



1 **Seasonal regime shifts in atmospheric aging of vehicular**
2 **water-soluble organic aerosols: evidence from**
3 **functionalization transformation indices and molecular**
4 **conformational modeling**

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17 **Abstract:**

18 Vehicular water-soluble organic aerosols (WSOA) critically impact urban air
19 quality and climate, yet their molecular-level responses to seasonal aging remain
20 unclear. This study integrates FT-ICR MS with a three-tier framework that includes
21 core molecular screening, functionalization transformation index quantification, and
22 three-dimensional conformational modeling to decipher seasonal evolution of tunnel
23 WSOA. Summer core molecules are dominated by saturated, low-nitrogen aliphatics
24 and lipids (88.5%), whereas winter cores shift to unsaturated, high-nitrogen aromatics
25 and CRAMs (93.4%). Functionalization transformation index diagnostics shows
26 summer hydroxylation dominates ($HI = 33,471$), while winter exhibits net hydroxyl
27 loss ($HI = -2,787$) and positive carbonylation ($CNI = 989$), suggesting a regime shift
28 from $\bullet OH$ -dominated photochemistry in summer to $NO_3\bullet/O_3$ -enhanced chemistry in
29 winter. Conformational modeling revealed opposite diurnal reorganizations, where
30 summer encapsulation enriched hydrogen bond acceptors (HBA) by 48 yet reduced
31 solvent-accessible polar surface area (PSA) by $790 \text{ \AA}^2$, whereas winter hydration
32 depleted HBA by 78 yet expanded PSA by $1,638 \text{ \AA}^2$. Molecular conjugation, rather than
33 bulk polarity, primarily governs chromophore activity. This framework moves beyond
34 elemental composition to three-dimensional structural interpretation, providing
35 transferable, experimentally constrained parameters for chemical transport models,
36 refining predictions of brown carbon light absorption properties, and offering a
37 mechanistic basis for season-specific air pollution mitigation strategies.

38 **Keywords:** Vehicle emission, Water-soluble organic aerosols, FT-ICR MS,
39 Functionalization transformation index, VSOMM2, Atmospheric aging



40 **1 Introduction**

41 Water-soluble organic aerosols (WSOA) are a pivotal fraction of total organic
42 aerosols (OA) with a mass contribution of 20%-80%, profoundly influencing global
43 climate radiative forcing, urban air quality, and human health (Sun et al., 2025; Cai et
44 al., 2020; Lee et al., 2022; McNeill et al., 2015) due to their unique hygroscopicity, light
45 absorption capacity, and multiphase reaction activity (Tan et al., 2024; Laskin et al.,
46 2025; Ma et al., 2018; Ma et al., 2019). Despite their significant impacts, WSOA remain
47 poorly characterized and understood, primarily due to their diverse emission sources
48 (biogenic, biomass burning, fossil fuel, industry) and complex atmospheric aging
49 processes (gas-phase photochemical oxidation, heterogeneous reactions, and aqueous-
50 phase processing) (Xu et al., 2017; Hu et al., 2022; Srivastava et al., 2022; Shrivastava
51 et al., 2025). However, the synergistic and competitive interactions among multiple
52 aging pathways, together with the regulatory effects of seasonal meteorological
53 variations, cause substantial deviations between model simulation results and field
54 observation data of OA levels (Huang et al., 2025a; Shrivastava et al., 2017).
55 Accordingly, elucidating the atmospheric aging pathways of WSOA is critical for
56 evaluating their environmental and climatic impacts.

57 Field and modeling studies confirm that atmospheric aging pathways exhibit
58 strong seasonal dependence, governed by shifts in oxidation conditions and
59 meteorological conditions (Rogers et al., 2025; Wang et al., 2021; Zhang et al., 2026).
60 Summer features intense photochemical oxidation under high solar radiation and
61 temperature, alongside aqueous-phase dark reactions facilitated by elevated humidity
62 and aerosol liquid water, jointly regulating secondary organic aerosols (SOA) formation
63 (Freney et al., 2018; Zhang et al., 2024a). In contrast, cold seasons suppress
64 photochemistry but enhance aqueous-phase heterogeneous reactions, promoting
65 organosulfur production under haze, while seasonal NH₃ variability further modulates



66 gas-aerosol partitioning and SOA yield (Han et al., 2023; Yang et al., 2025a; Lv et al.,
67 2022). Although previous studies have advanced the understanding of atmospheric
68 aging processes, these studies still suffer from notable research limitations. On the one
69 hand, most investigations have focused on bulk chemical characterization over a single
70 season, lacking continuous molecular-level tracking across seasonal transitions (Gu et
71 al., 2023; Duan et al., 2019). On the other hand, molecular comparative studies of
72 secondary organic carbon report only compositional differences, without linking
73 molecular property changes to pathway shifts (Kim et al., 2024). These knowledge gaps
74 are particularly acute for vehicular WSOA, a dominant urban OA source (Zhao et al.,
75 2022), where research has focused on source contributions (Zhang et al., 2024b), SOA
76 formation mechanisms and potential (Li et al., 2026a), and health effects (Delaval et al.,
77 2025). Nevertheless, systematic investigation into the molecular transformation of
78 vehicular WSOA and its coupling with seasonal aging pathway shifts remains critically
79 lacking.

80 Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), with
81 its ultra-high mass resolution and mass accuracy, is capable of distinguishing thousands
82 of molecular species in complex organic mixtures and has been widely applied in
83 environmental geochemistry and atmospheric chemistry research (Jennings et al., 2022;
84 Lechtenfeld et al., 2024; Tang et al., 2020). Actually, FT-ICR MS-based studies have
85 successfully identified the molecular signatures of various environmental and source-
86 emitted WSOA species (Zhong et al., 2023; Chen et al., 2025). Yet, most existing
87 studies only conduct qualitative statistical analysis of basic molecular parameters (such
88 as elemental formula distribution, O/C, H/C, DBE, and AI_{mod}), while neglecting
89 quantitative diagnosis of molecular transformation pathways, such as functionalization
90 transformation index and reaction network analysis, which are essential for elucidating
91 aging mechanisms (Chen et al., 2025; Qi et al., 2022). Notably, recent applications
92 extend FT-ICR MS data to track molecular transformations during photodegradation
93 and biological treatment, and integration with models like VSOMM2 enables predicting
94 dissolved organic matter structure (Dwinandha et al., 2024; Hu et al., 2025; Zhao et al.,



2023; Ye et al., 2025). These exploratory studies suggest that deep mining of FT-ICR MS datasets, through quantification of potential molecular transformation reactions and construction of three-dimensional models, holds promising prospects for unraveling the molecular evolution of organic mixtures. Unfortunately, no comprehensive study has systematically investigated the molecular responses of atmospheric WSOAs to shifts in atmospheric aging pathways.

To bridge these critical gaps and systematically decipher how seasonal variations in atmospheric aging pathways drive the molecular evolution of vehicular WSOA, this study employs road tunnels as natural atmospheric reactors to capture real-world aging gradients across diurnal (day/night) and seasonal (summer/winter) scales. Based on FT-ICR MS data, we propose a novel analytical framework for WSOA molecules, which integrates molecular characterization, quantitative functionalization transformation index diagnostics, and three-dimensional molecular modeling. This framework aims to achieve three interrelated research objectives: (1) to characterize the seasonal divergence in bulk chemical composition and molecular-level features of vehicular WSOA, identifying core molecular clusters and their physicochemical property shifts; (2) to quantify the dominant atmospheric aging pathways and their respective transformation index during in-tunnel transport, thereby establishing linkages between molecular responses and pathway shifts; (3) to construct three-dimensional structural models spanning the aging gradient, enabling quantitative assessment of seasonal and diurnal variations in molecular conformation, and to establish the potential linkage between molecular conformation and chromophore activity. This integrated framework moves beyond conventional qualitative fingerprinting toward a mechanistic understanding of molecular-level transformation dynamics. The outcomes are anticipated to significantly reduce uncertainties in predicting secondary organic aerosol formation in urban environments, refine source-oriented climate model parameterizations, and provide a molecularly informed basis for designing targeted, season-specific air pollution mitigation strategies in traffic-dominated regions.

