



Revealing the Underestimation of Anthropogenic Organosulfates in Atmospheric Aerosols in Urban Regions

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ABSTRACT

Organosulfates (OSs) are important component of organic aerosols, which serve as critical tracers of secondary organic aerosols (SOA). However, molecular composition, classification, and formation driving factors of OSs at different atmospheric conditions have not been fully constrained. In this work, we integrated OSs molecular composition, precursor-constrained positive matrix factorization (PMF) source apportionment, and OSs-precursor correlation analysis to classify OSs detected from PM_{2.5} samples collected from three different cities (Beijing, Taiyuan, and Changsha). This new approach enables the accurate classification of OSs from molecular perspective. Compared with conventional classification methods, we found the mass fraction of Aliphatic OSs and nitrooxy OSs (NOSs) increased by 22.0%, 17.8%, and 10.3% in Beijing, Taiyuan, and Changsha, respectively, highlighting the underestimation of Aliphatic OSs and NOSs in urban regions. The formation driving factors of Aliphatic OSs and NOSs were further investigated. We found that elevated aerosol liquid water content promoted the formation of Aliphatic OSs and NOSs only when aerosols transition from non-liquid state to liquid state. In addition, enhanced inorganic sulfate mass concentrations, and O_x (O_x = NO₂ + O₃) concentrations, as well as decreased aerosol pH commonly facilitated the formation of Aliphatic OSs and NOSs. These results reveal the underestimation of OSs derived from anthropogenic emission, highlighting the potential indicative role of Aliphatic OSs and NOSs in urban SOA.

KEY WORDS: non-target analysis; high-resolution mass spectrometry; secondary organic aerosol; PMF source apportionment



1. Introduction

Due to the diversity of natural and anthropogenic emissions and the complexity of atmospheric chemistry, investigating the chemical characterization and formation mechanisms of secondary organic aerosols (SOA) remains challenging. Among SOA components, organosulfates (OSs) have emerged as key tracers as their formation is primarily governed by secondary atmospheric processes (Iinuma et al., 2007a; Iinuma et al., 2007b; Surratt et al., 2007; Surratt et al., 2008). Moreover, OSs significantly influence the aerosol physicochemical properties, including acidity (Riva et al., 2019; Zhang et al., 2019), hygroscopicity (Estillore et al., 2016; Ohno et al., 2022; Hansen et al., 2015), and light-absorption properties (Fleming et al., 2019; Jiang et al., 2025). Therefore, a deeper understanding of OS abundances, sources, and formation drivers is crucial for elucidating SOA formation and its properties.

Quantifying OS abundances is vital to assess their contribution to SOA. However, this is difficult due to the large number and structural diversity of OS molecules and the lack of authentic standards. Most studies quantify a few representative OSs using synthetic or surrogate standards (Wang et al., 2020; Wang et al., 2017; Huang et al., 2018b; He et al., 2022), while non-target analysis (NTA) with high-resolution mass spectrometry (HRMS) offers broader molecular characterization (Huang et al., 2023a; Wang et al., 2022b; Cai et al., 2020). Although NTA combined with surrogate standards allows molecular-level (semi-)quantification, overall OS mass concentrations remain underestimated, and many OSs remain unidentified (Lukács et al., 2009; Cao et al., 2017; Tolocka and Turpin, 2012; Ma et al., 2025).

Accurate classification of OSs by their precursors is essential for reliable quantification and mechanistic insights. OSs from specific precursors generally share similar elemental compositions, with characteristic ranges of C atoms, double bond equivalents (DBE), and aromaticity equivalents (Xc). For example, isoprene-derived OSs typically contain 4–5 C atoms; monoterpene- and sesquiterpene-derived OSs usually have 9–10 and 14–15 C atoms, respectively (Lin et al., 2012; Riva et al., 2016b; Wang et al., 2019a; Surratt et al., 2008; Riva et al., 2015). An “OSs precursor map,” correlating molecular weight and carbon number based on chamber studies, has been developed to classify OSs accordingly (Wang et al., 2019a). However, these approaches often oversimplify OSs formation by relying solely on elemental composition, leaving many OSs without identified precursors.

The formation mechanisms of OSs remain incompletely understood, though several driving factors have been identified through controlled chamber experiments and ambient observations. For instance, increased aerosol liquid water content (ALWC) enhances OSs formation by promoting the uptake of gaseous precursors (Edwards et al., 2017; Brown et al., 2012). Inorganic sulfate can also affect OSs formation by acting as nucleophiles via epoxide pathway (Eddingsaas et al., 2010; Wang et al., 2020; Cooke et al., 2024). However, meteorological conditions vary across cities, meaning the relative importance of these factors may differ by location. Thus, evaluating these formation drivers under diverse atmospheric conditions is essential. Identifying both common and region-specific drivers is key to a comprehensive understanding of OSs formation mechanisms.

