



1 **Black Carbon Aging Sustained by Chemical Evolution in Wintertime Haze**
2 **over the East Asian Outflow: Evidence from Airborne Measurements**

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27 **Abstract**

28 Evaluating atmospheric aging remains crucial for robust air quality management. We conducted
29 airborne observations over the Yellow Sea during a haze event to elucidate how dynamic chemical
30 transitions govern the physical aging of refractory black carbon (rBC).

31 Over December 15-17, 2025, the flight-mean NR-PM₁ and rBC mass concentration varied from 3.8
32 $\pm 1.3 \mu\text{g m}^{-3}$ to $18.9 \pm 5.8 \mu\text{g m}^{-3}$ and $201.2 \pm 41.6 \text{ ng m}^{-3}$ to $581.8 \pm 136.4 \text{ ng m}^{-3}$, respectively. During
33 a NO₃⁻ explosion (mean $8.7 \mu\text{g m}^{-3}$), the maximum NO₃⁻ concentration coincided with peak rBC internal
34 mixing parameter, F_{thick} under high RH (74%) sustained since the previous evening, exceeding NH₄NO₃
35 deliquescence RH. These conditions likely promoted nighttime aqueous NO₃⁻ formation on rBC
36 surfaces. As strong northerly winds subsequently shifted the air mass, the SO₄²⁻ mass fraction rose
37 sharply, nonetheless, F_{thick} continued to elevate alongside the benzene/toluene ratio. Throughout this
38 evolution, the organic aerosol fraction increased progressively, suggesting a constant supply of
39 condensable mass via multi-channel pathways. Coating sensitivity analysis revealed that smaller rBC
40 (<155 nm) responded linearly during the early stages, while larger rBC (>156 nm) exhibited a delayed
41 sensitivity. Both were most sensitive to NO₃⁻, NH₄⁺, and organic aerosol, with aromatic and oxygenated
42 VOCs playing key roles in organic coating. These findings suggest that physical rBC aging is
43 fundamentally governed by major aerosol composition and size-dependent mass requirements.

44 Our findings highlight the need for an integrated mitigation framework targeting NO_x, aromatic
45 VOCs, and BC.

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56 **1. Introduction**

57 Aerosols significantly impact regional air quality and the global climate system. Black carbon (BC),
58 a primary aerosol of incomplete combustion and light-absorbing, plays a critical role in regional air
59 quality and global climate systems (Bond et al., 2013). While fresh BC aerosols are largely hydrophobic
60 and chemically inert, in the atmosphere they undergo complex aging processes, by which BC aerosols
61 are internally mixed with other components. Through coagulation and condensation, they form coating
62 materials and ultimately changed in morphology, size, chemical composition, and light-absorption
63 properties, signifying their air quality and climate impacts (Mishra et al., 2026).

64 While condensation of low volatile and oxygenated gases forms secondary aerosol on BC surfaces,
65 the amount of secondary aerosol coating and its formation rate depend on complex atmospheric
66 chemical and physical state and meteorology. In urban atmosphere, interplay of gas and aerosol loadings,
67 local meteorology, and related oxidation pathways directly affect the degree of BC aging. In
68 summertime with marine air influence, majority of BC aerosols (more than 70%) remained in bare or
69 thinly coated and the rate of coating formation was a few nm per hour in daytime (Lim et al., 2023).
70 Substantially coated BC aerosols were observed only at nighttime with relative humidity > 75% and
71 Temperature <30 °C. In contrast, during winter haze periods, BC aerosols were thickly coated and
72 highly associated with the chemical oxidation state of the atmosphere (Lim et al., 2025). While NO₃⁻
73 formation on BC surfaces has been reported in urban China (Zhou et al., 2022; Wei et al., 2023), recent
74 studies further demonstrate nighttime aqueous chemistry driving NO₃⁻ formation associated with BC
75 coating (Cui et al., 2022; Lim et al., 2023). The synergistic effects of high pollutant concentrations and
76 high humidity accelerate the formation of BC coatings, often exhibiting a distinct diurnal pattern driven
77 by daytime photochemical activity (Zhang et al., 2021).

78 Despite extensive monitoring in urban areas, atmospheric accumulation and aging of urban plumes
79 and their impacts on pollution evolution remained still uncertain. In this regard, several regional
80 background sites (e.g., Gosan Climate Observatory, Noto ground-based research observatory, etc.) have
81 served as important places for monitoring regional outflows. Recently, Yu et al. (2025) reported
82 comprehensive observations of BC physical properties in relation to combustion indicators in the
83 Yellow Sea based on multi-seasonal airborne measurements. The Yellow Sea, situated between the
84 massive emission sources of the Asian countries and downwind receptor regions, servers as a critical
85 place for observing the real-time physical aging and chemical evolution of continental outflows over an
86 open marine boundary layer (e.g., Takegawa et al., 2020). In particular, as emission sources and
87 intensity are rapidly changing in East Asia (Kanaya et al., 2020), establishing comprehensive multi-



pollutant mitigation strategies requires a precise understanding of how these evolving chemical environments dictate secondary aerosol coatings and BC physical aging.

In this study, we present a recent airborne measurement over the Yellow Sea during a wintertime 3-day haze episode occurred in December, 2025. We investigate interplay of bulk chemical composition of fine aerosol and BC physical aging, focusing on temporal evolution from the pre-episode period through the stagnant aging phase to the haze clearance.

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2. Methodology

2.1. Aircraft and Airborne measurements

Airborne observations were performed aboard a customized Beechcraft 1900D research aircraft. To continuously monitor flight dynamics (e.g., altitude, latitude, and longitude) and ambient meteorological parameters (e.g., temperature, pressure, and wind vectors), an Aircraft Integrated Meteorological Measurement System (AIMMS-30, Aventech Research Inc., Canada) was installed on the aircraft (Seo et al., 2019). For aerosol sampling, ambient air was drawn through a commercial isokinetic Airborne Aerosol Inlet (Droplet Measurement Technologies, USA). The inlet flow rate was strictly maintained at 100 L min⁻¹ to mitigate potential sampling artifacts and particle losses associated with flow distortion during high-speed flight.

A wintertime high-pollution episode over the Yellow Sea was investigated using six research flights conducted from 15 to 17 December 2025. During this period, two flights were performed each day, one in the morning and one in the afternoon, to capture the temporal evolution of the pollution episode. The aircraft departed from Taean Airfield (36°40' N, 126°16' E) and conducted measurements primarily over the Yellow Sea. Most observations were carried out at an altitude of approximately 300 m, while selected flight segments included stepwise ascents up to about 2.5 km to characterize the vertical distribution of aerosols.

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2.2 Airborne instruments

Single Particle Soot Photometer Concentrations and physical properties of refractory black carbon (rBC) were determined on a single-particle basis using a Single Particle Soot Photometer (SP2, Droplet Measurement Technologies, USA) (Schwarz et al., 2006). As rBC-containing particles traversed a continuous intra-cavity Nd:YAG laser beam (1064 nm), they were heated to their vaporization point



118 (~4000 K), emitting thermal radiation detected by incandescence channels (Moteki and Kondo, 2010).

119 The incandescence channel of the SP2 used in this study was calibrated using size-selected Aquadag
120 particles (Acheson Inc., USA). Aquadag particles with mobility diameters ranging from 80 to 450 nm
121 were selected to establish the calibration curve between the peak intensity of the incandescence signal
122 and rBC mass. The scattering channel was calibrated using polystyrene latex (PSL) spheres (Applied
123 Physics Inc., USA), and the scattering response was evaluated at particle diameters of 150, 200, 220,
124 269, 300, 350, 400, and 450 nm. Based on these calibrations, the measurable single-particle rBC mass
125 range was determined to be 0.23–25.4 fg, corresponding to an rBC mass-equivalent diameter (D_c) range
126 of 99.6–465.0 nm. The detectable optical diameter (D_{opt}) range for purely-scattering particles was
127 determined to be 174.0–434.1 nm.

