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Molecular evolution of oxygenated organic molecules in a cloud-influenced forested mountain environment

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Abstract. Atmospheric oxygenated organic molecules (OOMs) link the oxidation of volatile organic compound to secondary organic aerosol formation, yet their molecular evolution in cloud-influenced forested mountain environments remains poorly constrained. Here, gas-phase OOMs were measured using an iodide-adduct chemical ionization mass spectrometer at a high-altitude forested station in southeastern China during autumn 2023. Among the 1503 identified OOMs, isoprene-derived OOMs were primarily controlled by daytime OH-initiated oxidation, whereas monoterpene-derived OOMs were driven by coupled OH and NO_3 chemistry. Positive matrix factorization resolved nine distinct OOM factors, revealing that biogenic oxidation dominated OOM production during warm periods (mean temperature ~20 °C), accounting for 68–79% of the total OOMs, whereas anthropogenic and regional transport factors became prominent during cooler periods (below 15 °C), accounting for up to 63% of the total budget. Cloud processes exerted a pronounced influence on OOM composition through competitive wet scavenging and multiphase chemistry. During cloud events, isoprene-derived and monoterpene-derived organic nitrates (MT-ONs) decreased by 75% and 46%, respectively, while the relative contribution of MT-ONs increased from 23% to 40%, indicating distinct cloud-processing mechanisms and hydrolysis pathways. Furthermore, the contribution of sulfur-containing OOMs increased substantially, highlighting the importance of aqueous-phase formation pathways. These results demonstrate that cloud processing influences the composition and sources of OOMs in forested mountain atmospheres and should be considered when evaluating the atmospheric fate of biogenic oxidation products.

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1 Introduction

Biogenic volatile organic compounds (BVOCs), primarily emitted by terrestrial vegetation, constitute the largest sources of reactive carbon in the atmosphere (Guenther et al., 1995). Once released, BVOCs are oxidized by atmospheric oxidants such as hydroxyl radicals (OH·), ozone (O_3), and nitrate radicals (NO_3·), producing a wide range of oxygenated organic molecules (OOMs). Due to their low volatility and high condensability, OOMs are pivotal drivers of secondary organic aerosol (SOA) formation and new particle formation (NPF) (Hallquist et al., 2009; Ehn et al., 2014; Bianchi et al., 2019). By modulating aerosol mass loading and cloud condensation nuclei (CCN) activity, OOMs significantly influence atmospheric radiative forcing, air quality and regional climate (Sun and Ariya, 2006; Hoyle et al., 2009; Tröstl et al., 2016). Consequently, understanding the molecular composition, formation mechanisms, and atmospheric evolution of OOMs has become a central topic in atmospheric chemistry, particularly BVOCs-derived species.

Recent advancements in chemical ionization mass spectrometry (CIMS) have enabled the real-time, molecular-level characterization of atmospheric OOMs. Among these techniques, iodide-adduct CIMS (I-CIMS) has emerged as a robust tool for detecting multifunctional oxygenated organic compounds and organic nitrates (ONs), facilitating extensive investigations into atmospheric oxidation processes (Lee et al., 2014; Lee et al., 2016; Ye et al., 2021; Sun et al., 2025). Previous field campaigns using I-CIMS have revealed substantial variability in OOM composition and formation pathways across diverse environments. While boreal forest OOMs are typically dominated by highly oxygenated monoterpene-derived autoxidation products (Mohr et al., 2019), those in temperate and tropical forests have highlighted the importance of isoprene oxidation products (Zha et al., 2024) reflecting differences in BVOC emission patterns and oxidation regimes. In contrast, urban observations have further demonstrated the significant contribution of anthropogenic volatile organic compounds (AVOCs) and high-NO_x levels to the formation of oxygenated ONs and other nitrogen-containing OOMs (Li et al., 2026; Zhang et al., 2026c). Collectively, these studies indicate that the molecular characteristics of OOMs are strongly controlled by the interplay between precursor emissions and local atmospheric oxidation regimes.

Compared to well-studied forest and urban areas, high-altitude mountain sites represent a unique atmospheric environment where local biogenic emissions, regional transport, and free-tropospheric influences frequently interact. In southeastern China, mountain stations are often surrounded by dense subtropical forests and enveloped in clouds due to complex topography and monsoon circulations (Shen et al., 2025; Liu et al., 2025; Ding et al., 2025). Cloud processes can substantially alter the abundance and composition of OOMs through wet scavenging, aqueous-phase oxidation, and gas-particle partitioning (Ervens et al., 2011; Mcneill, 2015; Herrmann et al., 2015). Moreover, cloud droplets provide reactive media for multiphase oxidation and can modify the fate of ONs through dissolution and hydrolysis, potentially reshaping the molecular composition of OOMs (Takeuchi and Ng, 2019; Wang et al., 2021). These processes may alter both the volatility distribution and source contributions of OOMs, ultimately affecting SOA formation and atmospheric oxidative capacity. Despite the growing number of I-CIMS field measurements worldwide, molecular-level observations of OOMs at mountain sites remain limited. In particular, the

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effects of cloud processing on OOM composition, volatility characteristics, source apportionment, and the formation of biogenic ONs has not been comprehensively investigated.

