



Supplement of

Comparative nitrogen speciation in marine and coastal urban aerosols of the Greater Bay Area and implications for PM_{2.5}-bound nitrogen deposition

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Section S1. Compositional contrast between operationally ship-influenced and retained marine samples

Ship emissions may intermittently influence aerosol measurements conducted aboard a research vessel. To assess the compositional basis for the operational ship-plume screening and characterize the associated differences in aerosol composition, we compared 16 samples classified as operationally ship-influenced with the 75 samples retained for characterization of the marine atmosphere. The operational classification was based on the ship-plume screening procedure described in Section 2.2 of the main manuscript. Because NO_x was used in the operational screening, the NO_x difference between the two groups was evaluated descriptively and was not regarded as independent validation of the classification. The sample-mean NO_x concentration was 87.7 ± 66.1 ppb in the operationally ship-influenced samples, compared with 6.61 ± 7.81 ppb in the retained marine samples (Table S1). This marked contrast is expected from the classification procedure and shows that the operationally ship-influenced group contained periods with substantially elevated NO_x .

Carbonaceous aerosol measurements that were independent of the NO_x screening showed a consistent contrast between the two groups. The mean EC concentration was 2.09 ± 2.94 $\mu\text{g m}^{-3}$ in the operationally ship-influenced samples and 0.60 ± 0.57 $\mu\text{g m}^{-3}$ in the retained marine samples. The mean was approximately 3.5 times higher in the ship-influenced group, and the distributions differed significantly according to a two-sided Mann–Whitney U test ($p=0.016$). OC was also higher in the operationally ship-influenced group (5.65 ± 4.58 versus 3.30 ± 2.33 $\mu\text{g m}^{-3}$; $p=0.004$). Consequently, TC, calculated consistently as $\text{OC} + \text{EC}$, was approximately twice as high in the operationally ship-influenced samples (7.74 ± 7.42 versus 3.90 ± 2.78 $\mu\text{g m}^{-3}$; $p=0.003$). WSOC showed a similar difference, with concentrations of 3.52 ± 3.11 and 2.36 ± 2.87 $\mu\text{g m}^{-3}$ in the operationally ship-influenced and retained marine groups, respectively ($p=0.002$).

The corresponding differences in the bulk nitrogen components were less pronounced. Mean IN concentrations were 0.24 ± 0.21 and 0.29 ± 0.23 $\mu\text{g m}^{-3}$ in the operationally ship-influenced and retained marine groups, respectively ($p=0.217$). Mean ON concentrations were 0.17 ± 0.20 and 0.11 ± 0.06 $\mu\text{g m}^{-3}$, respectively ($p=0.276$), while mean TN concentrations were 0.41 ± 0.26 and 0.40 ± 0.26 $\mu\text{g m}^{-3}$ ($p=0.929$). The ON/TN ratio tended to be higher in the operationally ship-influenced samples ($43.5 \pm 23.0\%$) than in the retained marine samples ($31.7 \pm 13.2\%$), although this difference was not statistically significant ($p=0.066$). WSTN measured using the TOC–TN analyzer was also not significantly different between the groups ($p=0.086$). These results indicate that the contrast associated with operationally identified ship-plume influence was more consistently expressed in the carbonaceous aerosol components than in the bulk nitrogen concentrations.

Most major water-soluble ions did not differ significantly between the two groups. No significant differences were found for Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ , K^+ , or Ca^{2+} , with p values ranging from 0.101 to 0.963. Na^+ was higher in the operationally ship-influenced group (0.49 ± 0.23 versus 0.35 ± 0.15 $\mu\text{g m}^{-3}$; $p=0.005$), as was Mg^{2+} (0.04 ± 0.02 versus 0.03 ± 0.02 $\mu\text{g m}^{-3}$; $p=0.020$). However, Na^+ and Mg^{2+} are major constituents of sea salt and are affected by sampling location, wind conditions, sea state, and marine aerosol production. Their differences therefore cannot be attributed specifically to ship emissions.

Concentrations in Table S1 are reported as mean $\pm$ standard deviation to maintain consistency with the summary statistics used in the main manuscript. Several variables, particularly NO_x , EC, TC, and NH_4^+ , showed right-skewed distributions and high-concentration observations. We therefore used two-sided Mann–Whitney U tests rather than parametric tests to evaluate the

group differences. The resulting p values assess differences in the distributions of observations between the two groups; they should not be interpreted as direct tests of the arithmetic means. The EC comparison was the primary source-related comparison, while the remaining component-wise tests were exploratory. The reported p values were not adjusted for multiple comparisons and are therefore interpreted together with the magnitude, direction, and source specificity of the observed differences.

Taken together, the substantially higher EC, OC, TC, and WSOC concentrations provide composition-based support for separating samples with evident fresh ship-plume influence from the retained marine samples. The less pronounced differences in bulk nitrogen and the absence of statistically significant differences in most major ions indicate that the compositional contrast was not uniform across aerosol components. The operational screening should therefore be viewed as a procedure for identifying samples with evident fresh ship-plume influence rather than as evidence that the retained marine samples were completely unaffected by all shipping-related emissions. Contributions from diluted, aged, or regionally transported ship emissions cannot be excluded from the retained marine group.

Table S1. Chemical composition of the operationally ship-influenced and retained marine samples. Values are reported as mean $\pm$ standard deviation. Group differences were evaluated using two-sided Mann–Whitney U tests. The reported p values were not adjusted for multiple comparisons. Tests other than the primary EC comparison are exploratory.

Variable	Unit	Operationally ship-influenced (n = 16)	Retained marine (n = 75)	p
NO _x ¹	ppb	87.7 $\pm$ 66.1	6.61 $\pm$ 7.81	—
OC	$\mu\text{g m}^{-3}$	5.65 $\pm$ 4.58	3.30 $\pm$ 2.33	0.004
EC	$\mu\text{g m}^{-3}$	2.09 $\pm$ 2.94	0.60 $\pm$ 0.57	0.016
TC ²	$\mu\text{g m}^{-3}$	7.74 $\pm$ 7.42	3.90 $\pm$ 2.78	0.003
WSOC	$\mu\text{g m}^{-3}$	3.52 $\pm$ 3.11	2.36 $\pm$ 2.87	0.002
WSTN ³	$\mu\text{g m}^{-3}$	0.59 $\pm$ 0.43	0.42 $\pm$ 0.26	0.086
IN	$\mu\text{g m}^{-3}$	0.24 $\pm$ 0.21	0.29 $\pm$ 0.23	0.217
ON	$\mu\text{g m}^{-3}$	0.17 $\pm$ 0.20	0.11 $\pm$ 0.06	0.276
TN	$\mu\text{g m}^{-3}$	0.41 $\pm$ 0.26	0.40 $\pm$ 0.26	0.929
ON/TN	%	43.5 $\pm$ 23.0	31.7 $\pm$ 13.2	0.066
Cl [−]	$\mu\text{g m}^{-3}$	0.11 $\pm$ 0.15	0.06 $\pm$ 0.08	0.237
SO ₄ ^{2−}	$\mu\text{g m}^{-3}$	1.63 $\pm$ 1.33	1.30 $\pm$ 0.93	0.643
NO ₃ [−]	$\mu\text{g m}^{-3}$	0.26 $\pm$ 0.18	0.22 $\pm$ 0.18	0.390
Na ⁺	$\mu\text{g m}^{-3}$	0.49 $\pm$ 0.23	0.35 $\pm$ 0.15	0.005
NH ₄ ⁺	$\mu\text{g m}^{-3}$	0.30 $\pm$ 0.37	0.26 $\pm$ 0.28	0.963
K ⁺	$\mu\text{g m}^{-3}$	0.05 $\pm$ 0.04	0.03 $\pm$ 0.03	0.456
Mg ²⁺	$\mu\text{g m}^{-3}$	0.04 $\pm$ 0.02	0.03 $\pm$ 0.02	0.020
Ca ²⁺	$\mu\text{g m}^{-3}$	0.09 $\pm$ 0.05	0.07 $\pm$ 0.03	0.101

Notes:

¹ NO_x was used in the operational screening and is presented descriptively without a significance test.

² TC was calculated as OC + EC for both groups.

³ WSTN denotes water-soluble total nitrogen measured using the TOC-TN analyzer.

Section S2. Ion chromatography consistency checks and filter-sampling sensitivity

The marine ion dataset comprises 75 retained filters (A: 19; B: 44; C: 12). The initial analytical workflow required separate anion and cation sequences with repeated system reconfiguration, and notable between-batch variability was observed. All retained filters were subsequently re-analyzed using a dual-channel Thermo Scientific IC system that permitted paired anion and cation measurements without manual column exchange. The IC data presented in the discussion-stage manuscript were obtained using the initial workflow; the remeasured concentrations of all eight ions replace those data throughout the final manuscript.

All charge-balance calculations used atmospheric ion mass concentrations expressed on a common air-volume basis. Ion equivalent concentrations (neq m^{-3}) were calculated as $1000c_i/E_i$, where c_i is the mass concentration ($\mu\text{g m}^{-3}$) and E_i is the equivalent weight (g eq^{-1}). Total measured anion equivalents were calculated from Cl^- , SO_4^{2-} and NO_3^- , and total measured cation equivalents from Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} . Procedural blanks and routine quality assurance and quality control checks were performed following the laboratory's standard analytical procedures.

The group C/A ratio is the ratio of the group-mean cation equivalents to the group-mean anion equivalents, not the mean of individual C/A ratios. In the remeasured marine data, C/A is 1.10, 1.13 and 1.14 in regions A, B and C, respectively (Table S2). Sixty of the 75 filters fall within the descriptive interval 0.8–1.2 (Fig. S1). This interval is a visual consistency band, not an analytical acceptance criterion. In region C, NH_4^+ supplies 25.60 neq m^{-3} , compared with 40.74 neq m^{-3} of sulfate; other measured cations contribute 26.77 neq m^{-3} . Thus, NH_4^+ alone does not balance sulfate, but a large deficit of measured cation equivalents is not evident. Charge balance does not determine aerosol pH, establish complete neutralization or identify unique ion pairings.