128 The mass median diameter (MMD) of rBC was determined by fitting the rBC core mass size
129 distribution with a log-normal function. To ensure a robust fit and minimize uncertainties at the
130 detection limits, the log-normal fitting was performed based on observed rBC core sizes within the 100–
131 250 nm range. As rBC-containing particles traverse the SP2 laser, the sequential process of coating
132 evaporation and core incandescence results in a measurable time lag between their respective signal
133 maxima. Therefore, individual rBC-containing particles were classified based on their mixing state
134 which were determined by the lag time between the peaks of the scattering and incandescence signals
135 of the individual particle. In this study, particles with a lag time of less than 2 μ s were classified as
136 “uncoated/thinly coated” rBC, whereas those with a lag time of 2 μ s or longer were classified as “thickly
137 coated” rBC. The number fraction of thickly coated rBC particles (F_{thick}) was then calculated for each
138 ensemble dataset as the ratio of the number of thickly coated rBC particles to the total number of
139 mixing-state-distinguishable rBC particles.

140 **HR-ToF-AMS Measurements** The mass concentrations and chemical compositions of non-
141 refractory submicron particulate matter with an aerodynamic diameter of less than 1 μ m (NR-PM₁),
142 including organics, sulfate, nitrate, and ammonium, were characterized in real-time utilizing a High-
143 Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc., USA)
144 (DeCarlo et al., 2006). When the ambient air entered the HR-ToF-AMS inlet, aerosols were passed to a
145 pressure-controlled inlet (PCI) that was installed upstream inlet for making a constant flow rate of 1.3
146 LPM independent of altitude changes (Ban et al., 2024). Inside the instrument, sampled aerosols were
147 passed through the critical orifice and aerodynamic lens to make a narrow beam of particles under a
148 vacuum environment in the chamber from installed turbo pumps (Ban et al., 2024; Park et al., 2020). A
149 chopper positioned inside the chamber alternates between open and closed states, thereby controlling



the particle beam's access to the vaporizer (Canagaratna et al., 2007). The passed aerosols directed onto a heated standard vaporizer operating at 600 °C, where the non-refractory components were flash-vaporized and subsequently ionized via 70 eV electron impact (Alfarra et al., 2004; Jayne et al., 2000). Within the ToF chamber, the generated ions are segregated by their mass-to-charge (m/z) ratios based on flight-time differences, enabling both species identification and subsequent concentration quantification from the measured signal intensities (Park et al., 2025). To ensure sufficient temporal resolution for capturing rapid atmospheric variations during the flights, the HR-ToF-AMS was operated exclusively in Fast-MS (FMS) mode (Kimmel et al., 2011). Mass spectral data processing and quantification were carried out utilizing the Igor Pro-based software packages, SQUIRREL (v1.67) and PIKA (v1.27) (DeCarlo et al., 2006). Calibrations for the instrumental sensitivity, ionization efficiency (IE) and relative ionization efficiencies (RIEs) were performed using ammonium nitrate (NH_4NO_3), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), and ammonium chloride (NH_4Cl) particles produced by an aerosol portable atomizer (TSI Incorporated, USA) (Canagaratna et al., 2007). The determined IE and RIE values were subsequently applied to the dataset to quantify aerosol mass concentrations

PTR-TOF-MS Measurements Gas-phase volatile organic compounds (VOCs) were measured aboard the research aircraft using a Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-TOF-MS 1000, Ionicon Analytik GmbH, Innsbruck, Austria) operated in H_3O^+ mode (de Gouw and Warnenke, 2007; Blake et al., 2009). Ambient air was introduced into the reaction drift tube via 1.5m long heated (at 80) PEEK tubing with a flow rate of about 100 ml min^{-1} . The instrument was operated over the mass range of m/z 10-390 at a drift tube pressure of 2.4 mbar and temperature of 80 °C, corresponding to an E/N of approximately 130 Td (where E = electric field strength, N = gas number density, 1 Td = 10^{-17} V cm^2), and full mass spectra were acquired at 1Hz (Jordan et al., 2009; Müller et al., 2014).

For each research flight, instrumental backgrounds were determined using VOC-free zero air generated by a heated catalytic converter operated at 400 °C. A gravimetric 13-component VOC standard mixture (Ionicon Analytik GmbH, Innsbruck, Austria; ~1 ppm), containing methanol, acetonitrile, acetaldehyde, acetone, dimethyl sulfide, isoprene, methyl vinyl ketone, methyl ethyl ketone, benzene, toluene, styrene, ethylbenzene, and α -pinene, was dynamically diluted with the zero air through internal mass flow controllers (MFCs) and supplied to the PTR-ToF-MS to establish compound-specific sensitivity factors at low-ppb levels.

The raw mass spectra were processed using PTR-MS Viewer (v.3.3.17) to determine the mixing ratios of the target VOCs. Mixing ratios were calculated by applying compound-specific sensitivity factors obtained from calibration experiments. These sensitivity factors were expressed as normalized



counts per second per ppb (ncps ppb^{-1}). The resulting 1 Hz VOC dataset was subsequently synchronized with the aerosol and meteorological datasets for integrated analysis.

All datasets obtained from the onboard instruments were synchronized to the time stamp of AIMMS-30. Data of meteorology, NR-PM₁, and VOCs were processed at a 1 s time resolution and then averaged to 1 min intervals. The rBC mass concentration and physical properties were calculated at the same 1 min resolution and integrated with the aerosol chemical composition, VOCs, meteorological, and flight-position datasets for subsequent analysis.

3. Results and Discussion

3.1. Overview of the wintertime fine aerosol episode

The NR-PM₁ chemical composition and rBC properties evolved dynamically over the three-day airborne observations, captured across six distinct research flights (RF1–RF6). Figure 1 illustrates the temporal evolution of the event including meteorology, trace gases, NR-PM₁ composition and concentrations, and rBC concentrations and information of size and mixing state, categorized into distinct stages according to pollution levels and aerosol aging. The detailed data is shown in Table 1.

Initial Baseline condition (RF1, Dec. 15 AM): During the initial period under moderate southwesterly winds, RF-specific mean NR-PM₁ concentration was as low as $6.5 \pm 2.2 \mu\text{g m}^{-3}$ varying from $3.1 \mu\text{g m}^{-3}$ to $10.2 \mu\text{g m}^{-3}$. Major PM inorganic species, NO_3^- and SO_4^{2-} were 2.4 ± 1.1 and $1.5 \pm 0.5 \mu\text{g m}^{-3}$, respectively. Both CO and CO₂ were minimal.

The rBC mass concentration (M_{rBC}) was relatively low at $201.2 \pm 41.6 \text{ ng m}^{-3}$. Notably, the rBC mass-size distribution exhibited bimodal with mode 1 ($\sim 151 \text{ nm}$) and mode 2 ($\sim 297 \text{ nm}$). The F_{thick} value (0.62) revealed that the rBC particles remained consistent with remote background levels (Lim et al., 2022, 2023), showing minimal impact from anthropogenic pollution and its atmospheric processing. Consequently, this stage reflects background conditions, showing no discernible impact from heavy pollution sources.

Pollution inflow (RF2, Dec. 15 PM): As both temperature and RH (peaking at 80%) rose in the afternoon, both NR-PM₁ and M_{rBC} gradually increased despite PBLH development. In Figure 2, which illustrates the vertical profiles of M_{rBC} , F_{thick} , and concentrations of NR-PM₁ and its species, concentrations of these species elevated toward upper altitude up to 1.1 km. While MMD in mode 1 declined slightly to 150 nm, F_{thick} exhibited a subtle increase to 0.63 ± 0.06 , which suggests the inflow initiation of aged aerosols. The concurrent rise in CO and CO₂ concentrations resulted in a slightly



214 increased CO/CO₂ ratio of 0.50±0.20. This gradual enhancement in both aerosol loading and the
215 CO/CO₂ ratio reflects the continuous transport of regional pollutants, indicating the transition from
216 background conditions to an active inflow and aging regime.

