



Nonlinear Effects of Relative Humidity on the Light Absorption of Water-Soluble Brown Carbon: Molecular-Level Constraints under Different Pollution Levels

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Abstract. Brown carbon (BrC) plays an important role in aerosol light absorption, yet its relative humidity (RH) dependent optical evolution remains poorly constrained. Based on field observations and ultra-high-resolution mass spectrometry, this study reveals that the light absorption of water-soluble BrC is nonlinearly regulated by the interplay between pollution level and RH. The mass absorption efficiency at 365 nm shows a biphasic response to RH. It increases with RH, reaching a maximum in the range of approximately 50%–60% RH, and then decreases when RH exceeds this threshold. Molecular-level analysis reveals that RH may alter the chemical fate of water-soluble BrC chromophores, steering their formation and attenuation pathways while concurrently reshaping their optical absorption profiles. In the low-to-moderate RH regime, liquid-phase chemical processing drives the accumulation of chromophores. Beyond the inflection point, increasing aerosol liquid water activates several synergistic suppression pathways, including oxidative bleaching, hydrolytic cleavage of N/S-containing chromophores, and physical dilution. High pollution levels may partially offset the RH-driven suppression effects. These findings challenge static parameterizations of BrC in models and highlight the necessity of incorporating RH-driven molecular restructuring into radiative forcing assessments.

1 Introduction

Brown carbon (BrC) refers to a class of organic aerosols that exhibit significant light absorption in the near-ultraviolet to visible spectral range. Its sources include primary emissions from biomass burning and fossil fuel combustion, as well as secondary organic aerosols formed through photochemical oxidation or aqueous-phase reactions of volatile organic compounds (Laskin et al., 2015; Laskin et al., 2025; Yan et al., 2015; Yan et al., 2017). As an important type of light-absorbing aerosol,



BrC has a substantial impact on the assessment of global radiative forcing and is a key contributor to the current uncertainty in radiative effect evaluations. Climate model estimates indicate that the direct radiative effect of BrC ranges from +0.03 to +0.6 W m⁻² (Wang et al., 2022). This wide uncertainty range reflects the current insufficient understanding of BrC optical properties and their environmental evolution patterns. Previous studies have shown that the optical characteristics of BrC are influenced by multiple physical and chemical factors, including the characteristics of primary emission sources (e.g., biomass burning, fossil fuel combustion), secondary formation processes (e.g., photochemical evolution and aqueous-phase reactions of volatile organic compounds), coexisting components (e.g., inorganic salts, metals), particle pH, solar radiation, atmospheric oxidation processes, and key environmental parameters such as relative humidity (RH) (Al-Abadleh et al., 2021; Chen et al., 2022; Duan et al., 2025). As one of the most dynamically varying environmental parameters in the atmosphere, RH can range from below 10% in arid regions to nearly 100% under cloud/fog conditions. Previous studies have indicated that RH can regulate the physicochemical properties of particulate matter through multiple pathways, thereby exerting complex effects on the light-absorption characteristics of BrC (Chen et al., 2024a; Duan et al., 2025; Kasthuriarachchi et al., 2020). Specifically, RH determines the water content of particles, which in turn influences their size, refractive index, and morphology. Simultaneously, RH can modulate particle phase state and viscosity, restricting the diffusion of gaseous oxidants into the particle phase and the migration of internal reactants (Price et al., 2022). Furthermore, liquid water under high-RH conditions can participate in aqueous-phase reactions, affecting the formation and transformation of secondary organic aerosols (Rogers et al., 2025; Top et al., 2025). Finally, RH may also act synergistically with solar radiation to further influence the photochemical aging processes of BrC (Duan et al., 2025).

Existing research has made certain progress in understanding how humidity modulates the light-absorption properties of BrC, yet significant complexity and controversy remain. Laboratory studies have revealed the highly context-dependent nature of the influencing mechanisms. On one hand, the direction of RH's effect is strongly governed by the chemical structure of precursors. For instance, aromatic compounds may exhibit enhanced light absorption under high RH due to nitration reactions, whereas heterocyclic compounds show the opposite trend (Chen et al., 2024a). On the other hand, the source and aging pathway of BrC are equally crucial. For example, photochemical bleaching of biomass-burning-derived BrC accelerates under high RH, while non-biomass sources may remain insensitive (Duan et al., 2025). Furthermore, aqueous-phase formation experiments further indicate that the influence of RH is non-monotonic, with a potential peak in formation efficiency occurring within the 55%–65% RH range (Kasthuriarachchi et al., 2020). However, these laboratory findings are usually based on simplified systems with limited RH ranges, making it difficult to fully represent the mixed-precursor conditions, complex aging processes, and synergistic effects of multiple factors (e.g., radiation, oxidants) in the real atmosphere.

Currently, field-based studies exploring the influence of RH on BrC light absorption remain very limited. High-time-resolution observations targeting haze episodes over the North China Plain found that the light-absorption capacity of total BrC and water-soluble BrC (Ws-BrC) increased with increasing RH, peaked at approximately 65% RH, and subsequently declined as RH rose further (>65%) (Jiang et al., 2023; Tao et al., 2024). In addition, another study on Ws-BrC based on measurements from 10 sites across central and eastern China also identified a nonlinear effect of RH on BrC light absorption, with an



absorption peak at around 60% RH (Chen et al., 2025). This non-monotonic pattern resonates notably with the high-value RH interval of 55%–65% identified in laboratory aqueous-phase formation experiments (Kasthuriarachchi et al., 2020). However, the underlying mechanisms have not been elucidated at the molecular level, nor have the discrepancies in RH-dependent patterns under different pollution backgrounds been systematically examined. This disconnect between laboratory-derived mechanistic understanding and field-based observations underscores a critical research gap. Specifically, there is a lack of studies that systematically resolve the quantitative relationships between RH and the formation, evolution, and optical properties of BrC within the complex context of real-world environments. Therefore, there is an urgent need to conduct systematic field observations covering a wide range of RH and spanning multiple pollution gradients.

By integrating observations with molecular-level approaches such as ultra-high-resolution mass spectrometry (Jiang et al., 2018; Laskin et al., 2025), it is essential to elucidate the chemical nature of RH's influence at the chromophore level. Such efforts are necessary to bridge the cognitive gap between idealized laboratory conditions and the complexity of the real atmosphere. Against this backdrop, this study successfully captured distinct meteorological-pollution episodes during a winter field campaign at a coastal site in Qingdao, China, spanning from clean conditions to heavy pollution and accompanied by significant variations in RH. This study aims to address the current gap in field observations regarding the systematic linkage between RH and BrC light-absorbing properties at the molecular level, thereby providing critical observational evidence and mechanistic explanations for more accurate assessments of BrC's climate radiative effects.

2 Materials and methods

2.1 Sample Collection

Field observations were conducted at a suburban site on the campus of Shandong University (Qingdao, China) from February 4 to 19, 2021. The sampling site was situated near the Yellow Sea, surrounded by a traffic road and rural villages, with no significant industrial sources or tall buildings in the vicinity. During the sampling period, ambient PM_{2.5} (particles with an aerodynamic diameter $\leq 2.5 \mu\text{m}$) was collected using a medium-volume sampler (TH-150A, Tianhong, Wuhan, China) operated at a flow rate of 100 L min⁻¹. The samples were collected on prebaked quartz fiber filters (2500 QAT-UP, Pall Corporation, NY, USA). A total of 32 samples were obtained, comprising both daytime samples (8:00 am to 5:30 pm local time, UTC+8h, 9.5 hours) and nighttime samples (6:00 pm to 7:30 am the following day, 13.5 hours). Two field blank samples were collected on February 3 and February 20, 2021, respectively, following the same protocol but without activating the sampler pump. Notably, the sampling period included Chinese Lunar New Year's Eve (February 11) and the Spring Festival day (February 12), which may have influenced local emission patterns.