Table S2. Equivalent balance of measured inorganic ions. AE and CE denote total measured anion and cation equivalents, respectively; mean equivalents are expressed in neq m^{-3} .

Record	n	Mean AE	Mean CE	CE/AE
A	19	27.18	29.87	1.1
B	44	31.29	35.28	1.13
C	12	45.92	52.37	1.14
Urban filters	23	36.22	44.94	1.24
Urban MARGA hourly	533	32.09	36.35	1.13

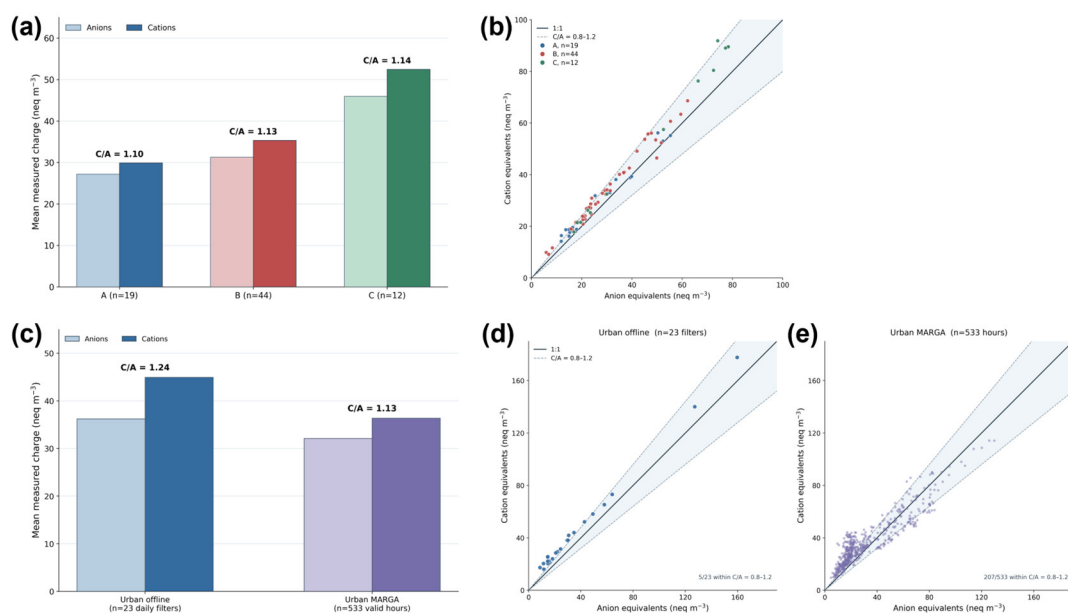


Figure S1. Ion-equivalent balance of major measured inorganic ions in marine and urban aerosols. (a) Mean measured anion and cation equivalents in marine regions A, B, and C, with the corresponding cation-to-anion (C/A) ratios indicated above the bars. (b) Sample-level relationship between total measured 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.

S2.1 Urban filter and MARGA comparison

Urban filter-based ion measurements were compared with concurrent online MARGA observations to assess their consistency. Four dates (12, 14 and 22 July and 3 August 2024) showed pronounced discrepancies between the two methods. An additional comparison with XRF measurements showed generally consistent concentrations for the corresponding metal elements measured by MARGA and XRF, after conversion to a common elemental-mass basis. This agreement suggests that the discrepancies may involve particular filter-based ion measurements rather than general bias in the MARGA record. Contamination affecting individual ions, sample handling or analytical variability are possible explanations, although the available comparisons do not establish the cause.

We therefore examined a 19-filter sensitivity subset excluding these four dates. Valid hourly MARGA observations were averaged over each local calendar day (00:00–24:00), without interpolation of missing hours, and paired with filter measurements using the dates recorded in the source workbook. These comparisons are aligned by calendar day rather than matched to the exact sampling windows. Table S3 reports results for the same 19 date pairs for each ion.

Within this subset, nitrate showed little filter–MARGA covariance ($r = -0.066$), with a filter/MARGA ratio of means of 0.79. Sulfate and ammonium covaried more closely ($r = 0.87$ and 0.841 , respectively), although their ratios of means were also approximately 0.79. The discrepancies therefore were not confined to nitrate and cannot be attributed uniquely to nitrate volatilization. Differences in gas adsorption, sample handling, calibration and temporal coverage may also contribute.

The four dates were excluded only from this ion-method sensitivity comparison. The corresponding urban bulk-N and AMS records were retained because comparisons with and without these dates did not materially alter the main conclusions. This stability supports retaining those records but does not rule

out bias in individual ion measurements. MARGA was used as the urban ion record because it provides hourly observations without prolonged filter collection; the urban method comparison was not used to derive a quantitative correction for marine filter measurements.

Table S3. Comparison of urban offline-filter and online MARGA ion measurements for 19 paired dates. Concentrations are reported as mean $\pm$ sample SD ($\mu\text{g m}^{-3}$); r is the descriptive Pearson correlation. Filter/MARGA is the ratio of means, not a mean of pairwise ratios.

Ion	MARGA daily	Filter	Filter/MARGA	r
NO_3^-	0.26 ± 0.12	0.20 ± 0.08	0.79	-0.07
SO_4^{2-}	1.07 ± 0.77	0.85 ± 0.77	0.79	0.87
NH_4^+	0.38 ± 0.21	0.31 ± 0.22	0.80	0.84
Cl^-	0.15 ± 0.08	0.10 ± 0.09	0.69	0.25
Na^+	0.16 ± 0.09	0.17 ± 0.09	1.07	0.91
K^+	0.03 ± 0.02	0.03 ± 0.03	1.12	0.79
Mg^{2+}	0.02 ± 0.01	0.03 ± 0.01	1.25	0.87
Ca^{2+}	0.01 ± 0.02	0.01 ± 0.07	0.96	0.55

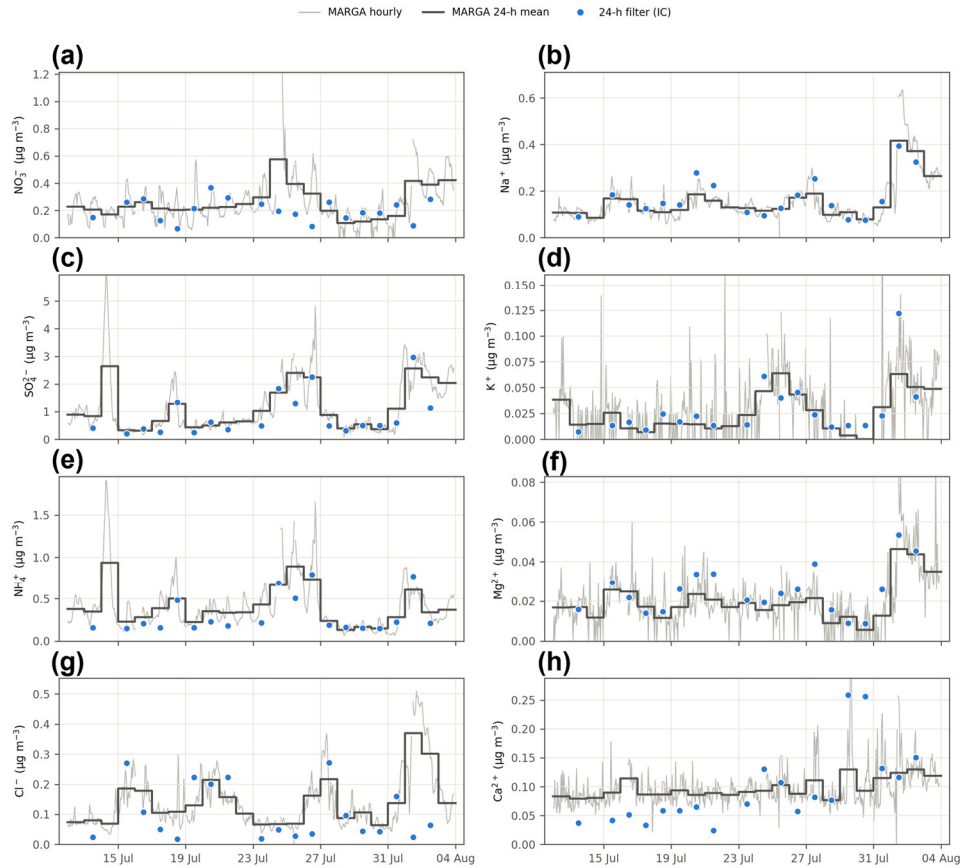


Figure S2. Urban filter and MARGA ion comparison (19 retained date pairs). Grey lines show hourly MARGA concentrations, black steps show calendar-day means, and blue points show retained filter measurements plotted at the midpoint of their labelled date. Pearson r is calculated from the paired daily values.

S2.2 Marine filter-artifact sensitivity

Marine filters integrated 1.2–17.1 h of actual pump-on time (mean 3.8 h; median 2.8 h), compared with 24 h for urban filters. Sixty-nine of the 75 marine filters experienced an active-sampling temperature range of ≤ 3 °C. Shorter collection times and smaller temperature ranges distinguish most marine filters from daily urban filters, but neither demonstrates negligible volatilization under persistently warm conditions.

Hourly urban MARGA observations were used to describe ambient nitrate partitioning, defining F as the molar amount of PM_{2.5} nitrate divided by the sum of PM_{2.5} nitrate and gaseous HNO₃. Temperature and F ranges were calculated within windows of two, three, four or five consecutive hourly observations (Fig. S3). Larger temperature ranges generally coincided with greater F variability, especially in longer windows. These variations describe ambient gas–particle partitioning rather than measured losses from filters; overlapping windows are descriptive and do not constitute independent replicates. The observed F ranges were therefore not used to derive marine filter-loss corrections.