217 **Stagnation and Nitrate explosion (RF3, Dec. 16 AM):** Meteorological conditions shifted to
218 atmospheric stagnation as wind speed dropped (4.1 m s⁻¹) and relative humidity (RH) rose to 74%.
219 Under these conditions, the most striking change was the explosive secondary formation of NO₃⁻, which
220 spiked by 209 % to reach 8.7 µg m⁻³, completely dominating the NR-PM₁ mass (Table 1 and figure 1).
221 While less pronounced than nitrate, sulfate, and ammonium, organic aerosols also exhibited concurrent
222 increases. Similarly, M_{rBC} rose dramatically to 469.9 ng m⁻³, accompanied by significant increases in
223 CO and CO₂ levels. In vertical profiles, highly elevated concentrations of aerosol species were prevalent
224 in altitudes up to 1.8 km in this morning period.

225 This period is characterized by a rapid transition into a stagnation-driven regime, where the synergy
226 between stagnant air masses and sustained high humidity (mean RH 74%) likely acted as a major driver
227 for the coincident explosion of NO₃⁻.

228 **Pollution accumulation (RF4, Dec. 16 PM):** After a slight shower (e.g., 1 mm in Incheon, a western
229 coastal city), aerosol concentrations dramatically reduced especially at altitudes above 1 km. However,
230 under continued stagnation and even higher humidity (RH 76%) in the afternoon, O₃ concentration
231 reached its maximum for the entire event period peaking to 60 ppbv at ~600 m in altitude. While NO₃⁻
232 levels declined ~5 µg m⁻³, organic aerosols remained relatively stable ~5.4 µg m⁻³. F_{thick} continued to
233 rise despite a lower rate of coating increase (ΔF_{thick}/Δt). This simultaneous occurrence of pollutant
234 accumulation intensified regional accumulation and aging evolution of the winter pollution.

235 **Peak pollution (RF5, Dec. 17 AM):** During this stage, winds shifted sharply from westerly flow to
236 strong northwesterly reaching 15.4 m s⁻¹. Despite these high velocities that would typically ventilate the
237 region, overall pollution levels reached their campaign maximum. NR-PM₁ concentrations continued
238 the upward trend initiated the previous afternoon, with M_{rBC}, CO, CO₂, F_{thick} all recording their peak
239 values of 581.8 ± 136.4 ng m⁻³, 0.37±0.14ppmv, 459.6±4.1ppmv, and 0.71±0.03, respectively.

240 While NO₃⁻ decreased to 4.9 µg m⁻³, but SO₄²⁻ concentration rose by 109 % to 2.9 µg m⁻³, coinciding
241 with a peak in CO (0.37 ppmv). Furthermore, the mass peak of the second rBC size mode (~295 nm)
242 grew substantially. These extreme values and the decoupled chemical shift demonstrate the direct influx
243 of a heavily aged air mass from northern coal-combustion regions.

244 **Clearance (RF6, Dec. 17 PM):** Sustained strong winds (11 m s⁻¹) eventually swept away the
245 polluted plume in the afternoon. All aerosols, including NR-PM₁ and M_{rBC} reached their minimum



246 values for the entire event period. Gaseous pollutants, such as CO, CO₂, and NO₂, also dropped to their
247 lowest recorded levels. F_{thick} returned to a low value of 0.6, comparable to the initial baseline—
248 signifying a return to remote background conditions. This dramatic reduction in both mass and rBC
249 mixing state confirms the clearance of the 3-day winter haze episode over the Yellow Sea.

250

251 3.2. Regional continuity of rBC physical aging driven by shifting chemical drivers

252 During the observation period, NR-PM₁ and rBC mass concentrations exhibited a steady increase
253 (Figure 1). However, NR-PM₁ chemical composition and the physical evolution of the rBC aerosols
254 showed a distinctive contrast during the progression of the winter haze episode. RF-specific analysis
255 shows that F_{thick} smoothly increased from 0.62 ± 0.04 , ultimately reaching a campaign maximum of
256 0.71 ± 0.03 on Dec. 17 am (Table 1). While the baseline concentration of NR-PM₁ rose steadily
257 throughout the event, the underlying chemical composition underwent a remarkable transition rather
258 than a simple continuous accumulation. During the atmospheric stagnation on Dec. 16 AM, NO₃⁻ spiked
259 to an overwhelming $8.7 \mu\text{g m}^{-3}$ on altitude average. In contrast, on Dec. 17 AM, when F_{thick} reached its
260 peak, NO₃⁻ dropped to $4.9 \mu\text{g m}^{-3}$, while SO₄²⁻ doubled from the previous afternoon ($1.4 \mu\text{g m}^{-3}$) to 2.9
261 $\mu\text{g m}^{-3}$. The monotonic increase in internal-mixing degree of rBC aerosols, occurring despite the abrupt
262 shift in dominant inorganic species, demonstrates that the continuous physical aging of primary
263 combustion aerosols is sequentially sustained by discrete transitions in the regional chemical drivers.

264 **NO₃⁻ explosion** On Dec. 16 AM, the pronounced NO₃⁻ peak serves as a key case for investigating
265 secondary aerosol formation mechanism under stagnant, high-humidity outflow conditions. After initial
266 increase in aerosol mass on Dec. 15 PM, during the morning of Dec. 16, the atmosphere was
267 characterized by stagnant and humid conditions (RF-mean wind speed and RH of 4.1 m s^{-1} and 74%,
268 respectively). It was highly probable that more pronounced atmospheric stability and near-saturated
269 humidity prevailed during the preceding night as the nocturnal boundary layer became increasingly
270 stable. Ground-based observations at Anmyeon-island, the western tip of Korea, showed that the surface
271 RH gradually increased from 66% at 20:00 on December 15 to 74% at 10:00 on December 16,
272 supporting the presence of nocturnal humidification prior to the aircraft measurements.

273 This RH range exceeded the deliquescence RH (DRH) of NH₄NO₃ under 0-5 °C conditions (55-
274 60%), and this DRH can be further reduced in internally mixed secondary inorganic aerosols containing
275 sulfate, nitrate, and ammonium (Seinfeld and Pandis, 1998). Therefore, the Dec. 16 AM case likely
276 provided favorable conditions for hygroscopic growth and increased aerosol liquid water (ALW)
277 content, thereby promoting the gas-to-particle partitioning of HNO₃ and NH₃ in aqueous phase and



278 contributing to the observed particulate NO_3^- enhancement.

279 It has been reported that nighttime heterogeneous reactions, such as the hydrolysis of N_2O_5 , were
280 active through aqueous chemistry, being drivers of NO_3^- coating on BC aerosols in urban environments
281 (Cui et al., 2022, Lim et al., 2023). The nocturnal marine boundary layer (MBL) over the Yellow Sea is
282 often shallow and stably stratified, favoring persistent moisture accumulation and elevated relative
283 humidity even within the overlying residual layer (Yun and Ha, 2022; Zhai et al., 2020), which often
284 makes marine fog. In vertical distributions (Figure 2), the peak of NO_3^- concentration was observed at
285 ~ 1.1 km on Dec. 15 PM, but this high-concentration layer extended up to altitudes of 1.8 km by the
286 morning of Dec. 16. This vertical expansion suggests that aerosols and their precursors persisted within
287 the nocturnal residual layer from the previous evening through the following morning.

288 Consequently, it is likely that newly formed particles and NO_3^- precursors confined within this low-
289 altitude residual layer were exposed to high-humidity conditions overnight. Such an environment aloft
290 could have provided a favorable medium for aqueous-phase processing (Saarikoski et al., 2023) and the
291 heterogeneous hydrolysis of N_2O_5 , although direct nocturnal observations were limited in the current
292 daytime aircraft study. The event maximum of NO_3^- ($12.5 \mu\text{g m}^{-3}$) coincided temporally with the peak
293 of F_{thick} (0.8). It suggests that under promoted NO_3^- formation, $\text{HNO}_3/\text{NO}_3^-$ could condense on rBC
294 surfaces and further grow in mass within the residual layer during the night.

295 The sudden explosion of NO_3^- mass in the following morning can therefore be explained by
296 boundary layer dynamics. This vertical coupling mechanism is also supported by Lim et al. (2022a),
297 whose ground-based and balloon measurements during the KORUS-AQ campaign demonstrated that
298 aerosols accumulating within the upper residual layer are entrained downward into the shallow
299 boundary layer upon morning vertical mixing. Similarly, in the current study, the morning vertical
300 mixing could facilitate the downward entrainment of this nocturnal airmass. At the surface, highly
301 humid conditions (RH 74%) exceeded the DRH of NH_4NO_3 ($\sim 55\text{--}60\%$ at $0\text{--}5^\circ\text{C}$) or even DRH of mixed
302 SIA salts, actively promoting *in-situ* aqueous reactions. This synergistic interplay between humid
303 conditions and vertical mixing likely triggered rapid gas-to-particle conversion, driving the explosive
304 NO_3^- concentration and thick rBC coatings observed on Dec. 16 AM.