2 Materials and Methods



124 **2.1 Vehicular WSOA sample preparation**

125 Sampling was conducted in two urban tunnels (Jinhua, Xi'an and Yuehaihu,
126 Yinchuan) during summer (Jinhua: May 29 to Jun. 5, Yuehaihu: July 7 to 14) and winter
127 (Jinhua: Dec. 2 to 12, Yuehaihu: Dec. 16 to 23) of 2025. The selection of the two tunnels,
128 the layout of sampling points, and the overall sampling methodology followed the
129 protocols established in our previous study (Tan et al., 2026). No structural or
130 operational changes occurred during sampling periods. This study focuses on the
131 contrast between summer and winter because they exhibit the most pronounced
132 differences in photochemical intensity, temperature, and relative humidity, thereby
133 enabling an analysis of how dominant aging pathways influence molecular evolution.
134 A detailed description can be found in Supplement Text S1 and Text S2. A total of 24
135 PM_{2.5} samples and 8 blank samples were collected using medium-volume aerosol
136 samplers (ZR-3930, 100L/min) with pre-baked quartz filters (500°C for 6 hours,
137 82.6mm, Whatman, USA) (Supplement Table S1 and S2). Daytime and nighttime 12-h
138 samples were obtained and stored at -20°C in foil. Before analysis, filters were
139 acclimatized to ambient conditions in darkness for 30 min. Then, half of the filter was
140 extracted with 10 mL ultrapure water via sonication (40 kHz, 25±2°C, 30 min), settled
141 for 10 min, and filtered through 0.22 µm PTFE. In line with our previous study, three
142 consecutive extractions were adopted (Tan et al., 2026). Procedural blanks, processed
143 identically, demonstrated negligible interference (<3% of sample signal for both
144 absorbance and WSOC concentration).

145 **2.2 FT-ICR MS experiments and data analysis**

146 Water-soluble organic components were isolated from the sample solution by
147 filtration through a 0.22µm PTFE membrane. Briefly, the filtrate (40 mL) was acidified
148 to pH 2 and loaded onto an Agilent Bond Elut PPL cartridge pre-conditioned with
149 methanol and 0.01 mol/L HCl (Tan et al., 2026; He et al., 2026). 错误!未找到引用源。 After
150 rinsing with 3 mL MS-grade water to remove salts, the cartridge was dried under
151 vacuum. Retained organics were eluted with methanol, concentrated to dryness under
152 N₂, and reconstituted in 100 µL methanol for MS analysis. Mass spectra were acquired



153 using a 15 T FT-ICR MS (Bruker Solarix) in negative-ion electrospray ionization (ESI⁻)
154 mode. Key settings: ion accumulation time 0.2 s, mass range 100–1600 Da, 4M data
155 points, and 300 co-added scans. External calibration with 10 mmol/L sodium formate
156 yielded a mass accuracy < 1 ppm. Molecular formulas were assigned for peaks at *m/z*
157 100–800 using combinations of ¹²C, ¹H, ¹⁶O, ¹⁴N (0–3), and ³²S (0–1), with constraints
158 $0.2 \leq H/C \leq 2.3$ and $0 \leq O/C \leq 1.2$. Intensity-weighted molecular parameters (e.g., *O/C_w*,
159 *H/C_w*, *N/C_w*, *S/C_w*, *DBE_w*, *AI_{mod,w}*) were calculated from the assigned formulas to
160 characterize the molecular signatures. The details of calculation methods are provided
161 in our previous study (Tan et al., 2026).

162 **2.3 Quantitative assessment of potential functional group transformations** 163 **between daytime and nighttime aerosol samples**

164 Based on the molecular formulas identified by FT-ICR MS, this study performed
165 a quantitative assessment of potential molecular transformation pathways between
166 daytime and nighttime tunnel aerosol samples. The analytical framework was adapted
167 from established methods used to quantify biochemical reaction networks (Hu et al.,
168 2025), and further modified to represent atmospheric aging processes. Net changes in
169 elemental composition across daytime-nighttime molecular pairs were used to quantify
170 the gain or loss of key functional groups. The following stoichiometric relationships
171 were applied to define candidate transformation pathways:

172 Hydroxylation: $C_cH_hO_oN_nS_s + x[O] \rightarrow C_cH_hO_{o+x}N_nS_s$

173 Carboxylation: $C_cH_hO_oN_nS_s + x[O] \rightarrow C_cH_{h-2x}O_{o+2x}N_nS_s$

174 Carbonylation: $C_cH_hO_oN_nS_s + x[O] \rightarrow C_cH_{h-2x}O_{o+x}N_nS_s + xH_2O$

175 where *c*, *h*, *o*, *n*, and *s* represent the number of atoms of the elements (C, H, O, N, S) in
176 the molecular formula, and are all integers. Corresponding reaction indices, including
177 Hydroxylation Index (HI), Carboxylation Index (CXI), and Carbonylation Index (CNI),
178 were computed to characterize the overall magnitude of each pathway. A detailed
179 description can be found in Supplement Text S3. For each transformation pathway *j*,
180 the total reaction index was calculated as (Hu et al., 2025):

$$181 \text{ Reaction Index}_j = \sum_{m=1}^n RI_{j,m} \quad (1)$$



182 where m denotes each daytime molecular formula, and $RI_{f,m}$ represents the net change
183 in functional groups associated with a given daytime-nighttime molecular pair. A
184 positive index value indicates a net loss of that functional group from daytime to
185 nighttime, whereas a negative index indicates a net gain. All calculations were
186 performed using Python (version 3.11), using the core molecular formulas from
187 daytime and nighttime samples collected during the same season. It should be
188 emphasized that the reaction indices (HI, CXI, CNI) quantify stoichiometrically
189 possible transformations based on the net changes in elemental composition between
190 daytime and nighttime molecular formulas. These indices diagnose candidate
191 transformation pathways rather than directly measured reaction fluxes or rates.
192 Nevertheless, it provides a theoretical framework to diagnose dominant molecular
193 transformation pathways underlying diurnal changes in atmospheric organic aerosols
194 (Hu et al., 2025).

195 **2.4 Molecular modeling of vehicular WSOA representative groups**

196 To elucidate the structural characteristics of WSOA molecules, molecular models
197 were constructed for the three distinct molecular groups (b(+), b(0), and b(-)) identified
198 via Spearman correlation analysis (Supplement Text S4). The modeling approach was
199 adapted from established frameworks for DOM and has been optimized in this study
200 for FT-ICR MS data derived from the WSOA. For each correlation group, a
201 representative molecular model was built using the VSOMM 2
202 (<https://somm.boku.ac.at/>) (Escalona et al., 2021). The detailed descriptions of the
203 model refer to Supplement Text S5. The primary input for each model was the FT-ICR
204 MS data from samples belonging to that specific group. 110 representative molecules
205 were generated for each group model, denoted as Model(+), Model(0), and Model(-).

206 The advanced input mode of VSOMM 2 was employed, specifying organic carbon
207 fractions (carbonyl, carboxyl, aromatic, acetal, hydroaliphatic, and aliphatic). These
208 component proportions were estimated based on the previous study and were iteratively
209 adjusted during model calibration (Duarte et al., 2015). pH was set from extract
210 measurements. The solvent was water with 200 molecules to represent the aqueous



211 particle phase, with Na⁺ as the counterion. The GROMOS 54A7 force field was applied
212 for energy minimization and molecular dynamics simulation to obtain a stable
213 supramolecular structure. Model performance was validated by comparing statistical
214 distributions of key parameters (MW, DBE, AImod, O number) from 110 model
215 molecules against those from FT-ICR MS data, using root mean square error (RMSE)
216 of relative frequency distributions. Acceptance required RMSE<0.3 for each parameter
217 (Zhao et al., 2023). The final, optimized input parameters (organic carbon fractions) for
218 the three group models are archived in the Supplement Table S3 and S4.

219 Following the generation of the PDB coordinate files by VSOMM 2, the models
220 were further processed and analyzed using Schrödinger (Maestro 13.7). The Protein
221 Preparation Wizard was used to add hydrogens, assign bond orders, and perform
222 restrained minimization with the OPLS4 force field, converging heavy atoms to a root-
223 mean-square deviation of 0.03 nm (Supplement Text S6). This refined 3D structural
224 model enabled subsequent quantitative analysis of molecular conformational
225 parameters, including solvent-accessible polar surface area (PSA), hydrogen bond
226 donor/acceptor (HBD/HBA) counts, molecular hydrophilicity (AlogP), and the number
227 of rotatable bonds and residues, across different seasons, diurnal periods, and optical
228 activity categories.

229 **3. Results and Discussion**

230 **3.1 Seasonal variations of molecular characteristics in urban tunnel WSOA**

231 To investigate seasonal molecular characteristics of WSOA in urban tunnels,
232 daytime and nighttime samples from two tunnels within each season were integrated to
233 minimize tunnel-specific, episodic, and diurnal interferences, yielding relatively stable
234 seasonal fingerprints. The intensity-weighted values were then calculated based on
235 relative peak intensities for different elemental compositions (e.g., CHO, CHON,
236 CHON₂), elemental ratios (O/C, H/C, N/C, and S/C), and compound classes.

237 As shown in Fig. 1, the molecular characterization of WSOA from urban tunnels
238 reveals statistically significant seasonal differences between summer and winter.