In this study, we employed non-target analysis (NTA) using ultra-high performance liquid chromatography (UHPLC) coupled with high-resolution mass spectrometry (HRMS) to characterize



OSs molecular composition in PM_{2.5} samples from three cities. Identified OSs were classified by their VOCs precursors—including aromatic, aliphatic, monoterpene, and sesquiterpene VOCs—via precursor-constrained positive matrix factorization (PMF). Mass concentrations were quantified or semi-quantified using authentic or surrogate standards. Additionally, spatial variations in OSs concentrations and co-located environmental factors were analyzed to distinguish both common and site-specific drivers of OSs formation.

2. Methodology

2.1 Sampling and Filter Extraction

Field observations were conducted during winter (December 2023 to January 2024) at three urban sites: Beijing, Taiyuan, and Changsha. In Beijing, PM_{2.5} samples were collected at the Peking University Atmosphere Environment Monitoring Station (PKUERS; 40.00°N, 116.32°E), as detailed in previous studies (Wang et al., 2023a). Sampling in Taiyuan and Changsha took place on rooftops at the Taoyuan National Control Station for Ambient Air Quality (37.88°N, 112.55°E) and the Hunan Hybrid Rice Research Center (28.20°N, 113.09°E), respectively (see Figure S1).

Daily PM_{2.5} samples were collected on quartz fiber filters ($\phi = 47$ mm, Whatman Inc.) from 9:00 to 8:00 local time the next day. In Beijing and Taiyuan, RH-resolved sampling was performed using an RH-resolved sampler, stratifying daily samples into low ($RH \leq 40\%$), moderate ($40\% < RH \leq 60\%$), and high ($RH > 60\%$) RH regimes. Due to persistently high RH in Changsha, a four-channel sampler (TH-16, Wuhan Tianhong Inc.) collected samples without RH stratification. Consequently, Beijing and Taiyuan collected one or more samples daily, whereas Changsha collected one sample per day. Considering the potential overestimate of monoterpene OSs detected due to the reaction of SO₂ on filters (Brüggemann et al., 2021), a denuder coated with NaCl and Na₂CO₃ was installed upstream of the sampler to remove SO₂. A total of 40, 64, and 30 samples were obtained from Beijing, Taiyuan, and Changsha, respectively. The sampled filters were stored in a freezer at -18 °C, and the duration from sampling to analysis was 40 days. Prior to analysis, all samples were equilibrated for 24 hours under controlled temperature (20 ± 1 °C) and RH (40-45%). Average daily PM_{2.5} mass concentrations and RH during sampling are summarized in Table S1.

Sample extraction followed established protocols (Wang et al., 2020). Briefly, filters were ultrasonically extracted with LC-MS grade methanol (Merck Inc.), filtered through 0.22 μ m PTFE syringe filters, and evaporated under a gentle stream of high-purity N₂ (>99.99%). The dried extracts were then redissolved in 2 mL of LC-MS grade methanol for analysis.

During the campaign, gaseous pollutants (SO₂, NO₂, O₃, CO) were monitored using automatic analyzers. PM_{2.5} and PM₁₀ mass concentrations were measured by tapered element oscillating microbalance (TEOM). Water-soluble ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, SO₄²⁻) were analyzed with the Monitor for Aerosols and Gases in ambient Air (MARGA) coupled with ion chromatography. Organic carbon (OC) and elemental carbon (EC) were quantified by online OC/EC analyzers or carbon aerosol speciation systems. Trace elements in PM_{2.5} were determined by X-ray fluorescence spectrometry (XRF). Additionally, VOCs concentrations were measured using an online



gas chromatography-mass spectrometry (GC-MS) system with a one-hour time resolution in Taiyuan and Changsha. Table S2 summarizes the monitoring instruments deployed at each site.

2.2 Identification of Organosulfates

The molecular composition of PM_{2.5} extracts was analyzed using an ultra-high performance liquid chromatography (UHPLC) system (Thermo Ultimate 3000, Thermo Scientific) coupled with an Orbitrap HRMS (Orbitrap Fusion, Thermo Scientific) equipped with an electrospray ionization (ESI) source operating in negative mode. Chromatographic separation was achieved on a reversed-phase Accucore C18 column (150 × 2.1 mm, 2.6 μm particle size, Thermo Scientific). For tandem MS acquisition, full MS scans (m/z 70–700) were collected at a resolving power of 120,000, followed by data-dependent MS/MS (ddMS²) scans (m/z 50–500) at 30,000 resolving power. Detailed UHPLC-HRMS² parameters are provided in Text S1.

