section 3.2, without attributing all elevated ammonium to direct inland NH_3 transport. Over-water trajectories on 26 July do not exclude earlier continental influence, but the 24 h trajectories alone cannot establish that earlier contribution. The revised Figure 4 caption specifies the arrival height, software, meteorological-data provider, and the daily, hourly and sample-specific trajectory schedules.

The revised manuscript (Sect. 3.2), lines 426–428, now reads:

“These concurrent enhancements are consistent with an increased contribution from regional secondary aerosol containing ammonium and sulfate, potentially formed from continental precursors before or during transport over coastal waters.”

The figure is now revised and included in Section 3.2:



(Revised Figure 4) Figure R2. 24 h backward air-mass trajectories arriving at a height of 20 m during the summer 2024 GBA campaign, generated using MeteoinfoMap software with meteorological input data obtained from the National Oceanic and Atmospheric Administration (NOAA). (a) Daily trajectories arriving at the Tsuen Wan urban site during 12 July–3 August 2024. (b) Hourly trajectories arriving at Tsuen Wan during 24–26 July. (c) Sample-specific trajectories for the moving marine sampling locations, with arrival times and intervals determined by the individual filter sampling schedule. (d) Corresponding marine trajectories during 24–26 July. Trajectories for 24, 25 and 26 July are shown in green, blue and red, respectively, and those for other dates in black.

Lines 271-274: The spatial distribution of sulfate is confusing. Please describe the distribution of sulfate aerosols using the observed data or add a figure to describe it. Why is sulfate shaped more by regional background transport and the marine boundary layer? The authors need to elaborate the reasons more clearly.

Response: We thank the reviewer for this comment. Following the additional IC reanalysis undertaken in response to Reviewer 2's concerns, we updated the ion data in Table 1 and revised Section 3.1. The revised mean sulfate concentrations were 1.06 ± 0.73 , 1.23 ± 0.81 , and $1.96 \pm 1.34 \mu\text{g m}^{-3}$ in regions A, B, and C, respectively. Thus, sulfate showed the same numerical regional ordering as ammonium, and the previous statement that sulfate was lower in region C has been removed.

To describe the observed distribution more clearly, we have added **(New Figure S5) Figure R3** in the SI, showing individual marine sulfate measurements colored by region together with the hourly and daily-mean urban MARGA observations. This comparison reveals substantial episode-related variability. In particular, sulfate in region C averaged $0.71 \pm 0.08 \mu\text{g m}^{-3}$ during 21–22 July but increased to $3.21 \pm 0.44 \mu\text{g m}^{-3}$ during 1–2 August, with six filters collected during each visit. Urban daily-mean sulfate likewise increased from 0.61–0.64 to 2.24–2.57 $\mu\text{g m}^{-3}$ during these respective periods. Both records also showed elevated sulfate during 24–26 July. Consequently, the higher campaign mean in region C partly reflects the sampling of an enhanced regional episode and should not be interpreted as a persistent west-to-east spatial gradient.

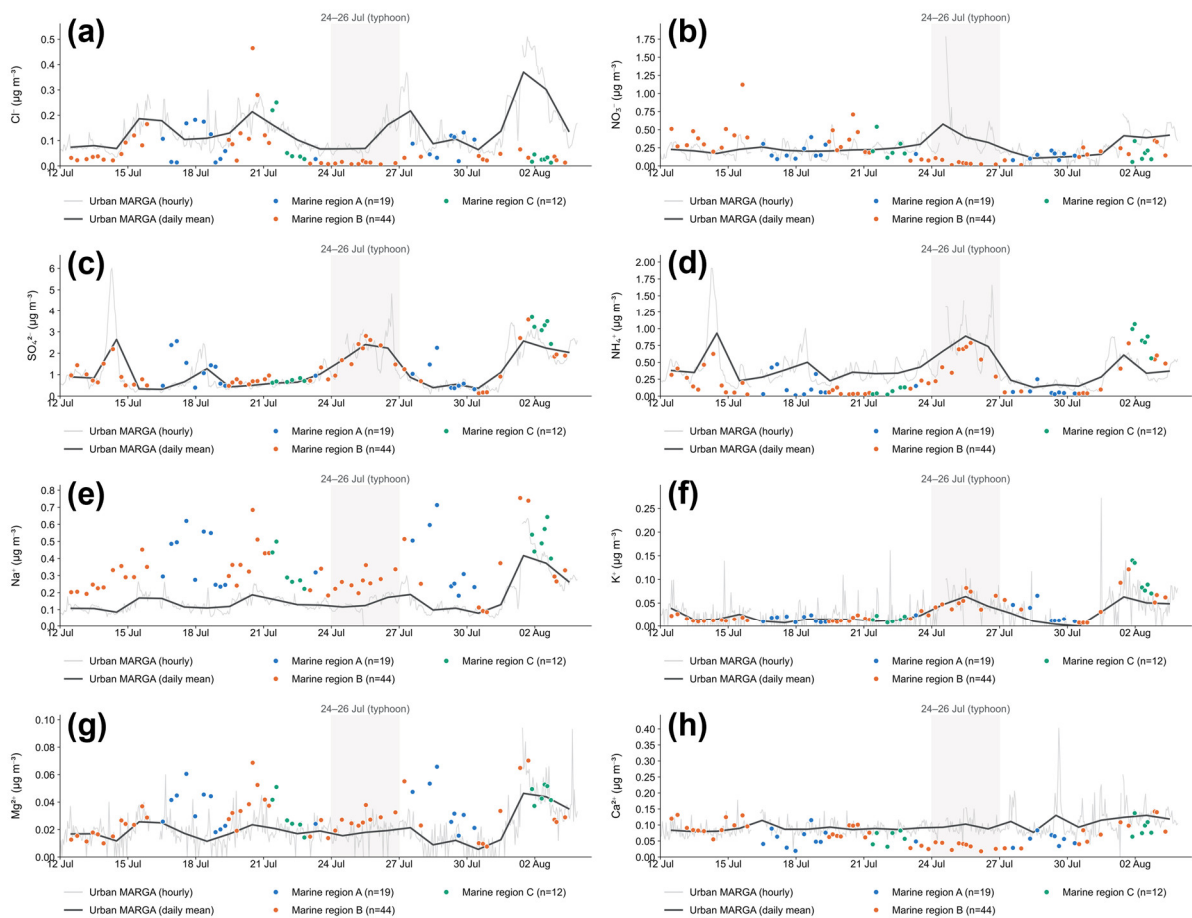
Sulfate also covaried strongly with ammonium in the marine samples (descriptive Pearson $r = 0.93$, $n = 75$). Their co-enhancement, together with the corresponding sulfate episodes at the urban site, is consistent with an appreciable contribution from regional secondary inorganic aerosol. Previous Hong Kong studies have similarly identified regional transport and secondary formation as important influences on fine-particle sulfate (Bian et al., 2014; Chow et al., 2022).

We have therefore replaced the earlier general attribution with an observation-based explanation. Regional transport and secondary formation remain plausible contributors, whereas the specific attribution to marine-boundary-layer processing has been removed because our measurements cannot distinguish sulfate formed locally over coastal waters from sulfate formed elsewhere and subsequently transported to the sampling area.

The revised manuscript (Sect. 3.1), lines 322–333, now reads:

“Sulfate concentrations averaged 1.06 ± 0.73 , 1.23 ± 0.81 , and $1.96 \pm 1.34 \mu\text{g m}^{-3}$ in regions A, B, and C, respectively, following the same numerical regional ordering as ammonium. However, these regional mean concentrations incorporate substantial temporal variability. Within region C, sulfate increased from $0.71 \pm 0.08 \mu\text{g m}^{-3}$ during 21–22 July to $3.21 \pm 0.44 \mu\text{g m}^{-3}$ during 1–2 August; urban MARGA observations showed a corresponding increase between these periods (Fig. S5c). Sulfate was also elevated in both records during 24–26 July and covaried strongly with ammonium concentrations (descriptive Pearson $r = 0.93$). These observations are consistent with a regional secondary inorganic aerosol influence on the coastal and marine measurements, in agreement with previous Hong Kong studies (Bian et al., 2014; Chow et al., 2022). The higher mean sulfate concentration in region C therefore reflects both the locations sampled and the atmospheric episodes encountered during the cruise. The available observations cannot separately quantify the contributions of local sulfate formation and regional transport.”

The figure added in the SI is copied below:



(New Figure S5) Figure R3. Time series of marine filter-based and urban MARGA ion concentrations during 12 July–3 August 2024. Panels show (a) Cl^- , (b) NO_3^- , (c) SO_4^{2-} , (d) NH_4^+ , (e) Na^+ , (f) K^+ , (g) Mg^{2+} and (h) Ca^{2+} . Light-grey and dark-grey lines represent urban hourly observations and daily means, respectively. Blue, orange and green points represent marine filters from regions A ($n = 19$), B ($n = 44$) and C ($n = 12$), respectively. Shading indicates the typhoon-influenced period of 24–26 July. Concentrations are expressed as ion mass ($\mu\text{g m}^{-3}$). Each marine point represents an individual sampling-period average.

Lines 279-281: The ratios did not vary a lot. In my view, the difference (34.6% vs. 32% vs. 27%) may not be significant. Is the ON contribution significantly different between the three regions? How about the significance level of their difference?

Response: We thank the reviewer for this observation. The mean ON/TN fractions were $34.7 \pm 11.7\%$, $31.7 \pm 13.7\%$, and $26.9 \pm 13.1\%$ in regions A, B, and C, respectively. Although these means decreased numerically from west to east, the overall regional difference was not statistically significant (Kruskal–Wallis $p = 0.224$). We have therefore revised the manuscript to describe this ordering as a descriptive pattern rather than a statistically significant regional difference.

To clarify this pattern, we also examined the corresponding IN concentrations, which averaged 0.17 ± 0.12 , 0.31 ± 0.21 , and $0.45 \pm 0.35 \mu\text{g N m}^{-3}$ in regions A, B, and C, respectively. Unlike ON/TN, IN showed a significant overall regional difference in the filter-level comparison (Kruskal–Wallis $H = 10.52$, $p = 0.005$). Dunn’s post hoc tests with Holm adjustment indicated higher IN in B and C than in A (adjusted $p = 0.0108$ and 0.0124 , respectively), whereas the B–C difference was not significant (adjusted $p = 0.520$). These results describe differences among the sampled regional records; they do

not separate geographic effects from sampling-date variability or account for temporal dependence among filters.

The numerically higher ON/TN fraction in region A thus coincided with lower IN rather than greater absolute ON abundance. Importantly, the significant IN differences do not imply significant differences in ON/TN. We have removed the implication that the regional ON/TN fractions alone demonstrate stronger marine biological emissions.

The revised manuscript (Sect. 3.1), lines 338–348, now reads:

“Mean ON/TN fractions were $34.7 \pm 11.7\%$, $31.7 \pm 13.7\%$ and $26.9 \pm 13.1\%$ in regions A, B and C, respectively, with no statistically significant overall regional difference (Kruskal–Wallis $p = 0.224$). In contrast, mean IN concentrations were 0.17 ± 0.12 , 0.31 ± 0.21 and 0.45 ± 0.35 $\mu\text{g N m}^{-3}$, respectively, and differed significantly among regions (Kruskal–Wallis $p = 0.005$). Holm-adjusted Dunn tests indicated higher IN concentrations in B and C than in A (adjusted $p = 0.011$ and 0.012 , respectively), but no significant difference between B and C (adjusted $p = 0.520$). These filter-level comparisons do not account for temporal dependence or separate regional differences from the atmospheric episodes sampled. The numerically higher ON/TN fraction in A was primarily driven by lower IN rather than higher absolute ON concentrations, as mean concentration was lowest in A (Table 1). Thus, the ON/TN pattern alone does not establish stronger marine-biogenic ON contributions. Limited and uneven regional sampling may also constrain the ability to detect differences in ON/TN.”