To address these knowledge gaps, a field campaign was conducted at a high-altitude forested mountain site in southeastern China during autumn 2023. Online measurements of OOMs were performed using an I-CIMS, together with complementary observations of BVOCs, trace gases, meteorological parameters, and aerosol chemical composition. The objectives of this study were to (1) characterize the molecular composition and volatility distribution of OOMs in this unique environment, (2) investigate the oxidation pathways of major biogenic OOMs and ONs, (3) quantify the contributions of different OOM sources and formation processes using positive matrix factorization (PMF), and (4) evaluate how cloud processing affects OOM composition and source profiles. This work provides new insights into the formation and evolution of OOMs in forested mountain environments and enhances our understanding of cloud–aerosol–chemistry interactions.

2 Sampling and methods

2.1 Sampling site and instruments

The field campaign was conducted at the Shanghuang Eco-Environmental Observatory of the Chinese Academy of Sciences (hereafter, SH; 119.51° E, 28.58° N), located in Jinhua, Zhejiang Province, China, at an elevation of 1128 m above sea level. The site is a representative mountaintop background station in southeastern China. The observation period lasted from 22 September to 21 October 2023. Surrounded by dense forests, the site is strongly influenced by active biogenic emissions (Zhang et al., 2024). In addition, frequent cloud events occurred during the campaign due to the combined effects of the East Asian monsoon climate and mountainous terrain. More detailed descriptions of the site can be found in Wang et al. (2025).

Gaseous OOMs were measured using an I-CIMS (Tofwerk AG, Switzerland). The sampling inlet was located on the rooftop of the third floor of the SH station. Ambient air was drawn through approximately 5 m of perfluoroalkoxy (PFA) Teflon tubing at a total flow rate of 10 L min^{-1}, resulting in a residence time of approximately 0.35 s before entering the instrument. Of the flow, ~1.8 L min^{-1} was introduced into the ion–molecule reaction region (IMR) of the I-CIMS. In the IMR, analyte molecules were ionized via adduct formation with iodide reagent ions (I^-). The iodide ions were generated by passing high-purity nitrogen over a permeation tube containing methyl iodide (CH_3I), which was maintained at approximately 60 °C, and subsequently ionizing the resulting vapor in a soft X-ray ion source (Lee et al., 2014). The reagent ions selectively clustered with oxygenated organic molecules, forming iodide adduct ions that were subsequently transferred into a time-of-flight mass spectrometer (ToF-MS) for mass analysis (Junninen et al., 2010). To ensure data quality, instrument background measurements were performed every 2–3 days throughout the campaign. The I-CIMS operated with a time resolution of 1 s, enabling continuous real-time monitoring of atmospheric OOMs. VOCs were simultaneously measured using a Vocus proton-transfer-reaction time-of-flight mass spectrometer (Vocus PTR-MS; Tofwerk AG, Switzerland). Instrument operation and data processing followed the same procedures as those applied during the 2022 measurement campaign at the same site (Zhang et al., 2024).

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Meteorological parameters, including air temperature and relative humidity (RH), were measured using a standard meteorological probe (HC2S3, Campbell Scientific Inc., USA). Wind speed and wind direction data were obtained from the ERA5 reanalysis dataset (Hersbach et al., 2023). Ambient O_3 concentrations were measured using a gas analyzer (Model 49i, Thermo Scientific Inc., USA), while nitrogen dioxide (NO_2) concentrations were determined using a thermal dissociation laser-induced fluorescence (TD-LIF) system (Di Carlo et al., 2013). The chemical composition of fine particulate matter ($PM_{2.5}$) was measured using a Time-of-Flight Aerosol Chemical Speciation Monitor (ToF-ACSM; Aerodyne Research Inc., USA). Detailed descriptions of the aerosol chemical composition measurements and data processing procedures can be found in Zhang et al. (2026b). It should be noted that cloud events were automatically identified using a ground-based counterflow virtual impactor (GCVI; Brechtel Manufacturing Inc.) (Shingler et al., 2012). To maintain consistency with previous analyses of cloud processing at the SH site, the cloud-event numbering used in this study follows that reported by Zhang et al. (2026b). A summary of the instruments deployed during the campaign is provided in Table S1.