305 This process highlights the potential role of the Yellow Sea boundary layer that functions as a
306 dynamic processing region rather than a passive transport corridor. Here, while advected continental
307 plumes are inherently subject to dilution and scavenging during transport, their aging is counteractively
308 and substantially accelerated by the vertical coupling of nocturnal processing aloft and morning
309 entrainment, directly determining the surface-level pollution intensity.



310

311 **Shift to SO_4^{2-} -dominant regime** Another pronounced chemical transition was observed on the
312 morning of December 17, when westerly winds shifted to strong northwesterly winds (15.4 m s^{-1})
313 accompanied by decreases in temperature and RH. Despite the strong northwesterly winds, which
314 would typically enhance atmospheric ventilation in this region (Lim et al., 2018, 2022), NR- PM_{10}
315 gradually increased with an elevated mass fraction of SO_4^{2-} (from 12-14% on Dec. 16 to 19% on Dec.
316 17 AM). The other species were stable in concentrations relative to those of last afternoon flight. In
317 parallel, both M_{rBC} and F_{thick} increased further. These simultaneous changes in meteorology and aerosol
318 composition suggest that the observed increase in F_{thick} was predominantly driven by a shift in the
319 dominant source region associated with the changing wind regime, rather than being solely governed
320 by localized chemical evolution. In particular, the enhanced SO_4^{2-} fraction implies the inflow of
321 regionally transported and more chemically aged continental air masses.

322 It is further supported by the benzene-to-toluene (BZ/TOL) ratio (Table 2 and Figure 3), which is
323 widely used as an indicator of emission characteristics and photochemical aging (Gelencsér et al., 1997).
324 Throughout Dec. 15 and 16, the BZ/TOL ratio remained relatively high, ranging from 1.27 to 1.51,
325 indicating that the air mass had already undergone substantial photochemical aging during regional
326 transport. However, on the onset of strong northwesterly winds on Dec. 17, the BZ/TOL ratio further
327 increased to 1.84, suggesting the inflow of an even more aged airmass with weaker influence from fresh
328 vehicular emissions. Under these conditions, the rBC aerosols observed over the Yellow Sea were likely
329 coated with complex aerosol mixtures.

330 Despite this air mass replacement, organic aerosols ($4.2 \mu\text{g m}^{-3}$) and NO_3^- ($4.9 \mu\text{g m}^{-3}$) maintained
331 relatively high concentrations in the morning time. Their persistence highlights that they function as
332 fundamental background pollutants in northeast Asia consistently supplied by urban outflow. In
333 particular, the mass fraction of organic aerosol to NR- PM_{10} gradually and progressively increased from
334 19.6 ± 2.0 on Dec. 15 AM to 29.6 ± 24.8 on Dec. 17 AM, tracking the monotonic rise in F_{thick} (Figure
335 1 and 3). This highlights that unlike secondary inorganics (NO_3^- and SO_4^{2-}) that are highly sensitive to
336 discrete meteorological triggers facilitating oxidation pathways (Lim et al., 2022b), organic aerosols
337 function as a ubiquitous chemical baseline driven by multi-channel formation pathways.

338

339 3.3. Evolution of rBC coating sensitivity across airmass aging stages

340 Figure 3 illustrates time series of BZ/TOL ratio and methanol to acetone ratio (MOH/ACT). As
341 mentioned above, BZ/TOL ratio remained elevated between 1.27 and 1.84 throughout event period. In



parallel, MOH/ACT ratio, which decreases with atmospheric oxidation because of the shorter lifetime of methanol relative to acetone, gradually declined from 1.66 on Dec. 15 AM to 1.32 on Dec. 16 PM. These trends indicate progressively enhanced photochemical aging of the continental outflow during transport.

To elucidate the temporal evolution of the coating sensitivity (ΔF_{thick}), we analyzed size-resolved variations across three distinct rBC core size ranges. Specifically, ΔF_{thick} was quantified as the difference in mean ΔF_{thick} between the lower ($< 25\text{th}$ percentile) and upper ($> 75\text{th}$ percentile) concentration groups for each chemical species from the initial stage to the clearance phase for the entire event period (Figure 4 and 5). This approach provides critical insights into the chemical and physical mechanisms underlying rBC aging over the Yellow Sea.

3.3.1 Size-dependent sensitivity to aerosol species

Figure 4 illustrates the sensitivity of rBC coating states to aerosol species across different rBC core groups. For smaller rBC cores (Bin 1 and Bin 2, < 155 nm), positive ΔF_{thick} values were distinctly observed up to 0.16 during the early stages of pollution accumulation (from Dec. 15 AM to Dec. 16 AM). The ΔF_{thick} to NO_3^- and NH_4^+ tended to increase linearly, peaking on Dec. 16 AM in conjunction with the NO_3^- -rich event under elevated RH (Sect. 3.2). In contrast, other chemical species showed no discernible temporal trends in relation to these size bins. These results demonstrate that smaller rBC aerosols over the Yellow Sea are preferentially sensitive to the initial increase in aerosol loading, and that the enhanced concentrations of bulk NO_3^- and NH_4^+ serve as the primary coating materials during the early stages of haze development.

In contrast, larger rBC cores (Bin 3, ≥ 156 nm) exhibited a prolonged response to the evolving pollution event. For Bin 3, the coating sensitivity to NO_3^- , NH_4^+ , and organic aerosols continuously increased through first two days, peaking on Dec. 16 PM. During this period, ΔF_{thick} reached as high as 0.25, surpassing the values observed in smaller bins. As the regional aging process deepened over the Yellow Sea, the coating sensitivity of larger rBC particles intensified.

These findings demonstrate that during the early stages of the episode, smaller rBC cores exhibit a rapid response due to their large surface-to-volume ratios (Kodros et al., 2018; Liu et al., 2018; Peng et al., 2023). Consequently, condensation of secondary species resulted in a large ΔF_{thick} . In contrast, larger rBC particles require a greater absolute mass of condensed vapors to cross the thickly-coated threshold. Under low concentrations of precursors or bulk aerosols, these larger cores are therefore likely to maintain a high degree of mixing-state heterogeneity. This size-dependent mass requirement



374 fundamentally explains why the coating sensitivity evolves more dynamically in rBC size ranges.

375

376 3.3.2 Coating sensitivity to VOC groups

377 To further elucidate the gas-phase precursor VOCs driving the formation of the secondary organic
378 coating on rBC aerosol, we investigated the coating sensitivity of rBC aerosols to VOC groups. Volatile
379 organic species were classified into four functional categories: (1) “Light-weight C₂-C₅ VOCs”
380 (including C₃H₆ and C₃H₄), (2) “aromatic VOCs” (including Benzene, toluene, styrene, Ethylbenzene,
381 Xylene, trimethylbenzene), (3) biogenic VOCs (Isoprene and pinene), and (4) “Oxygenated VOCs
382 (OVOCs)”, which encompassed a broad range of carbonyls and organic acids such as formaldehyde,
383 methanol, acetone, and methyl ethyl ketone.

384 Overall, the coating sensitivity to VOCs (maximum ΔF_{thick} up to ~ 0.15) was smaller than particulate
385 organic aerosols (maximum ΔF_{thick} reaching ~ 0.2). Given that VOCs must first undergo gas-phase
386 oxidation and phase partitioning to become condensable organic mass, contrary to aerosol, already-
387 condensed phase, this difference is physically well explained (Massoli et al., 2015). In parallel, among
388 the VOC groups, light-weight VOCs and biogenic VOCs exhibited minimal sensitivities ($\Delta F_{\text{thick}} < 0.1$)
389 with no temporal trends across all size bins, which is consistent with their high volatility and suppressed
390 wintertime emissions.