2.2 Chemical Analysis

PM_{2.5} mass concentrations were determined by gravimetric analysis. A small punch (1.5 cm²) of each quartz filter was analyzed for organic carbon (OC) and elemental carbon (EC) using a thermal/optical carbon analyzer (Sunset Lab, USA) following the



NIOSH 5040 protocol. For water-soluble components, a subsample was extracted with 15 mL of deionized water. One aliquot of the extract was used to measure water-soluble ions (e.g., Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- , Br^- , NO_3^- , PO_4^{3-} and SO_4^{2-}) using an ion chromatograph (Dionex, ICS-600, Thermo Fisher Scientific, USA). The aerosol liquid water content (ALWC) and particle pH were estimated using the ISORRPIA-II thermodynamic model operated in forward mode, assuming the particles were in a metastable state, with input parameters including measured water-soluble ions (e.g., SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+}), ambient temperature, and RH (Guo et al., 2015). Another aliquot was analyzed for water-soluble organic carbon (WSOC) using a Carbon Nitrogen Elemental Analyzer (Vario Macro Cube, Elementar, Germany). Additionally, six saccharides (e.g., levoglucosan, mannosan, galactosan, glucose, erythritol, arabitol) were quantified using a Dionex ion chromatography (IC) system (ICS-3000, Thermo Fisher Scientific Inc., MA, USA), with the high-performance anion-exchange chromatography coupled to pulsed amperometric detection (HPAEC-PAD). Further details on the analytical procedures and quality control measures are available in our previous study (Yan et al., 2024).

2.3 Absorption and Fluorescence Spectroscopy Analysis

The water extracts were filtered using 0.45 μm PTFE syringe filters (Pall, USA). Wavelength-resolved absorption coefficients (200–700 nm) of the water extracts were quantified using a TIDAS UV/visible light spectrophotometer (J&M Analytik AG, Germany), equipped with a 1-meter-long liquid waveguide capillary cell (LWCC-3100, World Precision Instruments, Sarasota, FL) connected via fiber optic cables (FO-600-SMA1M, World Precision Instruments, Sarasota, FL). The absorption coefficients (Abs , Mm^{-1}) and mass absorption efficiency at 365 nm (MAE_{365}) were calculated following the method described by Chen et al. (2023). Fluorescence excitation-emission matrix (EEM) spectra were acquired using a fluorescence and absorbance spectrometer (DuettaTM, Horriba scientific, USA) with excitation wavelength (Ex)/ emission wavelength (Em) ranges of 200–600 nm (5 nm increments for Ex, 2 nm for Em) and 5 nm slit width. Blank EEMs were obtained using the same method, and the independent Raman scans at Ex = 350 nm were routinely performed using Milli-Q water (Millipore, 18.2 $\text{M}\Omega$ cm, 25 °C). The inner filter effect was automatically corrected, and the influence of Rayleigh scattering was eliminated via the EzSpec software. All the EEM data were normalized by the water Raman peak area (Ex = 350 nm, Em = 385–410 nm), and the data were ultimately presented in Raman units (RU).

2.4 ESI-FT-ICR-MS Measurement and Data Analysis

Eleven samples representing different types of days were selected for a detailed molecular characterization of water-soluble organic matter. Subsamples from each quartz filter were extracted using ultrapure water for approximately 30 minutes. The water extracts were then filtered through a 0.22 μm PTFE membrane (Anpel, China) and adjusted to pH 2.0 using 1 M HCl. The acidified extracts were then passed through a preconditioned solid-phase extraction (SPE) cartridge (Oasis HLB, 30 μm , 60 mg/cartridge, Waters Corporation Milford, MA, USA). Organic components retained on the cartridge were eluted with 2% (v/v) ammonia/methanol, evaporated to dryness under a gentle stream of N_2 , and redissolved in 1 mL of methanol. The final solutions were infused into an electrospray ionization (ESI) source (negative ionization mode) of a Fourier-transform ion



cyclotron resonance mass spectrometer (FT-ICR-MS, 9.4 T SolariX XR, Bruker Daltonics GmbH, Bremen, Germany) at a
130 flow rate of 180 $\mu\text{L h}^{-1}$ through an Apollo II electrospray source. In each molecular spectrum, thousands of molecular formulas
(~1000–9000) were detected, with m/z values ranging from 150–650 Da. Molecular formulas were determined using an
algorithm for D-labeled ultra-high-resolution mass spectrometry (UHRMS) spectra (FTMSDeu) (Yan et al., 2024). Identified
formulas were classified into five major compound categories, including CHO (compounds containing carbon, hydrogen, and
oxygen), CHON (compounds containing carbon, hydrogen, oxygen, and nitrogen), CHOS (compounds containing carbon,
135 hydrogen, oxygen, and sulfur), CHONS (compounds containing carbon, hydrogen, oxygen, nitrogen, and sulfur) and halogen-
containing compounds (HCCs, compounds containing chlorine (Cl), bromine (Br), or iodine (I)). The elemental composition
of each compound was assigned as $\text{C}_c\text{H}_h\text{O}_o\text{N}_n\text{S}_s\text{Cl}_l\text{Br}_k\text{I}_i$, where the subscripts represent the number of atoms for each element.
Aromaticity and unsaturation were evaluated by calculating double bond equivalents (DBE) and the modified aromaticity
index (AI_{mod}), after excluding formulas that violate the nitrogen rule, contain odd-electron ions, or have $\text{DEB} < 0$. For more
140 details, please refer to our previous studies (Chen et al., 2023; Yan et al., 2024). The volatility distribution was estimated using
the element-based method according to the linear correlation between the logarithm of C^* and the number of carbon and
oxygen in the molecule (Donahue et al., 2011), with parametrization and treatment following the approaches of Chen et al.
(2024b) for CHO and CHON compounds and Li et al. (2016) for CHOS and CHONS groups.

3. Results and Discussion

145 3.1 Nonlinear Response of WSOC Optical Properties to Pollution and Relative Humidity

The observation period encompassed a wide range of pollution and RH regimes. Clean days (daily average $\text{PM}_{2.5} < 75 \mu\text{g m}^{-3}$, RH: 49.3%–59.1%) served as a low-pollution, low-RH baseline. Foggy days (RH > 90%, visibility < 10 km, $\text{PM}_{2.5}$
comparable to clean days, from the night of Feb. 13 to the night of Feb. 14) were determined to probe the influence of RH
under low-pollution conditions. To isolate the effect of RH under high pollution levels, two haze subtypes including dry haze
150 (daily $\text{PM}_{2.5} > 120 \mu\text{g m}^{-3}$, visibility < 10 km, RH: 40%–49%, from night of Feb. 5 to night of Feb. 6) and wet haze (daily
 $\text{PM}_{2.5} > 120 \mu\text{g m}^{-3}$, visibility < 10 km, RH: 80%–90%, night of Feb. 10) were distinguished. Additionally, Chinese New Year's
Eve (the night of Feb. 11), characterized by intense firework and firecracker emissions and coinciding with high RH (>80%),
served as an extreme-emission case (FW) to test the interplay between primary source strength and high RH. Overall, the five
pollution-humidity regimes defined in this study spanned wide gradients of both $\text{PM}_{2.5}$ mass loading and ambient RH.
155 Two central optical metrics, the absorption coefficient at 365 nm (Abs_{365}) and the mass absorption efficiency (MAE_{365}),
revealed a consistent yet non-monotonic pattern across regimes. The combined ranking followed the order: Dry haze > Wet
haze > FW > Clean days > Foggy days (see Fig. 1a). This ranking reveals three key principles. First, pollution enhanced light
absorption. Both dry and wet haze produced substantially higher Abs_{365} and MAE_{365} than clean days, indicating that elevated
 $\text{PM}_{2.5}$ loading increased the abundance and/or efficiency of water-soluble light-absorbing chromophores (see Fig. S1). Second,
160 high RH generally suppresses light absorption. On foggy days, with the highest RH and ALWC, the weakest absorption was



observed across all regimes, and wet haze yielded markedly lower values than dry haze despite comparable particle mass concentrations. Third, the superimposed effect of special emissions can partially counteract the RH-driven suppression. During the FW period, Abs_{365} exceeded both clean and foggy levels, confirming the presence of chromophoric BrC from pyrotechnic sources (Rawat et al., 2022). However, MAE_{365} remained lower than both dry and wet haze, suggesting that the fireworks-emitted BrC itself may consist largely of weakly-absorbing components and high RH suppressed the light-absorption efficiency of FW-derived organics.