Lines 344-357: The variation of ON and IN during the typhoon period is interesting, but more explanations are needed. Why only $\text{NH}_4\text{-N}$ increased, but there were not obvious variations for the concentrations of $\text{NO}_3\text{-N}$ or ON?

The authors attributed the higher $\text{NH}_4\text{-N}$ during the typhoon period to the transport of continental/inland air masses. However, some air masses on 26 July were from the ocean. Why did the continental air masses not lead to higher ON or nitrate during the typhoon period?

Response to the two comments: We thank the reviewer for these closely related questions and address them together. Reanalysis of the marine filters shows that the episode was not an isolated increase in $\text{NH}_4^+\text{-N}$. Among the nine retained region-B filters collected during 24–26 July, mean $\text{NH}_4^+\text{-N}$ was 0.41 $\mu\text{g N m}^{-3}$, compared with 0.15 $\mu\text{g N m}^{-3}$ in the other region-B filters; SO_4^{2-} increased concurrently from 1.03 to 2.00 $\mu\text{g m}^{-3}$. By contrast, $\text{NO}_3^-\text{-N}$ was lower during the episode (0.010 versus 0.069 $\mu\text{g N m}^{-3}$), while bulk ON showed no corresponding increase (0.11 versus 0.12 $\mu\text{g N m}^{-3}$). A concurrent sulfate–ammonium enhancement was recorded at the urban site (MARGA SO_4^{2-} : 2.11 versus 1.01 $\mu\text{g m}^{-3}$; NH_4^+ : 0.76 versus 0.35 $\mu\text{g m}^{-3}$). These observations support an increased contribution from regional secondary aerosol containing ammonium and sulfate, potentially formed from continental precursors before or during transport.

The over-water trajectories on 26 July do not necessarily contradict this interpretation. Transport over water during the final 24 h does not exclude earlier continental influence on an already formed aerosol, although these trajectories alone cannot establish that earlier contribution. We have therefore removed the statement that all elevated particulate ammonium resulted from inland air masses bringing gaseous NH_3 directly to the sampling location.

Continental influence does not necessarily produce synchronous increases in ammonium, nitrate and ON. These components depend on different precursor sources and formation pathways: ammonium-containing sulfate aerosol involves NH_3 and sulfur precursors, nitrate depends on the production and partitioning of HNO_3 derived from NO_x , and ON comprises diverse primary and secondary compounds whose abundances depend on their own sources and processing histories. Consequently, an air mass enriched in ammonium and sulfate need not also be enriched in nitrate or ON.

For nitrate, mean shipboard NO_x was lower during the episode (1.90 versus 9.81 ppb in the other region-B filters), consistent with weaker exposure to recent NO_x -rich outflow, although this measurement alone cannot constrain the HNO_3 concentration in aged air. Reaction of HNO_3 with sea salt also requires an available HNO_3 supply and does not necessarily retain the resulting nitrate within $\text{PM}_{2.5}$. For ON, neither OC nor WSOC showed a concurrent episode-wide increase, consistent with the absence of a parallel enhancement in bulk organic aerosol and bulk ON. We therefore interpret the episode primarily as a sulfate–ammonium enhancement, rather than a uniform increase in all continentally influenced nitrogen components, and have revised the discussion accordingly.

The revised manuscript (Sect. 3.2), lines 420–441, now reads:

“During the typhoon-influenced period (24–26 July 2024), changes in regional meteorological conditions and air-mass transport pathways coincided with enhanced sulfate and ammonium concentrations in both marine and urban aerosols (Figs. 4, S5 and S8). In the nine marine filters collected in region B during this period, mean NH_4^+ –N was $0.41 \mu\text{g N m}^{-3}$, compared with $0.15 \mu\text{g N m}^{-3}$ in the other region-B samples, while mean sulfate concentrations were 2.00 versus $1.03 \mu\text{g m}^{-3}$. Urban MARGA observations showed corresponding enhancements in sulfate (2.11 versus $1.01 \mu\text{g m}^{-3}$) and ammonium (0.76 versus $0.35 \mu\text{g m}^{-3}$). These concurrent enhancements are consistent with an increased contribution from regional secondary aerosol containing ammonium and sulfate, potentially formed from continental precursors before or during transport over coastal waters. In contrast, mean marine NO_3^- –N concentrations were lower during the episode than in the other region-B samples (0.01 versus $0.07 \mu\text{g N m}^{-3}$), while bulk ON showed no corresponding enhancement (0.11 versus $0.12 \mu\text{g N m}^{-3}$).”

“These differing responses are compatible with differences in precursor sources and atmospheric processing among the N components. Formation of ammonium-containing sulfate aerosol involves NH_3 and sulfur precursors, whereas particulate nitrate depends on the production and gas–particle partitioning of HNO_3 derived from NO_x . ON encompasses diverse primary and secondary compounds whose abundances reflect their respective sources and processing histories. Consequently, continental influence that enhances ammonium and sulfate need not simultaneously enhance nitrate or ON. Mean shipboard NO_x was also lower during the episode (1.9 versus 9.8 ppb), consistent with weaker recent influence from NO_x -rich emissions, although NO_x concentrations do not directly constrain HNO_3 availability in aged air. Neither OC nor WSOC showed a concurrent enhancement, consistent with the absence of a parallel increase in bulk ON. Together, these observations support a regional sulfate–ammonium enhancement rather than a uniform increase in all aerosol N components.”

Why continental air masses lead to enhanced particulate NH_x through gas-to-particle partitioning? More evidence is needed. Are there any other possibilities?

Response: We have revised this mechanistic interpretation. The data do not require enhanced uptake of NH_3 at the ship to explain the observed NH_4^+ increase. A more direct explanation consistent with the measurements is the transport of pre-existing, ammonium-containing sulfate aerosol, potentially accompanied by further secondary processing during transport. The strong SO_4^{2-} – NH_4^+ co-variation and the concurrent sulfate–ammonium enhancement at the urban site support this regional-aerosol interpretation. Because NH_4^+ alone does not provide sufficient charge to neutralize all measured sulfate, we do not assume that the particles consisted solely of $(\text{NH}_4)_2\text{SO}_4$; other measured cations may also contribute. Local NH_3 partitioning remains possible, but it cannot be distinguished from upstream particle formation and transport without colocated marine NH_3 , HNO_3 , and size-resolved composition. We have accordingly replaced the previous definitive gas-to-particle-partitioning statement with this evidence-based explanation.

The revised manuscript (Sect. 3.2), lines 426–428, now reads:

“These concurrent enhancements are consistent with an increased contribution from regional secondary aerosol containing ammonium and sulfate, potentially formed from continental precursors before or during transport over coastal waters.”

In addition, back trajectories of air masses on 24 July (in yellow) in Figure 4 are difficult to read. Please change the color.

Response: In the (Revised Figure 4) Figure R2, the trajectories for 24 July have been changed from yellow to a clearly distinguishable green to improve contrast and visual separation from the other trajectories. The trajectory lines have also been thickened to further improve their visibility and readability in the figure.

The updated trajectories are shown in Figure 4 (caption, lines 443–449) and reproduced above as Figure R2. The caption states: “Trajectories for 24, 25 and 26 July are shown in green, blue and red, respectively, and those for other dates in black.”

The authors emphasized “Ecosystem Implications” in the title and calculated aerosol nitrogen deposition in Section 3.4. To what extent would these aerosol nitrogen depositions impact the marine ecosystem of the Greater Bay Area?

Response: We thank the reviewer for highlighting the need to align the title and discussion with the scope of our measurements. We have now replaced “Ecosystem Implications” in the title with “Implications for PM_{2.5}-Bound Nitrogen Deposition” and revised Section 3.4 accordingly. The estimated summer campaign–mean PM_{2.5}-bound N dry-deposition flux over the marine environment was 0.036 mg N m⁻² d⁻¹. This estimate characterizes one component of atmospheric N supply to GBA coastal waters; it does not quantify its contribution to phytoplankton N demand or demonstrate changes in marine productivity. Gaseous N, coarse particles and wet deposition were not included, and the ecological response also depends on N bioavailability and the nutrient and physical conditions of the receiving waters. We therefore focus the revised discussion on the magnitude, chemical composition and uncertainty of PM_{2.5}-bound N dry deposition, with ecological relevance presented only as context rather than a demonstrated outcome.

The revised manuscript (Title), lines 1–2, now reads:

“Comparative Nitrogen Speciation in Marine and Coastal Urban Aerosols of the Greater Bay Area and Implications for PM_{2.5}-Bound Nitrogen Deposition”

The revised manuscript (Sect. 3.4), lines 597–598, now reads:

“These estimates represent only the fine-particle (PM_{2.5}-bound) contribution to nitrogen dry deposition; coarse-mode particulate nitrogen and gas-phase reactive nitrogen species were not included.”

The revised manuscript (Conclusions), lines 693–695, now reads:

“Our deposition estimates provide a campaign-specific constraint on fine-particle atmospheric N inputs for such assessments, but do not establish changes in seawater nutrient stoichiometry, productivity or ecosystem state.”

And how about the levels of nitrogen nutrients in coastal seawater of the Greater Bay Area? If the waters are eutrophic, aerosol nitrogen deposition may not have an obvious influence on the marine ecosystem in this area.

Response: We agree that the importance of atmospheric N deposition depends on the nutrient status of the receiving waters. In nutrient-rich waters where N does not limit phytoplankton growth, additional atmospheric N may produce little immediate productivity response. However, nutrient conditions are spatially heterogeneous across the GBA: Pearl River-influenced waters receive substantial land-derived nutrient inputs, whereas eastern coastal waters, including Mirs Bay, are less directly affected by the Pearl River plume (Li et al., 2020). This contrast does not, by itself, establish N limitation or a greater biological response to atmospheric deposition in the eastern waters. Seawater nutrient concentrations and biological responses were not included in the present aerosol analysis and therefore cannot determine the local nutrient-limitation regime or quantify the ecological effect of the estimated deposition. Consistent with the revised title, we have narrowed the discussion to PM_{2.5}-bound N deposition and removed implications of a demonstrated ecosystem response. Future assessments would require a more complete atmospheric N deposition budget, together with concurrent seawater nutrient and biological measurements, to evaluate its importance relative to other nutrient sources.

The revised manuscript (Conclusions), lines 695–702, now reads:

“These potential implications warrant particular consideration in the eastern GBA coastal waters, including Mirs Bay in region C (Fig. 2a), where summer waters are less directly affected by nutrient-rich Pearl River discharge and have been reported to exhibit relatively low nutrient concentrations (Li et al., 2020; Lo et al., 2025). Atmospheric N inputs could have greater relative importance where other nutrient inputs are smaller, although lower nutrient concentrations alone do not establish N limitation. The contribution of aerosol inorganic and organic N to bioavailable nutrient supply and local productivity in these waters therefore merits further assessment through coordinated deposition, seawater nutrient and biological measurements.”

Reviewer #2

Comments:

The manuscript presents a genuinely valuable and rare dataset, pairing shipboard PM_{2.5} nitrogen speciation over the GBA coastal ocean with concurrent urban sampling at Tsuen Wan. The authors employed a multi-method approach, and utilizing molecular AMS fragments to investigate ON oxidation states is a sensible strategy to add mechanistic depth. However, the primary concerns holding the paper back are methodological rather than presentational, specifically regarding comparability and quantitation. The core marine-urban contrasts are confounded because the authors compare irregularly spaced, sub-daily marine filters against 24-hour urban integrals, and they evaluate filter-IC data, which is subject to known artifacts, against artifact-free MARGA data. Furthermore, the AMS oxidized/reduced ON diagnostics are biased by co-extracted inorganic nitrate, the offshore gradient statistics fail to account for spatial-temporal autocorrelation, and the authors build headline conclusions on insufficient evidence—such as determining ship-influenced ON chemistry based on only four samples, or annualizing deposition fluxes from a three-week summer window. In summary, while the dataset is suitable for publication in this journal, the manuscript requires a major revision to address analytical artifacts, reanalyze the data, and temper the interpretive claims to align with what the measurements can robustly support.