391 In contrast, aromatics and OVOCs demonstrated pronounced positive ΔF_{thick} values, directly
392 implying their active role as primary precursors of SOA. For smaller rBC cores (Bin 1 and Bin 2), this
393 positive sensitivity was distinctly evident during the early to intermediate stages of the episode (Dec.
394 15 AM to 16 AM). Conversely, larger rBC cores (Bin 3) exhibited a delayed but substantial progressive
395 increase in ΔF_{thick} , peaking on Dec. 16 PM with ΔF_{thick} reaching up to ~ 0.15 for both aromatics and
396 OVOCs.

397 Crucially, the temporal evolution of ΔF_{thick} was not exclusively governed by the chronological
398 kinetic timescales required for multi-step SOA coating, which typically ranged from 5 to 19 hours (Cui
399 et al., 2022), but was fundamentally amplified by the spatial heterogeneity of the Yellow Sea. In figure
400 5a, for TVOCs, ΔF_{thick} relative to the baseline conditions (the lower 25th percentile TVOCs
401 concentration on the morning of 15 December) was the largest on Dec. 17 AM. At the stage of maximum
402 aging (Dec. 17 AM), the air mass overlying the Yellow Sea reached a state of 'regional airmass aging
403 saturation'. As the entire aerosol population became uniformly and heavily coated, both the spatial
404 gradient and the morphological heterogeneity were eliminated, causing the coating sensitivity to both
405 VOCs and aerosols to drop.



406

407 **4. Conclusions**

408 To elucidate how dynamic chemical transitions govern physical aging of rBC aerosol during the
409 haze episode, comprehensive airborne observations were conducted over the Yellow Sea during a
410 wintertime haze event in December 2025. As the winter episode progressed from an initial baseline
411 (RF1) and regional inflow (RF2) to stagnation-driven accumulation (RF3–RF4), a peak regional aging
412 (RF5) and final clearance (RF6), bulk NR-PM₁ chemical composition underwent a drastic transition
413 from a stagnant NO₃⁻-dominated regime to a long-range transported SO₄²⁻-rich plume rather than simple
414 continuous accumulation. Coinciding with changes in aging indicator of BZ/TOL ratio and MeOH/ACT
415 ratio, F_{thick} progressively elevated.

416 While the remarkable chemical shift from NO₃⁻ and SO₄²⁻-dominant regimes coincided with a
417 progressive increase in RF-mean F_{thick}, the RF-mean F_{thick} was tightly coupled with the continuous
418 accumulation of the organic aerosol mass fraction. These findings highlight that the rBC core serves as
419 an active atmospheric surface for the secondary formation of major inorganic species, while the multi-
420 pathway oxidation of diverse VOC precursors ensures a steady organic matrix that sequentially sustains
421 physical aerosol aging.

422 A size-dependent rBC coating sensitivity analysis to aerosols and VOCs highlights the fundamental
423 role of core-size-resolved mass requirements in determining rBC aging kinetics, revealing that smaller
424 cores undergo rapid initial encapsulation while larger cores drive the intensified physical transformation
425 as the air mass progressively matures toward atmospheric aging on a regional scale. Furthermore, rBC
426 coating was sensitive to aromatics and OVOCs preferentially, suggesting that these volatile groups
427 served as the primary drivers of secondary organic coating mass accumulation during the episode.

428 These results suggest that mitigation strategies of winter haze should consider coordinated
429 reductions in NO_x, aromatic VOCs, and primary combustion emissions. Given that BC coating has been
430 enhanced despite reductions in BC mass concentrations, which is SOA-driven (Shen et al., 2024), such
431 a strategy must optimize the reduction ratios to effectively suppress the recent and fast enhancement of
432 both SOA and ozone, thereby improving regional air quality management.

433 Our findings are broadly consistent with previous studies in Northeast Asia reporting enhanced rBC
434 physical aging during winter haze episodes driven by secondary inorganic aerosol formation. Our
435 aircraft observations also demonstrate the evolution of rBC coating alongside changes in aerosol
436 chemistry over the Yellow Sea. However, this single winter episode-based study may not fully capture
437 seasonal variability, particularly during summertime when photochemical aging is more active under



438 cleaner atmospheric conditions. In addition, the relative contributions of individual chemical pathways
439 could not be distinguished. Future studies combining multi-season observations with mechanistic
440 analyses are needed to better evaluate the climatic implications of BC aerosols.

441

442 **Code availability**

443 The code for data analysis of this paper can be obtained from <https://zenodo.org/records/20586737>.

444

445 **Data availability**

446 The original data will be available from the corresponding author upon request.

447

448 **Author contributions**

449 SL supervised the project, designed the methodology, performed the validation, and wrote the
450 original draft. SC carried out data curation, formal analysis, visualization, and figures preparation, and
451 YH performed formal analysis and visualization. JC, SK, TL, JK contributed to investigation, JP and
452 MS contributed to project administration. THL contributed to secured funding and manuscript review
453 and editing.

454

455 **Competing interests**

456 The authors declare that none of the authors has any competing interest.

457

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463

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491 Tables

492 Table 1. Summary of meteorology, gases, and aerosol components observed during each airborne
493 measurement of 15 to 17 Dec. 2025 over the Yellow Sea. Values are 5th percentile–95th percentile
494 values (mean ± standard deviation).

	Dec. 15 AM	Dec. 15 PM	Dec. 16 AM	Dec. 16 PM	Dec. 17 AM	Dec. 17 PM
Temp.	3.8–5.4	3.0–7.5	6.3–9.4	7.2–9.9	2.6–4.8	2.9–4.7
(°C)	(4.6 ± 0.8)	(5.8 ± 1.5)	(8.2 ± 1.2)	(8.5 ± 0.8)	(3.9 ± 0.8)	(3.8 ± 0.8)
RH	47.8–62.9	59.9–79.2	61.9–78.9	71.6–81.1	62.7–74.5	61.8–68.5
(%)	(57.3 ± 4.7)	(65.8 ± 5.9)	(73.9 ± 5.0)	(76.3 ± 3.0)	(68.6 ± 3.7)	(65.3 ± 2.7)
WS	2.8–6.9	3.5–9.5	1.5–8.6	1.2–8.0	3.0–24.3	8.7–12.8
(m s ⁻¹)	(5.0 ± 1.6)	(6.5 ± 2.2)	(4.1 ± 2.3)	(3.6 ± 2.1)	(15.4 ± 7.3)	(11.0 ± 1.3)
WD	227	229	235	229	355	342
(°)	(189–298)	(179–256)	(223–32)	(229–25)	(218–105)	(322–350)
NO ₂	3.6–8.2	2.8–7.4	3.8–6.8	3.1–7.8	3.3–6.6	1.3–3.4
(ppbv)	(6.0 ± 1.5)	(4.9 ± 1.4)	(5.2 ± 1.0)	(5.0 ± 1.5)	(4.6 ± 1.0)	(2.4 ± 0.7)
O ₃	43.3–49.4	47.1–55.9	42.8–54.9	47.8–58.9	39.7–46.3	50.7–53.1
(ppbv)	(46.4 ± 2.1)	(51.7 ± 3.1)	(46.0 ± 3.5)	(54.4 ± 3.5)	(42.8 ± 2.4)	(51.8 ± 0.8)
CO	0.08–0.29	0.09–0.38	0.11–0.57	0.11–0.46	0.14–0.60	0.06–0.29
(ppmv)	(0.18 ± 0.07)	(0.22 ± 0.09)	(0.29 ± 0.14)	(0.28 ± 0.11)	(0.37 ± 0.14)	(0.14 ± 0.08)
CO ₂	441.3–446.4	441.9–451.7	446.5–457.2	449.5–458.9	450.6–464.1	436.1–442.6
(ppmv)	(443.7 ± 1.6)	(446.5 ± 3.6)	(451.4 ± 3.3)	(453.3 ± 2.9)	(459.6 ± 4.1)	(438.4 ± 2.1)
CO/CO ₂	0.17–0.66	0.21–0.85	0.24–1.25	0.25–1.02	0.31–1.30	0.13–0.65
(ppbv/ppmv)	(0.41 ± 0.15)	(0.50 ± 0.20)	(0.64 ± 0.30)	(0.62 ± 0.24)	(0.80 ± 0.31)	(0.33 ± 0.18)
NR-PM ₁	3.1–10.2	3.6–12.2	8.5–26.2	8.1–15.6	4.9–19.5	2.2–6.6
(µg m ⁻³)	(6.5 ± 2.2)	(7.7 ± 2.8)	(18.9 ± 5.8)	(12.2 ± 2.3)	(14.7 ± 4.6)	(3.8 ± 1.3)
Org	0.7–1.8	0.8–2.3	2.7–5.3	2.5–5.0	2.0–5.3	1.1–2.7