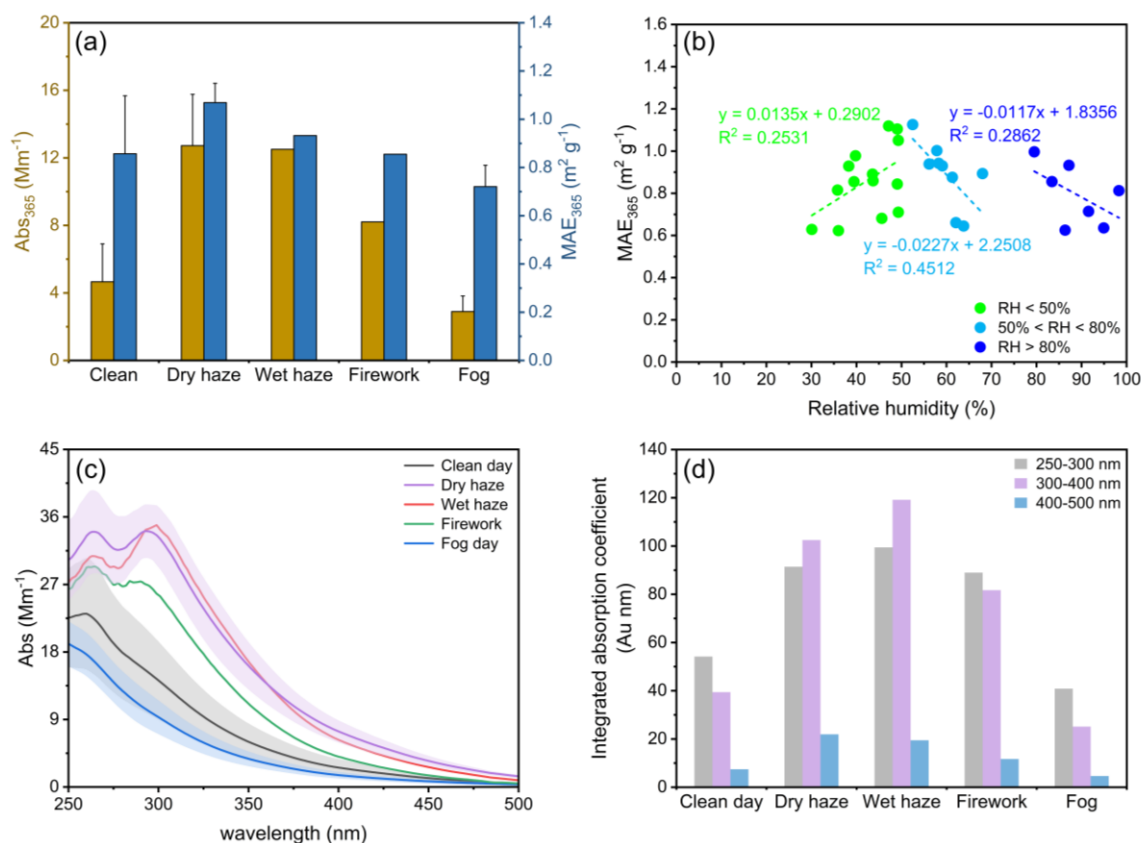


Figure 1. Variations in light absorption by WSOC in Qingdao. (a) Light absorption coefficient (Abs_{365}) and mass absorption efficiency (MAE_{365}) under different pollution scenarios, (b) variation of MAE_{365} with relative humidity, (c) spectral absorption across different pollution scenarios, and (d) integrated absorbance over different wavelength bands under different pollution scenarios.

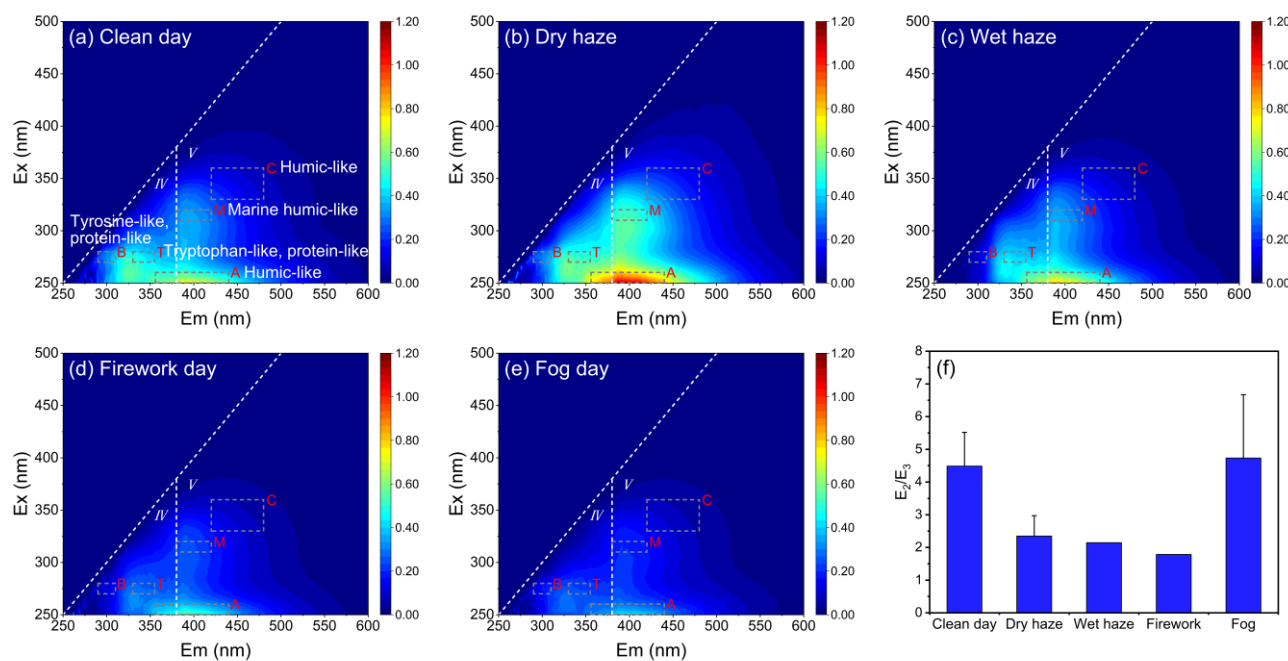
To isolate the humidity signal, we examined MAE_{365} as a function of ambient RH (see **Fig. 1b**). The response was distinctly non-linear with an inflection point near $RH \approx 50\%$ – 60% . This pattern aligned with findings from several previous field-based measurements conducted in China (Chen et al., 2025; Tao et al., 2024). Below this threshold, MAE_{365} rose progressively with increasing RH. However, above the inflection point, it decreased in a two-stage fashion, with a faster decline at moderately high RH (60% – 80%) followed by a slower decline at high RH ($>80\%$). This biphasic behavior indicated that the dominant role of RH switches from light-absorption-enhancing to light-absorption-suppressing as the atmosphere approaches water saturation. Previous studies have indicated that under low RH conditions, aerosols may become highly viscous and tar-like,



limiting internal reactions (Kidd et al., 2014). In contrast, high RH conditions make them more fluid, promoting the entry of oxidants such as ozone into the particle interior to initiate reactions, thereby accelerating bleaching (Schnitzler et al., 2022).