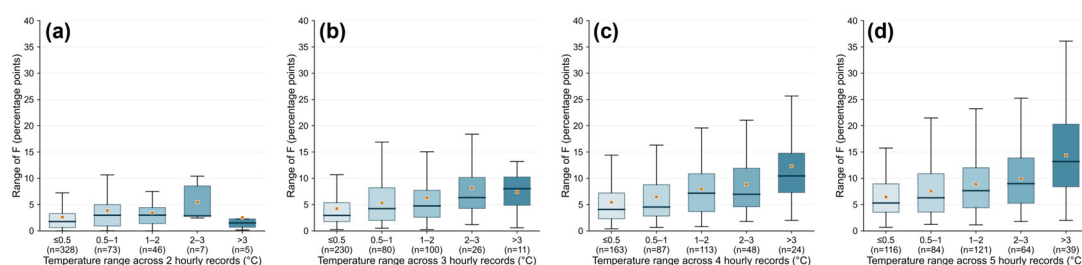


Figure S3. Variation in the particle nitrate fraction (F) in relation to temperature variability over different time windows. F is defined as the molar amount of nitrate in PM_{2.5} divided by the sum of PM_{2.5} nitrate and gaseous HNO₃. Boxplots show the range of F (percentage points) grouped by temperature 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.

Excluding the six filters with active-sampling temperature ranges above 3 °C (Table S4) changed mean nitrate from 0.224 to 0.228 $\mu\text{g m}^{-3}$ (+2.08%) and mean ammonium from 0.261 to 0.266 $\mu\text{g m}^{-3}$ (+1.85%). The ratio of mean NH₄⁺-N to mean NO₃⁻-N changed from 4.02 to 4.01 (−0.22%). Percent changes use unrounded values. All 75 filters were retained because the campaign summaries were insensitive to this exclusion. The 3 °C criterion is a sensitivity choice, not a validated boundary separating biased and unbiased filters. Without marine denuder or backup-filter data, the checks cannot quantify or bound the effect of volatilization, HNO₃ adsorption or a systematic bias shared by both subsets. No empirical marine artifact correction was applied, and no resolved marine–urban NH₄⁺-N/NO₃⁻-N contrast is claimed.

Table S4. Marine filters with active-sampling temperature ranges above 3 °C. Temperature ranges were calculated using observations during actual pump-on periods.

Filter	Region	Pump-on (h)	Temperature (°C)	Range (°C)
AoE09	B	2.42	26.1–31.1	5
AoE20	A	9.71	25.7–30.2	4.5
AoE23	A	2.94	26.1–29.6	3.5
AoE62	B	12.09	25.0–29.8	4.8
AoE76	B	2.22	25.2–28.9	3.7
AoE86	C	2.17	28.6–32.4	3.8

Section S3. Definition and calculation of distance to the continental mainland coastline

Distance to the continental mainland coastline was calculated separately for each of the 75 retained marine filters. This metric describes geometric proximity to the mainland and is distinguished from distance to the nearest shoreline, which may include islands, and from distance travelled along an air-mass trajectory.

The coastline was obtained from the Global Self-consistent, Hierarchical, High-resolution Geography (GSHHG) database, v2.3.7 (Wessel & Smith, 1996). We used the full-resolution Level-1 shapefile, GSHHS_f_L1.shp, which represents land–ocean boundaries. “Full resolution” denotes the original vector-data resolution tier rather than a uniform grid spacing. The continental-mainland polygon was selected, and island boundaries were excluded from the primary distance calculation. The mainland boundary was extracted and restricted to a domain extending from 111.8 to 116.0° E and from 20.2 to 24.3° N. Because the boundary was extracted before spatial clipping, artificial clipping edges were not treated as coastline.

For each filter, the representative sampling position was taken from the finalized per-filter coordinate record. These coordinates are the arithmetic means of the recorded sampling-start and sampling-end coordinates:

$$\lambda_i = \frac{\lambda_{i,\text{start}} + \lambda_{i,\text{end}}}{2}$$

$$\varphi_i = \frac{\varphi_{i,\text{start}} + \varphi_{i,\text{end}}}{2}$$

where λ_i and φ_i denote longitude and latitude, respectively. This convention uses the sampling endpoints to define one representative position; it does not represent the vessel’s sampling-start position, its position at the temporal midpoint, or a sampling-duration-weighted mean of the ship track.

The representative positions and coastline geometries were transformed from WGS84 geographical coordinates to a local azimuthal equidistant projection centred at 113.7° E, 22.2° N. The filter-level distance was calculated as

$$d_i = \frac{\min\{\|\mathbf{p}_i - \mathbf{q}\|_2 : \mathbf{q} \in C_{\text{mainland}}\}}{1000}$$

where $\mathbf{p}_i$ is the projected representative position, C_{mainland} is the set of projected mainland coastline segments, and the factor 1/1000 converts metres to kilometres. The calculation identifies the nearest point anywhere along the coastline segments rather than restricting the search to coastline vertices or manually selected reference points. No directional definition of “offshore” is imposed. In bays and estuaries, all surrounding mainland shoreline segments are eligible, including shores located behind or beside the sampling position. The resulting distances range from 2.00 to 53.89 km. The corresponding shortest connecting segments are shown in Fig. S4.

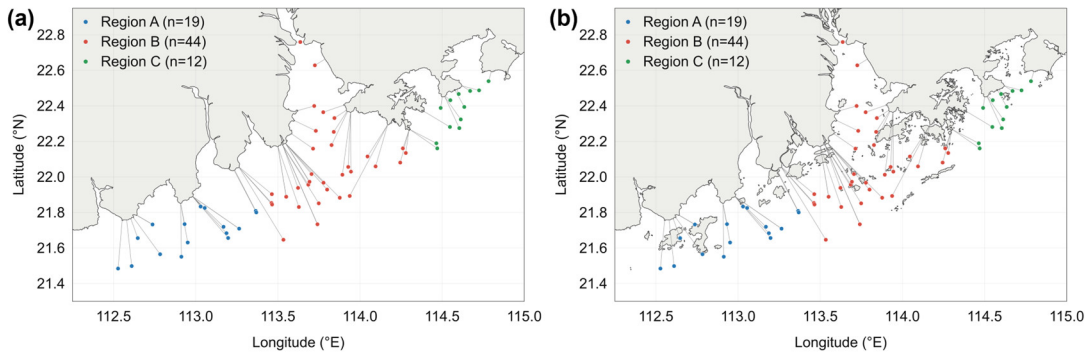


Figure S4. Marine sampling locations and shortest distances to the mainland coastline. **(a)** Map showing only the continental mainland coastline. **(b)** The same map with islands included for geographic context. Blue, red and green markers represent the sampling positions of retained marine filters 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.

The revised calculation supersedes the original minimum-distance estimates based on manually selected coastal reference points. It is nevertheless subject to the limitations of the representative-position convention and the coastline geometry represented in GSHHG. For moving or intermittently paused samples, a single midpoint of the start and end coordinates cannot describe the full spatial range sampled by the filter. Furthermore, excluding islands means that this metric is not a complete measure of proximity to all potential emission sources. It should therefore be interpreted as mainland proximity rather than atmospheric transport distance or source exposure.

Section S4. Within-day offshore gradient analysis and robustness checks

We analyzed bulk ON and IN concentrations in 75 retained marine filters collected over 23 local calendar dates. Each filter was assigned a distance to the continental mainland coastline based on the representative position defined in Section S3 (2.00–53.89 km), and the local date of its sampling-window midpoint.

S4.1 Primary regression model

ON and IN were analyzed separately by ordinary least squares, using natural-log concentration as the response and a separate intercept for each sampling date:

$$\ln(C_i) = \alpha_{d(i)} + \beta \frac{D_i}{10} + \varepsilon_i$$

Here, i identifies a filter; C is concentration; D is distance to the continental mainland coastline in kilometres; and $d(i)$ identifies the date assigned to that filter. The date-specific intercept α allows each day to have a different concentration baseline. The coefficient β describes the within-day distance association. The error term ε represents log-concentration variation not explained by the model, including unmeasured environmental influences and measurement variability. After fitting, a residual is calculated as observed minus fitted log concentration.

Because distance is divided by 10, the estimated percentage change per 10 km is:

$$100[\exp(\beta) - 1]$$

Date fixed effects account for between-day mean differences, but do not remove all within-day regional or meteorological variation.

S4.2 Statistical inference

Two-sided p values were obtained using a wild cluster bootstrap- t with 99,999 simulations. Filters from the same date formed one cluster. The model was first fitted with β constrained to zero. Each simulation added randomly weighted residuals to these constrained fitted values, using one common weight within each cluster, and refitted the full model. The observed and simulated slopes were standardized by their respective cluster-adjusted standard errors, using the CR1 finite-sample correction, and the resulting statistics were compared in absolute value. The 95% confidence limits were obtained by testing candidate slope values using the same procedure. Date clusters used equal-probability $+1/-1$ weights; cruise-period clusters used Webb six-point weights (Cameron et al., 2008; MacKinnon et al., 2023).

S4.3 Four separate robustness checks

Each check started from the primary model and was performed separately. Sampling-date fixed effects were retained throughout; date-level clustering was used except in Check 1.

(1) Cruise period clustering

The regression equation, all 75 filters and the 23 date-specific intercepts were unchanged. Only the bootstrap clustering unit changed from dates to eight consecutive cruise periods. Thus, the distance estimate was unchanged, while its p value and confidence interval could change. The periods were 12–15, 16–18, 19–20, 21–22, 23, 24–26 and 27–30 July, and 31 July–3 August. This clustering allows for dependence within longer time blocks but the periods have not been verified as independent air-mass episodes; inference assumes approximate independence between clusters.

(2) Longitude adjustment

295
$$\ln(C_i) = \alpha_{d(i)} + \beta \frac{D_i}{10} + \gamma L_i + \varepsilon_i$$

296 L is longitude centred at 113° E. This adds a linear longitude term to account for within-day

297 west–east variation. The distance and longitude coefficients were re-estimated together, with

298 bootstrap inference clustered by date.