Response: We appreciate the reviewer's focus on measurement comparability and the evidential basis of the interpretations. We address the five key questions first and provide the detailed methods, limitations and manuscript changes under the eight major comments. Where the available measurements cannot supply an empirical artifact bound or identify a source fraction, we state that limitation explicitly instead of presenting a sensitivity scenario as a correction.

Key questions

Q1. Are the marine–urban contrasts partly analytical rather than atmospheric? The authors adopted MARGA for the urban site precisely because it avoids artifacts like NH₄NO₃ volatilization and HNO₃ adsorption (lines 185–193). However, the authors compare this artifact-free data against marine filter-IC data, which suffers from exactly these biases. How much of the central N–NH₄⁺/N–NO₃[–] contrast (marine ≈ 1.8 vs urban ≈ 5.4) survives once these known marine filter artifacts are bounded?

Response: We thank the reviewer for highlighting these concerns. We repeated the water extraction of all filter samples and remeasured the major water-soluble ions using a newly acquired ion chromatography (IC) system. The corresponding ion concentrations and analyses have been updated throughout the manuscript. We also acknowledge that the original comparisons were not supported by sufficiently rigorous statistical testing. We have addressed this deficiency by aligning sampling time bases and applying appropriate statistical comparisons, including multiple-testing adjustment where applicable. These revisions have led us to revise or qualify several specific statements while retaining the main findings concerning bulk-N distributions and differences in extract-based N-containing fragment composition.

For the NH₄⁺–N/NO₃[–]–N comparison specifically, the original approximately 1.8 versus 5.4 contrast is no longer retained. Following marine IC reanalysis and averaging urban MARGA observations over the actual marine pump-on windows, the ratios of mean NH₄⁺–N to mean NO₃[–]–N are 4.0 and 5.2 for the marine and urban records, respectively. The urban-minus-marine difference is 1.2, with a 95% date-cluster bootstrap interval of –2.0 to +3.5. This interval describes campaign sampling uncertainty rather than analytical bias and does not support a resolved marine–urban ratio difference.

Marine filter artifacts cannot be quantitatively bounded from these measurements alone. Urban filter–MARGA comparisons and temperature-sensitivity analyses provide supporting diagnostics but cannot be transferred directly into marine artifact corrections; MARGA is also not assumed to be entirely artifact-free. We therefore withdraw the original strong ratio contrast and retain the descriptive finding

that campaign-mean $\text{NH}_4^+\text{-N}$ exceeds $\text{NO}_3^-\text{-N}$ in both measured records. The detailed evaluation is provided in **Reviewer #2's major comment #2**.

The revised manuscript (Sect. 3.2), lines 400–403, now reads:

“Campaign-mean $\text{NH}_4^+\text{-N}$ exceeded $\text{NO}_3^-\text{-N}$ in both environments (Fig. 3c–f). For the comparison using urban MARGA observations averaged over the actual marine pump-on windows, the ratios of mean $\text{NH}_4^+\text{-N}$ to mean $\text{NO}_3^-\text{-N}$ were 4.0 and 5.2 for the marine and urban records, respectively, with no statistically resolved difference between them (Sect. S5).”

Q2. How much of the $\text{NO}^+/\text{NO}_2^+$ contrast is driven by inorganic nitrate, and can AMS actually support the ON claims? The marine samples retain appreciable inorganic nitrate (lines 329–336), which directly contributes to $\text{NO}^+/\text{NO}_2^+$ (lines 237–238). The lower marine ratio is likely just a different mixing ratio of inorganic/organic nitrate, not proof of a less oxidized organic pool. More importantly, the capability of AMS to quantitatively measure organic nitrogen is inherently very limited. Coupled with the small sample size, the current data simply cannot bear the weight of the mechanistic conclusions drawn in Section 3.3.1. The authors must quantify the inorganic bias.

Response: We thank the reviewer for this comment. We have clarified the scope and limitations of the AMS measurements and refined our interpretation by considering the $\text{NO}^+/\text{NO}_2^+$ ratio together with the organic-nitrate-related fragments at m/z 75 and 76. Our assessment of inorganic nitrate interference and the corresponding revisions are detailed in our response to **Reviewer #2's major comment #3**.

The revised manuscript (Sect. 2.3.5), lines 249–254 and 274–278, now reads:

“Because extraction recovery, nebulization, particle transmission and fragmentation affect the measured signals, the N-containing organic fragments were used to compare relative composition rather than to quantify bulk ON or water-soluble ON concentrations. These fragment signals are distinct from bulk ON measured directly on filter punches and WSTN measured in water extracts, the latter comprising both inorganic and organic nitrogen.”

“These complementary spectral signatures were interpreted together to assess the relative prominence of oxidized organic-N signatures, particularly organic-nitrate-related functionality, across sample groups. This interpretation provides qualitative evidence of compositional differences, rather than a quantitative measure of organic-nitrate abundance or the mean oxidation state of bulk ON.”

Q3. Is the “unique ON chemistry” conclusion supportable at $n = 4$? The authors build two full paragraphs of complex mechanism (imidazole-like heterocycles, secondary amides) in Section 3.3.2 based on exactly four offline AMS ship-influenced samples (line 205). What is the sample-to-sample variability here? Does this sweeping claim survive it?

Response: We thank the reviewer for pointing out this limitation. The offline AMS analysis included only four ship-emission-influenced samples, and we agree that this small sample size does not support a broad or definitive mechanistic conclusion regarding “unique” ship-related ON chemistry. We have therefore substantially toned down Section 3.3.2. Specifically, we removed the term “unique” from the subsection title and revised the discussion to focus on the observed spectral characteristics rather than on definitive formation mechanisms. The elevated $\text{NO}^+/\text{NO}_2^+$ ratios, enhanced oxygenated organonitrogen contributions, and stronger imidazole-like fragment signals are now described as indicative features of the four ship-influenced samples, rather than as general characteristics of ship emissions.

Sample-to-sample variability is shown by the individual values in Fig. 5b–c for the $\text{NO}^+/\text{NO}_2^+$ ratio and $\text{C}_{\geq 3}$ fragment-signal fraction. The $\text{NO}^+/\text{NO}_2^+$ ratio of the four ship-influenced extracts was 7.7 ± 1.7

(mean $\pm$ SD). Section 3.3.2 explicitly treats the four-sample results as exploratory and calls for targeted measurements across a larger set of ship plumes.

Finally, the previous mechanistic discussion involving secondary amide and imidazole-like heterocycle formation has been shortened and reframed as a possible interpretation supported by previous literature, rather than as a mechanism demonstrated by the present dataset. The revised text now emphasizes that additional targeted ship-plume measurements with a larger sample size would be needed to establish whether these features are broadly representative of ship-influenced marine aerosols.

The revised manuscript (Sect. 3.3.2), lines 531–550, now reads:

“3.3.2 ON composition in ship-emission-influenced aerosols”

“The four ship-influenced water extracts exhibited compositional features that differed from those of the marine group. Their mean $\text{NO}^+/\text{NO}_2^+$ ratio was higher than that of the marine extracts (7.7 ± 1.7 ; BH-adjusted $p = 0.025$; Fig. 5b; Table S12), and their average spectra showed different relative contributions of oxygen-containing N fragments (Fig. S10c). Direct exhaust measurements have demonstrated that ships can emit particulate organic nitrates (Chen et al., 2024), providing a plausible source context for the nitrate-related signatures observed here. However, the dependence of $\text{NO}^+/\text{NO}_2^+$ on nitrate composition and instrument response also applies to these samples, so the ratio is interpreted as qualitative compositional evidence rather than a quantitative measure of organic-nitrate abundance or bulk-ON oxidation state.”

“The fraction of signals assigned to imidazole-like fragments was significantly higher in ship-influenced extracts than in marine and urban extracts (BH-adjusted $p = 0.004$ and 0.002 , respectively; Fig. S13; Table S12). Selected $\text{C}_x\text{H}_y\text{N}_2^+$ fragments are consistent with N-containing heterocycles, as demonstrated by standard-compound measurements (Ge et al., 2024). Laboratory studies have also shown that aqueous reactions of α -dicarbonyls with ammonium and amines can produce imidazoles and other N-containing heterocycles (Yang et al., 2023), offering a possible processing pathway. The present spectra, however, do not distinguish direct emissions from subsequent atmospheric formation. The four samples provide exploratory evidence rather than a representative ship-emission profile. Additional targeted measurements across a larger number of ship plumes would help establish the prevalence and formation pathways of these signatures.”

Q4. Is the offshore ON gradient robust to the confounding of distance, region, and time? The cruise progressed through regions A→C over three weeks, meaning offshore distance is heavily entangled with west–east position and sampling date. The trend test (lines 289–298) treats these distance bins as independent. How did the authors handle the strong temporal and spatial autocorrelation? Does the gradient survive a test that actually accounts for it?

Response: We replaced the original distance-bin inference with an individual-filter approach using sampling-day fixed effects and cluster-based uncertainty. The negative within-day ON association remains in the four separate sensitivity checks, but it is not interpreted as a source fraction or transport loss rate. The detailed analysis and its remaining limitations are given under **Reviewer #2’s major comment #5**.

The revised manuscript (Sect. 3.1), lines 353–360 and 367–370, now reads:

“To assess offshore gradients while accounting for differences among sampling dates, bulk IN and ON concentrations in the 75 marine samples were analyzed separately using regression models with sampling-day fixed effects. Natural-log concentrations were regressed on offshore distance, with a separate intercept for each sampling date, so that the estimated offshore

association was based on within-day variation. Sampling dates were assigned using the midpoint of each sampling window, and effects were expressed as percentage changes per 10 km offshore. Statistical inference used a wild cluster bootstrap with sampling dates as clusters to account for dependence among filters collected on the same day.”

“Bulk ON exhibited a significant negative within-day association with offshore distance, with an estimated decrease of 12.2% per 10 km (95% CI: –20.3% to –4.5%; $p = 0.007$; Fig. 2c). This association persisted across all four robustness checks, with estimated decreases of 10.1–14.2% per 10 km (all $p < 0.05$; Table S5), supporting the robustness of the observed ON gradient to the adjustments examined.”

Q5. What are the bulk ON measurement uncertainties, and do they support annualized deposition fluxes? The reported ON values (0.07–0.12 $\mu\text{g m}^{-3}$, Table 1) are extremely close to the detection limits of thermal-evolution methods, yet no LOD or uncertainty metrics are provided. Furthermore, the deposition fluxes (Table 2) are annualized from a brief 23-day summer window. Summer marine air does not represent the annual cycle. This extrapolation is unwarranted.

Response: We thank the reviewer for highlighting the need to clarify analytical sensitivity, measurement uncertainty, and the temporal representativeness of the deposition estimates. We have revised Section 2.3.1 to provide the relevant detection-limit and uncertainty information.

A low atmospheric concentration does not, by itself, establish proximity to the analytical detection limit, because the nitrogen mass analyzed also depends on the sampled air volume and the fraction of the filter deposit used for analysis. Yu et al. (2021) reported a nitrogen mass detection limit of 96 ng N for a 1 cm^2 filter aliquot, calculated as three times the standard deviation of replicate field-blank measurements. In our marine analyses, four 1 cm^2 punches were combined from an effective deposit area of 414 cm^2 . Using the published mass detection limit as a literature-based benchmark, and assuming that the same per-run mass threshold applies to the combined four-punch analysis, the estimated air-equivalent detection limit is approximately 0.039 $\mu\text{g N m}^{-3}$ for the mean sampling duration of 3.8 h at a flow rate of 1.13 $\text{m}^3 \text{min}^{-1}$. The regional mean ON concentrations reported in Table 1 exceed this representative benchmark.

Yu et al. (2021) estimated relative measurement uncertainties of 8.4% for IN and 14% for ON in their ambient-sample validation. As our measurements employed a similar thermal-evolution–MCR analytical method, we use these published values as reference estimates of measurement uncertainty for IN and ON. This information has now been added to Section 2.3.1.