Specifically, the elemental composition distribution (Fig. 1a) shows that summer samples are dominated by CHO and single-nitrogen CHON species ($p < 0.001$), while winter samples show a significantly higher enrichment in multi-nitrogenated and sulfur-containing compounds (CHON₂, CHON₂S and CHON₃S, $p < 0.001$; CHON₃, $p < 0.01$). The divergence may be associated with primary emission characteristics and seasonal aging conditions (Supplement Table S2). In summer, high temperatures improve engine combustion efficiency, reducing incomplete fuel cracking and favoring primary emissions of low-nitrogen oxygenated organics (CHO and CHON) (Johansson et al., 2016). Concurrently, intense solar radiation drives •OH-initiated photochemical reactions of gaseous precursors, further raising their abundance (Guo et al., 2022). In winter, cold start and incomplete combustion directly elevate the emission of complex nitrogen-containing organics, which may increase multi-nitrogen molecules (George et al., 2014; George et al., 2015; Drozd et al., 2016). Additionally, elevated relative humidity increases aerosol liquid water content, promoting multiphase reactions involving NO₂ and SO₂ that incorporate nitrogen and sulfur into organic frameworks, ultimately forming CHONS compounds (Yang et al., 2025a). Fig. 1b showed higher intensity-weighted H/C in summer (1.4) than winter (1.2, $p < 0.001$), indicating more aliphatic structures, consistent with the dominance of aliphatic/peptide compounds in summer (Fig. 1c). Winter WSOA exhibited significantly elevated N/C (0.034 vs. 0.02, $p < 0.001$), reflecting enhanced multi-nitrogenated molecules and implying that winter atmospheric conditions favor nitrogen incorporation during particle-phase aging processes (Ma et al 2025).

Figure 1c shows the seasonal variations in the intensity-weighted classification of organic categories in urban tunnels. Aliphatic/peptides and lipids were more abundant in summer ($p < 0.01$ and < 0.001 , respectively), while winter samples presented higher contributions of CRAMs, aromatics, and highly oxygenated organic compounds (HOCs) ($p < 0.01$, < 0.01 , and < 0.001 , respectively) (Fig. 1c). These variations are consistent with elemental features (Fig. 1a-b) and seasonal atmospheric conditions (Supplement Table S2). Strong summer photochemistry promotes ring-opening of primary aromatic



268 structures, generating aliphatic and peptide-like components, and oxidizes unsaturated
269 hydrocarbons to low-volatility oxygenated lipid species (Cheng et al., 2024). The
270 secondary formation of such lipid compounds may partially offset temperature-driven
271 volatilization losses (Yang et al., 2023). Conversely, the weakened winter
272 photochemical activity may reduce aromatic photodegradation, allowing more primary
273 aromatic precursors to persist. Cold-start operation further increases aromatic emission.
274 Furthermore, high winter humidity and aerosol liquid water facilitate acid-catalyzed
275 oligomerization and cross-linking of small carbonyls, promoting high-molecular-
276 weight CRAMs (Ji et al., 2020). Dissolved oxidants and gaseous pollutants in the
277 aqueous phases drive continuous oxidation and heteroatom substitution, possibly
278 increasing HOCs and N/S-containing derivatives (Jiang et al., 2025; Yang et al., 2025a).
279 These seasonal transformation characteristics are consistent with the higher N/C and
280 greater abundance of multi-nitrogenated and sulfur-containing molecules observed in
281 winter samples (Fig. 1a,b).

282 Seasonal differences in molecular structural saturation were further verified by
283 intensity-weighted structural parameters (Supplement Fig. S1). Winter exhibited
284 significantly higher mean DBE (9.2) than summer (7.3, $p < 0.01$), suggesting greater
285 unsaturated and aromatic moieties, matching the increased aromatics and HOCs (Fig.
286 1c). Slightly elevated AI_{mod} in winter (0.57) further supports stronger aromatic features
287 under weak photodegradation. A significant negative correlation between DBE and H/C
288 was observed across seasons (Supplement Fig. S2), with winter samples clustering at
289 lower H/C and higher DBE, while summer showed relatively higher H/C and lower
290 unsaturation. The consistent regression slope indicates that the intrinsic relationship
291 between molecular unsaturation and hydrogen content remains stable seasonally, yet
292 the clear separation of distributions suggests that environmental conditions modulate
293 structural evolution. Mass spectral distributions further support the seasonal divergence
294 in molecular composition and structure (Fig. 1d-g and Supplement Fig. S3). Winter
295 total mass spectra shifted toward higher m/z ranges, peaking at 500–600, compared to
296 a summer 400–500 peak (Fig. 1d). Similar shifts were observed for CRAMs and



aliphatic/peptides (Fig. 1e-g), implying that winter aqueous-phase aging and heteroatom modification may contribute to the generation of high-molecular-weight oligomeric molecules in tunnels WSOA.

Overall, seasonal environmental conditions strongly modulate the molecular evolution of WSOA in urban tunnels. Winter conditions tend to favor the retention of aromatic primary precursors and the secondary formation of highly unsaturated organic species. In comparison, intensive summer photochemical processing generally promotes the formation of aliphatic compounds with lower molecular unsaturation.

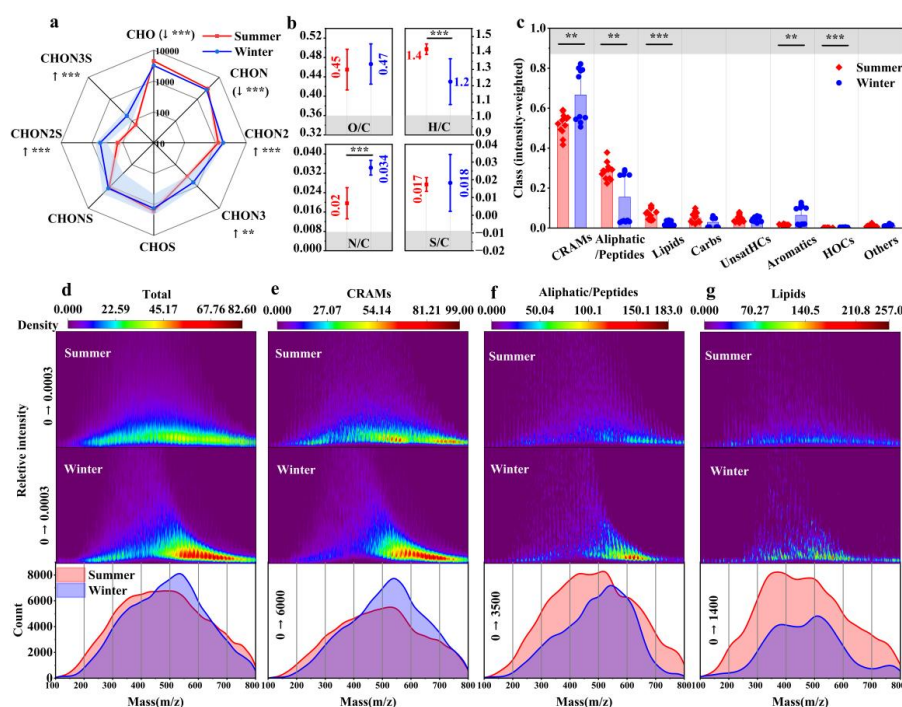


Figure 1. Seasonal variations of overall molecular characteristics of vehicle-emitted WSOA. Molecular composition is shown based on (a) elemental composition, (b) elemental ratio, and (c) compound classes, calculated based on relative intensity weights. Nitrogen-containing molecules are further classified based on the number of N atoms. CHON and CHONS denote one N atom, CHON2 and CHON2S denote two N atoms, and CHON3 and CHON3S denote three N atoms. Molecular formulas could be categorized into seven classes based on their H/C and O/C: (I) lipids ($1.5 < \text{H/C} \leq 2.0$, $0 \leq \text{O/C} \leq 0.3$), (II) aliphatic/peptides ($1.5 < \text{H/C} \leq 2.2$, $0.3 < \text{O/C} \leq 0.67$), (III) carboxylic-rich alicyclic molecules (CRAMs) ($0.67 < \text{H/C} \leq 1.5$, $0.1 \leq \text{O/C} < 0.67$), (IV) carbohydrates ($1.5 < \text{H/C} \leq 2.5$, $0.67 < \text{O/C} < 1.0$), (V) unsaturated hydrocarbons ($0.67 < \text{H/C} \leq 1.5$, $\text{O/C} < 1.0$), (VI) aromatic ($0.2 \leq \text{H/C} \leq 0.67$, $\text{O/C} < 0.67$), and (VII) highly oxygenated organic compounds (HOCs) ($0.6 < \text{H/C} \leq 1.5$, $0.67 \leq \text{O/C} \leq 1.0$) (Liu et al., 2025). Significance was evaluated by pair-sample t-test: *** represents $p \leq 0.001$, ** represents $p \leq 0.01$.