299 **(3) Diurnal adjustment**

300
$$\ln(C_i) = \alpha_{d(i)} + \beta \frac{D_i}{10} + \gamma_1 \sin(\frac{2\pi h_i}{24}) + \gamma_2 \cos(\frac{2\pi h_i}{24}) + \varepsilon_i$$

301 h is the local sampling-window midpoint time expressed in fractional hours. The sine and cosine

302 terms jointly represent a smooth 24-hour cycle. The distance coefficient was re-estimated with

303 both terms included; bootstrap inference remained clustered by date.

304 **(4) Typhoon period exclusion**

305 The primary regression equation was unchanged. The nine filters assigned to 24–26 July were

306 excluded, and the model was refitted using the remaining 66 filters and 20 date-specific

307 intercepts. Bootstrap inference was clustered by these 20 dates.

308 The negative within-day association between bulk ON concentration and offshore distance was

309 consistent across the primary analysis and all four robustness checks (Table S5). Estimated

310 decreases ranged from 10.1% to 14.2% per 10 km increase in offshore distance, with all two-

311 sided *p* values below 0.05. The association persisted when allowing dependence within longer

312 cruise periods, adjusting separately for longitude and diurnal variation, and excluding the

313 typhoon-influenced period. These results support the robustness of the observed ON gradient

314 to the specific temporal and spatial influences examined here. No statistically significant

315 offshore association was detected for IN in any specification.

316 **Table S5.** Offshore gradient analysis and robustness checks for bulk ON and IN. (Effects are expressed

317 as percentage changes per 10 km increase in offshore distance; *p* values are two-sided wild cluster

318 bootstrap values. Binning is used only for visualization in Fig. 2b–c, not for statistical inference.)

Analysis	Purpose and approach	ON Change (%); <i>p</i>	IN Change (%); <i>p</i>
Primary regression model	Control between-day mean differences using within-day regression with date-specific intercepts; cluster inference by date.	-12.2% <i>p</i> = 0.007	8.5% <i>p</i> = 0.511
Cruise period clustering	Allow dependence across neighbouring dates by clustering inference by eight cruise periods; keep the regression model unchanged.	-12.2% <i>p</i> = 0.023	8.5% <i>p</i> = 0.589
Longitude adjustment	Assess west–east variation by adding longitude to the primary regression model.	-12.2% <i>p</i> = 0.008	8.1% <i>p</i> = 0.509
Diurnal adjustment	Account for smooth diurnal variation by adding 24-hour sine and cosine terms to the primary regression model.	-10.1% <i>p</i> = 0.044	10.1% <i>p</i> = 0.514
Typhoon period exclusion	Assess typhoon-period influence by excluding 24–26 July and refitting the primary model on 66 filters from 20 dates.	-14.2% <i>p</i> = 0.003	9.0% <i>p</i> = 0.549

319 Notes: All analyses retain sampling-date fixed effects. The four robustness checks are conducted separately.

320 Inference is clustered by date except in the cruise-period clustering check. The primary model and cruise-period

321 clustering check have identical point estimates because only the inference changes.

322

Section S5. Temporal comparability of marine and urban bulk nitrogen and ion measurements

Marine filters integrated 1.17–17.07 h of actual sampling time (mean 3.84 ± 2.81 h), whereas urban bulk-N filters represented 24 h and urban MARGA provided hourly ion measurements. To assess the influence of these different integration times, marine bulk IN and ON measurements were aggregated by sampling date, and marine ion measurements were compared with urban MARGA observations summarized at hourly, daily and marine-sampling-window resolutions.

S5.1 Daily comparison of bulk IN and ON

Marine daily concentrations were calculated from 168 reconstructed pump-on segments, excluding sampler-off gaps and splitting segments crossing midnight between the corresponding local dates. Each filter concentration was assigned to its constituent active segments, and daily concentrations were calculated by weighting these concentrations by their actual sampling durations within each date. This approach assumes that the filter-average concentration applies throughout its active segments.

The aggregation yielded 23 dates paired with urban 24 h filters. Across these dates, mean marine IN and ON concentrations were 0.279 and $0.102 \mu\text{g N m}^{-3}$, respectively, compared with 0.215 and $0.140 \mu\text{g N m}^{-3}$ for the urban filters. These daily summaries provide a more consistent temporal basis for describing campaign-average concentrations than a direct comparison of individual marine and urban filters. However, marine sampling coverage ranged from 2.22 to 23.52 h per day, with a median of 10.13 h. The marine aggregates therefore represent sampled-period means rather than complete 24 h averages and do not recover unresolved within-filter variability.

S5.2 Hourly and daily comparison of inorganic ions

Figure S5 presents hourly urban MARGA concentrations and their daily means alongside individual marine filter measurements for the eight measured ions. Urban daily means were calculated from valid hourly observations within each local calendar date, without interpolation of missing hours. The hourly and daily curves illustrate how temporal averaging smooths short-term fluctuations and provide context for the marine observations, whose integration times fall between these two temporal resolutions.

Brief peaks in the urban hourly records are less pronounced in the daily means. At the broader event scale, sulfate concentrations were elevated in both marine and urban records around 24–26 July and again near the beginning of August. Marine Na^+ concentrations were generally higher than the urban daily means through much of the campaign, indicating that the marine–urban patterns differed among ions. The combined presentation allows concentration levels and the timing of elevated concentrations to be compared while making the different averaging times explicit.

For quantitative ion comparisons, urban MARGA observations were additionally averaged over the actual marine pump-on windows. The resulting ratios of mean $\text{NH}_4^+\text{-N}$ to mean $\text{NO}_3^-\text{-N}$ were 4.0 for marine filters and 5.2 for urban MARGA. These are ratios of mean N-equivalent concentrations, rather than averages of individual ratios. Although temporal matching improves comparability, it does not remove differences between the measurement methods or quantify marine filter artifacts. Accordingly, Fig. S5 is used to describe temporal patterns rather than to establish equivalent variability between the two environments.

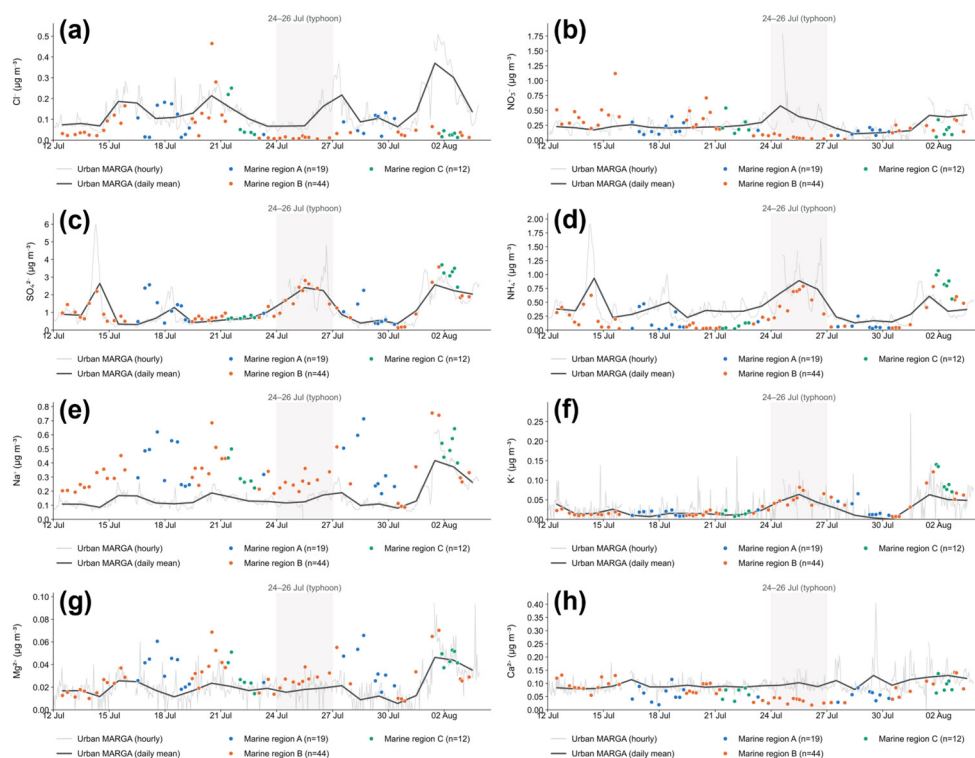


Figure S5. Time series of marine filter-based and urban MARGA ion concentrations during 12 July–3 August 2024. Panels show (a) Cl^- , (b) NO_3^- , (c) SO_4^{2-} , (d) NH_4^+ , (e) Na^+ , (f) K^+ , (g) Mg^{2+} and (h) Ca^{2+} . Light-grey and dark-grey lines represent urban hourly observations and daily 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.

Section S6. Calculation of PM_{2.5} dry deposition velocity (V_d) for marine and coastal urban environments

To provide a transparent basis for the dry deposition velocities used in the main text, we estimated representative PM_{2.5} particle dry deposition velocities using the size-segregated particle dry-deposition framework of Zhang et al. (2001). The calculation was performed separately for marine and coastal urban environments. A representative dry particle diameter of 0.5 μm and particle density of 1500 kg m^{-3} were used as the base case for both environments. The marine and urban surface roughness lengths were set to 2.0×10^{-4} m and 1.0 m, respectively. Neutral atmospheric stability was assumed. Because particle size and hygroscopic growth constitute important sources of uncertainty, additional sensitivity calculations were conducted by varying the representative dry particle diameter and by explicitly accounting for RH-dependent particle growth, as described below.

Governing equations

Following Zhang et al. (2001), the particle dry deposition velocity is calculated as

$$V_d = V_g + \frac{1}{R_a + R_s}$$

where V_d is the dry deposition velocity, V_g is the gravitational settling velocity, R_a is the aerodynamic resistance, and R_s is the surface resistance.