NTA was performed using Compound Discoverer (CD) software (version 3.3, Thermo Scientific) to identify chromatographic peak features (workflow details in Table S3). Molecular formulas were assigned based on elemental combinations C_cH_hO_oN_nS_s ($c = 1-90$, $h = 1-200$, $o = 0-20$, $n = 0-1$, $s = 1$) within a mass tolerance of 0.005 Da. Formulas with hydrogen-to-carbon (H/C) ratios outside 0.3–3.0 and oxygen-to-carbon (O/C) ratios beyond 0–3.0 were excluded to remove implausible assignments. Double bond equivalent (DBE) and Xc (Ma et al., 2022) were calculated using eqs. (1) and (2), where m and k were the fractions of oxygen and sulfur atoms in the π -bond structures of a compound (both m and k were presumed to be 0.50 in this work (Yassine et al., 2014)).

$$\text{DBE} = c - 0.5h + 0.5n + 1 \quad (1)$$

$$Xc = \frac{(3 \times (\text{DBE} - m \times o - k \times s) - 2)}{(\text{DBE} - m \times o - k \times s)} \quad (\text{if } \text{DBE} < (m \times o + k \times s) \text{ or } Xc < 0, \text{ then } Xc \text{ was set to } 0) \quad (2)$$

OSs were selected based on compounds with $\text{O/S} \geq 4$ and HSO₄[−] (m/z 96.96010) and/or SO₃[−] (m/z 79.95736) fragments were observed in their corresponding MS² spectra. Among them, if N number is 1, $\text{O/S} \geq 7$, and their MS² spectra showed ONO₂[−] (m/z 61.98837) fragment, these OSs were defined as nitrooxy OSs (NOSs).

2.3 Classification and Quantification/Semi-quantification of Organosulfates

Due to reversed-phase column limitations, concentration estimates of small OSs ($C \leq 7$) are highly uncertain (Liu et al., 2024); thus, only OSs with $C \geq 8$ were analyzed. Firstly, we used conventional classification approach following previous studies (Zhao et al., 2018; Wang et al., 2021; Deng et al., 2021; Xu et al., 2021; Mutzel et al., 2015; Brüggemann et al., 2020; Yang et al., 2024; Duporté et al., 2020; Huang et al., 2023b; Wang et al., 2022b; Riva et al., 2016a). All detected OSs and NOSs were classified into seven groups: Monoterpene OSs and NOSs, Aliphatic OSs, Aromatic OSs and NOSs, and Sesquiterpene OSs and NOSs (Table S4). NOSs from aliphatic precursors were not observed. Those without identified precursors were labeled Unknown OSs or NOSs.

Synthetic α -pinene OSs (C₁₀H₁₇O₅S[−]) and NOSs (C₁₀H₁₆NO₇S[−]) served for (semi-)quantifying Monoterpene and Sesquiterpene OSs and NOSs. Their detailed synthesis procedure was described in previous study (Wang et al., 2019b). Potassium phenyl sulfate (C₆H₅O₄S[−]) and sodium octyl sulfate (C₈H₁₇O₄S[−]) were used for Aromatic OSs and NOSs and Aliphatic OSs due to lack of authentic



standards (Yang et al., 2023; He et al., 2022; Staudt et al., 2014). Unknown OSs and NOSs were semi-quantified by surrogates with similar retention times (RT) (Yang et al., 2023; Huang et al., 2023b). Table 1 lists the standards, retention times, and quantified categories. Unknown OSs and NOSs were absent between 2.00–5.00 min and after 13.60 min.

Table 1 Chemical structure, UHPLC retention time, and quantified categories of standards used in the quantification/semi-quantification of OSs and NOSs

Formula (M-H)	m/z ([M-H] ⁻)	Chemical structure	UHPLC RT (min)	Quantified OSs categories
C ₆ H ₅ O ₄ S ⁻	172.99140		0.92	Aromatic OSs and NOSs, Unknown OSs and NOSs (RT 0.50-2.00 min)
C ₈ H ₁₇ O ₄ S ⁻	209.08530		10.30	Aliphatic OSs, Unknown OSs and NOSs (RT 10.00- 13.60 min)
C ₁₀ H ₁₇ O ₅ S ⁻	249.08022		7.73	Monoterpene OSs, Sesquiterpene OSs, Unknown OSs and NOSs (RT 5.00-10.00 min)
C ₁₀ H ₁₆ NO ₇ S ⁻	294.06530		9.26	Monoterpene NOSs and Sesquiterpene NOSs