	(1.2 ± 0.3)	(1.5 ± 0.5)	(4.2 ± 0.9)	(3.3 ± 0.8)	(4.2 ± 1.1)	(1.7 ± 0.5)
	1.0–4.7	1.2–4.4	2.1–13.2	3.0–6.9	1.3–6.9	0.3–1.7
NO ₃ [−]	(2.4 ± 1.1)	(2.8 ± 1.1)	(8.7 ± 3.5)	(5.2 ± 1.2)	(4.9 ± 1.7)	(0.8 ± 0.4)
	0.7–2.2	0.9–3.1	1.8–3.4	1.0–1.8	0.8–3.7	0.5–1.2
SO ₄ ^{2−}	(1.5 ± 0.5)	(1.8 ± 0.7)	(2.4 ± 0.6)	(1.4 ± 0.2)	(2.9 ± 1.0)	(0.7 ± 0.2)
	0.6–2.0	0.7–2.4	1.4–4.9	1.3–2.7	0.7–3.3	0.2–0.9
NH ₄ ⁺	(1.3 ± 0.4)	(1.5 ± 0.6)	(3.4 ± 1.1)	(2.1 ± 0.4)	(2.5 ± 0.8)	(0.5 ± 0.2)
	0.03–0.14	0.05–0.21	0.13–0.36	0.17–0.36	0.08–0.35	0.03–0.13
Chl	(0.08 ± 0.03)	(0.10 ± 0.05)	(0.24 ± 0.07)	(0.27 ± 0.06)	(0.26 ± 0.09)	(0.07 ± 0.03)
M _{rBC}	145.6–276.9	159.9–426.5	282.8–586.0	411.1–640.0	289.3–746.1	157.8–337.6
(ng m ^{−3})	(201.2 ± 41.6)	(276.6 ± 89.4)	(469.9 ± 98.7)	(550.5 ± 75.4)	(581.8 ± 136.4)	(228.2 ± 55.3)
MMD	158.4–168.9	157.7–166.4	156.3–166.1	153.5–164.3	164.3–172.8	160.8–171.3
(nm)	(163.8 ± 3.4)	(162.2 ± 2.9)	(161.5 ± 3.1)	(159.9 ± 3.2)	(168.6 ± 2.6)	(166.2 ± 3.4)
F _{thick}	0.56–0.68	0.54–0.74	0.47–0.70	0.54–0.71	0.66–0.73	0.57–0.68
	(0.62 ± 0.04)	(0.63 ± 0.06)	(0.62 ± 0.07)	(0.65 ± 0.05)	(0.71 ± 0.03)	(0.63 ± 0.03)

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507 Table 2. Summary of NR-PM and VOCs for each research flight. Values for NR-PM_I and its species
508 are mean ± standard deviation (with mass fraction), and VOCs are 5th percentile–95th percentile
509 values (mean ± standard deviation).

Component	Dec. 15 AM	Dec. 15 PM	Dec. 16 AM	Dec. 16 PM	Dec. 17 AM	Dec. 17 PM
NR-PM _I in µg m ⁻³ (mass fraction in %)						
NR-PM _I	6.48 ± 2.20	7.70 ± 2.82	18.9 ± 5.8	12.2 ± 2.3	14.7 ± 4.6	3.79 ± 1.33
Org	1.23 ± 0.33 (19.6)	1.53 ± 0.47 (20.3)	4.17 ± 0.89 (23.1)	3.29 ± 0.75 (27.2)	4.18 ± 1.05 (29.6)	1.72 ± 0.48 (46.6)
VOCs in ppbv						
TVOCs	14.9–16.3 (15.8 ± 1.5)	14.2–15.8 (22.6 ± 33.7)	17.3–19.2 (18.1 ± 1.5)	17.6–19.4 (18.7 ± 2.0)	15.9–19.2 (17.1 ± 2.3)	10.8–22.6 (18.5 ± 12.4)
Light VOCs (C ₂ –C ₅)	0.66–0.77 (0.71 ± 0.09)	0.61–0.67 (0.96 ± 1.39)	0.80–0.90 (0.85 ± 0.07)	0.78–0.88 (0.85 ± 0.09)	0.75–0.90 (0.82 ± 0.11)	0.53–2.25 (1.58 ± 1.75)
Aromatics (C ₆ –C ₈)	1.05–1.18 (1.13 ± 0.13)	0.96–1.10 (3.46 ± 10.90)	1.34–1.63 (1.48 ± 0.20)	1.19–1.49 (1.37 ± 0.23)	1.35–1.58 (1.43 ± 0.19)	0.83–5.28 (3.59 ± 4.66)
OVOCs	11.8–12.9 (12.5 ± 1.3)	11.3–12.8 (15.1 ± 15.0)	13.5–15.1 (14.3 ± 1.2)	14.1–15.7 (15.0 ± 1.7)	12.4–15.2 (13.4 ± 1.9)	8.23–9.54 (9.14 ± 1.15)
Biogenic VOCs	0.30–0.32 (0.31 ± 0.02)	0.26–0.28 (0.83 ± 2.62)	0.28–0.30 (0.29 ± 0.02)	0.27–0.29 (0.28 ± 0.01)	0.28–0.31 (0.30 ± 0.02)	0.25–1.43 (0.96 ± 1.21)
BZ/TOL ratio	1.31–1.42 (1.38 ± 0.10)	1.45–1.57 (1.51 ± 0.10)	1.14–1.40 (1.27 ± 0.16)	1.18–1.58 (1.38 ± 0.24)	1.77–1.90 (1.84 ± 0.12)	1.76–2.01 (1.89 ± 0.15)
MeOH/ACT ratio	1.45–1.82 (1.66 ± 0.39)	1.23–1.58 (1.36 ± 0.34)	1.36–1.57 (1.46 ± 0.15)	1.21–1.37 (1.32 ± 0.16)	1.38–1.55 (1.47 ± 0.12)	0.90–1.19 (1.21 ± 2.01)