(1) The gravitational settling velocity (V_g) is calculated as

$$V_g = \frac{\rho_p d_p^2 g C_c}{18\mu}$$

where ρ_p is particle density, d_p is particle diameter, g is gravitational acceleration, μ is the dynamic viscosity of air, and C_c is the Cunningham slip correction factor:

$$C_c = 1 + \frac{2\lambda}{d_p} [1.257 + 0.4\exp(-0.55d_p/\lambda)]$$

where λ is the mean free path of air molecules.

(2) The aerodynamic resistance (R_a) is calculated as

$$R_a = \frac{\ln(z_R/z_0) - \psi_H}{\kappa u^*}$$

Here, z_R is the reference height, z_0 is the surface roughness length, ψ_H is the stability correction, κ is the von Karman constant, and u^* is the friction velocity. Assuming neutral stability, $\psi_H = 0$, and u^* is estimated from the neutral logarithmic wind profile:

$$u^* = \frac{\kappa U}{\ln(z_R/z_0)}.$$

(3) The surface resistance (R_s) is calculated as

$$R_s = \frac{1}{\varepsilon_0 u^* (E_B + E_{IM} + E_{IN}) R_1'}$$

400 where $\varepsilon_0 = 3$, and E_B , E_{IM} , and E_{IN} are the collection efficiencies by Brownian diffusion,
 401 impaction, and interception, respectively. R_1 is the rebound correction factor.

402 Brownian diffusion is calculated as

$$403 \quad E_B = Sc^{-c}$$

404 where c is the land-use-dependent exponent, and Sc is the Schmidt number:

$$405 \quad Sc = \frac{\nu}{D}$$

$$406 \quad D = \frac{k_B T C_c}{3\pi\mu d_p}$$

407 where ν is the kinematic viscosity of air, D is the Brownian diffusivity, k_B is the Boltzmann
 408 constant, and T is air temperature.

409 The impaction efficiency is calculated as

$$410 \quad E_{IM} = \left(\frac{St}{a + St} \right)^2$$

411 where St is the Stokes number and a is the land-use-dependent empirical coefficient. For the
 412 marine surface, the smooth-surface form is used:

$$413 \quad St = \frac{V_g u^{*2}}{g\nu}$$

414 For the urban surface, the collector-radius form is used:

$$415 \quad St = \frac{V_g u^*}{gA}$$

416 where A is the characteristic collector radius.

417 For the urban surface, the interception efficiency is

$$418 \quad E_{IN} = \frac{1}{2} \left(\frac{d_p}{A} \right)^2$$

419 For the marine surface, A is not defined for the ocean land-use category, and therefore E_{IN} was
 420 set to zero. The rebound correction factor is

$$421 \quad R_1 = \exp(-St^{1/2})$$

422 **Hygroscopic particle growth**

423 The Zhang et al. (2001) scheme accounts for particle growth under humid conditions by
 424 replacing the dry particle radius with an RH-dependent wet radius following the empirical
 425 parameterization of Gerber (1985):

$$426 \quad r_w = \left[\frac{C_1 r_d^{C_2}}{C_3 r_d^{C_4} - \log_{10}(RH)} + r_d^3 \right]^{1/3}$$

where r_d and r_w are the dry and wet particle radii, respectively, expressed in cm; RH is relative humidity expressed as a fraction between 0 and 1; and C_1 , C_2 , C_3 , and C_4 are empirical coefficients that depend on aerosol type.

Table S6. Empirical coefficients used in the hygroscopic-growth parameterization for different aerosol types (Gerber, 1985; Zhang et al., 2001).

Aerosol growth parameterization	C_1	C_2	C_3	C_4
Sea salt	0.7674	3.079	2.573×10^{-11}	-1.424
Urban	0.3926	3.101	4.190×10^{-11}	-1.404
$(\text{NH}_4)_2\text{SO}_4$	0.4809	3.082	3.110×10^{-11}	-1.428

Because continuous shipboard RH measurements were unavailable, hourly observations from Waglan Island were used as a proxy for the marine environment. King's Park, the closest Hong Kong Observatory station to the Tsuen Wan site with continuous RH measurements, was used as the coastal urban proxy. During 12 July–3 August 2024, the campaign-mean RH values were $89.3 \pm 6.5\%$ at Waglan Island and $84.2 \pm 7.7\%$ at King's Park.

The RH -dependent growth calculation was applied as a sensitivity analysis rather than as a replacement for the dry-particle base case because the actual hygroscopic response of $\text{PM}_{2.5}$ depends on aerosol composition and mixing state, and was not measured directly. The calculated wet diameter was substituted for the dry diameter in the size-dependent terms of the Zhang et al. (2001) deposition scheme while the other base-case parameters, including the prescribed particle density, were retained.

For a dry diameter of $0.5 \mu\text{m}$, the sea-salt growth parameterization at $RH=89.3\%$ yielded a marine wet diameter of approximately $0.990 \mu\text{m}$ and a recalculated V_d of 0.074 cm s^{-1} . Using the urban growth parameterization at $RH=84.2\%$ yielded an urban wet diameter of approximately $0.705 \mu\text{m}$ and $V_d=0.105 \text{ cm s}^{-1}$. Because the ambient particles were internally mixed rather than pure sea salt or pure urban aerosol, an additional $(\text{NH}_4)_2\text{SO}_4$ -like sensitivity case was evaluated. This yielded wet diameters of approximately 0.861 and $0.773 \mu\text{m}$ and V_d values of 0.079 and 0.099 cm s^{-1} for the marine and coastal urban environments, respectively.

Input parameters

Table S7 summarizes the input parameters used in the calculation. Land-use-dependent parameters were taken from Zhang et al. (2001), with land-use category (LUC) 14 used for the ocean surface and LUC 15 used for the urban surface.

Table S7. Input parameters used for the Zhang et al. (2001)-based PM_{2.5} dry deposition velocity calculation.

Parameter	Marine	Coastal urban	Reference or source
U	5.5 m s ⁻¹	2.6 m s ⁻¹	Mean wind speed
d _p	0.5 μm	0.5 μm	Zhang et al. (2001)
ρ _p	1500 kg m ⁻³	1500 kg m ⁻³	Qi et al. (2020)
Z _R	10 m	10 m	Approximate 10 m wind reference
Z ₀	2 × 10 ⁻⁴ m	1.0 m	Qi et al. (2020); Zhang et al. (2001)
ψ _H	0	0	Neutral stability
κ	0.4	0.4	Constant
k _B	1.38 × 10 ⁻²³ J K ⁻¹	1.38 × 10 ⁻²³ J K ⁻¹	Constant
ε ₀	3	3	Zhang et al. (2001)
c	0.5	0.56	Zhang et al. (2001)
a	100	1.5	Zhang et al. (2001)
A	not applicable	0.01 m	Zhang et al. (2001)
T	298.15 K	298.15 K	Representative summer value
P	101325 Pa	101325 Pa	Near sea-level pressure
μ	1.81 × 10 ⁻⁵ kg m ⁻¹ s ⁻¹	1.81 × 10 ⁻⁵ kg m ⁻¹ s ⁻¹	Standard near-surface value
λ	6.65 × 10 ⁻⁸ m	6.65 × 10 ⁻⁸ m	Standard near-surface value
RH	89.3%	84.2%	Mean relative humidity

Using the prescribed particle diameter and atmospheric constants, the shared particle-related quantities are:

$$C_c = 1.336,$$

$$V_g = 1.508 \times 10^{-5} \text{ m s}^{-1} = 0.00151 \text{ cm s}^{-1},$$

$$D = 6.448 \times 10^{-11} \text{ m}^2 \text{ s}^{-1},$$

$$Sc = 2.371 \times 10^5.$$

Calculation results

Table S8 summarizes the intermediate variables and final dry deposition velocities for the marine and coastal urban base cases.

Table S8. Calculated intermediate variables and PM_{2.5} dry V_d for the marine and coastal urban base cases.

Variable	Marine	Coastal urban	Unit
u^*	0.207	0.452	m s^{-1}
R_a	130.7	12.7	s m^{-1}
E_B	2.05×10^{-3}	9.77×10^{-4}	—
St	4.31×10^{-3}	6.95×10^{-5}	—
E_{IM}	1.86×10^{-9}	2.14×10^{-9}	—
E_{IN}	0	1.25×10^{-9}	—
R_1	0.936	0.992	—
R_s	837.2	761.5	s m^{-1}
V_d	0.11	0.13	cm s^{-1}

Using the Zhang et al. (2001) scheme with a single representative 0.5 μm dry particle, the estimated PM_{2.5} dry deposition velocity was 0.11 cm s^{-1} for the marine environment and 0.13 cm s^{-1} for the coastal urban environment. The urban value is slightly higher than the marine value in this base calculation, despite the lower urban wind speed, because the much larger prescribed urban roughness length results in a higher friction velocity and lower aerodynamic resistance. This behavior is consistent with the Zhang et al. (2001) framework, in which fine-particle deposition depends strongly on friction velocity and surface roughness.

These values are retained as the dry-particle base cases. Because particle size and hygroscopic growth introduce additional uncertainty, their influence on V_d was further evaluated through sensitivity calculations.

Particle-size and hygroscopic-growth sensitivity

To quantify the sensitivity associated with the assumed representative particle size, the dry-particle calculation was repeated for diameters from 0.3 to 1.0 μm . The results are summarized in Tables S9–S10.

(a) Dry-particle diameter sensitivity

Table S9. Sensitivity of calculated PM_{2.5} dry deposition velocity (V_d) to the assumed representative dry particle diameter for the marine and coastal urban environments.

Dry particle diameter (μm)	Marine (V_d) (cm s^{-1})	Coastal urban (V_d) (cm s^{-1})
0.3	0.141	0.188
0.5	0.105	0.131
0.7	0.087	0.105
0.8	0.081	0.097
1	0.073	0.086

The resulting model-sensitivity ranges are therefore approximately 0.073–0.141 cm s^{-1} for the marine environment and 0.086–0.188 cm s^{-1} for the coastal urban environment.