To classify the Unknown OSs and NOSs, we first calculated the Xc of each specie. Those with DBE > 2 and Xc > 2.50 were designated as Aromatic OSs and NOSs (Yassine et al., 2014). Subsequently, constrained positive matrix factorization (PMF) analysis was performed using EPA PMF 5.0. Several OSs with known precursors served as auxiliary tracers to guide source apportionment. Specifically, C₁₁H₂₂O₅S and C₁₂H₂₄O₅S for long-chain aliphatic OSs (Yang et al., 2024); C₁₀H₁₀O₇S and C₁₁H₁₄O₇S for Aromatic OSs and NOSs (Riva et al., 2015); C₁₀H₁₈O₅S and C₁₀H₁₇NO₇S for Monoterpene OSs and NOSs, respectively (Surratt et al., 2008; Iinuma et al., 2007a); C₁₄H₂₈O₆S and C₁₅H₂₅NO₇S for Sesquiterpene OSs and NOSs, respectively (Wang et al., 2022b). These were selected due to their high detection frequency (>85%) and the highest average concentrations within their categories. Typical VOCs markers (isoprene, benzene, toluene, styrene, n-dodecane) were also included in the PMF model. Based on marker species, Unknown OSs and NOSs were further categorized into eight groups: Monoterpene, Aromatic, Aliphatic, and Sesquiterpene OSs and NOSs.

Correlation coefficients between classified OSs/NOSs and corresponding VOCs (Monoterpene OSs and NOSs vs. isoprene; Aromatic OSs and NOSs vs. benzene; Aliphatic OSs and NOSs vs. n-dodecane; Sesquiterpene OSs and NOSs vs. isoprene) were calculated, excluding species with R < 0.40. Given monoterpenes and sesquiterpenes primarily originate from biogenic sources and strongly correlate with isoprene (Guenther et al., 2006; Sakulyanontvittaya et al., 2008). Therefore, we checked the relationship between Monoterpene OSs and NOSs, Sesquiterpene OSs and NOSs, and isoprene.

To validate classification accuracy, MS² fragment patterns were analyzed (Table S5). Diagnostic fragments supported the assignments: Aliphatic OSs and NOSs showed sequential alkyl chain



cleavages ($\Delta m/z = 14.0157$) and saturated alkyl fragments ($[C_nH_{2n+1}]^+$ or $[C_nH_{2n-1}]^+$); Monoterpene OSs and NOSs displayed $[C_nH_{2n-3}]^+$ fragments; Aromatic OSs/NOSs exhibited characteristic aromatic substituent fragments ($[C_6H_5R-H]^+$; R = alkyl, carbonyl, -OH, or H). These fragment patterns confirm the reliability of our classification approach.

3. Results and Discussion

3.1 Concentrations, Compositions, and Classification of Organosulfates

Figure 1 shows the temporal variations of OSs and organic aerosols (OA) mass concentrations, as well as RH, during the sampling period across the three cities. The mean OSs concentrations were $(41.11 \pm 34.47) \text{ ng/m}^3$ in Beijing, $(57.39 \pm 39.23) \text{ ng/m}^3$ in Taiyuan, and $(102.06 \pm 80.54) \text{ ng/m}^3$ in Changsha. Table S6 summarizes the average concentrations of $PM_{2.5}$, OC, gaseous pollutants, OSs mass concentrations, and the mean meteorological parameters during sampling period for all three cities. OSs accounted for $0.64\% \pm 0.44\%$, $0.41\% \pm 0.24\%$, and $0.76\% \pm 0.34\%$ of the total OA in Beijing, Taiyuan, and Changsha, respectively.