2.2 Data analysis

2.2.1 Mass spectral data processing

The data obtained from the I-CIMS and Vocus PTR-MS were processed using the Tofware package (Tofwerk AG, v3.2.5) More than one thousand molecular ions were identified within the mass-to-charge ratio (*m/z*) range of 170–500 Th. These species mainly included oxygenated organic compounds, organic acids, and several inorganic species such as nitryl chloride and dinitrogen pentoxide. Because iodide-adduct chemical ionization exhibits high sensitivity toward multifunctional OOMs with moderate oxidation states and relatively high molecular polarity, while showing lower sensitivity toward weakly oxygenated and extremely highly oxidized species, the present study primarily focuses on OOMs containing more than two oxygen atoms. In particular, CHO and CHON compounds were selected for further analysis owing to their dominant contribution to the detected OOM pool.

A semi-quantitative approach was applied to estimate the mixing ratios of OOMs measured by the I-CIMS (Isaacman-Vanwertz et al., 2018; Ye et al., 2021). Instrument sensitivities were constrained using voltage-scanning experiments to establish the relationship between relative sensitivity and voltage. In addition, the dependence of ion transmission efficiency on analyte mass was parameterized to account for mass-dependent transmission effects. The detailed calibration procedures are provided in Text. S1. The Vocus PTR-MS was calibrated periodically throughout the campaign using a certified VOC standard gas mixture. The calibration enabled quantitative measurements of BVOCs, including isoprene and monoterpenes, as well as the major isoprene oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR). The resulting concentration data were subsequently used to investigate precursor–product relationships and oxidation pathways of OOM formation.

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2.2.2 PMF analysis

PMF analysis was conducted using the PMF Evaluation Tool (PET, v3.08) (Ulbrich et al., 2009). Following screening based on signal-to-noise ratio (S/N), data completeness, and molecular characteristics, a total of 576 OOM species were selected for PMF analysis. Details regarding the PMF data preparation and factor selection procedures are provided in the Text. S2. Following the evaluation of factor profiles, diurnal variations, precursor characteristics, and relationships with external tracers, the eleven-factor solution was selected as the most physically meaningful representation of the dataset. Among the resolved factors, nine were interpreted as atmospherically relevant sources or processes and were designated as Daytime ISO oxidation, Forenoon ISO+MT oxidation, Afternoon ISO oxidation, Afternoon ISO+MT oxidation, Nighttime ISO+MT oxidation, Nitrogen-containing species, Sulfur-containing species, Anthropogenic organic nitrates, and Regional transport. The remaining two factors (BG1 and BG2) were dominated by instrumental background signals and did not exhibit meaningful atmospheric characteristics, therefore, they were not considered in the subsequent analysis.

3 Results and discussion

3.1 Meteorology and trace gases

Figure 1 presents the diurnal variations of meteorological parameters and trace gases during the observation period. Based on the prevailing meteorology and pollutant concentrations, the campaign was divided into four representative periods: P1 (22-23 September), characterized by cloud influence but with relatively strong daytime solar radiation, and the RH approached saturation (99.8%); P2 (27-29 September), a warm and cloud-free period, which record the highest average temperature (22.4°C) and the most intense solar radiation; P3 (5-12 October) , a cold and dim period dominated by persistent precipitation, resulting in the lowest temperature (average: 11.5 °C) and minimal solar radiation; and P4 (16-20 October), a clear-sky period marked by elevated pollution levels with low RH. Affected by wet scavenging during cloud and precipitation events, $PM_{2.5}$ concentrations during P1 and P3 were substantially lower than those during the cloud-free periods (P2 and P4) (6.0 vs. 16.0 μg m^{-3}). In addition, $PM_{2.5}$ concentrations during P4 were the highest among all four periods, indicating the most severe pollution conditions during this stage. In contrast, the concentrations of O_3 and NO_2 began to increase after approximately 16:00 local time and reached maxima around 20:00, creating favourable conditions for nocturnal NO_3 radical formation and subsequent nighttime oxidation chemistry. Temporal variations during the observations and more detailed comparisons among the four periods are summarized in Fig. S1-S2 and Table. S2.