* represents $p \leq 0.05$. Mass and relative intensity distributions are shown for (d) total, (e) CRAMs, (f) aliphatic/peptides, and (g) lipid compounds.

3.2 Identification of core molecular formulas as potential vehicular emission markers

In this study, core molecular formulas were defined as those detected in 100% of samples within a season, minimizing interference from external inputs, transient traffic variations, and random noise, thus representing the most stable source-specific signatures of vehicular WSOA. Core molecules accounted for 18.4% (summer) and 14% (winter) of total molecules (Supplement Fig. S4), indicating higher summer chemical diversity.

Van Krevelen diagram clearly separated seasonal core molecules (Fig. 2a). Summer core molecules spanned broader O/C ranges, consistent with stronger photochemical oxidation, while winter core molecules were concentrated at lower H/C, indicating greater unsaturation. Consistent with the overall sample results in Fig. 1c, summer core molecules were dominated by CRAMs, aliphatic/peptide, and lipid compounds (88.5% combined). In winter, CRAMs and aromatic compounds became the dominant fractions (93.4%), with aliphatic/peptides dropping from 23.4% to 2.6% and lipids from 7.7% to 1.4% (Fig. 2a and Supplement Fig. S5). Seasonal differences in molecular unsaturation and nitrogen content of core molecules are illustrated in Fig. 2b. Summer core molecules showed a moderate correlation slope of 0.60 and a mean DBE of 7.3, whereas winter core molecules displayed a steeper slope (0.70) and a higher average DBE of 9.2. Furthermore, summer core molecules were overwhelmingly N0 (N-free) and N1 (single-N), contributing 96.58%, while winter increased N2 and N3 to 14.45% and reduced N0 from 59.1% to 47.14% (Supplement Table S5, S6 and Supplement Fig. S6). This seasonal variation mainly affected aromatic and CRAM species, with concomitant loss of low-nitrogen aliphatic/lipid components.

The alluvial diagram of core molecular composition quantifies seasonal shifts in compound classes and oxidation states based on the nominal oxidation state of carbon (NOSC) (Fig. 2c). A broader NOSC range (−1.8 to 2) was observed in summer, with higher values being more prominent in the low molecular weight region (<300 m/z).



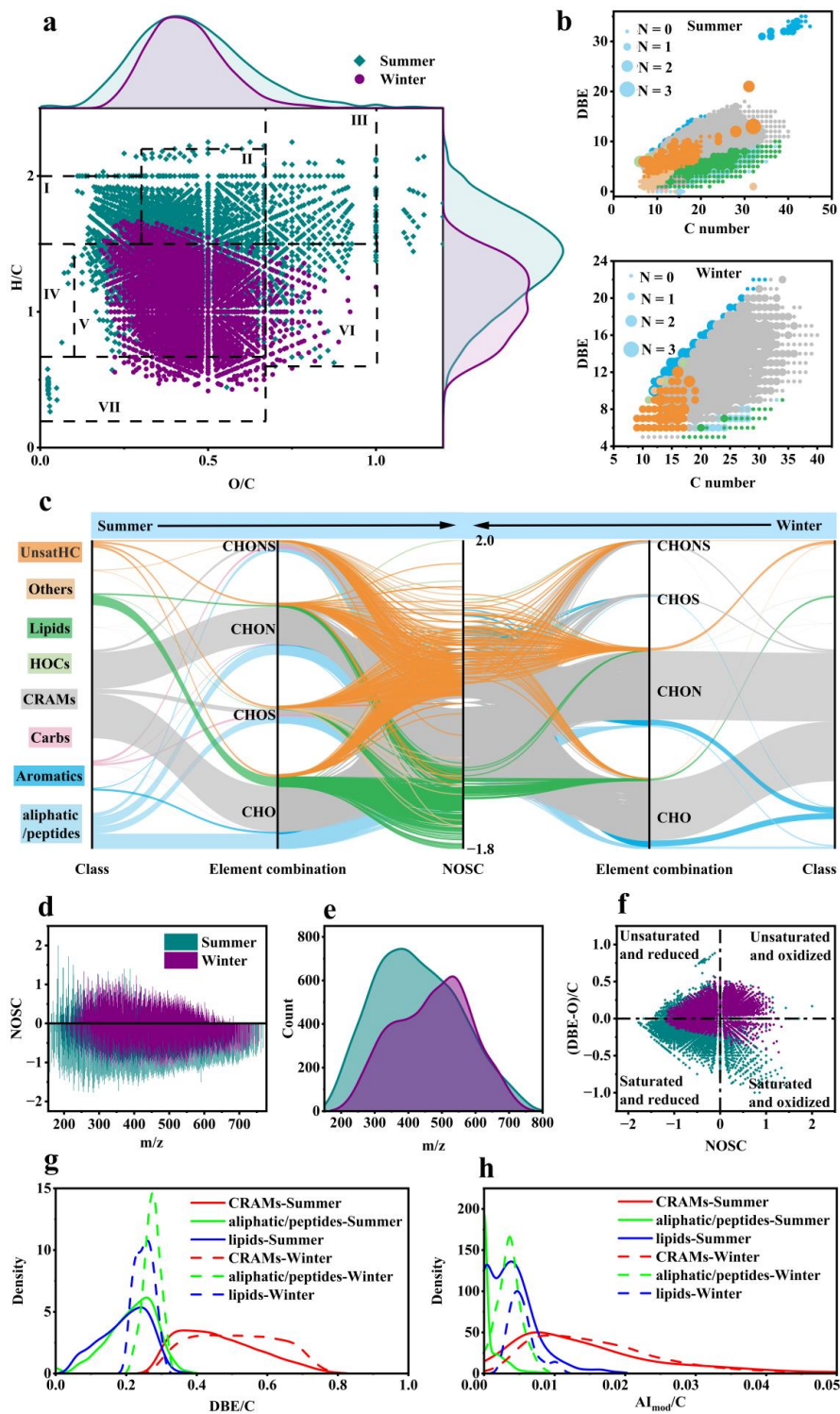
347 Winter exhibited a narrower NOSC (−1.2 to 1.3) shifted toward positive values,
348 especially in the 400–650 m/z range, dominated by CHON and CHO species (Fig. 2c,d).
349 These patterns likely arise from shifts in primary emissions and aging pathways.
350 Summer high temperatures and air-conditioning load increase emissions of reduced
351 aliphatic hydrocarbons from vehicles, which under intense solar radiation undergo rapid
352 functionalization and carbon-chain cleavage, yielding small, highly oxidized SOA
353 molecules (Zhang et al., 2023; Kroll et al., 2011). In winter, weaker photochemistry and
354 high humidity promote slower aqueous-phase functionalization of aromatics, forming
355 and accumulating medium-weight moderately oxidized products (e.g., CRAMs)
356 without reaching summer’s extreme oxidation levels (Fig. 2a and Supplement Fig. S5)
357 (Huang et al., 2025a; Wang et al., 2021). Mass count distribution confirms evident
358 seasonal differences in molecular size (Fig. 2e). Summer core molecules peaked at m/z
359 300–400, while winter ones peaked at m/z 500–600. This indicates a shift from
360 photochemical fragmentation in summer to liquid-phase polymerization in winter, a
361 pathway transition consistent with prior atmospheric observations (Guo et al., 2022).

362 The structural indices (DBE-O)/C and AI_{mod}/C reflect molecular structural
363 characteristics normalized by carbon number (Fig. 2f-h). Summer core molecules
364 featured 49.58% saturated and reduced compounds as the dominant fraction. In winter,
365 unsaturated oxidized and unsaturated reduced compounds increased to 31.67% and
366 36.85%, respectively, while saturated compounds declined markedly (Fig. 2f and
367 Supplement Table S5, S6). This aligns with VK and NOSC trends. Moreover, seasonal
368 conditions may reshape intrinsic structures within the same compound class (Fig. 2g,h
369 and Supplement Fig. S7). Aliphatic and lipid species consistently clustered at low
370 DBE/C (<0.4) and AI_{mod}/C (<0.01) for both seasons, but winter distributions shifted
371 slightly toward higher values with elevated density, indicating mild intramolecular
372 cyclization from aqueous oxidation. CRAMs dominated high DBE/C (0.35–0.80) and
373 AI_{mod}/C (0.01–0.05), with rightward shifts and broader distributions in winter. Low
374 winter temperatures suppressed the volatilization of CRAMs, promoting particle-phase
375 accumulation. Concurrently, elevated aerosol liquid water and acidity facilitate



376 condensation reactions of aromatic precursors, enhancing cyclization and aromaticity
377 (Yang et al., 2025b). These metrics indicate that summer photochemical processing
378 homogenizes WSOA toward saturated, low-aromatic structures, while winter aqueous
379 aging generally increases molecular unsaturation and aromaticity.