Regarding deposition, we agree that the 23-day summer campaign cannot represent the annual cycle, irrespective of analytical precision. We have removed the annualization and now report summer campaign–mean $\text{PM}_{2.5}$ -bound TN dry-deposition fluxes in $\text{mg N m}^{-2} \text{d}^{-1}$ in Table 2. The revised discussion explicitly identifies these as partial, campaign-specific estimates of atmospheric nitrogen input, rather than annual deposition budgets. The uncertainty associated with deposition velocity is addressed separately through the sensitivity analysis described in our response to **Reviewer #2’s major comment #7**.

The revised manuscript (Sects. 2.3.1 and 2.4), lines 192–198 and 287–289, now reads:

“For marine samples, four 1 cm^2 filter punches were combined for analysis. For this combined punch area, using the published N mass detection limit of 96 ng as a literature-based benchmark (Yu et al., 2021), an effective filter deposit area of 414 cm^2 , a sampling flow rate of 1.13 $\text{m}^3 \text{min}^{-1}$ and a mean sampling duration of 3.8 h, the estimated air-equivalent N detection limit was approximately 0.039 $\mu\text{g N m}^{-3}$. The regional mean IN and ON concentrations exceeded this estimated benchmark. Relative measurement uncertainties of 8.4% for IN and 14% for ON were reported in the ambient-sample validation of this method (Yu et al., 2021).”

“Fluxes calculated in $\text{mg N m}^{-2} \text{s}^{-1}$ were multiplied by 86,400 to obtain $\text{mg N m}^{-2} \text{d}^{-1}$. These estimates represent conditions during the summer campaign and were not annualized.”

Major comments

1. Marine filters ran 1.2–17.1 h (mean 3.8 ± 2.8 h; lines 138–139), meaning the marine record is effectively sub-daily and irregularly spaced, whereas the urban filters are 24-h integrals (line 153) and the urban nitrate/ammonium are hourly MARGA. Short filters capture transient peaks that 24-h integration smooths out, which inflates apparent marine variability and shifts marine concentration statistics relative to the urban site. This directly undermines the statement regarding “broadly comparable concentrations and temporal variability” (lines 321–324) and the distributional comparisons in Fig. 3. The authors must state the averaging times side by side, and either aggregate the marine data to a comparable time base or demonstrate that the mismatch does not drive the observed contrasts.

Response: We thank the reviewer for highlighting the different sampling integration times. Marine filters integrated 1.2–17.1 h of actual pump-on time (mean 3.8 ± 2.8 h), whereas urban bulk-N filters represented 24 h and urban MARGA provided hourly ion measurements. The integration times are stated together in Section S5, and Section 3.2 explains the shorter marine integrations relative to the urban 24 h filters. The Figure 3 caption identifies the measurement methods and clarifies that the distributions reflect their respective sampling resolutions. We have removed the statement concerning comparable temporal variability.

For bulk IN and ON, we added a daily comparison in Section 3.2 and Supplement Section S5. Marine measurements were aggregated by local calendar date using actual pump-on-duration weighting, excluding sampler-off periods and allocating segments crossing midnight to the corresponding dates. Across 23 paired dates, mean marine IN and ON concentrations were 0.28 and $0.10 \mu\text{g N m}^{-3}$, respectively, compared with 0.22 and $0.14 \mu\text{g N m}^{-3}$ for the urban filters. The 95% paired-date bootstrap intervals for the marine-minus-urban mean differences were -0.04 to $+0.15 \mu\text{g N m}^{-3}$ for IN and -0.11 to $+0.01 \mu\text{g N m}^{-3}$ for ON. Thus, the daily comparison did not resolve a difference in campaign-mean concentrations, although this does not establish equivalence. Marine daily coverage ranged from 2.2 to 23.5 h (median 10.1 h), so these aggregates represent sampled-period means rather than complete 24 h means.

For the inorganic ions, the hourly MARGA record allows the effect of temporal averaging to be displayed directly. We have added the **(New Figure S5) Figure R3** in SI showing urban hourly concentrations and daily means alongside the sub-daily marine filter measurements for all eight measured ions. The urban curves illustrate both short-term fluctuations and their smoothing under daily averaging, providing temporal context for the marine observations, whose integration times fall between these two scales. This presentation supports a descriptive comparison of concentration levels and the timing of elevated concentrations, while making the different temporal resolutions explicit. For quantitative ion comparisons, urban MARGA observations were additionally averaged over the actual marine pump-on windows.

Together, these additions address temporal comparability through daily aggregation of bulk N and time-resolved comparisons of the ions. We have removed the claim of comparable temporal variability and distinguish descriptive features of the individual-filter records from comparisons performed on aligned time bases.

The revised manuscript (Sect. 3.2), lines 392–399 and 403–405, now reads:

“Marine filters integrated shorter and more variable sampling periods than the urban 24-h filters. To improve temporal comparability, marine bulk-N concentrations were aggregated by local sampling date using actual pump-on duration as the weighting factor (Sect. S5). Across 23 paired dates, mean marine IN and ON concentrations were 0.28 and $0.10 \mu\text{g N m}^{-3}$, respectively,

compared with 0.22 and 0.14 $\mu\text{g N m}^{-3}$ in the urban samples. These concentrations were of similar magnitude, although marine daily aggregates represented only the sampled portions of each day and did not provide complete 24 h coverage. Accordingly, the individual-filter records in Fig. 3a–b provide descriptive temporal context rather than a basis for directly comparing temporal variability between the two environments.”

“Hourly and daily urban MARGA records are also shown alongside the marine filter measurements to illustrate ion variability at different temporal resolutions (Fig. S5).”

2. The authors adopt MARGA for the urban site specifically because filter sampling suffers semi-volatile NH_4NO_3 loss (lines 189–193). However, they then compare those artifact-free urban values against marine nitrate and ammonium measured by filter-IC, which is subject to exactly that loss and additionally to positive HNO_3 adsorption on quartz filters. The marine $\text{N-NH}_4^+/\text{N-NO}_3^-$ ratio (≈ 1.8) versus the urban ratio (≈ 5.4) (lines 325–328) is one of the headline contrasts of the manuscript, and it is heavily confounded by this inconsistency. Note also that in mass terms, the marine samples show NO_3^- (0.38–0.58 $\mu\text{g m}^{-3}$) exceeding NH_4^+ (0.19–0.25 $\mu\text{g m}^{-3}$) across all regions (Table 1), so the “ NH_4^+ -dominant” framing depends entirely on the nitrogen-mass conversion and on the assumption that filter nitrate is unbiased. The authors must bound the filter artifacts (e.g., using denuder or backup-filter data, or literature values for this specific sampler and duration) and propagate that uncertainty into the marine–urban ratio comparison.

Response: We thank the reviewer for highlighting the potential influence of sampling artifacts on the marine–urban comparison. A key mechanism underlying negative filter-based nitrate bias is the temperature-dependent volatility of ammonium nitrate. As temperature rises during sampling, the gas–particle equilibrium shifts towards gaseous NH_3 and HNO_3 , and nitrate previously collected on the filter may volatilize and be lost in the sampling airflow. Longer collection periods generally span a larger portion of the diurnal temperature cycle and therefore increase the likelihood that material collected under cooler conditions will subsequently experience warmer conditions. Consequently, the nitrate remaining on a filter may underestimate the particulate nitrate collected over the sampling period. Consistent with this mechanism, Zhang et al. (2026) observed an inverse relationship between temperature and the particle-phase nitrate fraction within the diurnal cycle, together with poorer agreement between filter-based and MARGA $\text{PM}_{2.5}$ nitrate measurements under warmer conditions.

To examine this relationship in our campaign, we used the hourly urban MARGA record to characterize nitrate partitioning over short sampling windows. The fine-particle nitrate fraction, F , was defined as $\text{PM}_{2.5}$ nitrate divided by the sum of $\text{PM}_{2.5}$ nitrate and gaseous HNO_3 , expressed on a common nitrate-equivalent molar basis. We calculated the within-window ranges of F and temperature for windows containing two, three, four and five consecutive hourly observations [(New Figure S3) Figure R4]. Larger temperature ranges were generally accompanied by greater variability in F , particularly in the longer windows, although the relationship was not monotonic in every category. These observations illustrate the variability of ambient nitrate partitioning over different sampling windows. They are not direct measurements of nitrate loss from a filter and were therefore not used as quantitative corrections for marine samples.

Together, this mechanism and the MARGA observations provide the rationale for examining sampling duration and within-sampling temperature variation in our campaign. Shorter collection periods with smaller temperature changes may reduce exposure to temperature-driven repartitioning, although they do not eliminate volatilization under persistently warm conditions. Adsorption of gaseous HNO_3 can separately produce a positive nitrate artifact. MARGA reduces these filter-related effects by collecting gases and particles separately into liquid solutions for prompt analysis, but is not assumed to be entirely artifact-free. We therefore evaluated the marine–urban comparison through IC reanalysis, temporal matching and the following sampling-condition sensitivity checks.

First, we repeated the water extraction and IC measurements and updated the marine–urban comparison. All filter samples were re-extracted with water, and the major water-soluble ions were

remeasured using a newly acquired IC system. Following this reanalysis and averaging urban MARGA observations over the actual marine pump-on windows, the ratios of mean $\text{NH}_4^+\text{-N}$ to mean $\text{NO}_3^-\text{-N}$ are 4.0 for marine filters and 5.2 for urban MARGA. The original approximately 1.8 versus 5.4 contrast has therefore been withdrawn. The 95% date-bootstrap interval for the urban-minus-marine difference is -2.0 to $+3.5$, which does not support a resolved difference. This interval describes campaign sampling uncertainty rather than analytical bias. The IC reanalysis improves the analytical basis of the comparison but does not correct artifacts occurring during filter collection.

Second, we examined marine sampling durations and temperature variations. Marine collection periods were generally much shorter than the 24 h urban filter collections: actual pump-on durations ranged from 1.2 to 17.1 h, with a mean of 3.8 h and a median of 2.6 h. Moreover, 69 of the 75 retained marine filters experienced temperature ranges of $\leq 3^\circ\text{C}$ during active sampling. Most marine filters therefore sampled a more limited portion of the diurnal temperature cycle. These conditions suggest less exposure to diurnal temperature changes than for 24 h collections, although they do not establish negligible sampling artifacts.

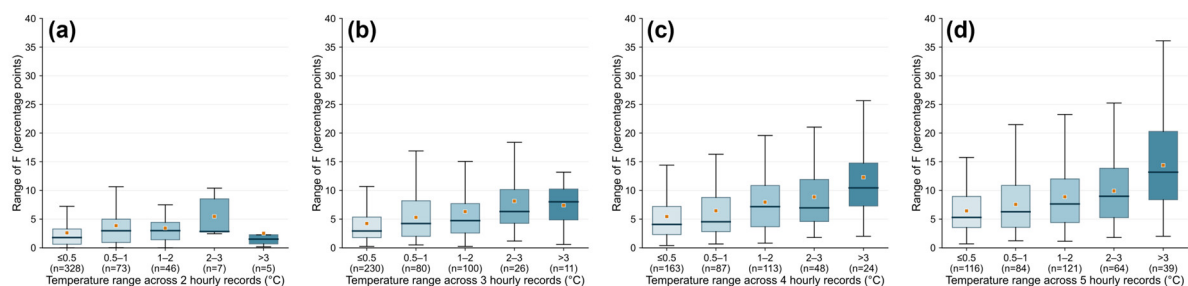
Finally, we tested whether the marine results were sensitive to filters experiencing larger temperature changes. Excluding the six marine filters with active-sampling temperature ranges $>3^\circ\text{C}$ changed mean NO_3^- and NH_4^+ concentrations by only $+2.08\%$ and $+1.85\%$, respectively. The ratio of mean $\text{NH}_4^+\text{-N}$ to mean $\text{NO}_3^-\text{-N}$ changed from 4.02 to 4.01 (-0.22%). Thus, the campaign-mean results were not driven by these six samples, and all 75 marine filters were retained. The 3°C criterion was used for sensitivity analysis, not as a validated threshold for the occurrence of artifacts.