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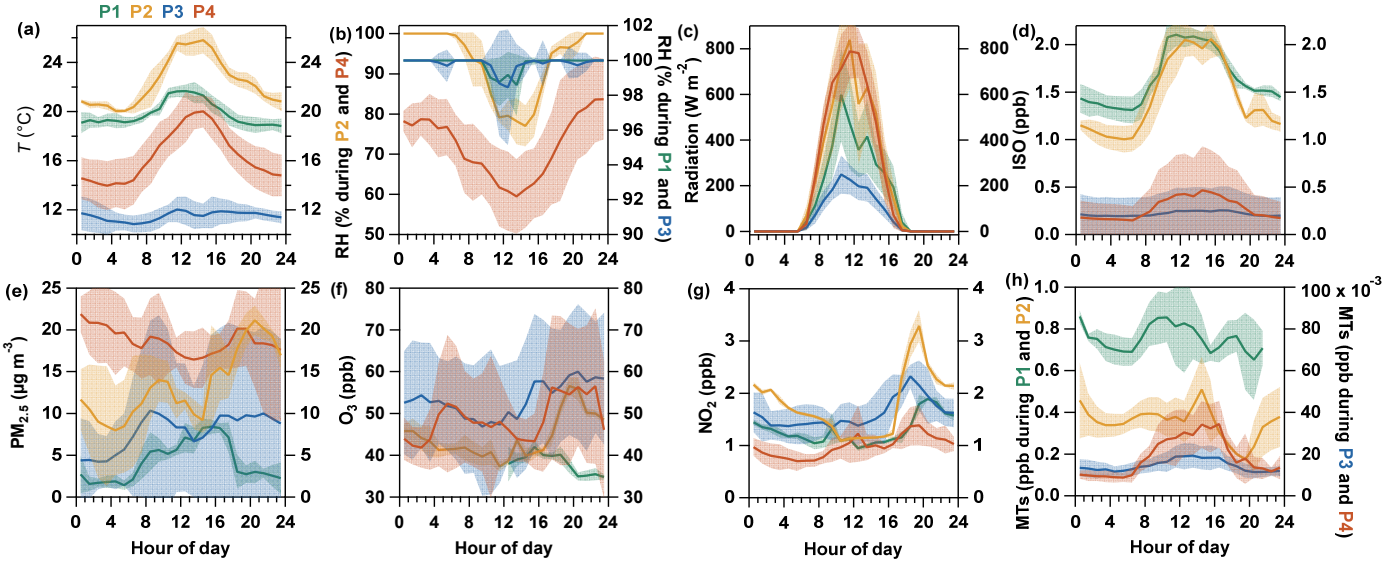

Figure 1: Diurnal variations of (a-c) meteorological parameters, (e) $PM_{2.5}$ concentrations, (f-g) trace gases, (d, h) isoprene and monoterpenes during the selected four periods. The shaded areas indicate one standard deviation (±1σ) around the mean values.

3.2 Overview of detected species by I-CIMS

A total of 1503 iodide-adduct ions were identified during the campaign. Based on elemental composition, these compounds were classified into five categories as shown in Fig. S3. Among them, CHO compounds, consisting solely of C, H, and O atoms, exhibited the largest contributions in both number and mixing ratio, with 701 species accounting for nearly half of the total mixing ratio. The second largest group was CHON compounds, containing C, H, O, and N atoms, comprising 583 species and contributing 29% of the total mixing ratio. As shown in the mass spectrum (Fig. 2a), CHO-OOMs exhibited a broad *m/z* distribution ranging from 170 to 480 Th. These compounds were mainly composed of organic acids, including small molecular carboxylic acids such as formic acid, acetic acid, glycolic acid, and lactic acid, as well as oxidation products derived from isoprene and terpenes, such as $C_4H_6O_3$, $C_5H_{10}O_3$, and $C_5H_8O_3$. In comparison, CHON-OOMs showed a relatively narrower *m/z* distribution, mainly concentrated between 180 and 380 Th. Major CHON species included amides (e.g., acetamide and hydroxyacetamide), nitrophenols (e.g., nitrophenol and methyl-nitrophenol), and ONs derived from isoprene and monoterpene oxidation (e.g., $C_{10}H_{15}NO_5$ and $C_{10}H_{15}NO_6$).

Figure 2b illustrates the variation in average carbon oxidation state (OS_c) as a function of carbon number for the two OOM classes. Overall, the average OS_c increased with decreasing carbon number for both CHO- and CHON-OOMs, indicating that functionalization and fragmentation reactions dominated the aging processes of OOMs (Hunter et al., 2017; Kroll et al., 2011). However, CHON compounds with two carbon atoms exhibited significantly lower OS_c values. This anomaly was mainly attributed to the high abundances of small amide compounds such as acetamide and hydroxyacetamide. At the relatively remote SH site, these compounds are likely influenced by regional transport associated with industrial emissions, a feature that is highly consistent with observations reported in 2022 (Zhang et al., 2024).