380 Overall, Summer is characterized by intense photochemical fragmentation, which
381 favors saturated, low-nitrogen aliphatic and lipid core compounds, whereas cold, humid
382 winters drive aqueous acid-catalyzed oligomerization, producing abundant unsaturated,
383 high-nitrogen aromatic and CRAM-dominated species. Crucially, the seasonal
384 structural changes in the core molecules are consistent with the overall molecular
385 variations (Fig. 1 and Fig. 2), implying that the overall seasonal patterns within tunnels
386 are not random but represent seasonal trends driven by core vehicular emissions and
387 subsequent atmospheric processing. This underscores the value of core molecules for
388 future research in precise identification of anthropogenic molecular fingerprints. It
389 should be noted that the 100% detection frequency criterion inevitably excludes
390 sample-specific unique compounds that may be chemically reactive or serve as
391 intermediates in atmospheric aging processes. Although non-core molecules are not
392 part of the stable ensemble, they could play important roles in dynamic reaction
393 pathways and warrant further investigation.





395 Figure 2. Characteristics of the core molecules between summer and winter. (a) Van Krevelen Diagram
396 with marginal density plots of core molecules. (b) DBE vs C number for core molecules in summer and
397 winter. The color of the dot represents different classes of compounds, as shown on the left in (2c). The
398 size of the dot reflects the number of N atoms in the molecule. (c) Alluvial diagram for comparing
399 compound classes, element combinations, and NOSC between summer and winter core molecules. (d)
400 Mass spectrum illustrating the relationship between mass and NOSC. (e) Mass distribution. (f) Scatter
401 plots of the core molecular redox states and saturation distributions based on (DBE-O)/C and NOSC. (g)
402 DBE/C and (h) AI_{mod}/C distribution for the core molecules of summer and winter.

403 **3.3 Diagnosing Seasonal Regime Shifts in Aging Pathways via the Potential** 404 **Molecular Functionalization Quantification**

405 To clarify diurnal functional group conversion mechanisms and quantify seasonal
406 oxidation pathway contributions, this study treats urban tunnels as atmospheric reactors.
407 Core molecular signatures represent overall seasonal variation (Section 3.2), so we
408 screened season-specific core molecules separately for daytime (emission reactant end)
409 and nighttime (aged product end), using net day-to-night functional group changes to
410 quantify seasonal pathway differences. The tunnel's relatively enclosed environment
411 minimizes external transport and mixed sources, while stable traffic emissions ensure
412 diurnal changes reflect in-situ aging rather than source fluctuations, justifying the
413 reactor hypothesis.

414 Figure 3a and 3b present the diurnal molecular partitioning of summer and winter
415 WSOA based on VK classification, with clear seasonal disparities. Summer shared
416 molecules accounted for 60.2% of total formulas, while winter shared molecules
417 increased to 68.8%. The 8.6% higher shared fraction in winter indicates weaker diurnal
418 molecular turnover, attributed to suppressed photochemical activity under low solar
419 radiation, which restrains compositional renewal and enhances diurnal stability (Huang
420 et al., 2025b). Unique molecule elemental distributions showed summer molecules
421 concentrated at low O/C (0–0.2) and H/C (0.8–1.2), while winter centered at O/C from
422 0.2 to 0.6 and H/C from 1.0 to 1.5, reflecting lower overall oxidation for summer-unique
423 species but higher oxygen incorporation in winter-unique ones. Notably, within the
424 same season, day-unique and night-unique distributions were nearly identical, with
425 divergence occurring primarily between seasons rather than diurnally, implying that
426 seasonal ambient conditions exert a stronger influence on elemental structure than



427 diurnal aging.

428 Functional group transformation indices (Fig. 3c,d) were quantified for
429 hydroxylation (HI), carboxylation (CXI), and carbonylation (CNI). In summer, all three
430 functionalization pathways exhibited positive net flux, showing obvious net generation
431 from day-to-night evolution. HI reached 33,471, approximately 5.6-fold CXI (5,992)
432 and 5.3-fold CNI (6,304), establishing hydroxylation as the dominant inferred pathway
433 (Fig. 3c). Increased functional groups were mainly distributed among CRAMs,
434 aliphatic/peptides, and lipids, suggesting photochemical oxidation preferentially acts
435 on aliphatic- and lipid-rich primary emission, introducing hydroxyl, carboxyl, and
436 carbonyl groups to form stable oxygenated derivatives. For hydroxylation, the largest
437 daytime-to-nighttime transitions occur within the CRAMs (81399 in summer and
438 83557 in winter; Supplement Table S7), indicating that CRAMs serve as both primary
439 reservoir and major recipient. Cross-conversion between CRAMs and unsaturated
440 hydrocarbons was also prominent (e.g., CRAMs-d to unsaturated hydrocarbons-n =
441 12198, unsaturated hydrocarbons-d to CRAMs-n = 11,528, Supplement Table S7),
442 suggesting hydroxyl addition converts unsaturated aliphatic structures into more
443 oxygenated, aromatic-like condensed systems, especially enhanced in summer via
444 photochemical ring-closure or cross-linking reactions. Aliphatic/peptides and lipids
445 showed significant bidirectional exchange (e.g., summer hydroxylation:
446 aliphatic/peptides-d to lipids-n = 7010, lipids-d to aliphatic/peptides-n = 6765,
447 Supplement Table S7), implying hydroxylation facilitates structural rearrangement
448 between peptide- and lipid-like domains through cleavage or condensation of
449 ester/amide bonds under oxidative conditions. Thus, summer functionalization is a
450 complex network of functional group introduction and skeletal transformation, with
451 hydroxylation as the primary driver.

452 In contrast, winter presented a completely different pathway evolution (Fig. 3d).
453 HI turned negative (-2,787), indicating net loss of hydroxyl groups. CXI was -174,
454 with generation and consumption balanced. CNI maintained a weak positive value
455 (989), becoming the sole net formation pathway. The sharp reversal of HI reflects that