(b) RH/hygroscopic-growth sensitivity for a 0.5 μm dry particle

Table S10. Sensitivity of calculated $\text{PM}_{2.5}$ dry deposition velocity (V_d) to RH-dependent hygroscopic particle growth in the marine and coastal urban environments.

Environment	RH (%)	Growth parameterization	Wet diameter (μm)	V_d (cm s^{-1})
Marine	89.3	Sea salt	0.990	0.074
Marine	89.3	$(\text{NH}_4)_2\text{SO}_4$	0.861	0.079
Coastal urban	84.2	Urban	0.705	0.105
Coastal urban	84.2	$(\text{NH}_4)_2\text{SO}_4$	0.773	0.099

Although hygroscopic growth increases the effective particle diameter, the calculated V_d decreases for these accumulation-mode particles. This behavior reflects the non-monotonic size dependence of particle dry deposition: within approximately the 0.1–2 μm range, the decrease in Brownian-diffusion efficiency with increasing size occurs before gravitational settling becomes sufficiently strong to dominate deposition. The RH-adjusted values fall within the broader particle-size sensitivity ranges shown above.

The sensitivity ranges should not be interpreted as statistical confidence intervals. Rather, they quantify the first-order model sensitivity to two important but incompletely constrained parameters: particle size and hygroscopic growth. Because a size-resolved $\text{PM}_{2.5}$ nitrogen distribution and particle-specific hygroscopicity were not measured during the campaign, a uniquely constrained bulk V_d cannot be derived.

508 **Table S11.** Summary of sampling times, sailing distances, high-NO_x ship-emission notes
509 (exclude from marine samples), and notes on ship stops for the 91 cruise samples.

Sample ID	Date	Start Time	End Time	Duration (h)	Sailing distance (km)	Ship emission influence	Ship stops
AoE01	2024/7/12	10:52:00	12:46:35	1.91	27.6		
AoE02	2024/7/12	15:48:50	20:48:45	2.48	27.7		
AoE03	2024/7/12-13	21:22:50	7:45:10	2.08	22.3		
AoE04	2024/7/13	8:57:40	12:21:30	2.14	22.0		
AoE05	2024/7/13	13:17:20	18:26:55	2.18	21.3		
AoE06	2024/7/13-14	20:15:10	0:02:40	1.88	18.7		
AoE07	2024/7/14	5:48:30	10:04:50	2.24	21.2		
AoE08	2024/7/14	13:12:40	15:46:40	2.57	27.4	✓	
AoE09	2024/7/14	15:53:05	18:18:05	2.42	28.3		
AoE10	2024/7/14	19:36:50	23:34:10	1.89	24.2		
AoE11	2024/7/15	5:30:10	7:39:50	2.16	27.6		
AoE12	2024/7/15	8:41:40	11:39:50	2.97	13.4	✓	
AoE13	2024/7/15	14:05:20	16:10:00	1.72	13.0		
AoE14	2024/7/15	19:11:25	21:25:50	2.24	17.5		
AoE15	2024/7/15-16	21:34:40	7:23:00	9.54	126.5	✓	
AoE16	2024/7/16	10:18:50	15:57:50	5.65	17.1		
AoE17	2024/7/16	16:30:05	19:25:00	2.50	28.8	✓	
AoE18	2024/7/16-17	19:44:45	0:21:10	3.49	30.0		
AoE19	2024/7/17	0:37:20	7:16:30	6.65	0.0		✓
AoE20	2024/7/17	9:14:20	18:56:40	9.71	0.0		✓
AoE21	2024/7/17-18	19:41:50	3:09:00	7.45	0.0		✓
AoE22	2024/7/18	3:27:00	5:59:30	2.54	13.2	✓	
AoE23	2024/7/18	6:34:30	10:20:40	2.94	30.3		
AoE24	2024/7/18	10:51:40	14:22:45	2.58	24.3	✓	
AoE25	2024/7/18	14:46:00	17:20:40	2.28	18.3		
AoE26	2024/7/18	18:42:25	23:16:00	3.46	38.6		
AoE27	2024/7/18-19	23:36:30	5:06:50	4.30	40.6		
AoE28	2024/7/19	5:37:50	9:09:00	2.80	30.8		
AoE29	2024/7/19	9:30:50	12:48:10	2.61	29.4		
AoE30	2024/7/19	13:11:00	16:52:00	2.54	28.6		
AoE31	2024/7/19	18:10:20	20:58:40	2.81	0.0		✓
AoE32	2024/7/19-20	21:12:10	1:43:20	3.11	47.0		
AoE33	2024/7/20	6:21:30	10:16:45	2.57	36.1		
AoE34	2024/7/20	10:37:10	15:07:00	2.48	29.5		
AoE35	2024/7/20	15:49:00	19:19:30	2.52	29.2		
AoE36	2024/7/20	20:15:00	22:53:00	2.09	18.7	✓	
AoE37	2024/7/20-21	23:07:40	3:48:40	3.84	35.6		
AoE38	2024/7/21	4:06:40	7:26:50	2.95	28.8		
AoE39	2024/7/21	7:48:30	11:12:30	2.77	33.9		
AoE40	2024/7/21	11:39:30	15:42:40	3.07	36.2		
AoE41	2024/7/21-22	22:04:20	4:01:00	5.94	0.0		✓
AoE42	2024/7/22	4:21:30	8:20:00	3.02	26.2		
AoE43	2024/7/22	8:49:50	12:19:20	2.53	31.3	✓	
AoE44	2024/7/22	13:04:20	16:40:20	2.44	32.5		
AoE45	2024/7/22	17:31:10	21:29:20	2.43	30.4		
AoE46	2024/7/22-23	22:00:50	4:56:40	6.93	185.2		
AoE47	2024/7/23	5:11:00	9:24:30	4.23	0.0		✓
AoE48	2024/7/23	9:32:10	16:43:40	7.19	0.0		✓
AoE49	2024/7/23-24	16:50:10	0:22:30	7.54	0.0		✓
AoE50	2024/7/24	0:28:30	7:49:10	7.34	0.0		✓
AoE51	2024/7/24	8:10:10	14:11:30	6.02	0.0		✓
AoE52	2024/7/24-25	17:39:10	1:04:30	7.42	0.0		✓
AoE53	2024/7/25	1:10:20	8:28:50	7.31	0.0		✓
AoE54	2024/7/25	8:36:50	10:22:50	1.77	0.0		✓
AoE55	2024/7/25	10:27:00	14:55:10	4.47	49.8		
AoE56	2024/7/25	15:02:50	19:46:20	4.73	0.0		✓
AoE57	2024/7/25-26	19:54:20	12:58:40	17.07	0.0		✓
AoE58	2024/7/26	13:30:00	16:38:40	3.14	0.0	✓	
AoE59	2024/7/26	16:45:40	23:19:00	6.56	0.0		✓
AoE60	2024/7/26-27	23:25:30	11:43:10	12.29	0.0		✓
AoE61	2024/7/27	12:32:00	16:01:20	3.38	131.0		
AoE62	2024/7/27-28	17:00:40	5:06:00	12.09	0.0		✓
AoE63	2024/7/28	7:07:00	9:47:40	2.03	22.9		
AoE64	2024/7/28	10:31:10	14:31:00	2.88	36.9	✓	
AoE65	2024/7/28	15:05:40	17:12:50	2.12	27.0		
AoE66	2024/7/28	18:23:50	21:52:10	2.14	28.2	✓	
AoE67	2024/7/28-29	22:20:00	0:26:00	1.58	22.9	✓	
AoE68	2024/7/29	6:05:40	8:40:10	2.03	26.6		
AoE69	2024/7/29	9:18:40	11:57:35	2.08	20.7		
AoE70	2024/7/29	12:39:00	17:22:40	2.84	29.8		
AoE71	2024/7/29	18:20:20	22:49:30	3.18	40.6		
AoE72	2024/7/30	5:43:10	9:57:40	2.44	32.8		
AoE73	2024/7/30	10:46:30	14:24:00	2.41	29.6		
AoE74	2024/7/30	15:03:00	18:48:00	2.24	28.6		
AoE75	2024/7/30	19:09:45	23:37:10	2.68	33.5		
AoE76	2024/7/31	9:45:10	13:00:00	2.22	26.4		
AoE77	2024/7/31	13:20:10	17:19:00	2.31	32.3	✓	
AoE78	2024/7/31	17:51:00	19:47:30	1.86	23.9	✓	
AoE79	2024/7/31	20:29:30	22:34:45	1.46	18.2	✓	
AoE80	2024/8/1	6:36:20	10:22:30	2.58	29.0		
AoE81	2024/8/1	10:52:50	14:36:20	1.92	23.5	✓	
AoE82	2024/8/1	15:16:50	18:50:20	2.53	37.0		
AoE83	2024/8/1	19:20:50	22:38:50	2.33	32.5		
AoE84	2024/8/1-2	22:58:00	0:08:00	1.17	17.5		
AoE85	2024/8/2	5:52:00	8:44:50	1.88	26.3		
AoE86	2024/8/2	9:06:20	11:52:40	2.17	29.4		
AoE87	2024/8/2	12:11:30	14:20:10	1.86	19.9		
AoE88	2024/8/2	14:42:40	19:36:30	4.90	63.4		
AoE89	2024/8/2	20:04:00	21:39:00	1.58	20.5		
AoE90	2024/8/2	22:01:20	23:59:50	1.98	27.9		
AoE91	2024/8/3	6:14:00	10:01:40	3.02	38.4		

Table S12. Pairwise statistical comparisons of relative organic and nitrogen-containing AMS metrics in marine, urban, and ship-influenced water extracts.