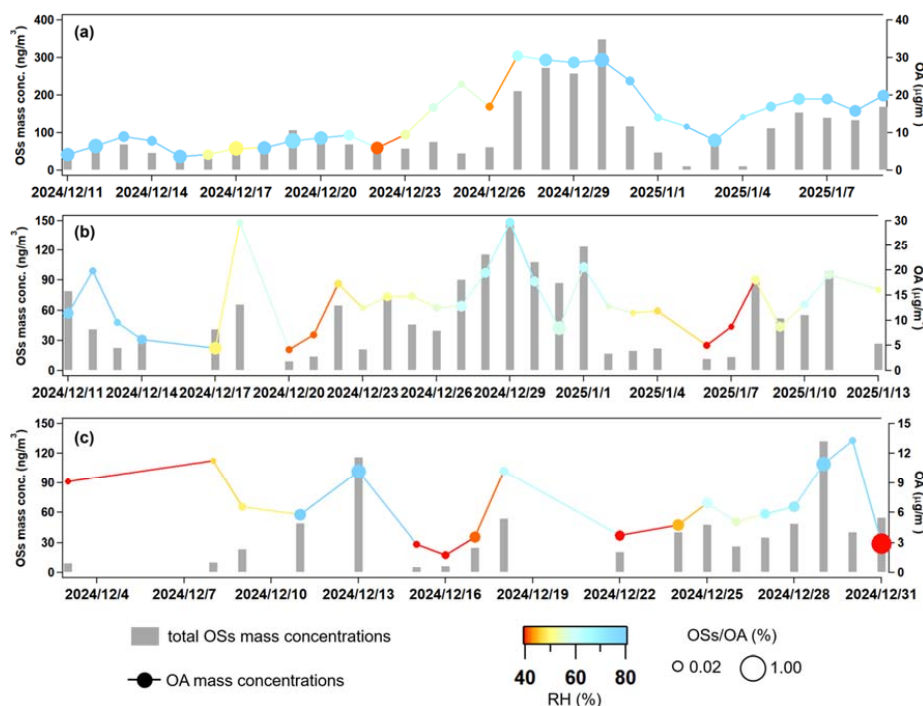


Figure 1 Temporal variations of daily total OSs mass concentrations and average OA mass concentrations in (a) Changsha, (b) Taiyuan, and (c) Beijing. The markers of OA mass concentrations are colored by average RH during sampling period, and marker sizes indicate the OSs/OA mass concentration ratios.

The highest OSs mass concentrations and OSs/OA ratios were observed in Changsha. As shown

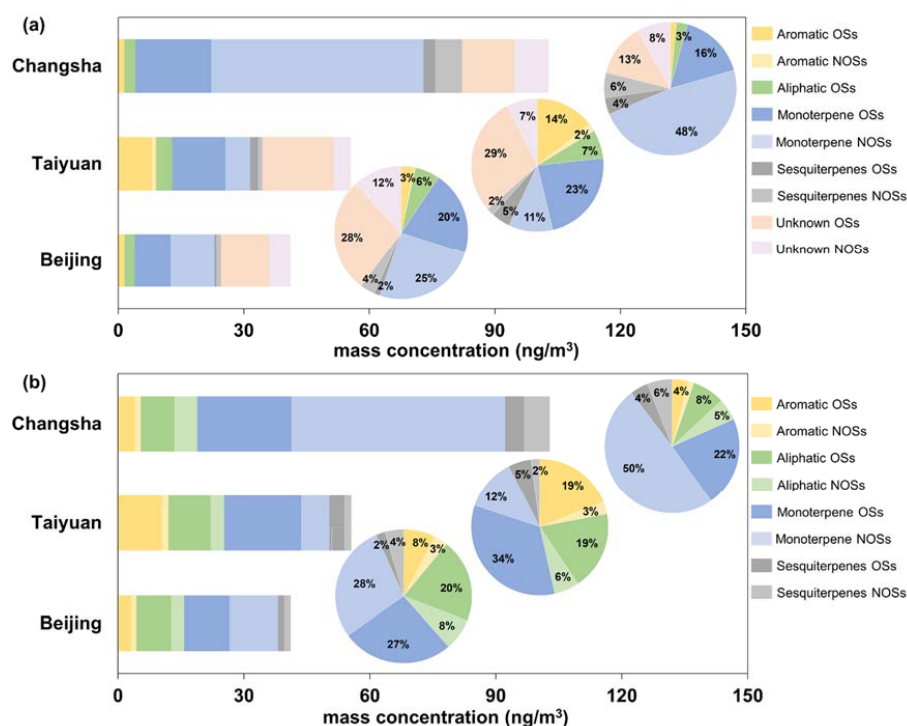


207 in Figure 1(a), a distinct episode with OSs mass concentrations exceeding 300 ng/m^3 occurred between
 208 December 27th and 31st, leading to the elevated OSs mass concentrations in Changsha. During this
 209 period, RH remained consistently above 70%, and the resulting increase in ALWC facilitated OSs
 210 formation through aqueous-phase reactions (Cheng et al., 2016b; Wu et al., 2018; Zheng et al., 2015).
 211 Furthermore, as shown in Figure S2, concentrations of Ba and K—tracers for fireworks emissions—
 212 were elevated, indicating intense fireworks activity. The high ALWC accelerated the heterogeneous
 213 conversion of SO_2 from fireworks into particulate sulfate (Figure S3), further promoting OSs
 214 formation (Xu et al., 2024; Wang et al., 2020). Additionally, transition metals such as Fe and Mn,
 215 emitted during fireworks combustion (Figure S2), catalyzed OSs formation (Huang et al., 2019; Huang
 216 et al., 2018a). Collectively, these factors contributed to the pronounced OSs mass concentration
 217 observed during this period.