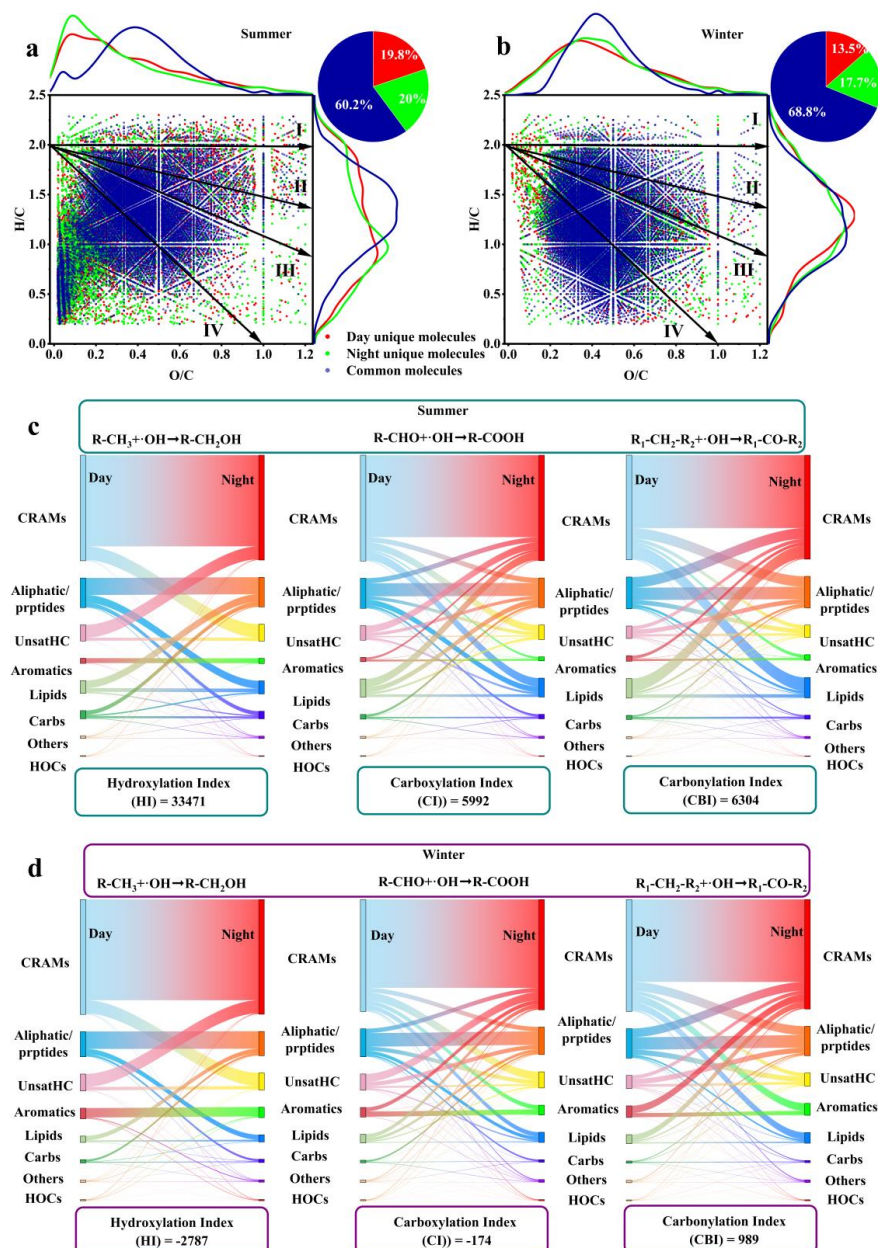


low temperature and weak photochemistry greatly inhibit OH-driven functionalization. Additionally, low temperature shifts gas-particle partitioning, causing semi-volatile hydroxyl-containing compounds to escape to the gas phase, leading to net depletion (Shahin et al., 2025). Carbonylation persistence may relate to heterogeneous reactions initiated by ozone and $\text{NO}_3\bullet$ under weak light conditions, making it the residual pathway in cold seasons (Lin et al., 2025). Despite negative HI, absolute transition counts between categories remained high (e.g., CRAMs self-conversion 83,557, CRAMs and unsaturated hydrocarbons exchange 10,981 vs 10,838, Supplement Table S7), indicating substantial inter-category transformation still occurs (Lim et al., 2010). While carboxylation transition counts (e.g., CRAMs-d to CRAMs-n = 31,889) were comparable to summer (29,666, Supplement Table S7), the net flux balanced, suggesting dynamic equilibrium between photochemical formation and acid-catalyzed decarboxylation in colder, more acidic particles (Klodt et al., 2021). Carbonylation weak positive index (989) was supported by persistent transitions like CRAMs-d to aliphatic/peptides-n (6,473) and reverse (6,244, Supplement Table S7), only slightly lower than summer, implying $\text{NO}_3\bullet$ -driven carbonyl formation is less temperature-sensitive and may even be enhanced in winter due to longer nights favoring $\text{NO}_3\bullet$ accumulation (Li et al., 2026b; Ng et al., 2017).

Overall, summer relies on strong photochemistry driving hydroxylation, carboxylation, and carbonylation with high molecular replacement. Winter suffers from suppressed hydroxylation, and only carbonylation is maintained, governed by weak photochemistry, low-temperature partitioning, and $\text{NO}_3\bullet/\text{O}_3$ -dominated heterogeneous chemistry. The proposed reaction indices are based on stoichiometric pairing of daytime and nighttime molecular formulas, representing potential transformation pathways rather than directly measured reaction fluxes. Future integration with online radical measurements would validate assignments. Nevertheless, this functional group index framework effectively distinguishes dominant seasonal oxidation pathways, overcoming traditional molecular characterization that merely describes phenomenological differences, and provides data-driven insight into transformation



485 pathways. The acquired seasonal pathway indexes also offer valuable quantitative
 486 support for optimizing OA aging simulations in atmospheric chemical models.



487
 488 Figure 3. Quantitative analysis of possible functionalization of WSOA between summer and winter. **a**:
 489 Van Krevelen Diagram (VKD) with marginal density plots of molecular formulae unique to daytime
 490 samples, nighttime samples, and common to the two samples in summer. **b**: VKD with marginal density



491 plots of molecular formulae unique to daytime samples, nighttime samples, and common to the two
492 samples in winter. **c:** Potential hydroxylation, carboxylation, and carbonylation transformation index
493 between daytime and nighttime in summer. **d:** Potential hydroxylation, carboxylation, and carbonylation
494 transformation index between daytime and nighttime in winter.

495 **3.4 Conformational Controls on the Chromophore Activity of Seasonally Aged** 496 **WSOA**

497 This study employed the VSOMM2 model and the Schrödinger platform to
498 construct 12 molecular models representing four periods (summer/winter,
499 daytime/nighttime) across three absorption categories (positively, uncorrelated, and
500 negatively correlated with b_{405}), designated Model(b+), Model(b0), and Model(b-)
501 (Supplement Fig. S8). Model validation via RMSE (<0.3) for MW, DBE, AI_{mod} , and O
502 number confirmed adequate representation of experimental molecular diversity
503 (Supplement Fig. S9-S12) (Zhao et al., 2023). Subsequently, conformational
504 descriptors were extracted, including AlogP, number of hydrogen bond
505 acceptors/donors (HBA, HBD), number of residues and rotatable bonds, and polar
506 surface area (Polar SA). All conformational parameters derived from VSOMM2
507 assume an idealized aqueous particle phase (Na^+ only, 200 H_2O molecules, no inorganic
508 salts). These simplifications ignore the complex inorganic matrix of ambient aerosols
509 (sulfate, nitrate, ammonium, chloride) and variable relative humidity effects. Therefore,
510 the model outputs are used exclusively to infer relative seasonal and diurnal
511 conformational trends, not absolute physicochemical properties. The results revealed
512 pronounced differentiation across seasons, diurnal periods, and light absorption
513 categories (Supplement Fig. S13).

514 Despite comparable seasonal totals of HBA (summer 763.7, winter 777.3) and
515 HBD (summer 746.4, winter 739.9), summer and winter WSOA exhibit distinct
516 molecular conformations marked by a large AlogP gap and opposite diurnal solvent-
517 accessible PSA evolution (Supplement Fig. 4a,e). In summer, sustained nocturnal high
518 RH enables aqueous-phase oxidation (Gu et al., 2023), while acid-catalyzed
519 heterogeneous reactions produce organosulfates and ether-containing rearrangements
520 (Chen et al., 2023; Lin et al., 2012). Consequently, summer nighttime enriches HBA by



521 48.0 and depletes HBD by 53.3, while rotatable bonds and residue numbers decrease
 522 (−54.3 and −35.7), indicating oxidative fragmentation into smaller, more oxygenated
 523 products (Fig. 4b-f and Supplement Fig S14) (Hettiyadura et al., 2021).
 524 Summer AlogP shifts from −181.8 to −194.0, indicating enhanced nocturnal
 525 hydrophilicity (Supplement Fig. S14). Paradoxically, nighttime PSA decreases from
 526 18787.8 to 17997.5 Å², despite rising HBA (Fig. 4b,e and Supplement Fig. S14),
 527 consistent with an encapsulation effect where newly formed polar acceptors become
 528 buried within molecular interiors via concurrent oligomerization, decoupling total
 529 acceptor count from surface polarity (Li et al., 2021). In contrast, winter nights invert
 530 this signature, with HBA decreasing by 78.0, HBD increasing by 65.7, and both residue
 531 numbers(62.7) and rotatable bonds (92.7) rise by 62.7 and 92.7 (Fig. 4b-f and
 532 Supplement Fig. S14). This reversal aligns with non-photochemical aqueous processing,
 533 such as acid-catalyzed epoxide hydration (Yang et al., 2025a), which preferentially
 534 generates hydroxyl/carboxyl moieties (HBD species) and promotes aldol condensation
 535 and acetalization, constructing larger polymeric frameworks with flexible aliphatic
 536 linkages (Yasmeen et al., 2010). Winter AlogP decreases from 7.1 (day) to −30.6 (night),
 537 driven by HBD accumulation, while nighttime PSA rises from 17156.8 to 18794.3 Å²
 538 (Supplement Fig. S14), indicating net exposure of solvent-exposed polar groups
 539 (Papazian et al., 2022; Yang et al., 2025a).

540 Despite near-equal total HBA/HBD (Fig. 4h, j), summer-averaged PSA (18392.6
 541 Å²) exceeds winter (17,975.6 Å²), because summer HBA moieties remain solvent-
 542 accessible (Fig. 4l), whereas the winter compact oligomer encapsulates many acceptor
 543 sites, consistent with prior encapsulation findings (Li et al., 2021). Summer and winter
 544 mean AlogP differ by an order of magnitude (−187.9 vs −11.8) (Fig. 4g), yet winter
 545 nighttime PSA (18794.3 Å²) nearly equals summer daytime value (18787.8 Å²). This
 546 decoupling implies that winter oligomerization (HBD accumulation) and summer
 547 oxygenation (HBA enrichment) can yield comparable exposed polar surfaces under
 548 intensive aqueous aging, despite fundamentally different intrinsic molecular
 549 hydrophilicity (Lim et al., 2010). Furthermore, minimal seasonal contrast in average



550 residue counts (summer 713.2, winter 692.4, Fig. 4k) supports that winter
551 acid-catalyzed oligomerization largely offsets suppressed photochemical fragmentation,
552 yielding comparable mean molecular dimensions via different oxidative trajectories (Ji
553 et al., 2022).