180 Spectral features corroborated this non-linear response. Under polluted scenarios (dry haze, wet haze, FW), the absorption spectra exhibited a bimodal distribution with a pronounced peak around 300 nm, similar to the absorption spectra observed in polluted Chinese cities (Chen et al., 2025), whereas clean days and foggy days displayed only a single peak below 300 nm (see **Fig. 1c**). Quantitatively, the 300–400 nm band contributed 45%–50% of the total integrated absorption during pollution episodes, and the 400–500 nm band accounted for ~10% in dry haze and ~8% in wet haze, with values far exceeding those

185 under clean or foggy conditions (**Fig. 1d**). This spectral red shift, together with lower E_2/E_3 absorbance ratios (the ratio of light absorption by WSOC at 250 and 365 nm) and enhanced humic-like fluorescence signatures (**Fig. 2**), indicated the accumulation of highly conjugated, high-molecular-weight chromophores in polluted air. Crucially, the long-wavelength enhancement partially retreated during wet haze and foggy days, indicating that such chromophores did not persist stably in the presence of abundant condensed water.



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Figure 2. The average fluorescence spectra of WSOC (a-e) and E_2/E_3 ratios (f) under different pollution scenarios (Note: Fluorescence intensities are normalized to WSOC concentrations. Colorbar units: RU (mg L⁻¹)⁻¹).

3.2 Molecular Basis of WSOC Light Absorption in Clean and Polluted Atmospheres

The divergent optical responses described in Sect. 3.1 originated from systematic differences in bulk chemical composition and ultimately in the molecular identity of the water-soluble chromophores. We therefore first examine the chemical regimes

195 that define each scenario before resolving the molecular-level drivers of light absorption. **Figure 3a** shows that PM_{2.5} mass



loading varied distinctly by a max factor of four across the five scenarios, following the order FW ($175.36 \mu\text{g m}^{-3}$) > dry haze ($156.55 \pm 24.76 \mu\text{g m}^{-3}$) > wet haze ($124.38 \mu\text{g m}^{-3}$) > clean days ($48.69 \pm 19.56 \mu\text{g m}^{-3}$) > foggy days ($43.13 \pm 4.17 \mu\text{g m}^{-3}$). More instructive than the mass loading alone were the contrasting secondary-formation signatures. Dry haze was characterized by the highest NO_3^- fraction and nitrogen oxidation ratio (NOR, 0.41 ± 0.05 ; **Fig. S2a**), highlighting the dominance of photochemical NO_x oxidation and active heterogeneous reactions under low-humidity polluted conditions (Feng et al., 2023). In contrast, foggy days and the FW period exhibited markedly elevated SO_4^{2-} proportion and sulfur oxidation ratios (SOR, 0.35 ± 0.08 and 0.67 , respectively), consistent with vigorous aqueous-phase oxidation of SO_2 at high ALWC under high RH (**Fig. S2b**) (Liang et al., 1999). The abundant ions co-emitted with metals during fireworks likely further catalyzed this process (Zhang et al., 2024). Wet haze was most notably distinguished by a large organic fraction, pointing to substantial aqueous secondary organic formation. Throughout both haze periods, secondary organic carbon (SOC, calculated based on the EC tracer method) dominated over primary organic carbon (POC), with the SOC/POC ratio reaching 2.2 in wet haze versus 1.4 in dry haze (**Fig. 3b**). Paradoxically, the WSOC/WIOC (water-insoluble organic carbon, difference between OC and WSOC) ratio fell to a minimum of 0.89 during wet haze, suggesting that either primary WIOC accumulated preferentially under stagnant high-RH conditions, or that secondary WSOC production did not outpace the accumulation of WIOC. By contrast, FW and foggy days showed OC characteristics closer to those of clean days, with $\text{POC} > \text{SOC}$ and $\text{WSOC} > \text{WIOC}$.

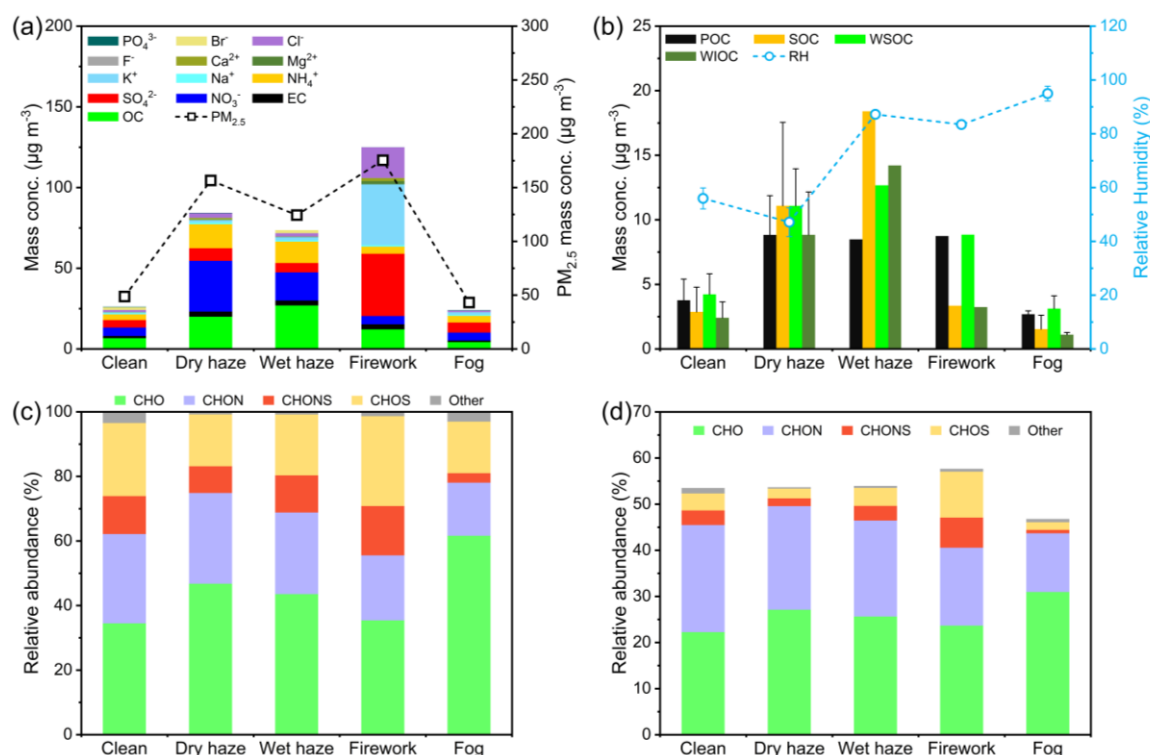


Figure 3. Variations in chemical composition of $\text{PM}_{2.5}$ (a) and organic components (b), and the relative abundance of different compound categories in WSOC (c) and potential Ws-BrC (d) under different pollution scenarios.



215 To link these bulk-chemical signatures to the optical properties of WSOC, we derived the molecular composition of WSOC
using ESI-FT-ICR-MS (see **Fig. 3c**) and identified potential Ws-BrC chromophores by the criterion $0.5C \leq DBE \leq 0.9C$ (Lin
et al., 2018). The relative abundance of the potential Ws-BrC chromophores exhibited moderate positive correlations with
 Abs_{365} ($r = 0.55$) and MAE_{365} ($r = 0.52$) (**Fig. S3**). These species accounted for 50%–60% of all detected WSOC molecules,
with their relative abundance following the order FW > wet haze > dry haze > clean days > foggy days (see **Fig. 3d**). This
220 order deviated from MAE_{365} or Abs_{365} trends, which can be plausibly attributed to negative-ion ESI's inherent bias towards
polar analytes and poor response for neutral/weakly polar chromophores (e.g., polycyclic aromatic hydrocarbons and
derivatives), as well as molecular composition classes of Ws-BrC discussed below.