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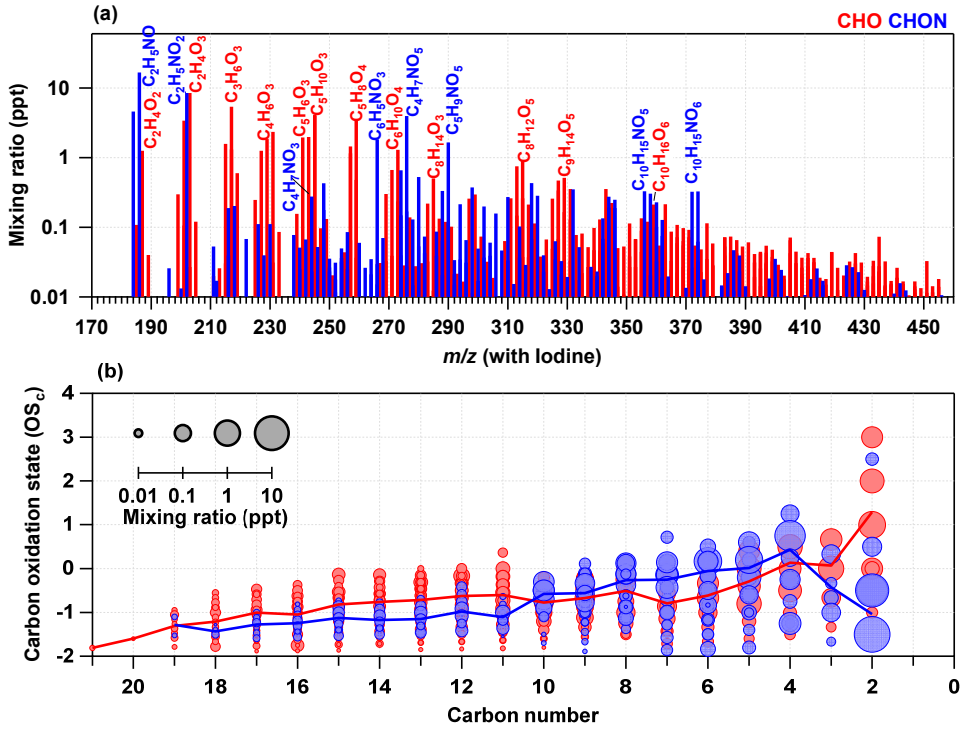

Figure 2: (a) The average spectra of CHO and CHON molecules measured during the observation period. (b) The average carbon oxidation state of CHO and CHON molecules varies with different carbon numbers. The circle size corresponds to the mixing ratio of the molecules.

Figure 3 presents the volatility distributions of CHO- and CHON-OOMs under different meteorological conditions. Overall, both classes were dominated by IVOCs, which accounted for 88% and 72% of CHO- and CHON-OOMs, respectively. In contrast, the contribution of LVOCs was less than 4% for both classes. Notably, under all meteorological conditions, the fraction of SVOCs in CHON-OOMs was consistently higher than that in CHO-OOMs, indicating that nitrogen-containing functional groups reduced molecular volatility. This result is consistent with previous observations conducted in Beijing during the winter of 2022 and summer of 2023 (Li et al., 2026). Previous studies have demonstrated that the addition of nitrogen-containing functional groups, particularly nitro and nitrate ester groups, can substantially decrease the saturation vapor pressure of organic molecules. Specifically, the introduction of one nitro group can reduce the saturation vapor pressure by approximately 0.34 orders of magnitude, while nitrate ester functionalities likewise contribute to lowering molecular volatility and enhancing condensability (Wu et al., 2021; Graham et al., 2023). These findings suggest that CHON-OOMs exhibit a stronger tendency to partition into the particle phase during gas–particle partitioning processes. Consistent with this finding, ONs have been shown to exhibit low volatility and readily partition into the particle phase with the NO_x concentrations lower than 6 ppb (Aruffo et al., 2022).

Furthermore, comparisons among different meteorological conditions revealed clear differences in volatility distributions. During cloud-influenced periods (P1 and P3), the contribution of IVOCs increased substantially, especially for CHON-OOMs

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(82% under cloudy conditions versus 68% under clear conditions). In contrast, the fraction of SVOCs increased by approximately 14% during cloud-free periods (P2 and P4). The enhanced contribution of IVOCs during cloudy periods is likely associated with both efficient wet scavenging of lower-volatility compounds and aqueous-phase processing within cloud droplets. Due to their stronger affinity for the condensed phase, SVOCs and LVOCs are more readily absorbed into cloud droplets and subsequently removed through aqueous-phase processing and wet deposition. At the same time, aqueous-phase oxidation and fragmentation can generate smaller and more volatile products that are released into the gas phase, leading to a relative enrichment of IVOCs. In contrast, under cloud-free conditions with stronger solar radiation and enhanced photochemical activity, continuous oxidation of VOC precursors can promote the formation of more oxygenated and lower-volatility products, thereby increasing the relative contribution of SVOCs. Additionally, the absence of cloud scavenging under clear conditions facilitates the accumulation of condensable species in the atmosphere. These results demonstrate that cloud processing and photochemical oxidation exert contrasting effects on OOM volatility, jointly shaping the gas-phase chemical composition of OOMs under different meteorological conditions.