554 The distribution of absorption correlation categories within the PSA-rotatable
555 bonds space reveals seasonal contrasts in the structural motifs associated with
556 chromophoric potential (Fig. 4m). Summer b⁺ molecules uniformly exhibit PSA
557 exceeding 18,900 Å² and rotatable bond counts above 1,260, consistent with conjugated
558 carbonyl or aromatic substructures within highly oxygenated photochemical products
559 (Jiang et al., 2023). Winter b⁺ shows two distinct regimes. One regime shows moderate
560 PSA around 17,900 Å² with low rotatable bonds near 900, characteristic of compact
561 aromatic oligomers (Fig. 4m). The other regime shows high PSA near 19,980 Å² with
562 elevated rotatable bonds around 1,180 (Fig. 4m). They may encompass both freshly
563 emitted aromatic cores and their oxygenated derivatives formed through nighttime
564 aqueous processing, with the latter retaining chromophoric moieties despite extensive
565 functionalization (Li et al., 2020). Moreover, winter b⁺ (WN-1) and b⁻ (WN-3) have
566 similar PSA (19,800 Å²) yet opposite optical behavior (Fig. 4m). This divergence in
567 optical behavior, despite comparable solvent-accessible polarity, points to fundamental
568 differences in molecular backbone conjugation. b⁺ molecules retain polycyclic
569 aromatic or conjugated carbonyl systems, while b⁻ species consist of non-conjugated
570 aliphatic oligomers with abundant hydroxyl/carboxyl groups that enhance polarity but
571 contribute little to visible absorption (Huang et al., 2020). Summer high residue counts
572 correlate with elevated PSA and rotatable bonds, reflecting fragmentation-induced
573 functionalization and flexibility (Fig. 4m). Winter samples, in contrast, present two
574 distinct scenarios (high residue with high PSA/rotatable bonds vs low residue with low
575 PSA/rotatable bonds). Both extremes occur within the same nighttime period (WN),
576 implying that the winter nighttime aging process involves not only oligomerization
577 forming large polar flexible backbones, but condensation yielding smaller rigid
578 non-polar aggregates (Ji et al., 2022; Li et al., 2021; Al Nimer et al., 2019).



579 In summary, this study demonstrates that seasonal differences in WSOA light
580 absorption arise not from total functional group counts, but from conformation-level
581 reorganization driven by diel reaction pathways. Summer nighttime oxidative
582 fragmentation, coupled with an encapsulation effect, enriches HBA while reducing
583 surface polarity. Winter nighttime hydration and oligomerization preferentially
584 accumulate HBD and increase surface polarity. Both regimes can produce comparable
585 solvent-accessible PSA under certain conditions, yet molecular hydrophilicity and
586 backbone conjugation remain fundamentally distinct, confirming that chromophoric
587 activity is governed by backbone conjugation rather than overall polarity. Although our
588 models assume idealized aqueous phases, the primary objective is capturing relative
589 seasonal and diurnal conformational trends, and the consistency with optical b_{405}
590 correlations supports the approach. Future refinements incorporating explicit salt and
591 solvation will strengthen quantitative interpretation. The core contribution extends the
592 interpretive framework for BrC optical properties from elemental composition to three-
593 dimensional molecular organization, offering a structurally constrained perspective for
594 predicting the evolution of light absorption during atmospheric aging.

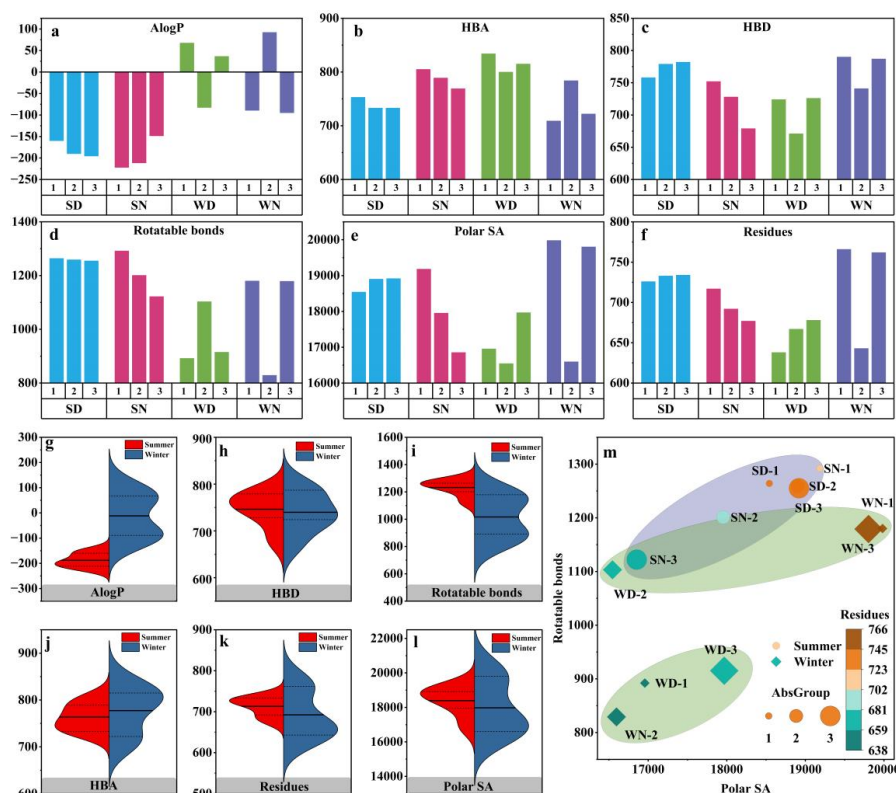


Figure 4. Characteristics of three-dimensional conformational parameters extracted from VSOMM2 and Schrödinger. a–f show the values of key conformational descriptors for summer and winter. g–l compare the seasonal averages of the same descriptors. m maps the distribution of optical activity categories within the conformational space defined by polar surface area (PSA) and rotatable bonds. Color bands represent the residue values of the molecular models; circles represent summer samples; diamonds represent winter samples; and 1, 2, and 3 denote molecular models that are positively correlated, uncorrelated, and negatively correlated with b_{405} , respectively.

3.5 Proposed conceptual framework linking seasonal conformational shifts to aerosol physicochemical functions

This study proposes a theoretical framework integrating seasonal molecular fingerprints, diurnal functionalization transformation indexes, and three-dimensional conformations (Fig. 5). Centered on molecular conformation, it links spatial structure to three core functionalities: hygroscopicity and cloud condensation nuclei (CCN) activity, heterogeneous aging kinetics, and BrC photobleaching persistence, providing novel insights into seasonal aerosol property differences. However, the framework is



611 intended to generate testable hypotheses for future laboratory and field studies, rather
612 than to establish definitive causal mechanisms.

613 Effective PSA, rather than O/C ratios or total HBA/HBD, governs water uptake.
614 Traditional parameterizations assume linear scaling between oxygenated groups and
615 water affinity, ignoring intramolecular spatial arrangement (Tan et al., 2024). However,
616 our data show PSA and HBA exhibit opposite diurnal trajectories (Supplement Fig.
617 S14). In summer, nighttime aging increases HBA (48.0) yet decreases PSA ($790 \text{ \AA}^2$),
618 indicating encapsulation that sequesters polar groups within hydrophobic interiors,
619 reducing accessible water-binding sites. Consequently, summer WSOA should exhibit
620 lower CCN activity than O/C-based proxies predict. In winter, nighttime processing
621 reduces HBA (78) yet increases PSA ($1,600 \text{ \AA}^2$) through surface hydration, enhancing
622 exposure of hydroxyl/carboxyl donors, thus promoting higher hygroscopic growth
623 relative to O/C estimates.