At comparable RH levels, clean atmospheric conditions contained a larger absolute number of molecular species and potential
Ws-BrC chromophores than polluted dry haze conditions (**Fig. S4**). CHON compounds dominated the WSOC and potential
225 Ws-BrC pool in both scenarios, followed by CHO species, while S-containing compounds (CHOS and CHONS) showed
substantially higher fractional abundances under clean conditions. Notably, despite the greater absolute count of potential Ws-
BrC chromophores in clean conditions, their relative abundance was slightly lower than that in dry haze conditions, alongside
an elevated fraction of S-containing chromophores (**Fig. 3d**). Molecular-level compositional differences between the two
scenarios were primarily responsible for their distinct Ws-BrC light absorption behaviors. For clean atmospheric conditions,
230 unique CHO molecules exclusive to clean days exhibited lower oxidation states and aromaticity, along with considerably lower
relative abundances, compared with dry haze day-specific molecules and ubiquitous compounds common to both scenarios
(**Table S1**). These molecular features indicated restricted extended π -conjugation structures, thereby weakening the light-
absorption capacity of Ws-BrC. Furthermore, S-containing chromophores enriched in clean air (**Fig. 3c** and **3d**) were identified
as highly unsaturated organosulfates with DBE values ranging from 3 to 15 (mean 7.83 ± 2.44) and O/S ratios of 6.04 ± 2.06 .
235 This compound class generally possesses low absorption cross-sections in the near-visible region (Qiu et al., 2025).
Additionally, WSOC in clean air mainly originated from primary organic aerosols. The substantially lower levoglucosan
concentrations observed during clean periods (**Fig. S5**) suggested negligible contributions of strongly light-absorbing aerosols
from primary combustion sources, including biomass burning and coal combustion. Collectively, the lower aromaticity of
clean-specific molecules, the predominance of weakly absorbing organosulfates, and the limited contribution of combustion-
240 derived primary aerosols jointly explain the lower MAE_{365} and Abs_{365} values in clean atmospheric environments. In contrast,
dry haze episodes exhibited a pronounced enhancement in WSOC light absorption, primarily driven by N-containing
chromophores, with supplementary contributions from highly oxidized CHO polymers. Dry haze-enriched CHO-class Ws-
BrC chromophores possessed higher O/C ratios and modified aromaticity indices (**Table S1**). These species may be formed
via oligomerization and condensation reactions of oxidized derivatives of anthropogenic volatile organic compounds,
245 producing highly oxidized macromolecules that enhance near-ultraviolet light absorption through the formation of
intermolecular charge-transfer complexes (Ervens et al., 2011). CHON compounds constituted the dominant fraction of the
Ws-BrC pool during dry haze events, accounting for approximately 50% of all potential chromophores, and their relative
abundance displayed a strongly positive correlation with MAE_{365} ($r = 0.76$; **Fig.S6**). Relative to clean conditions, CHON



compounds in dry haze exhibited significantly higher relative abundances, average carbon oxidation states (OSc), and O/N ratios (**Table S2**). These observations indicated that high-NO_x haze environments promoted the extensive incorporation of nitro (–NO₂) functional groups into aromatic and alicyclic molecular skeletons. This chemical transformation generated abundant nitroaromatic chromophores with extended π -conjugated systems and large molar absorption coefficients, which served as the primary drivers of enhanced Ws-BrC light absorption during haze pollution. Overall, the weak light absorption of WSOC in clean atmospheres was attributable to the scarcity of high-efficiency light-absorbing chromophores and to the absence of strongly absorbing combustion-derived primary aerosols. In contrast, the synergistic effects of nitro-functionalized CHON chromophores and highly oxidized CHO polymeric chromophores induced substantial light absorption enhancement during dry haze episodes.

3.3 Humidity-Driven Chromophore Pool Reconfiguration and Optical Evolution

In line with the evolution of optical absorption, the total number of WSOC molecules, the number of potential Ws-BrC formulas, and their relative abundances all displayed a non-monotonic response to increasing RH, characterized by an initial slight rise followed by a decline (**Fig. 4a-f**). To elucidate this pattern, the molecular-level compositional evolution of the water-soluble chromophore pool across the wide RH gradient was investigated to identify the key drivers of light absorption attenuation under high humidity.

3.3.1 Chromophore Accumulation Driven by Liquid-Phase Chemical Activation (RH < 60%)

As RH gradually increased from low to moderate conditions (from RH1 to RH6, 40%–60%), the total number of detected WSOC and potential Ws-BrC molecular species exhibited an increasing trend, accompanied by a concurrent rise in relative abundance of potential Ws-BrC (**Fig. 4**). Such enhancement could be tightly linked to the elevated ALWC (**Fig. 5a**). Increased water content can provide an aqueous medium for aqueous-phase reactions, facilitating secondary formation of organic aerosols and Ws-BrC (**Fig. 5b**) (Chen et al., 2026a; Chen et al., 2026b; Lim et al., 2010). Activation of aqueous-phase chemistry triggered molecular compositional evolution. The relative abundance of CHO compounds progressively decreased, whereas the contributions of N-containing chromophores (particularly CHON and CHONS species) and S-containing compounds (CHOS and CHONS) increased markedly. On the one hand, within the 40%–60% RH interval, the average particle pH was 3.58±0.82. The resulting weakly acidic environment may favor nitrogen-involved aqueous-phase reactions, such as Maillard reactions, thereby promoting the formation of CHON chromophores (Chen et al., 2026b; Tang et al., 2022). Consistent with this observation, the nitrogen oxidation ratio remained at a high level (**Fig. 5c**), supplying sufficient nitration precursors for the aqueous-phase generation of N-containing chromophores. On the other hand, SOR rose steadily with rising RH, driving the formation of inorganic sulfate. Moreover, the elevated SOR coincided with the enhanced relative abundances of CHOS and CHONS compounds (**Fig. 5d**), suggesting a coupling between the aqueous-phase formation of S-containing organics and the production of inorganic sulfate.