These checks support the stability of the measured campaign summaries to the exclusion examined, but cannot quantify a systematic artifact affecting the marine dataset. Without denuder or backup-filter measurements, we cannot provide an empirical marine artifact bound or propagate it into an artifact-corrected ratio. We therefore retain only the descriptive finding that campaign-mean measured $\text{NH}_4^+\text{-N}$ exceeds $\text{NO}_3^-\text{-N}$ in both environments, without claiming a resolved marine–urban ratio contrast. We also clarify that this statement refers to nitrogen-equivalent mass, the appropriate basis for comparing contributions to inorganic N, rather than to the masses of the ions themselves.

The revised manuscript (Sect. 2.3.2), lines 210–213, now reads:

“By collecting gases and particles separately into liquid solutions for prompt analysis, MARGA provides higher temporal resolution and reduces artifacts associated with prolonged filter collection and storage, including losses of semi-volatile ammonium nitrate (Zhang et al., 2026).”

The added figure in the SI is copied below:



(New Figure S3) Figure R4. Variation in the particle nitrate fraction (F) in relation to temperature variability over different time windows. F is defined as the molar amount of nitrate in $\text{PM}_{2.5}$ divided by the sum of $\text{PM}_{2.5}$ nitrate and gaseous HNO_3 . Boxplots show the range of F (percentage points) grouped by temperature range for (a) 2-h, (b) 3-h, (c) 4-h, and (d) 5-h observations. Orange dots represent mean values, center lines indicate medians, boxes represent the interquartile range, and whiskers indicate the data range. Sample sizes (n) are shown below each temperature-range category.

3. First, the offline AMS analyzes water-extracted, nebulized material, reporting water-soluble ON only, while the thermal-evolution IN/ON is from filter punches (bulk). The authors use “ON” for both without reconciling the two operational definitions; the manuscript needs to clarify which quantity is which throughout, and whether the bulk ON and AMS-derived ON fractions are actually consistent. Second, and more importantly, the $\text{NO}^+/\text{NO}_2^+$ ratio and the CHN-vs-CHON split are highly sensitive to the inorganic nitrate present in the extract. Because the marine samples retain appreciable nitrate (as argued by the authors regarding sea-salt processing, lines 329–336), a lower marine $\text{NO}^+/\text{NO}_2^+$ partly reflects a larger inorganic-nitrate contribution to those fragments rather than a genuinely less oxidized organic pool. The interpretation in Section 3.3.1 and the conclusion (lines 522–527) require this bias to be quantified or explicitly bounded; otherwise, the oxidized/reduced dichotomy remains unsupported.

Response: We thank the reviewer for highlighting the distinction between bulk ON measurements and extract-based AMS diagnostics, and for raising the potential influence of inorganic nitrate on their interpretation. We agree that the original terminology and some of the interpretive statements require clarification. Nevertheless, our interpretation draws on complementary spectral observations rather than the $\text{NO}^+/\text{NO}_2^+$ ratio alone.

First, we distinguish the quantities measured by the different methods. “Bulk ON” refers to the thermal-evolution/MCR measurement on filter punches, which encompasses both water-soluble and water-insoluble organic nitrogen. “WSTN” refers to water-soluble total nitrogen measured using the TOC/TN analyser. The offline AMS characterizes the non-refractory material detected following water extraction, nebulization and drying. Accordingly, we refer to its carbon-containing nitrogen signals as “AMS N-containing organic fragments”, and their normalized contributions as fragment-signal fractions. These fractions describe the composition represented in the extract spectra; they are not measurements of bulk ON mass or quantitative water-soluble ON concentrations. We therefore do not claim a quantitative mass-balance agreement between bulk ON and the AMS fragment fractions.

Second, the updated IC measurements provide relevant context. Mean NO_3^- concentrations were of similar magnitude in the marine filter samples and urban hourly MARGA observations (0.22 ± 0.18 versus $0.25 \pm 0.17 \mu\text{g m}^{-3}$, respectively; mean $\pm$ SD). In contrast, mean Na^+ was approximately 2.22 times higher in the marine samples (0.35 ± 0.15 versus $0.16 \pm 0.10 \mu\text{g m}^{-3}$). These campaign summaries characterize the ambient ionic composition; they do not directly quantify inorganic-nitrate contributions to the offline-AMS spectra. The possible direction of sea-salt-related interference also requires consideration. Bruns et al. (2010) reported substantially higher $\text{NO}^+/\text{NO}_2^+$ ratios for NaNO_3 than for NH_4NO_3 , approximately 80 and 2.4, respectively. Thus, if sea-salt-associated NaNO_3 contributes appreciably to the detected marine spectra and exhibits comparable fragmentation behaviour, it would tend to increase the marine ratio. The retention of nitrate in marine aerosol therefore does not, by itself, explain the lower marine $\text{NO}^+/\text{NO}_2^+$ ratio. We use these published results to illustrate a possible direction of interference, rather than as calibration endmembers for our instrument. Higher Na^+ alone does not establish nitrate speciation (Bruns et al., 2010; Day et al., 2022). Our interpretation combines the higher urban $\text{NO}^+/\text{NO}_2^+$ ratio with the more prominent signals and stronger covariation of the carbon-containing fragments assigned to CHNO_3^+ and CH_2NO_3^+ at nominal m/z 75 and 76 in urban extracts (Figs. S10 and S12). CH_2NO_3^+ has previously been reported as an organic-nitrate-related AMS fragment. These observations provide complementary evidence beyond the carbon-free NO^+ and NO_2^+ signals, although the fragment assignments do not identify unique parent molecules (Fry et al., 2011).

Thirdly, regarding the CHN/CHON comparison, carbon-free NO^+ and NO_2^+ ions are excluded from both families and therefore do not directly enter their signal sums. However, we agree that the CHN/CHON split is not itself a measure of nitrogen oxidation state: CHON fragments can also originate from compounds containing reduced nitrogen, including amides and amino acids. We therefore retain these families as descriptors of fragment composition.

Taken together, these diagnostics support the qualitative interpretation that organic-nitrate-related oxidized-N functionality is more prominent in the urban water-extract spectra. We retain this interpretation with appropriately qualified wording, without inferring a quantitative organic-nitrate fraction or the mean oxidation state of bulk ON.

The revised manuscript (Sect. 2.3.5), lines 249–254, now reads:

“Because extraction recovery, nebulization, particle transmission and fragmentation affect the measured signals, the N-containing organic fragments were used to compare relative composition rather than to quantify bulk ON or water-soluble ON concentrations. These fragment signals are distinct from bulk ON measured directly on filter punches and WSTN measured in water extracts, the latter comprising both inorganic and organic nitrogen.”

The revised manuscript (Sect. 3.3.1), lines 479–484 and 499–505, now reads:

“Importantly, oxygen-containing fragments do not necessarily indicate oxidized nitrogen functionality. Standard-compound measurements show that amides generate $C_nH_{2n}NO^+$ fragments and amino acids produce ions such as $C_2H_4NO_2^+$ and CH_4NO^+ (Ge et al., 2024); oxygen in these fragments therefore need not belong to a nitrate or nitro group. We interpret the CHN and CHON families as compositional descriptors and examine the complementary nitrate-related signatures below to assess evidence for oxidized organic-N functionality.”

“Laboratory measurements have shown that $NaNO_3$ can produce substantially higher NO^+/NO_2^+ ratios than NH_4NO_3 (Bruns et al., 2010). Consequently, if sea-salt-associated $NaNO_3$ contributed appreciably to the detected marine spectra with comparable fragmentation behavior, it would tend to increase rather than decrease the marine ratio. Under this assumption, a greater contribution from sea-salt associated $NaNO_3$ would not explain the lower observed marine ratio, although ambient Na^+ cannot establish nitrate speciation and literature ratios cannot substitute for instrument-specific calibration (Day et al., 2022).”

4. Section 3.1 argues that ON is dominated by continental sources and is rapidly attenuated during marine transport (lines 298–305), yet Section 3.3.1 attributes the marine reduced-N enrichment to marine biogenic origins (alkyl amines, amino acids, bubble-burst DOM; lines 385–391). These claims pull in opposite directions: if ON is continental and declines offshore, the marine-biogenic reduced-N pool is merely a minor, diminishing contributor. Thus, “enrichment in reduced-N fragments” is a relative statement about composition, not evidence of biogenic dominance. The manuscript offers no independent marine-biogenic tracer. The authors should test the biogenic attribution directly (e.g., using MSA if measured, examining the offshore trend of the CHN fraction itself, or correlating with wind speed/ocean-color productivity). As currently written, the biogenic-source language overreaches the available evidence.

Response: We thank the reviewer for identifying the overinterpretation of source contributions in our original discussion. Bulk ON concentrations and relative AMS fragment composition describe different properties. An offshore decrease in bulk ON can coexist with a relatively large contribution of reduced-N-related fragments in the water-extracted material. However, neither observation alone establishes the dominance of a particular source.

We have revised Section 3.1 to describe the offshore association as consistent with a coastal or continental contribution, while acknowledging possible effects of dilution, mixing, removal, and atmospheric processing. We no longer interpret this spatial association as demonstrating continental source dominance or rapid attenuation during transport, because the campaign does not quantify source fractions or follow the evolution of a single air mass.

In Section 3.3.1, we now distinguish relative fragment composition from source attribution. The mean CHN_1 contribution was numerically higher in marine extracts, but the marine–urban difference was not significant after Benjamini–Hochberg (BH) adjustment (adjusted $p = 0.098$). We have therefore removed the categorical statement that marine ON is dominated by reduced, biogenic nitrogen compounds. Marine biological emissions remain a possible contributor, but the present fragment

measurements do not establish their contribution relative to transported terrestrial emissions and atmospheric processing.

Previous evidence linking marine aerosol water-soluble ON to ocean productivity and wind speed provides context for this hypothesis (Altieri et al., 2016), rather than direct validation for our coastal campaign. We agree that independent source-sensitive measurements and appropriately matched biological and meteorological observations would be needed to test the marine-biogenic attribution. Accordingly, the revised Sections 3.1 and 3.3.1 and the Abstract emphasize the observed concentration association and relative extract composition, without attributing marine ON dominance to biological sources.

The revised manuscript (Sect. 3.1), lines 372–377, now reads:

“The negative ON association is consistent with a contribution from coastal or continental sources. Previous modelling has demonstrated that atmospheric transport links continental ON sources to deposition over the ocean, with chemical processing and removal influencing ON distribution (Kanakidou et al., 2012). Dilution, mixing and removal may therefore contribute to the observed offshore decrease, while atmospheric processing may further modify ON concentrations.”

The revised manuscript (Sect. 3.3.1), lines 463–474, now reads:

“The mean contribution of CHN_1 fragments, containing C, H and one N atom but no O, was numerically higher in marine than urban water extracts (64.6% versus 57.7%; Fig. 5a), although the difference was not statistically significant after Benjamini–Hochberg (BH) adjustment (adjusted $p = 0.098$; Table S12). Laboratory measurements of organic-N standards show that amines produce prominent CHN fragments, including $\text{C}_n\text{H}_{2n+2}\text{N}^+$ ions, supporting their interpretation as signatures compatible with reduced-N-containing precursors (Ge et al., 2024). Previous studies have reported amines and amino acids in marine aerosols (Calderón et al., 2007; Wedyan and Preston, 2008), while observations in remote marine environments have linked water-soluble ON to ocean productivity and wind-driven aerosol production (Altieri et al., 2016). These findings provide context for a possible marine contribution to the observed fragment composition. However, the CHN_1 fraction alone cannot distinguish this contribution from the influence of transported terrestrial material or atmospheric processing in the GBA coastal environment.”

5. The 75 marine samples are binned into six distance classes and tested with Mann–Kendall and Sen's slope (lines 289–298). However, offshore distance is heavily confounded with region (A→C, west→east) and sampling date, as the cruise progressed in space and time simultaneously. Furthermore, samples are spatially and temporally autocorrelated within persistent monsoon air masses, meaning the effective degrees of freedom are far below $n = 75$. The central contrast (that ON shows a significant offshore trend while IN does not) rests on p -values from a test that falsely assumes independence. The authors must (a) account for autocorrelation (e.g., blocking/clustering by air-mass episode, or reporting effective sample size), and (b) demonstrate that the ON gradient is not merely an artifact of the west–east regional gradient or temporal drift over the campaign. Similarly, Fig. 5 reports multiple Mann–Whitney comparisons with no stated correction for multiple testing.