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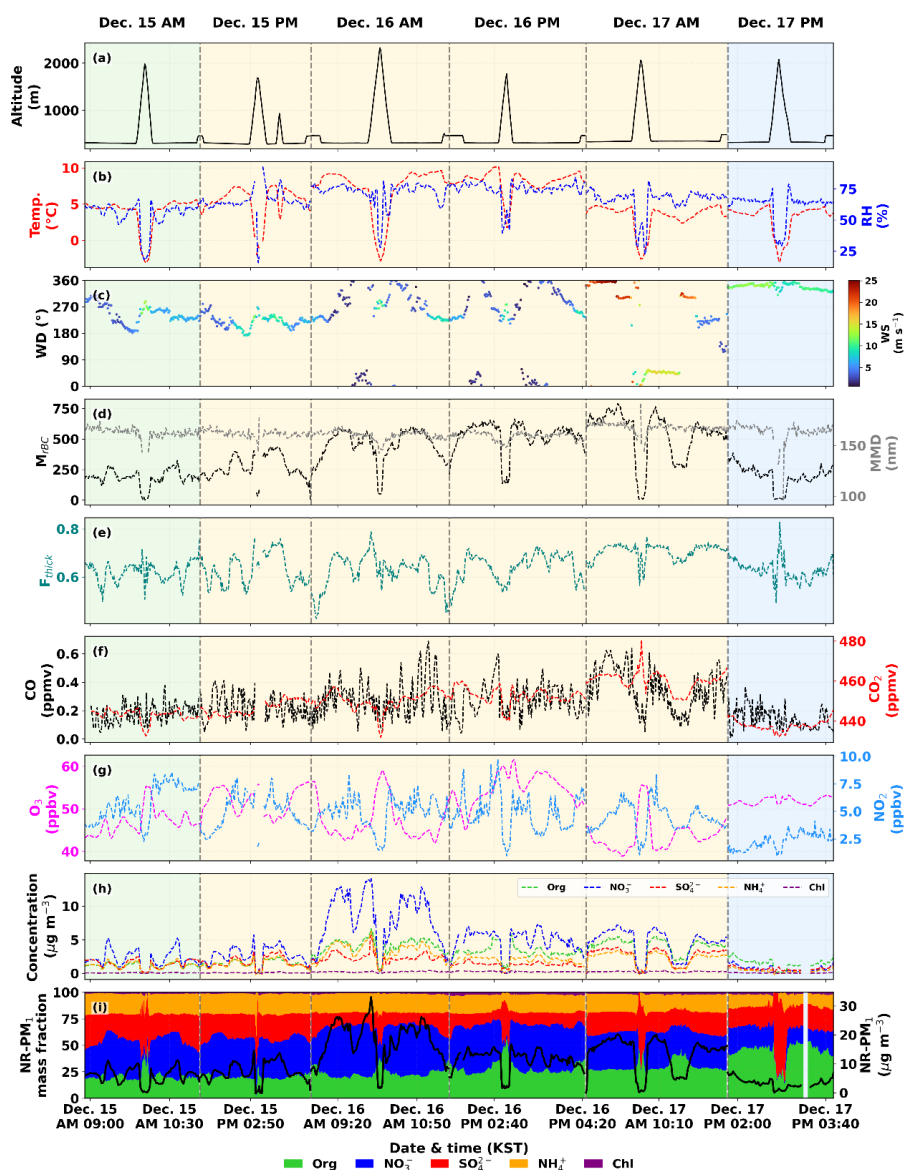
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517 Figures

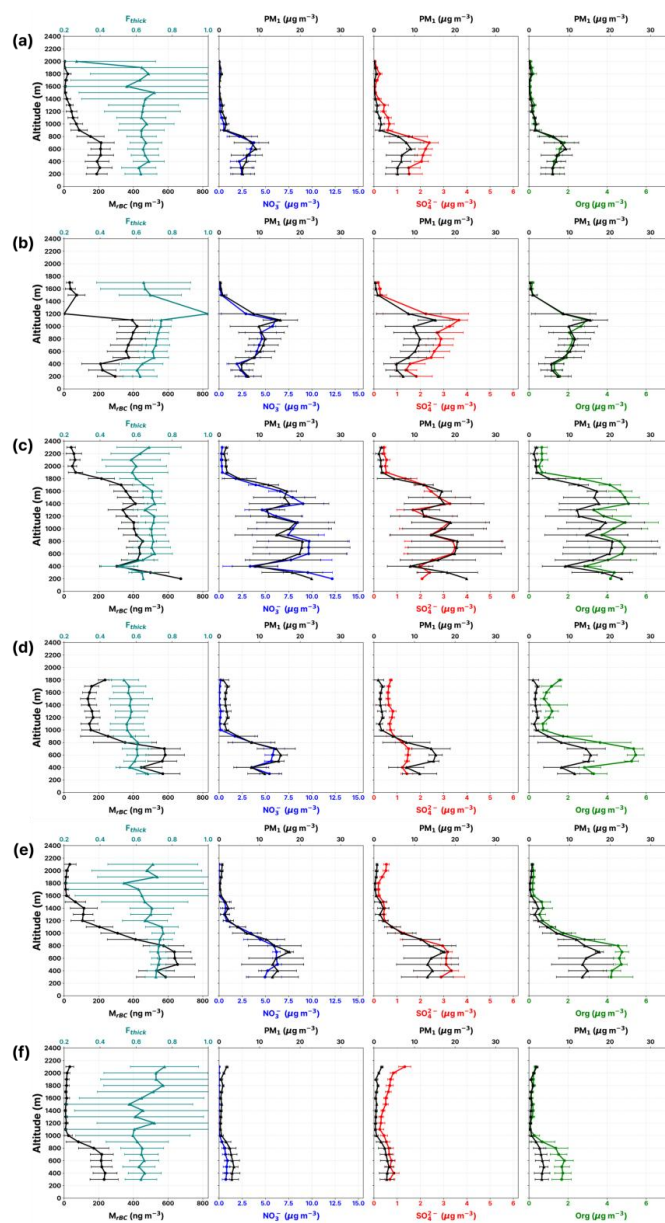
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520 Figure 1. Time series of meteorological parameters, trace gases, and aerosol properties observed during
521 all research flights over the Yellow Sea. The continuous timeline concatenates data from all
522 airborne measurements: (a) flight altitude; (b) ambient temperature ($^{\circ}\text{C}$) and relative humidity
523 (RH); (c) wind direction (WD) and wind speed (WS); (d) mass concentration of refractory
524 black carbon (M_{rBC}) and mass median diameter (MMD); (e) coating thickness fraction (F_{thick});
525 (f) CO and CO₂; (g) O₃ and NO₂; (h) chemical compositions of non-refractory submicron
526 particulate matter (NR-PM₁); and (i) mass fractions and total mass concentration of NR-PM₁.
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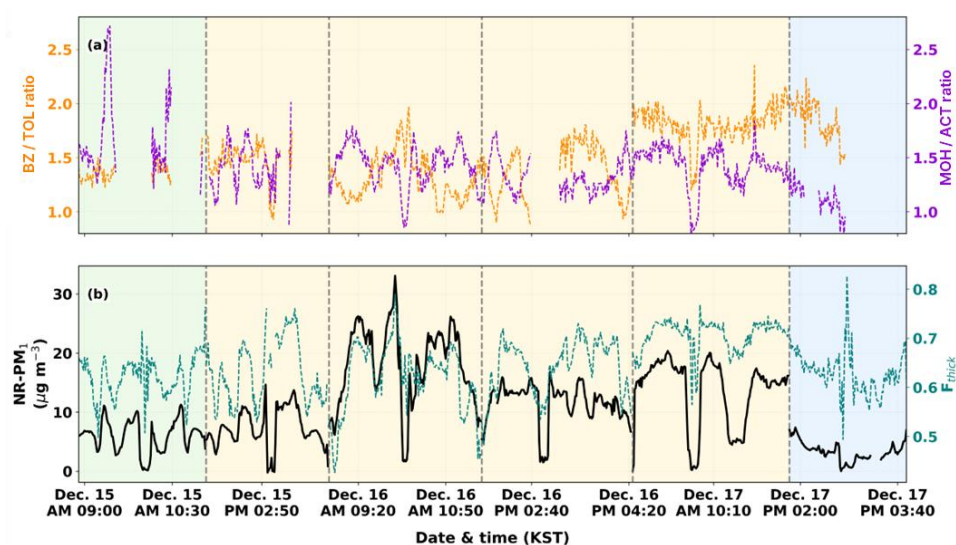


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530 Figure 2. Research flight-wise vertical profiles of rBC properties (M_{rBC} and F_{thick}) and NR-PM₁ species
 531 concentrations observed during the intensive periods: (a) Dec. 15 AM; (b) Dec. 15 PM; (c) Dec.
 532 16 AM; (d) Dec. 16 PM; (e) Dec. 17 AM; and (f) Dec. 17 PM. The error bars represent the
 533 standard deviations calculated at 100 m altitude intervals.