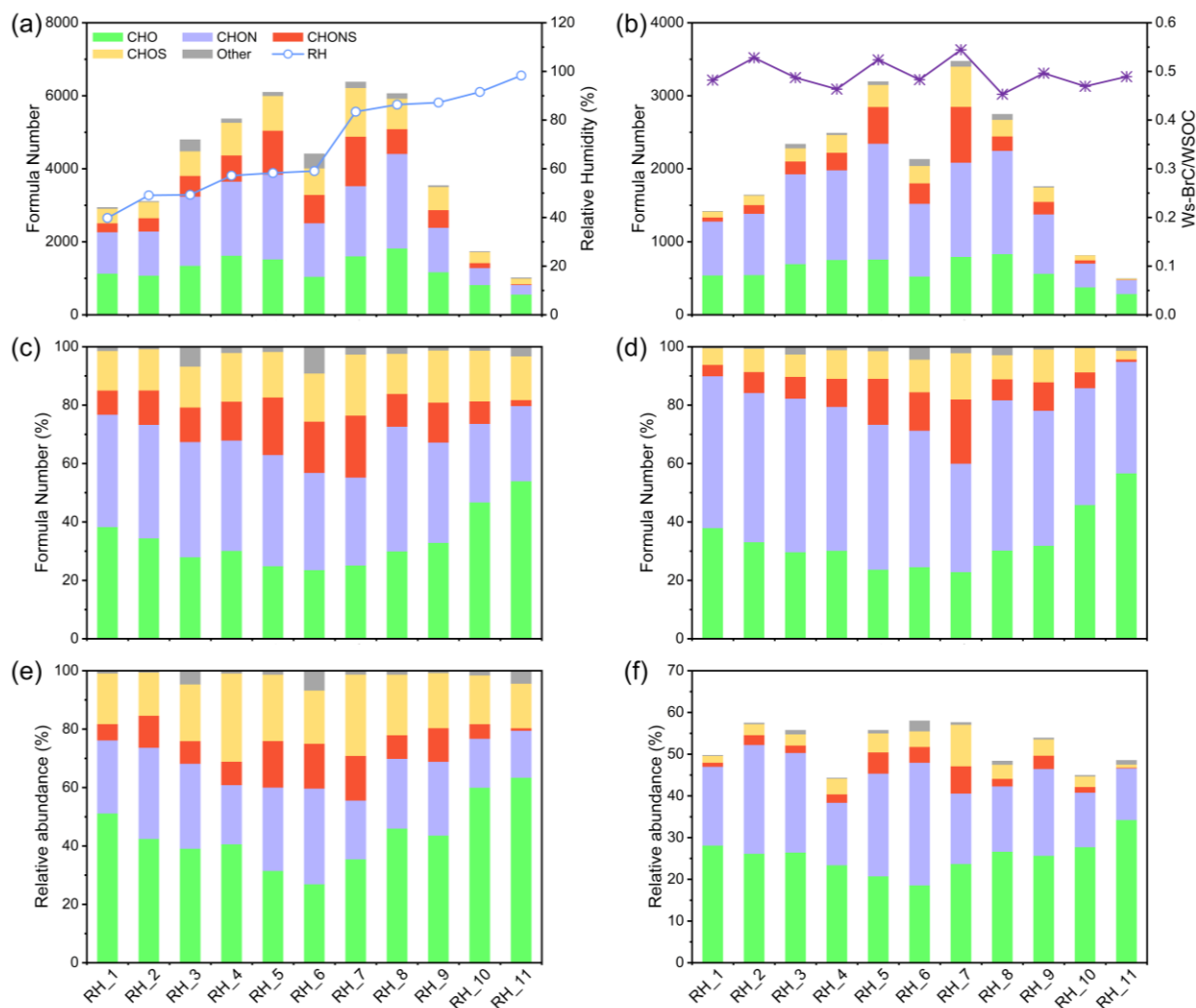


Figure 4. Molecular composition of WSOC and potential Ws-BrC under varying relative humidity (RH). (a, b) Number of molecular formulas, (c, d) fractional contributions of compound categories by number, and (e, f) relative abundance of categories. Left column (a, c, e) for WSOC and right column (b, d, f) for potential Ws-BrC. (Note: RH1–RH6: 40%–60%, and RH7–RH11: >80%)

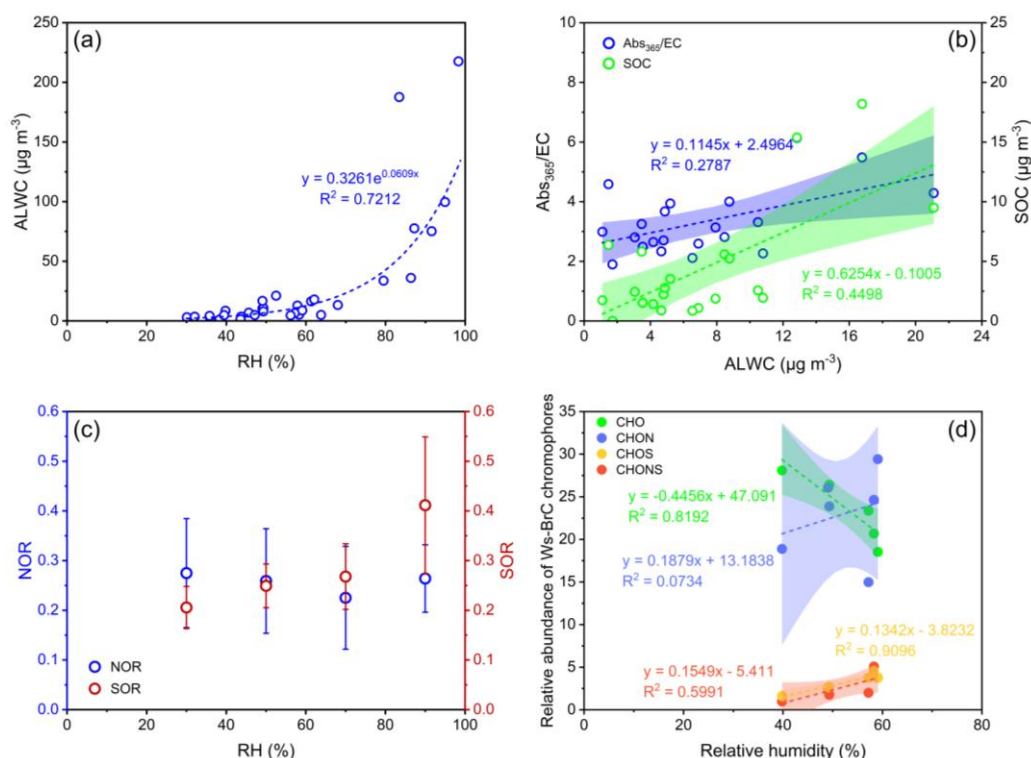


Figure 5. Effects of relative humidity (RH) and aerosol water content (ALWC) on atmospheric composition and optical properties. (a) Aerosol liquid water (ALWC) as a function of RH (0–100%), (b) correlations of ALWC (under RH<60%) with light absorption ($\text{Abs}_{365}/\text{EC}$) and secondary organic carbon (SOC), (c) evolution of oxidation ratios (NOR, SOR) with RH, and (d) variations of relative abundance of potential Ws-BrC compound categories with RH under low-moderate RH.

During the aforementioned process, aqueous-phase secondary oxidation and polymerization were the dominant reaction pathways. The molecular weights of potential Ws-BrC chromophores increased continuously, as evidenced by an elevated fraction of high-molecular-weight species with $m/z > 400$ (Fig. 6a). A pronounced surge in extremely low-volatility organic compounds (ELVOC) was observed, accompanied by a transition of the logarithm of saturation mass concentration ($\log_{10}C_0$) from positive to negative values (Fig. 6b and Fig. S7). These results indicated a progressive partitioning of reaction products toward the low-volatility particulate phase. The increased abundance of chromophores strengthened intermolecular interactions and aggregation, further elevating their molar absorption efficiency. Accordingly, chromophores exhibited a net accumulation state within this RH regime, driving a sustained increase in MAE_{365} as RH increased. Correlation analyses further supported the proposed mechanism. Under low-to-moderate RH conditions, WSOC molecules and potential Ws-BrC components that exhibited significantly strong positive correlations with RH were predominantly composed of CHON and CHOS compounds (Fig. 6c). Specifically, potential Ws-BrC, which was strongly and positively correlated with RH, accounted for 57.4% of total WSOC, statistically verifying the accumulation tendency of BrC across this humidity regime.