Response: We thank the reviewer for identifying the dependence and space–time confounding in the original offshore analysis. We agree that the original distance-bin trend tests did not adequately address the cruise sampling design. We have replaced that inference with a within-day analysis of the 75 retained marine filters, using sampling-day fixed effects and cluster-based uncertainty estimates.

The model compares log concentrations among filters collected on the same day, allowing each date to have its own concentration baseline. Thus, between-day changes do not determine the distance

coefficient. Clustering by day allows measurements from the same date to be dependent; days are clusters, rather than individual filters being treated as independent replicates.

In the primary model, ON decreased by 12.20% per 10 km offshore (95% CI: -20.26% to -4.45%; $p=0.0066$). No clear distance association was detected for IN (+8.48%; 95% CI: -12.85% to +37.80%; $p=0.511$). These estimates describe within-day associations during this campaign.

We retained four focused sensitivity checks (Table S5). Grouping neighbouring dates into eight cruise periods allows dependence to persist across days; the ON estimate remained -12.20% ($p = 0.0234$). Adding longitude addresses the west-east component within days (-12.15%; $p = 0.0081$). Adding 24-hour sine-cosine terms allows for diurnal variation (-10.09%; $p = 0.0442$). Excluding 24–26 July tests sensitivity to the typhoon period (-14.24%; $p = 0.0034$). IN was not significant in these checks. We therefore retain the negative within-day ON association. We have accordingly narrowed the interpretation and replaced Figure 2b–c with within-day comparisons, with the five core analyses summarized in the Supplement.

For Figure 5, we re-evaluated the two-sided comparisons and applied Benjamini–Hochberg (BH) adjustment across the complete family of 45 comparisons (Benjamini & Hochberg, 1995). Table S12 displays the 10 organic and N-containing metrics. The urban–marine contrasts in $\text{NO}^+/\text{NO}_2^+$ ($p_{\text{BH}} = 0.009$), $\text{CHN} > 1$ (0.016) and $\text{C} \geq 3$ (8.45×10^{-6}) remain significant; $\text{CHN}1$ and $\text{CHON}1$ do not (both 0.098). These sample-level tests characterize relative extract composition and do not remove temporal dependence.

The revised manuscript (Sect. 3.1), lines 358–372, now reads:

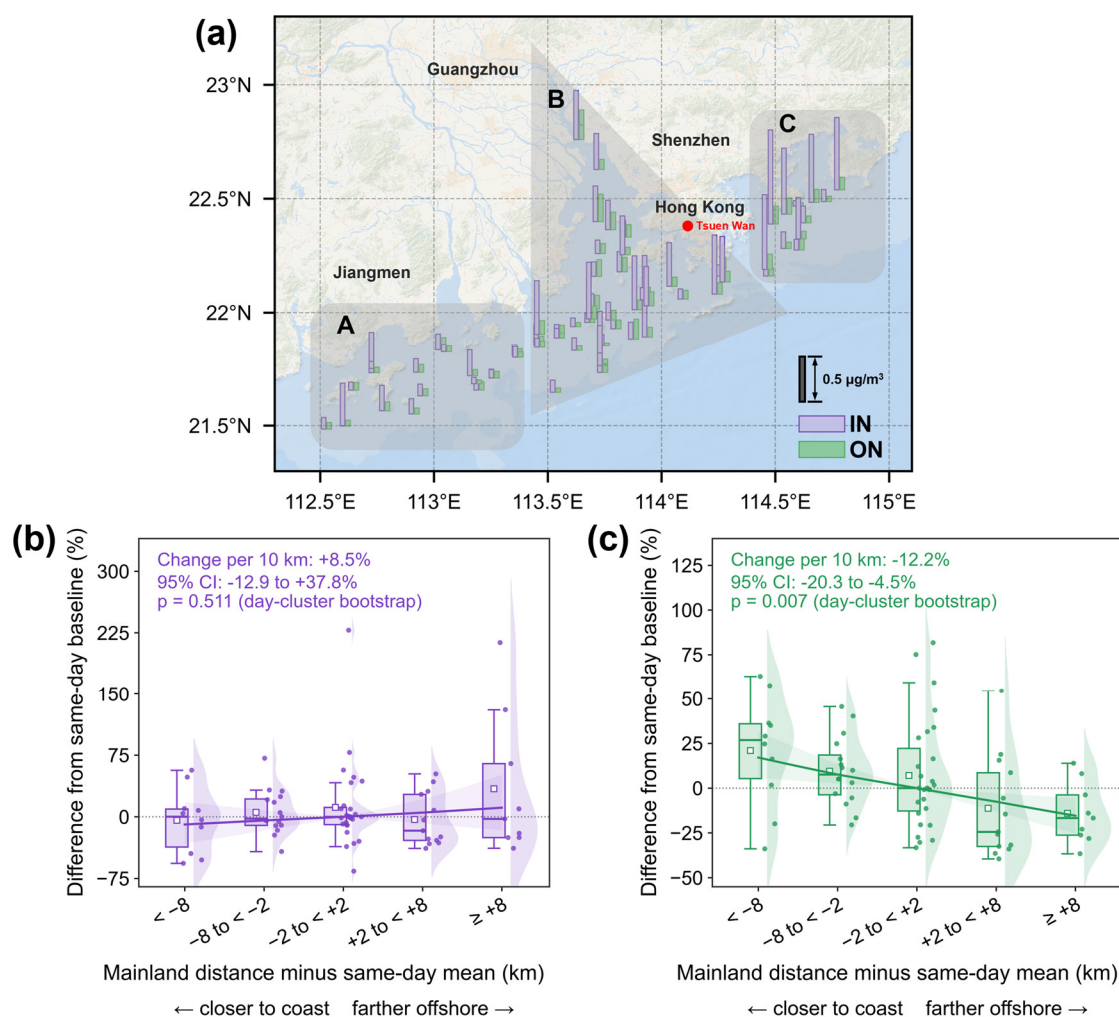
“Statistical inference used a wild cluster bootstrap with sampling dates as clusters to account for dependence among filters collected on the same day. Four separate robustness checks were conducted: (1) replacing sampling-date clusters with eight consecutive cruise-period clusters to assess sensitivity to temporal dependence across days; (2) adding longitude to the regression model to account for within-day west–east variation; (3) adding 24 h sine and cosine terms to account for diurnal variation; and (4) excluding samples collected during the typhoon period (24–26 July) and refitting the model to assess the influence of this episode. Each check was applied independently to the primary model, and all retained the sampling-day fixed effects (Sect. S4; Table S5).”

“Bulk ON exhibited a significant negative within-day association with offshore distance, with an estimated decrease of 12.2% per 10 km (95% CI: -20.3% to -4.5%; $p = 0.007$; Fig. 2c). This association persisted across all four robustness checks, with estimated decreases of 10.1–14.2% per 10 km (all $p < 0.05$; Table S5), supporting the robustness of the observed ON gradient to the adjustments examined. No statistically significant offshore association was detected for IN (estimated change: +8.5% per 10 km; 95% CI: -12.9% to +37.8%; $p = 0.511$; Fig. 2b).”

The revised Figure 5 caption (lines 490–492) now reads:

“Asterisks denote significant differences from two-sided Mann–Whitney U tests with Benjamini–Hochberg adjustment across 45 comparisons: * adjusted $p < 0.05$, ** adjusted $p < 0.01$, *** adjusted $p < 0.001$. Additional results are provided in Table S12.”

The revised Figure 2 in the manuscript is now copied below:



(Revised Figure 2) Figure R5. Spatial distributions and within-day offshore associations of bulk IN and ON in marine PM_{2.5} during summer 2024. (a) Spatial distributions of IN (purple bar) and ON (green bar) concentrations in PM_{2.5} samples collected during the research cruise campaign over the GBA oceanic region during summer 2024. Basemap source: Esri World Ocean Base; © Esri, Garmin, GEBCO, NOAA NGDC, and other contributors. (b–c) Percentage deviations of IN (b) and ON (c) concentrations from their same-day geometric means, grouped by relative mainland distance (each filter’s mainland distance minus the same-day arithmetic mean distance). Negative values indicate distances below the same-day mean. For example, the <−8 km bin includes filters whose distances to the mainland were more than 8 km shorter than the same-day mean distance. Sample sizes are n = 10, 16, 27, 13 and 9 filters from left to right (75 in total). Bins are used for visualization only; inference uses individual-filter log concentrations (Sect. S4).

6. The contamination criterion relies on a single threshold ($\text{NO}_x > 100 \text{ ppb}$ for $\geq 10 \text{ min}$; lines 148–150), which is high enough that diluted or aged ship plumes below 100 ppb would pass into the retained “marine” set—the exact set upon which the reduced-N/marine narrative depends. Concurrently, the authors build Section 3.3.2 (“Unique ON chemistry...”) entirely on only four AMS ship-influenced samples (line 205). The authors need to (a) justify the 100 ppb/10 min threshold or test sensitivity to it, (b) report the residual ship influence expected in the retained marine samples, and (c) substantially soften Section 3.3.2 and the corresponding conclusion, given the $n = 4$ limitation, unless more samples can be added.

Response: We agree that the $\text{NO}_x > 100$ ppb for ≥ 10 min criterion identifies evident fresh ship-plume episodes but cannot exclude diluted or aged ship influence. Section S1 now provides a composition-based evaluation of this operational separation. The 16 flagged samples had substantially higher sample-mean NO_x than the 75 retained samples (87.7 ± 66.1 versus 6.61 ± 7.81 ppb); because NO_x defined the screening, this contrast is reported descriptively. Independent carbonaceous measurements provided additional support: mean EC was approximately 3.5 times higher in the flagged group (2.09 ± 2.94 versus $0.60 \pm 0.57 \mu\text{g m}^{-3}$; two-sided Mann–Whitney $p = 0.016$), with higher OC, TC and WSOC concentrations as well (Table S1; exploratory, unadjusted tests). These results support separating samples with evident fresh plume influence, but do not establish the sensitivity of the chosen threshold or quantify residual shipping contributions. We therefore use “retained marine” rather than “ship-free” and explicitly acknowledge possible diluted, aged or regionally transported ship emissions. Section 3.3.2 remains explicitly exploratory ($n = 4$), removes “unique,” and avoids generalizing the four spectra to ship emissions as a whole. Individual values for the $\text{NO}^+/\text{NO}_2^+$ ratio and $\text{C} \geq 3$ fragment-signal fraction are shown in Fig. 5b–c.

The revised manuscript (Sect. 2.2), lines 153–162, now reads:

“This criterion identified 16 of the 91 filters, leaving 75 samples for concentration analyses. Hereafter, “marine samples” refers to these 75 retained filters but does not imply complete absence of ship-emission influence. Independent carbonaceous measurements supported this operational separation: mean elemental carbon (EC) concentrations were significantly higher in the ship-influenced group than in the retained marine group (2.09 ± 2.94 versus $0.60 \pm 0.57 \mu\text{g m}^{-3}$; two-sided Mann–Whitney $p = 0.016$), as were organic carbon (OC), total carbon (TC) and water-soluble organic carbon (WSOC) concentrations (Sect. S1; Table S1; Fig. S7). This screening identifies evident fresh ship-plume influence but may not exclude contributions from diluted, aged or regionally transported ship emissions in the retained marine samples.”

The revised manuscript (Sect. 3.3.2), lines 546–550, now reads:

“The present spectra, however, do not distinguish direct emissions from subsequent atmospheric formation. The four samples provide exploratory evidence rather than a representative ship-emission profile. Additional targeted measurements across a larger number of ship plumes would help establish the prevalence and formation pathways of these signatures.”