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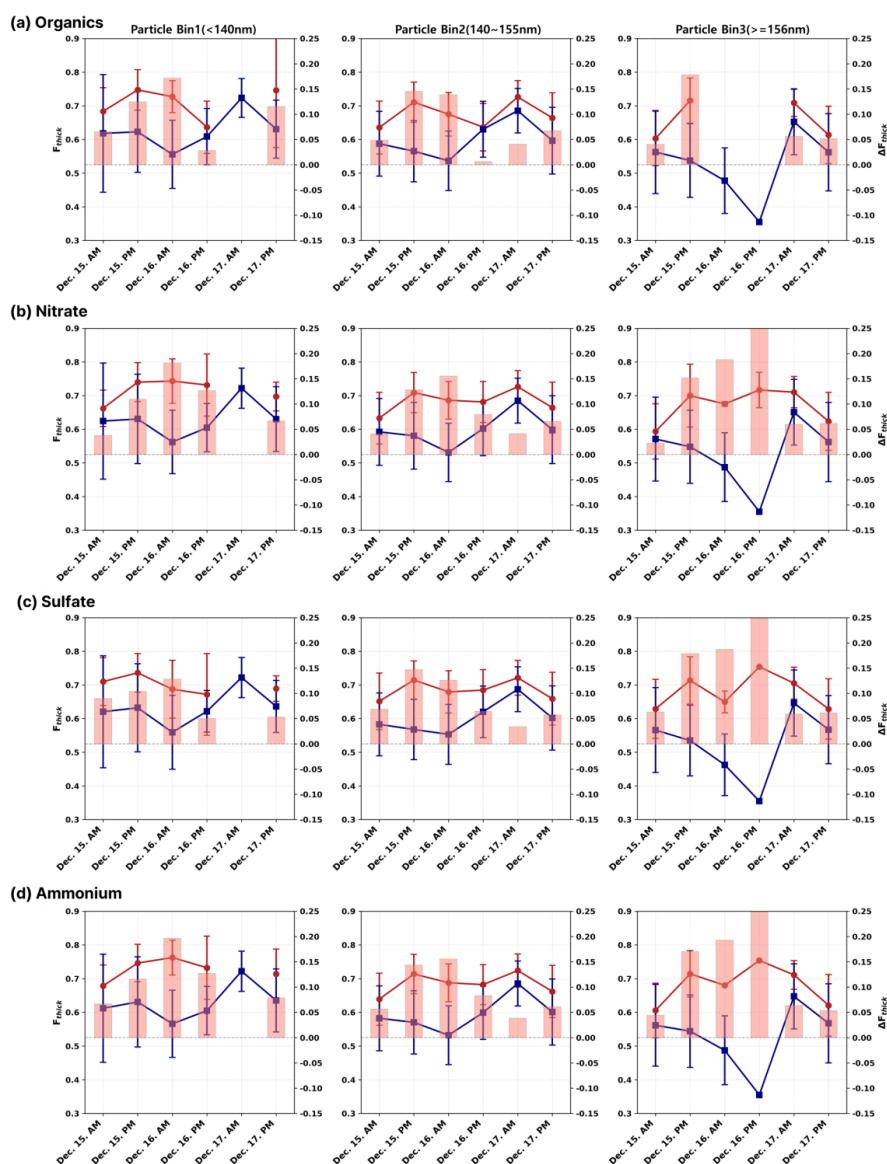


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536 Figure 3. Time series of VOC ratios and photochemical age during the intensive measurements. Panel
 537 (a) shows the time series of the BZ/TOL and MOH/ACT ratios, and panel (b) illustrates the
 538 time series of the non-refractory particulate matter (NR-PM₁), coating thickness fraction (F_{thick}).

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542 Figure 4. Size-resolved coating sensitivity of rBC to NR-PM₁ major component, (a) Organic, (b) NO₃⁻,

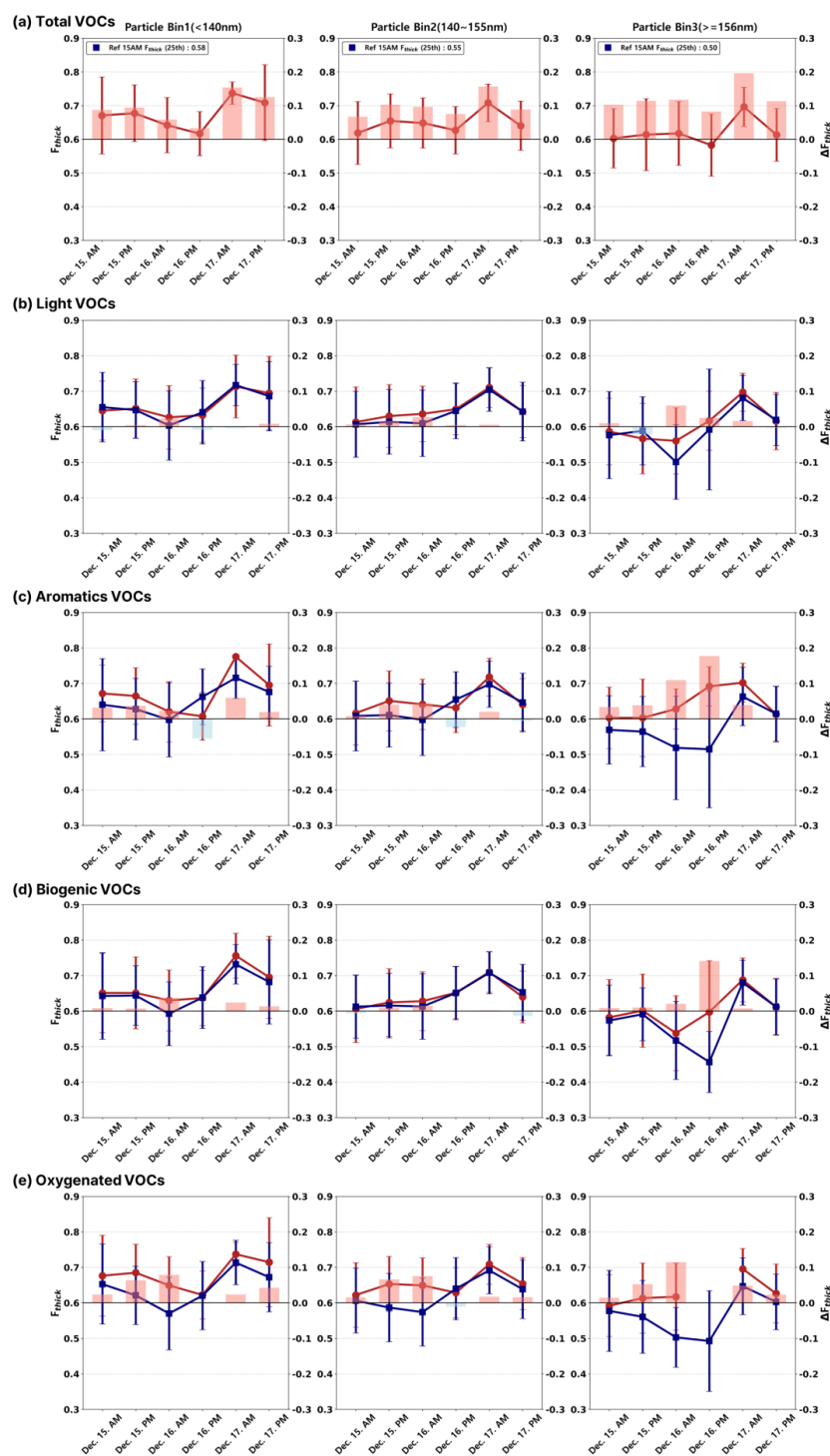
543 (c) SO₄²⁻, and (d) NH₄⁺. Bin 1 (≤140 nm), Bin 2 (140-155 nm), and Bin 3 (≥156 nm) indicate

544 size-dependent rBC group. The blue solid line represents the F_{thick} under the lower 25th

545 percentile mass concentrations of each corresponding aerosol species, while the red solid line



546 denotes the F_{thick} under the upper 25th percentile mass concentrations. The bar graph indicates
547 the difference F_{thick} between the upper and lower 25th percentile F_{thick} values.
548





550 Figure 5. Size-resolved coating sensitivity of rBC to various VOC groups: (a) total VOCs (TVOCs), (b)
551 light VOCs (C_2 – C_5), (c) aromatics (C_6 – C_8), (d) biogenic VOCs (BVOCs), and (e) Oxygenated
552 VOCs. For TVOCs only (a), the baseline F_{thick} for the lower condition was fixed using the values
553 obtained under the lower 25th percentile concentration on the morning of 15 December. The
554 blue solid line represents the coating thickness fraction F_{thick} under the lower 25th percentile
555 concentrations of each corresponding VOC group, while the red solid line denotes the F_{thick}
556 under the upper 25th percentile concentrations. The bar graph indicates the difference (ΔF_{thick})
557 between the upper and lower 25th percentile F_{thick} values.

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