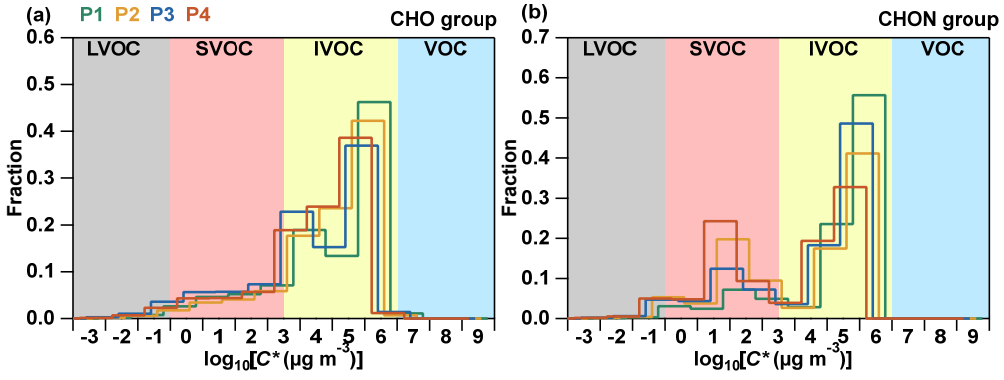

Figure 3: The volatility distribution of (a) CHO and (b) CHON molecules under different meteorological conditions, where the volatility of gaseous organic molecules is represented by the saturated mass concentration (C^*) of organic molecules at 298 K. Volatility was estimated following the parameterization developed by Li et al. (2016). For clarity, the distributions are shown with vertical offsets.

3.3 Diurnal pattern and oxidation pathways

3.3.1 Non-nitrate biogenic oxidation products

Figure 4 illustrates the diurnal variations of non-nitrate oxidation products derived from biogenic isoprene and monoterpenes under different meteorological conditions. Previous studies have identified $C_4H_{6,8}O_{3,4}$ and $C_5H_{6,8,10}O_{3,4}$ as typical oxidation products of isoprene, whereas $C_{9,10}H_{14,16}O_{4,5}$ are commonly regarded as characteristic oxidation products of monoterpenes (Yu et al., 1999; Wennberg et al., 2018; Li et al., 2020). Distinct diurnal patterns were observed among the four periods. During the cloud-influenced period P1, nearly all oxidation products exhibited pronounced afternoon maxima. This behaviour was likely driven by enhanced biogenic emissions under elevated temperature and solar radiation during the daytime, leading to increased concentrations of the precursor compounds, isoprene and monoterpenes (Fig. 1), and consequently promoting their

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photochemical oxidation even under cloudy conditions. In addition, the nearly saturated humidity and persistent cloud droplets during P1 may have further promoted the aqueous-phase oxidation of water-soluble intermediates, facilitating the formation of oxygenated products through cloud processing (Altieri et al., 2006). In contrast, during the cloud-influenced period P3, both temperature and solar radiation were substantially lower than those during P1. As biogenic emissions are highly sensitive to temperature and radiation (Hakola et al., 2006), the emissions of isoprene and monoterpenes were strongly suppressed, resulting in insufficient precursor availability and consequently the lowest concentrations of their oxidation products among all four periods. During the warm and cloud-free period P2, the concentrations of these oxidation products gradually increased throughout the afternoon and reached their maxima around 20:00 local time, suggesting sustained production from daytime BVOC oxidation and subsequent accumulation under favourable meteorological conditions. Similar diurnal patterns have previously been reported in the Landes forest in France (Li et al., 2020). During the cloud-free but relatively cooler period P4, lower temperatures were less favourable for photochemical oxidation, leading to reduced concentrations of oxidation products and more subdued diurnal variations compared with P2. Overall, the results suggest that the abundance and diurnal evolution of biogenic non-nitrate OOMs are primarily governed by the interplay between biogenic precursor emissions and photochemical oxidation, with cloud conditions exerting a secondary modulation through changes in radiation, humidity, and aqueous-phase processing.