218 Figures 2(a) and 2(b) shows the average mass concentrations and fractions of different OSs
 219 categories across the three cities, based on conventional and our new classification approach,
 220 respectively. As displayed in Figure 2(b), Monoterpene OSs and NOSs dominated detected OSs across
 221 all cities, contributing 55.2%, 46.8%, and 72.3% to total OSs, respectively. Biogenic-emitted
 222 monoterpene is the precursor of Monoterpene OSs and NOSs. However, monoterpenes are primarily
 223 biogenic precursors, their limited emissions during winter cannot fully explain the high mass fractions
 224 of Monoterpene OSs and NOSs. Recent studies have highlighted anthropogenic sources, particularly
 225 biomass burning, as significant contributors to monoterpene (Wang et al., 2022a; Koss et al., 2018).
 226 The $\text{PM}_{2.5}$ source apportionment analysis (Text S2, Figure S4) confirmed that biomass burning
 227 substantially contributed to $\text{PM}_{2.5}$ across all cities. The highest total mass fractions of Monoterpene
 228 OSs and NOSs in Changsha are mainly attributed to the high RH (Table S6), which facilitates their
 229 formation via heterogeneous reactions (Hettiyadura et al., 2017; Wang et al., 2018; Ding et al., 2016a;
 230 Ding et al., 2016b; Li et al., 2020).

231 In Taiyuan, the total mass fractions of Aromatic OSs and NOSs (21.2%) were significantly higher
 232 than those in Beijing (10.7%) and Changsha (4.6%). Aromatic OSs and NOSs primarily formed via
 233 aqueous-phase reactions between S(IV) and aromatic VOCs (Huang et al., 2020). Taiyuan exhibited
 234 the highest sulfate mass concentration among the three cities (Table S6), which promoted the
 235 formation of these species. Additionally, transition metal ions—particularly Fe^{3+} —catalyze aqueous-
 236 phase formation of Aromatic OSs and NOSs (Huang et al., 2020). High Fe mass concentration was
 237 observed in Taiyuan ($0.79 \text{ } \mu\text{g/m}^3$), further facilitated the formation of Aromatic OSs and NOSs.

238 The highest total mass fractions of Aliphatic OSs and NOSs was observed in Beijing (28.1%).
 239 The formation mechanisms of Aliphatic OSs and NOSs still remains highly uncertainty up to now.
 240 Potential pathways include heterogeneous reactions between SO_2 and alkenes (Passananti et al., 2016),
 241 as well as reactions between sulfate and photooxidation products of alkenes (Riva et al., 2016c). Their
 242 precursors, mainly long-chain alkenes, are predominantly emitted from fossil fuel combustion and
 243 vehicle emissions (He et al., 2022; Wang et al., 2021; Riva et al., 2016c; Tao et al., 2014; Tang et al.,
 244 2020). Since fossil fuel combustion and vehicle emissions substantially contributed to $\text{PM}_{2.5}$ in all
 245 cities (Figure S4), it is suggested that relatively low anthropogenic emissions and low RH promote the
 246 dominance of Aliphatic OSs and NOSs. Specifically, low anthropogenic emissions reduce the
 247 precursor concentrations for Monoterpene OSs/NOSs and Aromatic OSs/NOSs, while low RH limits
 248 their formation through aqueous-phase reactions.



249

250 **Figure 2** The average mass concentrations of different OSs categories (a) before and (b) after
 251 classification across three cities. The inserted pie chart indicates the average mass fractions of different
 252 OSs categories.

253 3.2 Formation Driving Factors of Aliphatic OSs and NOSs

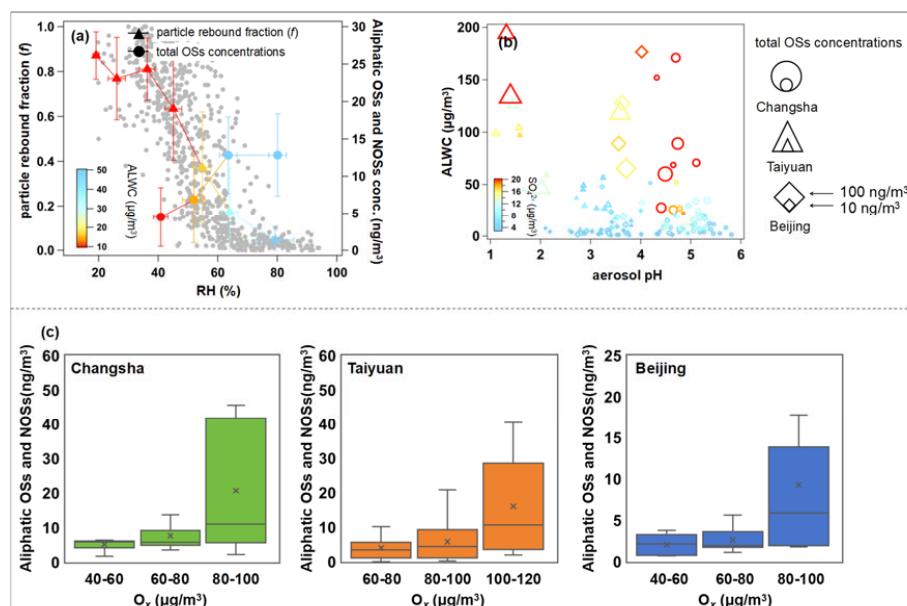
254 Compared with conventional classification approach (Figure 1(a)), we found Aliphatic OSs and
 255 NOSs increased markedly—by 22.0%, 17.8%, and 10.3% in Beijing, Taiyuan, and Changsha,
 256 respectively—with Aliphatic NOSs newly identified. Therefore, we further examined the formation
 257 drivers of Aliphatic OSs and NOSs.