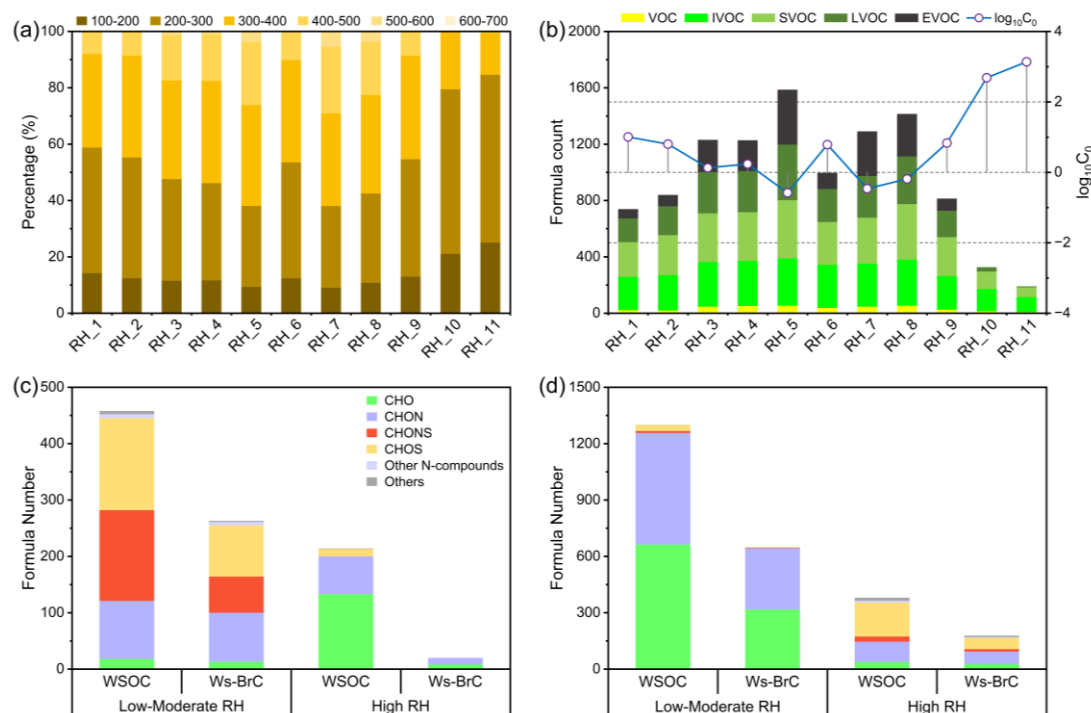


Figure 6. Relative humidity-driven molecular weight distribution (a) and volatility-resolved composition (b) of potential Ws-BrC chromophores, and strongly positive (c) and negative correlations (d) to WSOC and potential Ws-BrC under low-to-moderate versus high RH conditions.

3.3.2 Multiple Synergistic Bleaching Effects Driven by Exponential Growth in ALWC (RH > 80%)

The light-absorbing capacity of Ws-BrC decreased when RH exceeded approximately 60%. This threshold coincides well with the onset of exponential growth in ALWC (Fig. 5a). The sharp rise in ALWC may trigger a fundamental compositional rearrangement of the chromophore pool. Based on the integrated molecular evolution characteristics, the following synergistic mechanisms may collectively govern this attenuation process.

- (i) Oxidative Bleaching and Molecular Fragmentation.** High ALWC can significantly reduce particle-phase viscosity and facilitate the diffusion and mass transfer of oxidants (e.g., OH radicals) within particles, thereby driving oxidative ring-opening or cleavage reactions of conjugated chromophores (Angelaki et al., 2025; Liu et al., 2025; Schnitzler et al., 2020). Our observational data under RH conditions (RH > 80%) provided direct evidence to support this mechanism. The total number of detected WSOC and Ws-BrC molecules decreased markedly, with CHON chromophores exhibiting sharp reductions in both molecular number and relative abundance. In contrast, the contribution of CHO compounds rose significantly with increasing RH (Fig. 4). Further molecular fingerprint analyses revealed that CHO compounds under high RH exhibited reduced carbon numbers, lower double-bond equivalents (DBE; decreasing to 4.98 under foggy conditions), elevated H/C ratios, and lower carbon oxidation state (OSC; shifting toward a more reduced state) (see Fig. S8). Additionally, within this RH range, the $\log_{10} C_0$ values of CHO compounds exhibited an upward trend with increasing RH, accompanied by a marked increase in the



fractional contributions of semi-volatile organic compounds (SVOCs) and intermediate-volatility organic compounds (IVOCs) (Fig. S7a and S7b). Collectively, these lines of evidence indicated that initial conjugated structures were degraded into saturated, low-molecular-weight non-absorbing fragments (Hems et al., 2018).

(ii) Hydrolytic Cleavage of N/S-Containing Chromophores. Evolutions in molecular volatility and molecular weight provided direct evidence for the shift in reaction pathways. Within this high RH regime, the proportion of low-molecular-weight ($m/z < 300$) chromophores rose sharply as RH increased (Fig. 6a), and the $\log_{10}C_0$ values of potential Ws-BrC chromophores increased from negative to positive (Fig. 6b). Concurrently, ELVOCs and low-volatility organic compounds (LVOCs) diminished or even disappeared, while SVOCs and IVOCs increased substantially (Fig. 6b). Collectively, these trends indicated that the macromolecular BrC backbone underwent bond cleavage via hydrolysis, disrupting conjugated structures and thereby reducing the mass-specific light-absorption efficiency.

Correlation analysis further revealed the target selectivity of hydrolytic cleavage. The correlation between CHOS compounds and RH reversed from strongly positive (indicative of accumulation products) at low-to-moderate RH to strongly negative at high RH, signifying that S-containing chromophores acted as the primary targets of hydrolytic bleaching under high-humidity conditions, with their net change dominated by removal (Fig. 6c-d). Meanwhile, strongly light-absorbing CHON chromophores (particularly nitroaromatic compounds) exhibited evident reduction. Notably, SOR increased sharply under high-RH conditions, reflecting enhanced aqueous-phase SO_2 oxidation (Fig. 5c). Strong positive correlations between SOR and CHOS/CHONS-class chromophores ($r = 0.81$ and 0.60 , Fig. S9) verified that the formation of S-containing chromophores was coupled to aqueous-phase SO_2 oxidation processes. Nevertheless, this flux of formation did not result in net accumulation of CHOS chromophores, demonstrating that the rate of hydrolytic loss likely exceeded the formation rate at high RH, shifting the formation-removal balance toward loss.

In parallel, WSOC, which exhibited a significantly strong positive correlation with RH, became dominated by CHO compounds under high-RH conditions, among which potential Ws-BrC accounted for only 9.34%. Such a low fraction further suggested that the newly formed WSOC at increasing RH was dominated by non-light-absorbing species, and that the concurrent formation of light-absorbing WSOC was substantially suppressed. These findings were consistent with the reaction pathway in which macromolecular BrC underwent hydrolytic cleavage, disrupting conjugated light-absorbing structures and transforming them into colorless, low-molecular-weight CHO compounds.

(iii) Physical Dilution by Liquid Water. As RH increased, ALWC exhibited an exponential growth (Fig. 5a). The resultant aqueous-phase expansion may dilute the concentration of chromophores within individual particles, thereby directly reducing the light-absorption efficiency per unit carbon mass (Chen et al., 2026b; Jin et al., 2020). This physical dilution acted synergistically with the aforementioned chemical mechanisms to jointly amplify the attenuation of light absorption.

Foggy conditions ($\text{RH} = 95 \pm 4\%$, corresponding to the peak ALWC during this observation period) represented the extreme endpoint of the aforementioned bleaching process. Even under comparable $\text{PM}_{2.5}$ mass loadings (approximately $45 \mu\text{g m}^{-3}$), MAE_{365} decreased significantly from $0.94 \pm 0.01 \text{ m}^2 \text{ g}^{-1}$ on clean days to $0.67 \pm 0.06 \text{ m}^2 \text{ g}^{-1}$ on foggy days, and the intensities of all fluorescent components reached their minima (Fig. 2e). This observation was highly consistent with field reports



documenting suppressed brown carbon light absorption during fog events over the Indo-Gangetic Plain, as well as laboratory
evidence showing that the mass absorption efficiencies of aqueous-phase aerosol products peaked at approximately 55%–65%
RH and then declined thereafter (Izhar et al., 2020; Kasthuriarachchi et al., 2020).

In summary, the non-monotonic response of WSOC light absorption to RH can be interpreted as a transition from chromophore
accumulation to degradation, driven by compositional changes in the molecular composition as ALWC increases. Moderate
RH established a microenvironment favorable for chromophore formation and intermolecular aggregation, in which S-
containing (CHOS/CHONS) and N-containing (CHON) compounds jointly served as the major accumulated products and
drove the net increase in the chromophore pool. At high RH, synergistic pathways, including oxidative bleaching, hydrolytic
cleavage, and physical dilution, reshaped the chromophore pool and reduced its light-absorption efficiency. The role reversal
of CHOS compounds from accumulation products to dominant degraded species constituted the most direct and robust
molecular evidence supporting the high-RH bleaching mechanism.