7. While the dry-deposition arithmetic is internally consistent (yielding $\approx 0.14 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ from $\text{Ca} \approx 0.4 \mu\text{g N m}^{-3}$ and $V_d = 0.11 \text{ cm s}^{-1}$), the core issue is representativeness. Annual fluxes are extrapolated from a brief three-week summer window under southwest-monsoon marine air, which drastically underrepresents winter continental outflow and its characteristically higher IN. Consequently, reporting values in “ $\text{kg N ha}^{-1} \text{ yr}^{-1}$ ” overstates what a summer campaign can legitimately constrain; the authors must label these as summer-representative or campaign-scaled fluxes, not annual, unless robust support for the extrapolation is provided. Additionally, the marine–urban V_d difference (0.11 vs 0.13 cm s^{-1}) falls well within the uncertainty of a first-order size-segregated scheme. Calling them the “same order” (lines 477–478) carries little actual information. The authors should state the V_d uncertainty range and temper the deposition comparison accordingly. Furthermore, they should note whether hygroscopic growth of sea-salt-influenced particles at high marine RH was considered, as this raises effective size and V_d .

Response: We thank the reviewer for this careful and constructive comment. We agree that the previous presentation overstated the temporal representativeness of the dry-deposition estimates and did not adequately quantify the sensitivity of the inferred deposition velocity. We have substantially revised the deposition analysis in the manuscript and Supplement to address all three issues raised by the reviewer.

First, we agree that the approximately three-week summer campaign cannot constrain annual nitrogen deposition over the GBA. The measurements were obtained from 12 July to 3 August 2024 under

predominantly southwesterly summer-monsoon conditions, whereas winter continental outflow may result in substantially different, and often higher, aerosol inorganic-N concentrations. We have therefore removed the interpretation of the calculated fluxes as annual deposition rates and no longer report the campaign results as annual fluxes in $\text{kg N ha}^{-1} \text{ yr}^{-1}$. Instead, we now report campaign-mean $\text{PM}_{2.5}$ -bound TN dry-deposition fluxes in $\text{mg N m}^{-2} \text{ d}^{-1}$. Using the base-case V_d calculation, these correspond to approximately $0.036 \text{ mg N m}^{-2} \text{ d}^{-1}$ for the marine environment and $0.040 \text{ mg N m}^{-2} \text{ d}^{-1}$ for the coastal urban environment. These values are explicitly described as summer campaign–representative estimates and are not extrapolated to annual deposition.

Second, we agree that the difference between the base-case V_d values of 0.11 cm s^{-1} for the marine environment and 0.13 cm s^{-1} for the coastal urban environment is too small to support a meaningful marine–urban contrast. We therefore removed the previous interpretation based on the two point estimates. To quantify the sensitivity of the first-order calculation, we repeated the Zhang et al. (2001) calculation using representative dry particle diameters between 0.3 and $1.0 \mu\text{m}$ while retaining the other base-case parameters. The resulting V_d values ranged from approximately 0.07 to 0.14 cm s^{-1} for the marine environment and from 0.09 to 0.19 cm s^{-1} for the coastal urban environment. We refer to these as model-sensitivity ranges rather than formal confidence intervals, because no size-resolved particle distribution was measured during the campaign. The strong overlap of these ranges indicates that the small difference between the base-case marine and urban V_d values cannot be resolved within the uncertainty of this first-order calculation. The manuscript has therefore been revised to avoid implying a meaningful difference between the two environments.

Third, we have now explicitly evaluated the influence of relative humidity (RH) and hygroscopic particle growth. Continuous shipboard RH measurements were not available during the 2024 cruise. We therefore used hourly RH observations from Waglan Island as a marine proxy and King’s Park as a coastal urban proxy. Waglan Island was selected as the marine meteorological proxy because its wind-speed conditions were broadly consistent with the shipboard observations. In the absence of continuous shipboard RH measurements, its RH observations were therefore used as the best available representation of the coastal marine environment. King’s Park is the closest Hong Kong Observatory station to the Tsuen Wan site with continuous RH observations. During the 12 July–3 August campaign, the mean RH values were 89.3% at Waglan Island and 84.2% at King’s Park.

Hygroscopic growth was incorporated following the Gerber (1985) parameterization used in Zhang et al. (2001), in which the prescribed dry particle radius is converted to an RH-dependent wet radius before recalculating the size-dependent deposition terms. Starting from the representative dry diameter of $0.5 \mu\text{m}$, the sea-salt growth parameterization yielded an effective wet diameter of approximately $0.99 \mu\text{m}$ at the marine RH of 89.3% , whereas the urban growth parameterization yielded approximately $0.70 \mu\text{m}$ at the urban RH of 84.2% . Propagating these wet diameters through the Zhang et al. (2001) scheme resulted in V_d values of approximately 0.07 and 0.11 cm s^{-1} for the marine and urban sensitivity cases, respectively. An additional ammonium-sulfate-like sensitivity calculation yielded V_d values of approximately 0.079 and 0.099 cm s^{-1} , respectively.

We note that hygroscopic growth increases the effective particle size, as pointed out by the reviewer, but it does not necessarily increase V_d for accumulation-mode particles. In the Zhang et al. (2001) framework, particles in approximately the 0.1 – $2 \mu\text{m}$ size range lie near the minimum of the deposition-velocity curve. Thus, as a $0.5 \mu\text{m}$ particle grows toward approximately 0.7 – $1.0 \mu\text{m}$, the reduction in Brownian diffusion can exceed the increase in gravitational settling, resulting in a modest decrease rather than an increase in V_d . Because the actual $\text{PM}_{2.5}$ is internally mixed and its hygroscopicity was not directly measured, these RH-adjusted calculations are treated as sensitivity tests rather than uniquely constrained V_d values.

Accordingly, the revised manuscript now (1) reports summer campaign–mean rather than annualized deposition fluxes, (2) provides quantitative V_d sensitivity ranges, (3) includes an explicit RH/hygroscopic-growth sensitivity analysis in the Supplement, and (4) no longer interprets the small difference between the marine and urban point estimates as a meaningful deposition contrast. Our revised conclusion is that these estimates quantify the fine-particle component of atmospheric N input

to the coastal waters during the summer campaign, while sensitivity to the assumed deposition parameters precludes a firm conclusion about a marine–urban flux difference.

The revised manuscript (Sect. 3.4), lines 563–569 and 573–588, now reads:

“To constrain representative V_d values, we conducted a first-order calculation following the size-segregated particle dry-deposition scheme of Zhang et al. (2001), as described in Sect. S6, where the governing equations, input parameters (Table S7), and calculated intermediate and final results (Table S8) are summarized. For a representative dry particle diameter of 0.5 μm , the base-case V_d values were 0.105 cm s^{-1} for the marine environment and 0.13 cm s^{-1} for the coastal urban environment. Varying the dry particle diameter from 0.3 to 1.0 μm yielded ranges of 0.07–0.14 and 0.09–0.19 cm s^{-1} , respectively (Table S9).”

“We further evaluated sensitivity to hygroscopic growth using the RH-dependent parameterization included in Zhang et al. (2001). Campaign-mean RH was 89.3% at Waglan Island, used as a marine proxy because continuous shipboard RH measurements were unavailable, and 84.2% at King’s Park, used as the coastal urban proxy. Depending on the assumed aerosol hygroscopicity, the resulting V_d values were approximately 0.074–0.079 cm s^{-1} for the marine environment and 0.099–0.105 cm s^{-1} for the coastal urban environment (Table S10). In these model scenarios, hygroscopic growth did not increase V_d : the competing size-dependent deposition processes produced lower values than in the dry-particle base case. These calculations are sensitivity scenarios rather than observationally constrained corrections, because the particle size distribution and hygroscopicity were not measured during the campaign.”

“Using the dry-particle base-case V_d values, the summer campaign-mean $\text{PM}_{2.5}$ -bound TN dry-deposition fluxes were approximately 0.036 $\text{mg N m}^{-2} \text{d}^{-1}$ over the marine region and 0.040 $\text{mg N m}^{-2} \text{d}^{-1}$ at the coastal urban site (Table 2). These point estimates are of similar magnitude, and the sensitivity to the assumed deposition parameters precludes a firm conclusion about a marine–urban difference. The estimates nevertheless quantify the fine-particle component of atmospheric N input to the GBA coastal waters during the summer campaign.”

8. Using the region-mean ions in Table 1, the measured cations fall significantly short of the anions on a charge basis (cation/anion $\approx$ 0.64–0.66 in region C), and NH_4^+ ($\approx$ 13–15 neq m^{-3}) is far below what is needed to neutralize sulfate alone ($\approx$ 40–42 neq m^{-3}). This implies either the aerosol is strongly acidic with a large unmeasured H^+ pool, or there is a massive cation deficit in the IC data. For a submission to a high-tier venue relying on IC as a core method, providing an ion balance and a neutralization/acidity check is mandatory. The outcome directly affects the “ NH_4^+ -dominant” framing. The authors must add an ion-balance figure or table and adequately discuss this cation deficit.

Response: We thank the reviewer for identifying the substantial cation deficit implied by the originally submitted Table 1. This comment prompted us to reassess the ion measurements and reanalyse the corresponding marine filters using a newly acquired Thermo Scientific ion chromatography (IC) system in our Department.

The original measurements were performed using an older IC system that required manual exchange of the separation columns between anion and cation analysis. Consequently, anions and cations were measured in separate analytical batches, with an interval of approximately 2–3 days between cation and anion analyses. This workflow involved repeated system reconfiguration and equilibration, as well as additional sample handling, and may therefore have increased susceptibility to between-batch analytical variability. Such variability could arise from differences in calibration performance, chromatographic conditions, or sample handling between the two analytical sequences. We regard these as potential

contributors to the original inconsistency rather than attributing the discrepancy to a uniquely established source of error.

The newly acquired IC system permits paired anion and cation analyses without manual column exchange. This configuration reduces repeated system reconfiguration and allows the two sets of measurements to be obtained closer together in time, reducing potential inconsistencies associated with the previous workflow. We have replaced all eight major-ion entries in Table 1 with the remeasured results. The revised regional groups contain 19, 44, and 12 retained marine filters in regions A, B, and C, respectively. We have also added Section S2 and Table S2 to the Supplement to document the measured-ion inventory and charge balance.

The revised ratios of mean cation to mean anion equivalents are 1.10, 1.13, and 1.14 in regions A, B, and C, respectively. For comparison, the corresponding ratios calculated from the originally submitted Table 1 were 0.70, 0.76, and 0.65; those original regional means preceded the A/B reassignment. At the individual-sample level, 60 of the 75 retained marine filters fall within the descriptive C/A range of 0.8–1.2: 14/19 in region A, 35/44 in region B, and 11/12 in region C. These results show substantially improved agreement between the measured cation and anion equivalents, although this descriptive range is not treated as an independent validation of analytical accuracy.