258 ALWC plays a key role in facilitate OSs formation (Wang et al., 2020). Using PM_{2.5} chemical
 259 composition and RH, ALWC was calculated via the ISORROPIA-II model (details in Text S3)
 260 (Fountoukis and Nenes, 2007). Given the direct influence of ambient RH on ALWC (Figure S5)
 261 (Bateman et al., 2014) and leveraging RH-resolved samples from Beijing and Taiyuan, we assessed
 262 RH effects on Aliphatic OSs/NOSs under low (RH < 40%), medium (40% ≤ RH < 60%), and high
 263 (RH ≥ 60%) conditions.

264 In Changsha, where RH remains consistently high, Aliphatic OSs and NOSs mass concentrations
 265 strongly correlated with RH (R = 0.78). In Beijing and Taiyuan, correlations increased from low to
 266 medium RH (Beijing: 0.53 to 0.82; Taiyuan: 0.38 to 0.77) but declined slightly at higher RH (Beijing:
 267 0.82 to 0.69; Taiyuan: 0.77 to 0.72). The initial correlation rise reflects ALWC-enhanced sulfate-driven
 268 heterogeneous OSs formation (Wang et al., 2016; Cheng et al., 2016a), while the decline at elevated



269 RH is unexplained.



270

271 **Figure 3** (a) The measured particle rebound fraction (f) and total mass concentrations of Aliphatic OSs
 272 and NOSs as a function of RH, the plots were colored by the calculated ALWC concentrations in
 273 Taiyuan; (b) the relationship between aerosol pH and ALWC across three cities, the markers were
 274 colored by the inorganic sulfate mass concentrations, the marker sizes represented the total mass
 275 concentrations of Aliphatic OSs and NOSs; (c) the box plot of total mass concentrations of Aliphatic
 276 OSs and NOSs at different O₃ concentration levels.

277 This threshold behavior aligns with aerosol phase transitions. Particle rebound fraction (f),
 278 indicating phase state, was measured in Taiyuan using a three-arm impactor (Liu et al., 2017). As RH
 279 exceeded 60%, f dropped below 0.2 (Figure 3(a)), signaling a transition from non-liquid to liquid
 280 aerosol states. This transition at RH > 60% aligns with prior field (Liu et al., 2017; Liu et al., 2023;
 281 Meng et al., 2024; Song et al., 2022) and modeling (Qiu et al., 2023) studies in Eastern China.
 282 Correspondingly, Aliphatic OSs and NOSs concentrations increased with RH below 60% but plateaued
 283 beyond that despite further humidity rises. These findings underscore aerosol phase state as a critical
 284 factor: initial liquid phase formation (RH < 60%) promotes heterogeneous OSs formation (Ye et al.,
 285 2018), whereas at higher RH, saturation of reactive interfaces limits further ALWC effects.

286 In addition, the increase in ALWC with rising RH altered aerosol pH (Figure 3(b)), which
 287 inhibited OSs formation via acid-catalyzed reactions (Duporté et al., 2016). In Changsha, as aerosol
 288 pH increased from below 1.0 to above 3.0, the average total mass concentrations of Aliphatic OSs and
 289 NOSs decreased significantly from 9.3 to 4.6 ng/m³ (Figure S6), with further declines as pH increased.
 290 In Taiyuan, OS concentrations dropped from 12.2 to 6.8 ng/m³ as pH rose from below 4.5 to above
 291 5.0. However, in Beijing, total mass concentrations of Aliphatic OSs and NOSs remained stable within
 292 a narrow pH range of 3.2–3.9. Elevated ALWC facilitates aqueous-phase radical chemistry that forms



OSs via non-acid pathways, which can dominate over pH-dependent processes (Rudziński et al., 2009; Wach et al., 2019; Huang et al., 2019). Thus, pH-dependent suppression of aliphatic OSs and NOSs formation is common across urban aerosol pH ranges, but less evident when pH varies narrowly.