3.4 Extreme Case Validation: The Fireworks/Firecracker Episode

The intensive firework burning period provided an extreme experimental scenario, featuring concurrent heavy air pollution
(peak $\text{PM}_{2.5} = 175.4 \mu\text{g m}^{-3}$, the maximum observed in this study) and high RH ($\text{RH} \approx 83\%$). During this period, Abs_{365} of Ws-
BrC was approximately 1.8 times that on clean days and 2.8 times that on foggy days, suggesting that intense primary emissions
from fireworks contributed substantially to Ws-BrC. However, the MAE_{365} values in this episode were substantially lower than
those during dry haze and wet haze, and even slightly lower than values on clean days. This paradox of severe pollution yet
low light-absorption efficiency revealed that, despite the massive absolute loading of organic compounds, the light-absorbing
capacity of the firework-source organic aerosols was remarkably low on a per-unit-carbon basis.

On the one hand, the coexistence of abundant precursors and ALWC during the FW period favored condensation and
oligomerization reactions, facilitating the formation of highly aromatic, high-molecular-weight chromophoric species (Ji et al.,
2022; Kasthuriarachchi et al., 2025). This interpretation aligned with the extremely low E_2/E_3 ratio 1.79, compared with
 4.49 ± 1.03 for clean days and 2.05 ± 0.14 for wet haze, alongside pronounced enrichment of high-molecular-weight (300–600
Da, see RH7 in **Fig. 6a**) Ws-BrC molecules. On the other hand, firework emissions introduced large quantities of S-containing
precursors (e.g., originating from black powder) and metallic catalysts (Brink et al., 2019; Tian et al., 2014). These
simultaneously elevated concentrations of SO_2 and transition metal ions (e.g., Fe, Cu), combined with high ALWC sustained
at $\text{RH} \approx 83\%$, strongly promoted the formation of organosulfates and nitrooxy organosulfates (Huang et al., 2018). CHOS and
CHONS species collectively accounted for approximately 38% of the molecular count and roughly 29% of the relative
abundance of Ws-BrC, representing the highest proportion across all sampling scenarios. By contrast, the relative abundance
of CHON compounds was lower than that during haze episodes and clean days. Although these S-containing molecules
formally satisfy the unsaturation criteria for potential Ws-BrC constituents, they exhibited low intrinsic molar absorptivity.
Most of these species corresponded to organosulfates, thiosulfates, or polysulfides, (Xie et al., 2021; Yan et al., 2024), which
possessed weakly chromophoric structures and small absorption cross-sections (Zeng et al., 2020, 2021). Such weakly



absorbing S-containing species displaced strongly absorbing nitroaromatics and conjugated CHO chromophores, thereby diluting the pool of light-absorbing substances from a compositional perspective. This organosulfur substitution effect was further amplified under high-RH conditions. The polluted particles with higher transition-metal and H₂O₂ loadings could sustain enhanced endogenous ·OH radical production, accelerating bleaching chemistry relative to clean conditions (Lelieveld et al., 2021; Shahpoury et al., 2024). Meanwhile, elevated RH facilitated in-particle ·OH chemistry and promoted oxidative bleaching of pre-existing chromophores through enhanced aqueous-phase reactions (Li et al., 2018).

Collectively, the firework burning case validated the core hypothesis of this study under conditions of extreme emissions and high ambient humidity. Under coincident high-pollution and high RH conditions, vigorous absolute chromophore production cannot sustain high MAE when processes such as organosulfur substitution and oxidative bleaching are simultaneously intensified. This case further demonstrated that the optical response of Ws-BrC was governed not merely by the quantity of chromophores but, more critically, by chromophore chemical composition. RH reshapes BrC composition by modulating the balance among formation, functionalization, and degradation reactions, thereby constituting the fundamental mechanism by which atmospheric humidity regulates light absorption by atmospheric BrC.

4. Conclusions

This study reveals that the light-absorption properties of Ws-BrC are not static quantities but are dynamically and non-monotonically regulated by the interplay between pollution level and atmospheric RH. Across a wide pollution-humidity gradient, the MAE₃₆₅ of WSOC exhibits a characteristic biphasic response to RH, rising progressively below ~50%–60% RH, then declining above this threshold. This nonlinearity arises from RH-driven restructuring of the chromophore molecular pool. Under drier, polluted conditions, enhanced photochemical and multiphase nitration reactions introduce strongly absorbing nitro-functionalized chromophores (CHON) into the organic phase, while highly oxidized CHO polymers provide supplementary absorption. These nitro aromatic chromophores, rather than conventional aromatic conjugated systems, were identified as the principal molecular drivers of BrC absorption during haze events. When RH increases beyond the inflection point, the abundant ALWC simultaneously triggers synergistic suppression mechanisms that collectively shift the chromophore pool toward lower intrinsic absorption efficiency. This mechanistic framework explains why dry haze and wet haze, despite comparable PM_{2.5} loadings, display fundamentally different optical properties, and why foggy conditions produce the weakest absorption of all scenarios. Critically, elevated pollution may attenuate the amplitude of the humidity response at high RH and high-water content, as the sustained supply of abundant precursors may trigger complex concurrent reactions that partially offset the photo-bleaching of Ws-BrC. The fireworks influence period corroborates this framework in an extreme emission context, where intense aqueous-phase polymerization generates highly aromatic macromolecular chromophores, yet the concurrent surge in weakly absorbing S-containing compounds and accelerated oxidative bleaching suppress the effective absorption efficiency to below clean-day levels.



These findings carry significant implications for the representation of BrC in regional and global models. Current modeling frameworks commonly parameterize BrC absorption as a linear function of organic aerosol mass or secondary organic aerosol yield, often treating the mass absorption efficiency as a constant or a simple function of source type. Our results demonstrate that MAE is instead a highly dynamic quantity, co-regulated by pollution level and ambient RH in a non-linear fashion. Ignoring this RH dependence, particularly the substantial suppression of absorption efficiency above ~60% RH, is likely to introduce systematic biases in estimated BrC radiative forcing, especially in regions where high pollution and high RH coincide (e.g., winter haze in East and South Asia). The molecular mechanisms identified in this study, such as nitro-aromatic formation, organosulfate displacement, and aqueous-phase oxidative bleaching, provide a mechanistic basis for parameterizing BrC optical evolution in subsequent chemical transport models. Future efforts to constrain BrC climate impacts should therefore incorporate explicit coupling between ALWC, multiphase chemistry, and chromophore molecular identity, rather than relying solely on bulk organic carbon mass. From a measurement perspective, the demonstrated ionization bias of negative-mode ESI against neutral and weakly polar chromophores also calls for complementary analytical approaches in future molecular-level studies of atmospheric BrC to capture the full chromophore inventory.

Data availability

The data used in this study are available upon request from the corresponding author.

Author contributions

CY contributed to study conceptualisation and design. HC, BX, BJ, QF and RL performed the field measurements, laboratory analyses, and data collection. CY, HC, BX, BJ, QF and RL performed data processing, formal data analysis, and data validation. GZ, XZ and MZ provided resources. CY and HC visualized data. CY interpreted data and wrote the manuscript draft with contributions from all authors. CY acquired funding, supervised the project, and administered the project. All authors commented on and discussed the manuscript.

Competing interests

The contact author has declared that none of the authors has any competing interests.

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of the publisher.

Acknowledgements

We are grateful to Prof. Lingxiao Yang, Dr. Bin Chen, and Dr. Zhisheng Zhang for their support with the instrumentation and analyses of water-soluble ions, organic carbon, elemental carbon, and water-soluble saccharides.

Financial support

This study was supported by the National Natural Science Foundation of China (NO. 42205110, 42475189). Caiqing Yan is specifically supported by Taishan Scholars Program of Shandong Province (NO. tsqn201909018).

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