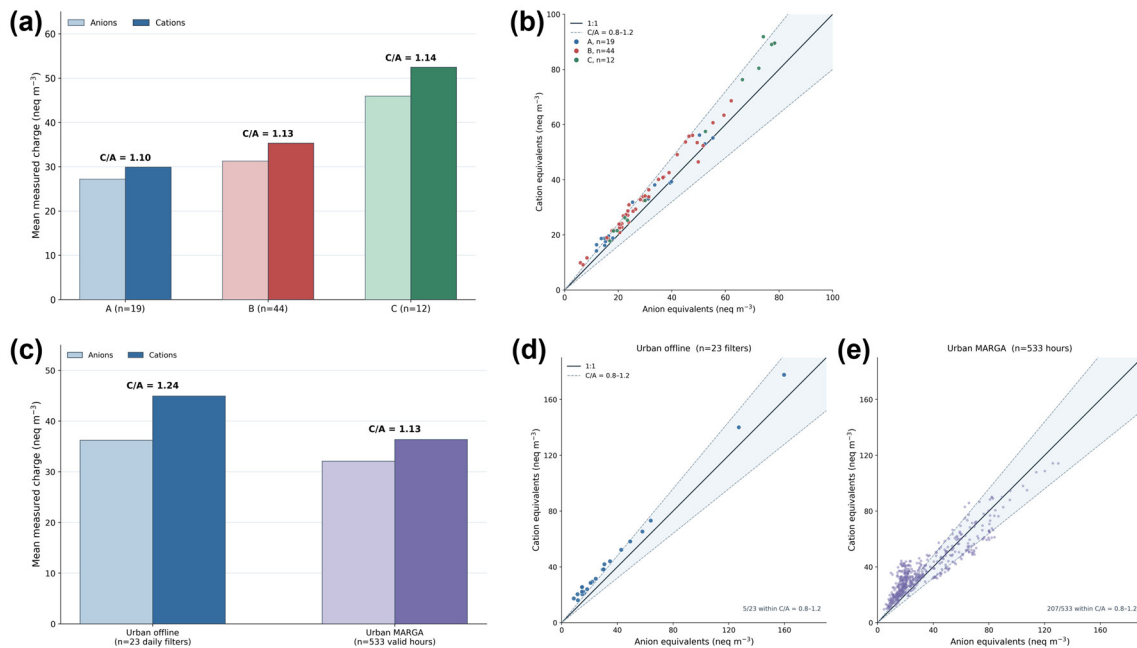
In region C, measured NH_4^+ contributes 25.60 neq m^{-3} , which remains insufficient by itself to balance SO_4^{2-} at 40.74 neq m^{-3} . However, the other measured cations contribute 26.77 neq m^{-3} , giving total measured cations of 52.37 neq m^{-3} compared with 45.92 neq m^{-3} of measured anions. Thus, the large missing-cation pool inferred from the original table is no longer evident in the revised regional mean. The remeasured results provide a more internally consistent basis for interpreting the aerosol ion composition.

We have also clarified that “ NH_4^+ -dominant” refers to NH_4^+ -N exceeding NO_3^- -N among the measured inorganic nitrogen species. It does not imply that NH_4^+ is the sole counterion of sulfate or that the aerosol is fully neutralized. Charge balance alone cannot establish aerosol pH, complete neutralization, or unique ion pairings.

The revised manuscript (Sect. 2.3.2), lines 202–207, now reads:

“The extracts were filtered and analyzed using a Dionex ion chromatography (IC) system (Thermo Scientific, USA), which permitted paired anion and cation analyses without manual column exchange. Calibration was performed using multi-ion standards, and field blanks were processed alongside the samples for blank correction. The consistency of the measured ionic composition was further assessed through cation–anion equivalent balance calculations, as described in Sect. S2 (Table S2; Fig. S1).”

The added figure in the SI is copied below:



(New Figure S1) Figure R6. Ion-equivalent balance of major measured inorganic ions in marine and urban aerosols. **(a)** Mean measured anion and cation equivalents in marine regions A, B, and C, with the corresponding cation-to-anion (C/A) ratios indicated above the bars. **(b)** Sample-level relationship between total measured cation and anion equivalents for marine samples, colored by region. **(c)** Mean measured anion and cation equivalents for the urban offline-filter and MARGA datasets. **(d)** Sample-level cation–anion relationship for the urban offline filter samples (n=23 filters). **(e)** Hourly cation–anion relationship for the urban MARGA measurements (n=533 hours). The solid line in panels **(b)**, **(d)**, and **(e)** denotes the 1:1 relationship, and the shaded region represents a C/A ratio of 0.8–1.2.

References:

- Altieri, K. E., Fawcett, S. E., Peters, A. J., Sigman, D. M., & Hastings, M. G. (2016). Marine biogenic source of atmospheric organic nitrogen in the subtropical North Atlantic. *Proc Natl Acad Sci U S A*, 113(4), 925-930. <https://doi.org/10.1073/pnas.1516847113>
- Benjamini, Y., & Hochberg, Y. (1995). Controlling The False Discovery Rate - A Practical And Powerful Approach To Multiple Testing. *J. Royal Statist. Soc., Series B*, 57, 289-300. <https://doi.org/10.2307/2346101>
- Bian, Q., Huang, X. H. H., & Yu, J. Z. (2014). One-year observations of size distribution characteristics of major aerosol constituents at a coastal receptor site in Hong Kong – Part 1: Inorganic ions and oxalate. *Atmospheric Chemistry and Physics*, 14(17), 9013-9027. <https://doi.org/10.5194/acp-14-9013-2014>
- Bruns, E. A., Perraud, V., Zelenyuk, A., Ezell, M. J., Johnson, S. N., Yu, Y., Imre, D., Finlayson-Pitts, B. J., & Alexander, M. L. (2010). Comparison of FTIR and Particle Mass Spectrometry for the Measurement of Particulate Organic Nitrates. *Environmental Science & Technology*, 44(3), 1056-1061. <https://doi.org/10.1021/es9029864>
- Calderón, S. M., Poor, N. D., & Campbell, S. W. (2007). Estimation of the particle and gas scavenging contributions to wet deposition of organic nitrogen. *Atmospheric Environment*, 41(20), 4281-4290. <https://doi.org/10.1016/j.atmosenv.2006.06.067>
- Chen, J., Fu, X., Wang, X., Dong, S., Chen, T., Xue, L., Zhou, Y., Sheng, L., & Wang, W. (2024). Unveiling the overlooked direct emissions of particulate organic nitrates from ship. *Environment International*, 185, 108487. <https://doi.org/10.1016/j.envint.2024.108487>
- Chow, W. S., Liao, K., Huang, X. H. H., Leung, K. F., Lau, A. K. H., & Yu, J. Z. (2022). Measurement report: The 10-year trend of PM_{2.5} major components and source tracers from 2008 to 2017 in an urban site of Hong Kong, China. *Atmospheric Chemistry and Physics*, 22(17), 11557-11577. <https://doi.org/10.5194/acp-22-11557-2022>
- Day, D. A., Campuzano-Jost, P., Nault, B. A., Palm, B. B., Hu, W., Guo, H., Wooldridge, P. J., Cohen, R. C., Docherty, K. S., Huffman, J. A., de Sá, S. S., Martin, S. T., & Jimenez, J. L. (2022). A systematic re-evaluation of methods for quantification of bulk particle-phase organic nitrates using real-time aerosol mass spectrometry. *Atmospheric Measurement Techniques*, 15(2), 459-483. <https://doi.org/10.5194/amt-15-459-2022>
- Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Brauers, T., Brown, S. S., Dorn, H. P., Dubé, W. P., Fuchs, H., Mensah, A., Rohrer, F., Tillmann, R., Wahner, A., Wooldridge, P. J., & Cohen, R. C. (2011). SOA from limonene: role of NO₃ in its generation and degradation. *Atmospheric Chemistry and Physics*, 11(8), 3879-3894. <https://doi.org/10.5194/acp-11-3879-2011>
- Ge, X., Sun, Y., Trousdell, J., Chen, M., & Zhang, Q. (2024). Enhancing characterization of organic nitrogen components in aerosols and droplets using high-resolution aerosol mass spectrometry. *Atmospheric Measurement Techniques*, 17(2), 423-439. <https://doi.org/10.5194/amt-17-423-2024>
- Gerber, H. E. (1985). Relative - Humidity Parameterization of the Navy Aerosol Model (NAM).
- Guo, C., Yu, J., Ho, T. Y., Wang, L., Song, S., Kong, L., & Liu, H. (2012). Dynamics of phytoplankton community structure in the South China Sea in response to the East Asian aerosol input. *Biogeosciences*, 9(4), 1519-1536. <https://doi.org/10.5194/bg-9-1519-2012>
- He, T., Li, J., Xie, L., & Zheng, Q. (2024). Response of chlorophyll-a to rainfall event in the basin of the South China sea: Statistical analysis. *Mar Environ Res*, 199, 106576. <https://doi.org/10.1016/j.marenvres.2024.106576>
- Hu, J., Tian, R., Yan, J., Zhang, X., Wang, S., Sun, H., Xu, H., Shen, S., & Zeng, Q. (2026). Distinct phytoplankton responses to dust in the Chinese marginal seas: role of synoptic circulation and air-sea heat exchange. *Biogeosciences*, 23(16), 5697-5714. <https://doi.org/10.5194/bg-23-5697-2026>
- Kanakidou, M., Duce, R. A., Prospero, J. M., Baker, A. R., Benitez-Nelson, C., Dentener, F. J., Hunter, K. A., Liss, P. S., Mahowald, N., Okin, G. S., Sarin, M., Tsigaridis, K., Uematsu, M., Zamora, L. M., & Zhu, T. (2012). Atmospheric fluxes of organic N and P to the global ocean. *Global Biogeochemical Cycles*, 26(3). <https://doi.org/10.1029/2011gb004277>

- Li, D., Gan, J., Hui, R., Liu, Z., Yu, L., Lu, Z., & Dai, M. (2020). Vortex and Biogeochemical Dynamics for the Hypoxia Formation Within the Coastal Transition Zone off the Pearl River Estuary. *Journal of Geophysical Research: Oceans*, 125(8). <https://doi.org/10.1029/2020jc016178>
- Lo, H. W., Yu, X., Chen, H., Chu, W. C., Chung, N. M., Lau, S. W., Li, J., Liang, S., Liao, K., Thomas, H. C. J., Wang, Z., Zhang, Z., Yu, J. Z., & Thibodeau, B. (2025). Tidal currents and atmospheric inorganic nitrogen contribute to diurnal variation of dissolved nutrients and chlorophyll a concentrations in Mirs Bay, Hong Kong. *Regional Studies in Marine Science*, 81, 103941. <https://doi.org/10.1016/j.rsma.2024.103941>
- Tan, S.-C., Shi, G.-Y., Shi, J.-H., Gao, H.-W., & Yao, X. (2011). Correlation of Asian dust with chlorophyll and primary productivity in the coastal seas of China during the period from 1998 to 2008. *Journal of Geophysical Research*, 116(G2). <https://doi.org/10.1029/2010jg001456>
- Wang, S. H., Hsu, N. C., Tsay, S. C., Lin, N. H., Sayer, A. M., Huang, S. J., & Lau, W. K. M. (2012). Can Asian dust trigger phytoplankton blooms in the oligotrophic northern South China Sea? *Geophysical Research Letters*, 39(5). <https://doi.org/10.1029/2011gl050415>
- Wedyan, M. A., & Preston, M. R. (2008). The coupling of surface seawater organic nitrogen and the marine aerosol as inferred from enantiomer-specific amino acid analysis. *Atmospheric Environment*, 42(37), 8698-8705. <https://doi.org/10.1016/j.atmosenv.2008.04.038>
- Yang, L., Huang, R.-J., Shen, J., Wang, T., Gong, Y., Yuan, W., Liu, Y., Huang, H., You, Q., Huang, D. D., & Huang, C. (2023). New Insights into the Brown Carbon Chromophores and Formation Pathways for Aqueous Reactions of α -Dicarbonyls with Amines and Ammonium. *Environmental Science & Technology*, 57(33), 12351-12361. <https://doi.org/10.1021/acs.est.3c04133>
- Yu, X., Li, Q., Ge, Y., Li, Y., Liao, K., Huang, X. H., Li, J., & Yu, J. Z. (2021). Simultaneous Determination of Aerosol Inorganic and Organic Nitrogen by Thermal Evolution and Chemiluminescence Detection. *Environmental Science & Technology*, 55(17), 11579-11589. <https://doi.org/10.1021/acs.est.1c04876>
- Zhang, L., Gong, S., Padro, J., & Barrie, L. (2001). A size-segregated particle dry deposition scheme for an atmospheric aerosol module. *Atmospheric Environment*, 35(3), 549-560. [https://doi.org/10.1016/S1352-2310\(00\)00326-5](https://doi.org/10.1016/S1352-2310(00)00326-5)
- Zhang, Z., Liao, K., & Yu, J. Z. (2026). Assessing temperature-dependent bias in offline filter-based nitrate measurements: insights from multi-year PM_{2.5} and PM₁₀ comparisons with MARGA. *ACS ES&T Air*, (In press).