To investigate the formation pathways of these non-nitrate biogenic oxidation products, the contributions of OH radicals and O_3 to their oxidation processes were evaluated using a kinetic approach (Text S3 and S5). The results indicate that isoprene oxidation was overwhelmingly dominated by OH radicals at both 20:00 and 09:00, with the reaction rate of isoprene + OH being approximately 15 times higher than that of isoprene + O_3. This finding is consistent with previous laboratory studies showing that the reaction rate constant of isoprene with OH radicals is several orders of magnitude larger than that with O_3 (Zhang et al., 2000; Khamaganov and Hites, 2001). In contrast, monoterpene oxidation exhibited a more complex oxidation regime. The estimated oxidation rate of monoterpenes by OH radicals was only about 1.5 times higher than that by O_3, suggesting that both oxidants contributed substantially to monoterpene processing. This result is consistent with the observed diurnal patterns of monoterpene-derived oxidation products and indicates the coexistence of daytime photochemical oxidation and ozonolysis pathways at the SH site. The contrasting oxidation regimes of isoprene and monoterpenes likely contribute to the distinct molecular composition and temporal evolution of their oxidation products under different meteorological conditions.

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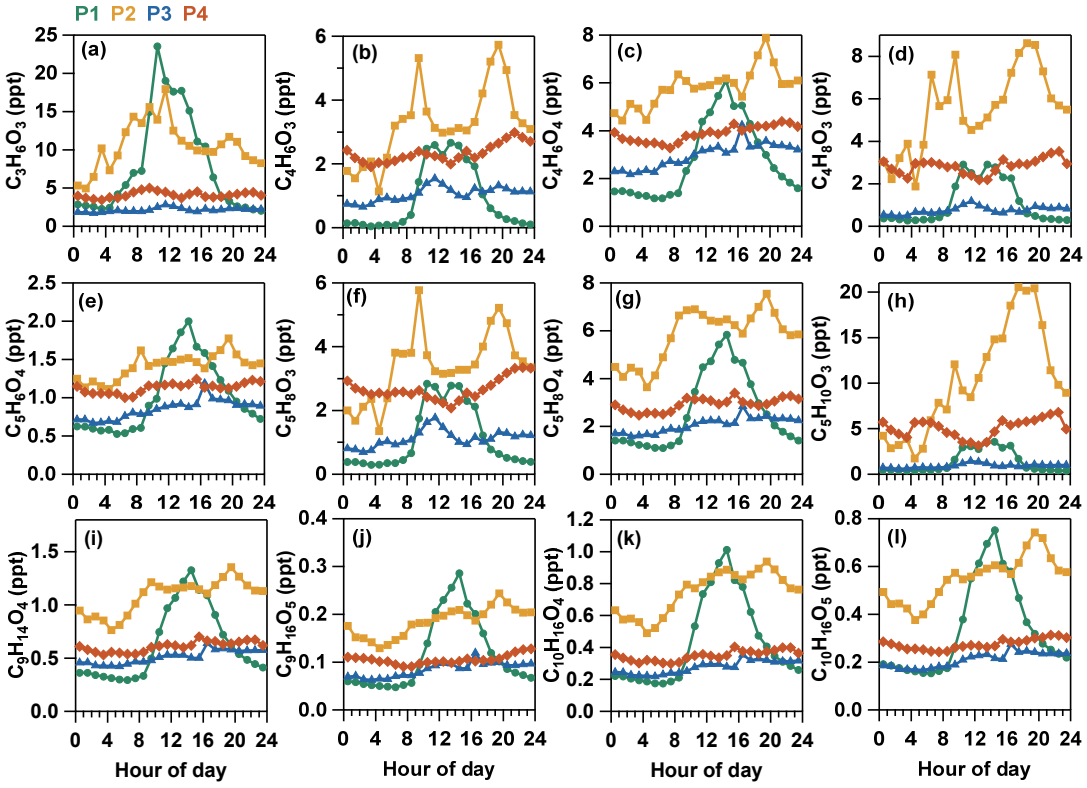

Figure 4: Diurnal variations of (a-h) isoprene and (i-l) monoterpene non-nitrate oxidation products during four periods.

3.3.2 Biogenic organic nitrates

ONs constituted an important class of gaseous OOMs at the SH site. During the observation period, a total of 47 ON species were identified, of which more than 80% were biogenic organic nitrates (Fig. S5). Figure 5 presents the diurnal variations of isoprene-derived organic nitrates (ISO-ONs) and monoterpene-derived organic nitrates (MT-ONs). As shown in the figure, except for P1 period, both species exhibited pronounced nocturnal maxima under all other meteorological conditions, with concentrations peaking at approximately 20:00 local time and decreasing substantially during daytime. Similar diurnal patterns have also been reported by Li et al. (2020) in the Landes forest in France, where biogenic ONs exhibited pronounced nighttime maxima associated with enhanced nocturnal oxidation chemistry. Kinetic calculations evaluating the relative contributions of NO_3-initiated oxidation pathways are provided in Text S4 and S6. The results indicate that ozonolysis contributed substantially to ISO-ON formation, with the oxidation rate of isoprene by O_3 estimated to be approximately 8.6 times higher than that by NO_3 radicals. In contrast, monoterpenes reacted more efficiently with NO_3 radicals, and the estimated oxidation rate of monoterpenes by NO_3 was approximately 1.65 times higher than that by O_3. These findings suggest that while O_3 oxidation plays an important role in the production of ISO-ONs, both NO_3-initiated oxidation and ozonolysis contribute significantly to MT-ON formation at the SH site. In contrast to the other ON species, $C_{10}H_{15,17}NO_6$ exhibited pronounced daytime peaks during