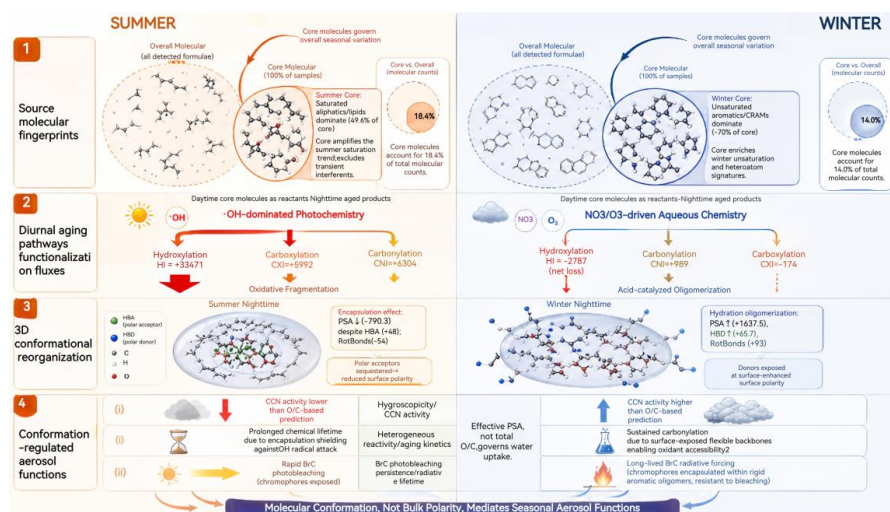
624 Conformational steric accessibility modulates aging rates. Summer HI (+33,471)
625 and winter HI (−2,787) reflect not only oxidant availability but also conformational
626 reorganizations. The summer encapsulation effect creates steric barriers shielding
627 hydroxyl groups from •OH attack, prolonging the lifetime of oxygenated products (Fig.
628 5). Winter's increased rotatable bonds (+92.7) produce flexible, open oligomers
629 maximizing surface accessibility for $\text{NO}_3\bullet$ and O_3 , sustaining positive CNI (989)
630 despite weak photochemistry (Fig. 5). This conformational arrangement facilitates
631 sustained oxidative attack, thereby maintaining carbonylation. Summer's rigidified
632 conformers undergo rapid functionalization saturation, while winter's flexible
633 backbones permit continued oxidation (Fig. 4, 5). Thus, conformation may regulate
634 both rates and pathways of heterogeneous aging, a factor currently absent in SOA
635 models. Notably, this hypothesized steric shielding effect warrants testing in controlled
636 oxidation experiments.

637 Steric burial versus solvent exposure of conjugated backbones dictates optical
638 persistence. Summer b(+) molecules uniformly occupy high PSA ($>18,900 \text{ \AA}^2$) and
639 high rotatable bonds ($>1,260$) (Fig. 4m), indicating extended, solvent-accessible



640 conjugated carbonyl and aromatic substructures directly susceptible to photolytic
641 cleavage, consistent with rapid summer photobleaching (Qiu et al., 2024). Winter b(+)
642 molecules exhibit two structures (one cluster at moderate PSA with low rotatable bonds,
643 another at high PSA with elevated rotatable bonds), both of which confer resistance to
644 photochemical degradation (Fig. 4m). The former resists photodegradation via physical
645 shielding from UV penetration, while the latter does so via energy dissipation or radical
646 quenching (Wong et al., 2017; Qiu et al., 2026). Notably, summer high PSA and high
647 rotatable species are aliphatic or lightly substituted aromatics (photolabile by backbone),
648 whereas winter counterparts are polycyclic aromatic CRAMs and multi-nitrogen
649 oligomers (photostable due to core rigidity and peripheral quenching) (Fig. 1, 2) (Masai
650 et al., 2025). Thus, winter BrC undergoes slower photobleaching, prolonging positive
651 radiative forcing during cold haze episodes, consistent with field observations of
652 enhanced winter BrC absorption in Northern China (Qiu et al., 2025).

653 This framework demonstrates that three-dimensional molecular conformation
654 mediates seasonally differentiated environmental impacts of vehicular WSOA.
655 Together with the functionalization transformation indexes (HI, CXI, CNI), these
656 descriptors form a transferable, experimentally constrained toolkit bridging FT-ICR
657 MS to chemical transport models, enabling refined predictions of CCN microphysical
658 activity, multiphase aging rates, and BrC absorption. However, modeling assumes a
659 simplified aqueous phase (Na^+ only, fixed H_2O , no salts), potentially affecting absolute
660 PSA. Conclusions are limited to vehicular WSOA in northwest Chinese urban tunnels
661 and require validation for other sources. Future work integrating multi-ion solvation
662 and atomic force microscopy characterization is needed to validate encapsulation under
663 real particle conditions.



664

665 Figure 5. A proposed conceptual framework linking seasonal molecular fingerprints, diurnal
666 functionalization transformation indices, and conformational reorganizations to hypothesized aerosol
667 physicochemical functions.

668 4 Conclusions

669 The integrated analytical framework developed in this study, consisting of core
670 molecular screening, functionalization transformation index quantification, and three-
671 dimensional conformational modeling, offers a transferable methodology for
672 investigating how seasonal aging pathways drive WSOA molecular evolution.
673 Although demonstrated for vehicular emissions in urban tunnels, it is adaptable to other
674 sources (biomass burning, coal combustion, biogenic emissions, industrial processes)
675 given appropriate diurnal or spatial aging gradients. Core molecular screening isolates
676 stable source-specific fingerprints by filtering sporadic external interferences, enabling
677 authentic identification of inherent emission signatures and their atmospheric
678 processing. Functionalization transformation index analysis, based on stoichiometric
679 pairing of daytime and nighttime molecular pools, moves beyond static compositional
680 description to quantify net gains and losses of key functional groups, effectively
681 distinguishing dominant seasonal oxidation pathways. These indexes (HI, CXI, CNI)
682 provide observationally constrained metrics that can be integrated into chemical
683 transport models, reducing uncertainties in predicting SOA formation, hygroscopic



684 growth, and CNN activity arising from oversimplified parameterizations of
685 functionalization and fragmentation processes.

686 The conformational modeling component reveals that chromophoric potential is
687 governed by the spatial arrangement and conjugation of molecular backbones rather
688 than by bulk functional group inventories or overall polarity. This insight reframes the
689 interpretation of brown carbon optical properties from a purely compositional
690 perspective to a structurally explicit one. The encapsulation effect, wherein polar
691 moieties become buried within molecular interiors, further highlights the need to
692 account for three-dimensional molecular organization when linking aerosol
693 composition to surface-active properties such as water uptake and heterogeneous
694 reactivity. These conformational differences across seasons carry direct implications for
695 BrC absorption assessments. Summer-dominant hydroxylation and fragmentation
696 pathways produce smaller, more oxygenated species with enhanced hygroscopicity that
697 modulate cloud albedo, whereas winter-favored oligomerization and nitrogen
698 incorporation generate larger, aromatic-rich species with stronger visible-light
699 absorption and potentially higher oxidative potential, which may influence both climate
700 forcing and health outcomes. These findings collectively underscore that molecular
701 conformation, not merely elemental composition, modulates the environmental and
702 climatic impacts of organic aerosols.

703 We acknowledge several limitations. The functionalization transformation index
704 diagnoses candidate transformation pathways rather than directly measured reaction
705 rates; the conformational models assume idealized aqueous particle phases without
706 considering inorganic salts, pH variability, or dynamic relative humidity; and the
707 current dataset is limited to two urban tunnels in northwestern China, requiring
708 extension to diverse sources and ambient environments to establish generalizability.
709 Nevertheless, the relative seasonal and diurnal conformational trends identified here
710 provide a structurally constrained, testable hypothesis for future laboratory oxidation
711 experiments and field campaigns. Future work should incorporate explicit salt effects
712 and dynamic solvation into conformational models, couple transformation indexes with



713 controlled oxidation studies to validate inferred pathways, and extend this framework
714 to biomass burning, industrial, and biogenic aerosols. Such efforts will ultimately
715 reduce uncertainties in climate forcing and health impact evaluations while supporting
716 the design of season-specific air pollution control strategies in anthropogenically
717 impacted regions.

718 **Data availability.**

719 The data are available upon request from the corresponding author Yanpeng Li
720 (liyanp01@chd.edu.cn).

721 **Supplement.**

722 Information for the description of the research tunnels and sampling methodology, FT-
723 ICR MS analysis and functionalization flux diagnostics, VSOMM2 modeling
724 parameters and 3D conformational refinement, Schrödinger-based molecular descriptor
725 calculation (Text S1-S6), and supplementary figures (Figure S1-S14) and tables (Table
726 S1-S7).

727 **CRedit authorship contribution statement**

728 **T.T.:** Conceptualization, Software, Formal analysis, Visualization, Data curation,
729 Writing – original draft, Investigation. **Y.L.:** Methodology, Validation, Writing – review
730 & editing, Supervision, Funding acquisition. **S.L.:** Investigation, Resources. **H.D.:**
731 Investigation, Resources, Writing – review & editing. **L.Z.:** Writing – review & editing.
732 **L.H.:** Writing – review & editing. **S.D.:** Writing – review & editing. **W.L.:** Writing –
733 review & editing. **J.C.:** Writing – review & editing, Supervision, Project administration.

734 **Competing interests.** The authors declare that they have no conflict of interest.

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