Inorganic sulfate plays a crucial role in OSs formation via sulfate esterification reactions (Xu et al., 2024; Wang et al., 2020). We thus examined its effect on the formation of Aliphatic OSs and NOSs. Figure 3(b) illustrates the relationships among ALWC, pH, inorganic sulfate mass concentration, and total mass concentrations of Aliphatic OSs and NOSs across all cities. A consistent positive correlation was observed, consistent with previous field studies (Lin et al., 2022; Wang et al., 2023b; Le Breton et al., 2018; Wang et al., 2018). This correlation was strongest when sulfate concentrations were below 20 $\mu\text{g}/\text{m}^3$. Below this threshold, total mass concentrations of Aliphatic OSs and NOSs increased significantly with inorganic sulfate, whereas above it, the correlation weakened. Additionally, inorganic sulfate mass concentration showed a clear positive correlation with ALWC (Figure 3(b)), suggesting that ionic strength did not increase linearly with sulfate mass. This likely reflects saturation effects in acid-mediated pathways, driven by limitations in water activity and ionic strength (Wang et al., 2020). Overall, these results highlight the nonlinear influence of inorganic sulfate on Aliphatic OSs and NOSs formation.

Atmospheric oxidative capacity, represented by O_x ($\text{O}_x = \text{O}_3 + \text{NO}_2$) concentrations, typically modulates OSs formation via acid-catalyzed ring-opening reactions pathways. As shown in Figure 3(c), total mass concentrations of Aliphatic OSs and NOSs exhibited significant increases with rising O_x levels across all cities. Especially, total mass concentrations of Aliphatic OSs and NOSs significantly increased across all cities when O_x concentrations raised from 60–80 $\mu\text{g}/\text{m}^3$ to > 80 $\mu\text{g}/\text{m}^3$. As shown in Figure S7, O_3 dominated the O_x composition during high- O_x episodes (> 80 $\mu\text{g}/\text{m}^3$) across all cities. Therefore, we inferred that high O_x conditions enhance the oxidation of VOCs (Zhang et al., 2022; Wei et al., 2024), leading to heterogeneous Aliphatic OSs and NOSs formation via acid-catalyzed ring-opening reactions pathways (Eddingsas et al., 2010; Iinuma et al., 2007a; Brüggemann et al., 2020).

4 Conclusions and Implications

In this study, we applied a non-target analysis (NTA) approach based on UHPLC-HRMS to investigate the molecular composition of OSs in $\text{PM}_{2.5}$ samples from three cities. By integrating molecular composition data, precursor-constrained PMF source apportionment, and OSs–precursor correlation analysis, we developed a comprehensive method for accurate classification of detected OSs, demonstrating superior discrimination between aliphatic OSs and nitrogen-containing OSs (NOSs). Conventional classification methods rely on laboratory chamber-derived precursor–OSs relationships (Wang et al., 2019a), which provide limited insight into the formation of aliphatic OSs and NOSs and tend to underestimate their mass fractions. The abundant Aliphatic OSs and NOSs detected in ambient $\text{PM}_{2.5}$ suggest complex formation pathways, such as OH oxidation of long-chain alkenes (Riva et al., 2016c) and heterogeneous SO_2 –alkene reactions in acidic environments (Passananti et al., 2016), which remain incompletely understood in laboratory studies. Our findings highlight the importance of emphasizing the formation of Aliphatic OSs and NOSs in urban atmospheres.



333 However, this approach depends on public molecular composition datasets, potentially
334 underestimating OSs mass concentrations in urban environments. For example, OSs identified here
335 accounted for less than 1% of total OA mass, whereas recent work (Ma et al., 2025) reported
336 approximately 20% contributions. Furthermore, OSs may become increasingly significant in OA,
337 particularly in coastal regions influenced by oceanic dimethyl sulfate emissions (Brüggemann et al.,
338 2020). Future work will focus on synthesizing OSs standards representing various precursors and
339 establishing a dedicated fragmentation database through multi-platform MS² validation to elucidate
340 OSs sources in more detail.

341 **Author Contributions**

342 Y.Q., J.W., and Z.W. designed this work. J.L., Y.Wei, C.L., J.Y., T.L., R.M., T.Z., W.F., J.Y., Z.F., Y.X.
343 and K.B. collected PM_{2.5} samples. Y.Q., J.W., T.Q., Y.B., and D.L. conducted UHPLC-HRMS
344 experiments. Y.Q., J.W., Z.G., and Y.Wang wrote this manuscript. Z.W., Y.Wang, and M.H. edited this
345 manuscript. All authors have read and agreed to submit this manuscript. Y.Q. and J.W. contributed
346 equally to this work.

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352 **Notes**

353 The authors declare that they have no conflict of interest.

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