Metric	U–M	U–M	S–M	S–M	S–U	S–U
	<i>p</i>	<i>p</i> BH	<i>p</i>	<i>p</i> BH	<i>p</i>	<i>p</i> BH
CHN ₁	0.030	0.098	0.008	0.041*	0.128	0.262
CHN _{>1}	0.002	0.016*	0.261	0.442	0.921	0.942
CHON ₁	0.029	0.098	0.044	0.116	0.216	0.393
CHON _{>1}	0.846	0.934	0.036	0.107	0.041	0.115
Amines	0.052	0.123	0.090	0.201	0.008	0.041*
Amides	0.047	0.118	0.536	0.799	0.022	0.083
Amino acids	0.218	0.393	0.684	0.879	0.818	0.934
Imidazole-like heterocycles	0.190	0.373	3.59E-04	0.004**	1.14E-04	0.002**
NO ⁺ /NO ₂ ⁺	0.001	0.009**	0.004	0.025*	0.974	0.974
C _{≥3} fraction	1.88E-07	8.45e-06***	0.900	0.942	0.018	0.072

Note:

1. U, urban (n = 23); M, marine (n = 45); S, ship-influenced (n = 4).

2. All tests are two-sided, using Mann–Whitney U tests with exact permutation inference for comparisons involving S. *p*BH denotes the Benjamini–Hochberg-adjusted *p* value across all 42 comparisons, including 12 inorganic-ion comparisons not displayed here. Significance is based on *p*BH: *** < 0.001, ** < 0.01, and * < 0.05. Values are rounded for display; *p* values do not indicate the direction of differences.

3. Comparisons use relative fractions or fragment-signal ratios rather than absolute concentrations. Organics is normalized to total AMS-reported component mass. The four CHN/CHON families and the four assigned functional groups are normalized to their respective four-category sums; these are not quantitative bulk ON mass fractions.

4. The C_{≥3} fraction includes N-containing organic fragments with at least three carbon atoms, normalized to the total N-containing organic-fragment signal; it is not a bulk ON mass fraction.



Figure S6. Photograph of the shipboard aerosol sampling configuration during the cruise campaign. Red boxes and arrows indicate the location of the high-volume air sampler on the upper deck outside the bridge and the nearby NO_x sampling inlet on the lower deck, illustrating their close proximity and the basis for using NO_x as an operational screen for ship-exhaust influence.

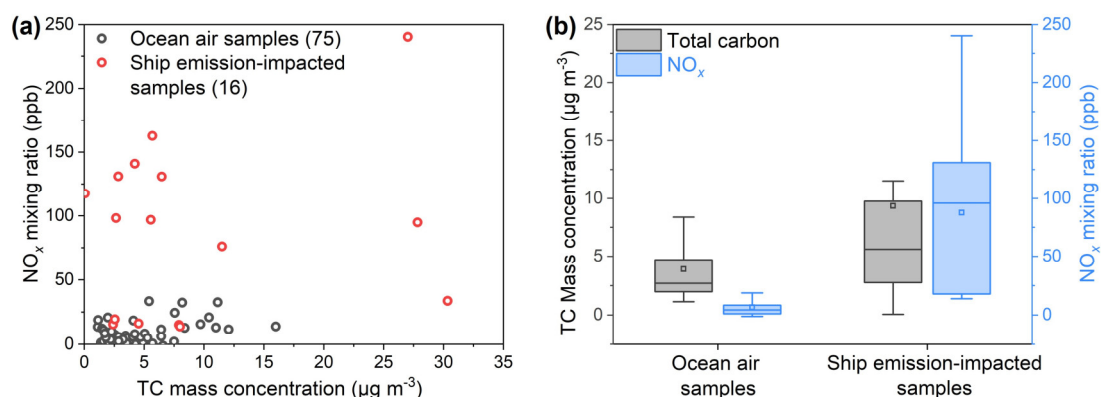


Figure S7. (a) Relationship between NO_x mixing ratio (ppb) and TC mass concentration ($\mu\text{g m}^{-3}$). Black symbols denote retained marine samples ($n = 75$) used in the subsequent analysis, and red symbols denote operationally ship-emission-influenced samples ($n = 16$), which were excluded from the retained marine dataset. (b) Box-and-whisker plots showing TC concentrations (gray boxes, left y-axis) and NO_x mixing ratios (blue boxes, right y-axis) for the retained marine and operationally ship-emission-influenced sample groups.

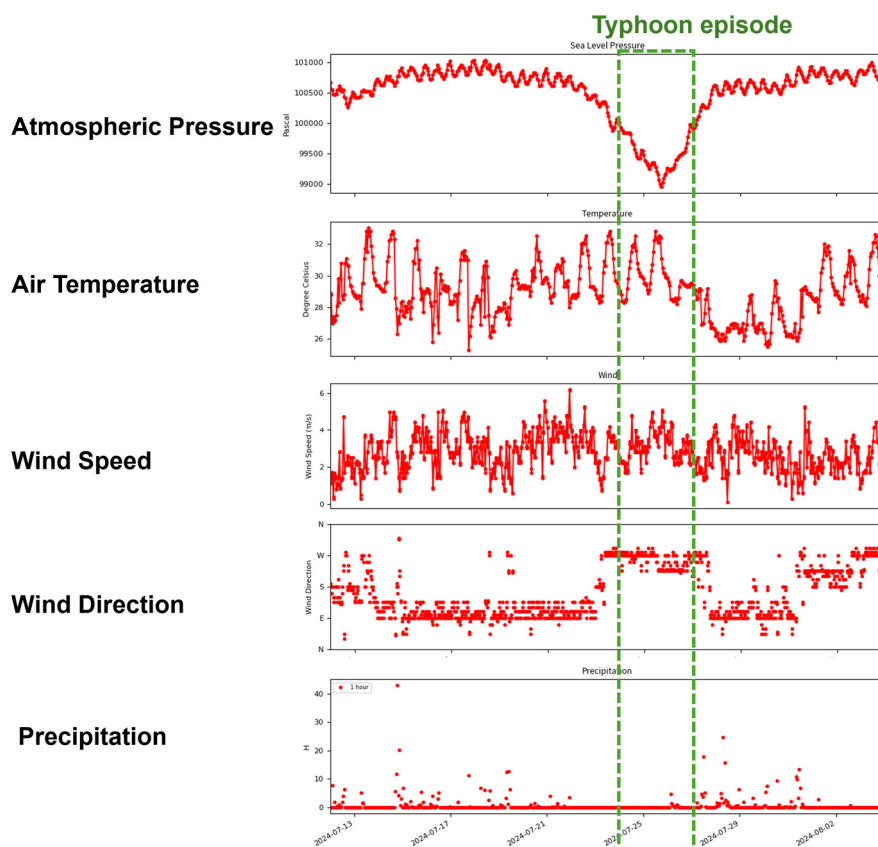


Figure S8. Time series of five key meteorological parameters, including atmospheric pressure, wind speed, wind direction, air temperature, and precipitation, measured at the King's Park station of the Hong Kong Observatory (HKO), located approximately 8 km southeast of the Tsuen Wan (TW) sampling site. The King's Park HKO station represents the closest station to the TW sampling site, with comprehensive observations of meteorological conditions. The green dashed box marks the typhoon-influenced period.

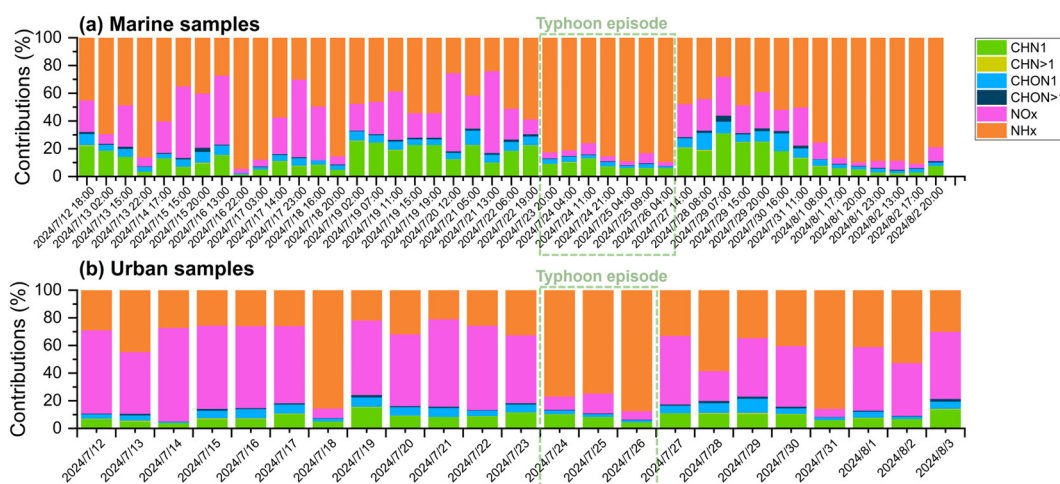


Figure S9. Time series of relative contributions of NH_x , NO_x , and the nitrogen-containing organic fragment classes (CHN and CHON classes) in marine and urban $\text{PM}_{2.5}$ water extracts, with the typhoon-influenced period highlighted.

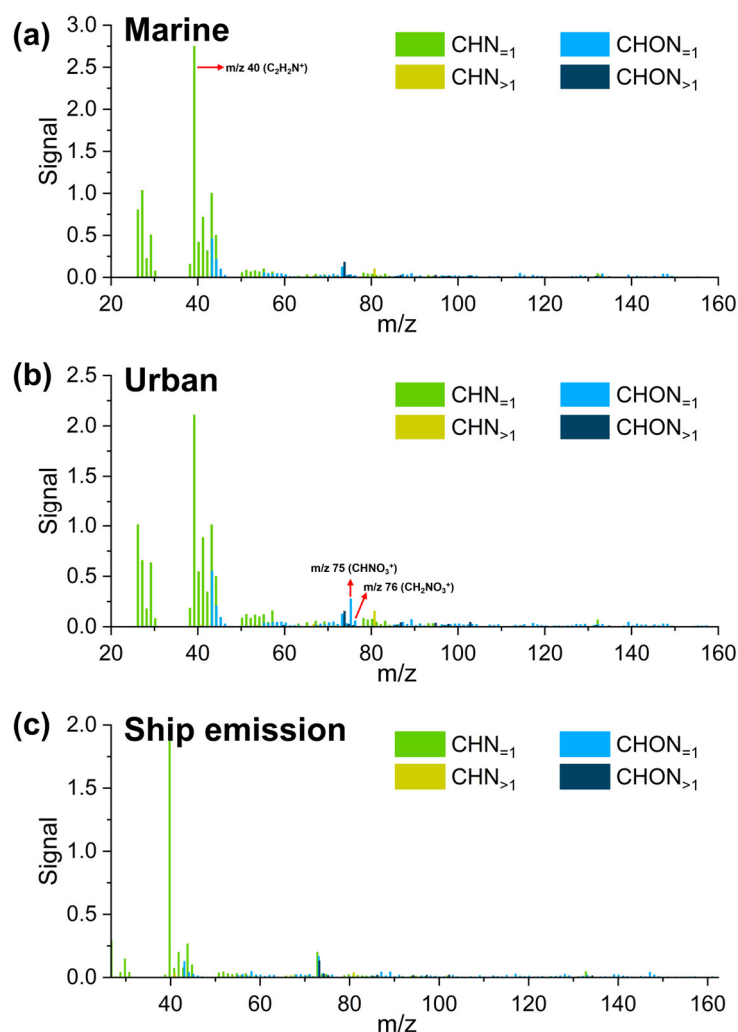


Figure S10. Mean mass spectra of nitrogen-containing organic fragments in (a) marine, (b) urban, and (c) ship-emission-influenced samples.

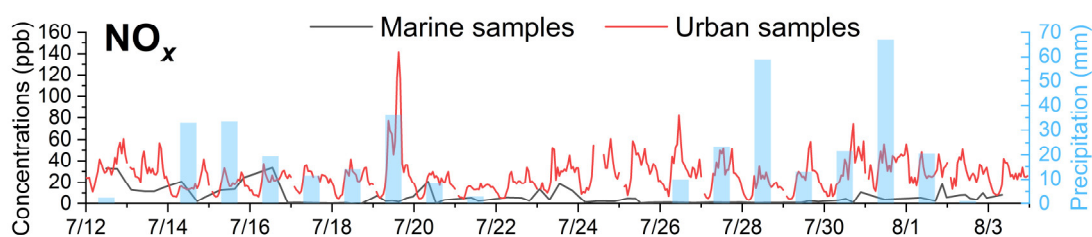


Figure S11. Time series of NO_x mixing ratios for marine (black line) and urban (red line) observations during the campaign. The urban NO_x data are reported at an hourly resolution, whereas the marine NO_x values are averaged over ~ 2 -hour intervals to match the corresponding filter sampling periods for the marine aerosol samples.

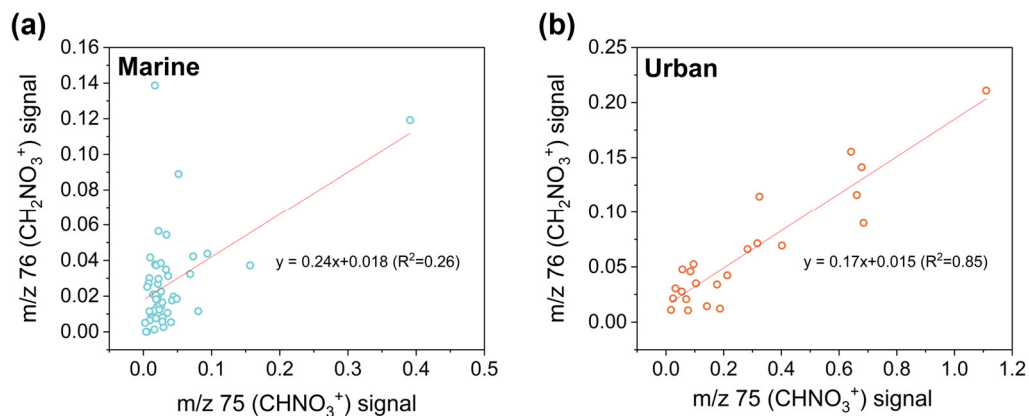


Figure S12. Relationship between CHNO_3^+ (m/z 75) and CH_2NO_3^+ (m/z 76) signals in (a) marine and (b) urban samples.

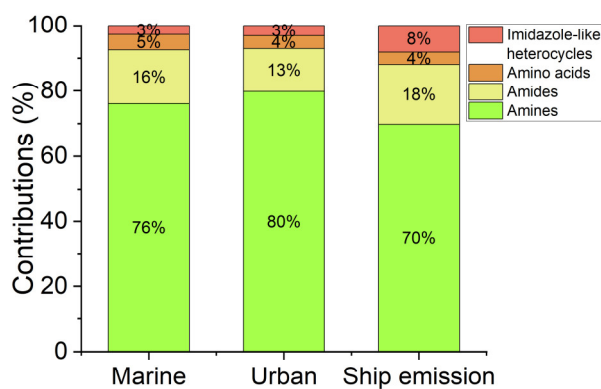


Figure S13. Comparative composition of reduced ON species in marine, urban, and ship-emission-influenced $\text{PM}_{2.5}$ samples.

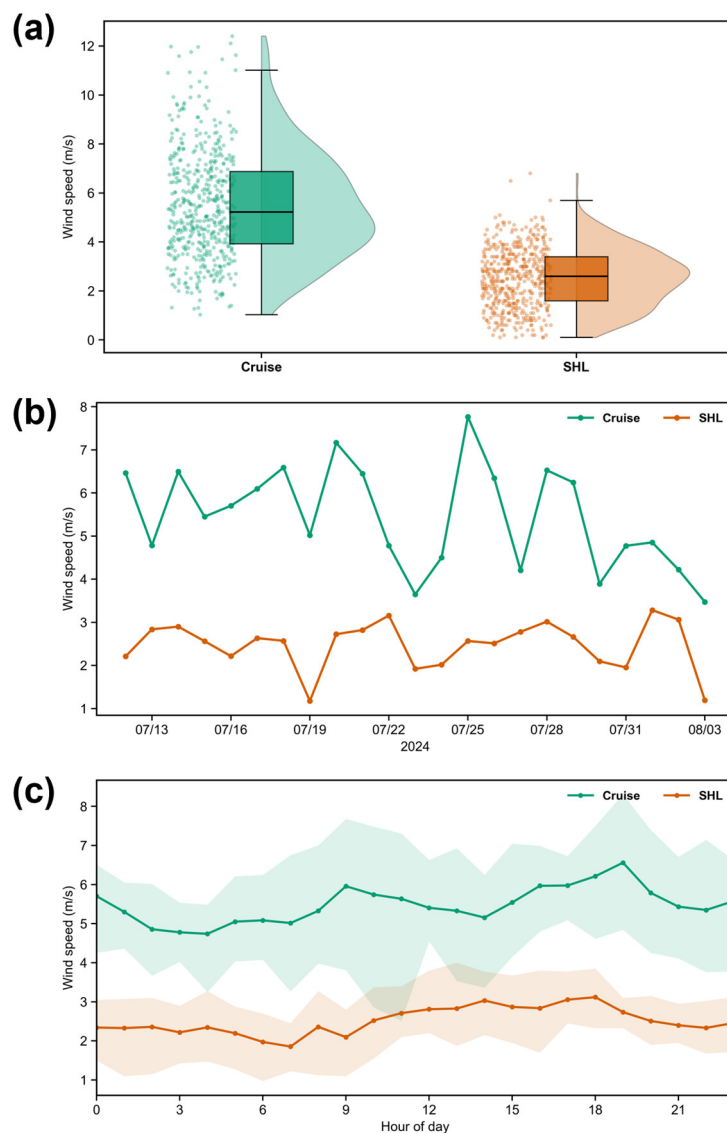


Figure S14. Wind speed comparison between the marine regions (shipboard observations) and the coastal urban site (SHL), used as a proxy for the coastal urban wind environment. **(a)** Box plots of the hourly wind speeds during the campaign period. **(b)** Daily mean wind-speed variations during the campaign period. **(c)** Mean diurnal patterns of wind speed, with shaded areas indicating variability.

References

- Cameron, A. C., Gelbach, J. B., & Miller, D. L. (2008). Bootstrap-Based Improvements for Inference with Clustered Errors. *The Review of Economics and Statistics*, 90(3), 414-427. <https://doi.org/10.1162/rest.90.3.414>
- Gerber, H. E. (1985). Relative - Humidity Parameterization of the Navy Aerosol Model (NAM).
- MacKinnon, J. G., Nielsen, M. Ø., & Webb, M. D. (2023). Cluster-robust inference: A guide to empirical practice. *Journal of Econometrics*, 232(2), 272-299. <https://doi.org/https://doi.org/10.1016/j.jeconom.2022.04.001>
- Qi, J., Yu, Y., Yao, X., Gang, Y., & Gao, H. (2020). Dry deposition fluxes of inorganic nitrogen and phosphorus in atmospheric aerosols over the Marginal Seas and

588 Northwest Pacific. *Atmospheric Research*, 245.
 589 <https://doi.org/10.1016/j.atmosres.2020.105076>
 590 Wessel, P., & Smith, W. H. F. (1996). A global, self-consistent, hierarchical, high-resolution
 591 shoreline database. *Journal of Geophysical Research: Solid Earth*, 101(B4), 8741-
 592 8743. <https://doi.org/https://doi.org/10.1029/96JB00104>
 593 Zhang, L., Gong, S., Padro, J., & Barrie, L. (2001). A size-segregated particle dry deposition
 594 scheme for an atmospheric aerosol module. *Atmospheric Environment*, 35(3), 549-
 595 560. [https://doi.org/10.1016/S1352-2310\(00\)00326-5](https://doi.org/10.1016/S1352-2310(00)00326-5)
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