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P2 period, indicating that their formation may be associated with the reaction of organic peroxy radicals (RO_2) with NO, a pathway that becomes more important under daytime photochemical conditions. Similar formation mechanisms have been reported for multifunctional MT-ONs in environments influenced by both BVOC emissions and anthropogenic NOx (Lee et al., 2016). These multiple formation pathways reflect the complex coupling between BVOC oxidation and nitrogen oxide chemistry, highlighting the diverse sources and formation mechanisms of ONs in the atmosphere of high-altitude background sites.

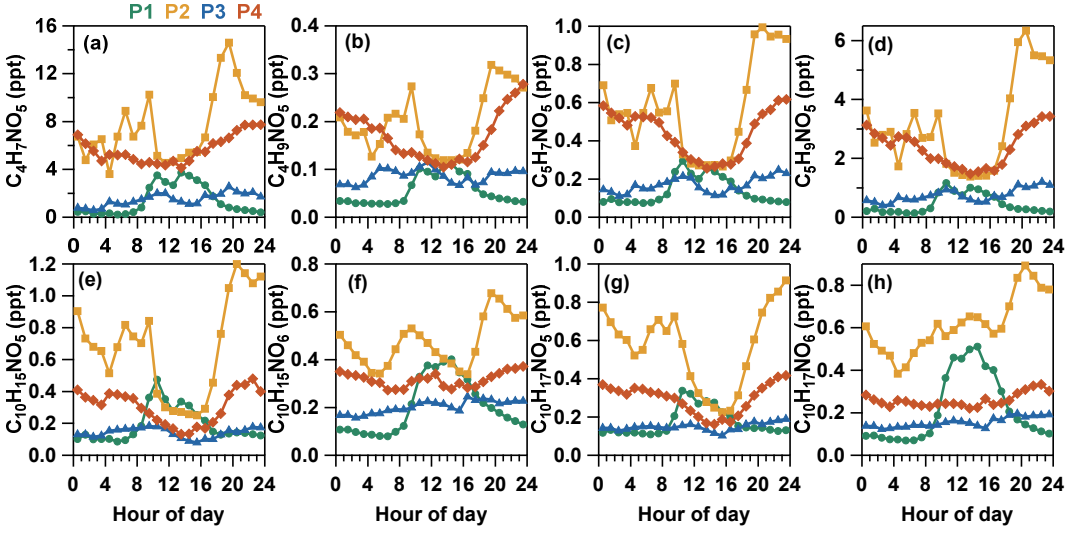

Figure 5: Diurnal variation of (a-d) isoprene and (e-h) monoterpene organic nitrates among the four periods.

As shown in Fig. 6, the contributions of ISO-ONs and MT-ONs varied substantially under different meteorological conditions. During the cloud-influenced periods (P1 and P3), the concentrations of both ISO-ONs and MT-ONs decreased markedly due to efficient wet scavenging, with reductions of 75% and 46%, respectively, compared to cloud-free conditions. To evaluate the influence of precursor variability, we additionally examined the ratios of ISO-ONs/isoprene and MT-ONs/monoterpenes (Fig. S6). The normalized ratios exhibited substantially different behaviours from the absolute concentrations, suggesting that precursor abundance alone cannot explain the observed variability in ONs. The elevated ONs/precursor ratios during P3 and P4 indicate that changes in oxidation conditions and ONs loss processes also played important roles. In addition to the overall decrease in concentration, their relative contributions also changed significantly during cloud events. The fraction of MT-ONs increased from 23% under cloud-free conditions to 40% during cloud-influenced periods, indicating distinct responses of ISO-ONs and MT-ONs to cloud processing. Several mechanisms may explain the enhanced contribution of MT-ONs during cloud events. First, the reaction rate of monoterpenes with NO_3 radicals is approximately one to two orders of magnitude higher than that of isoprene. Consequently, monoterpenes can be converted to MT-ONs more efficiently under conditions favourable for NO_3-initiated oxidation. This effect may be particularly important during cloud-influenced periods, when reduced solar radiation suppresses daytime OH oxidation and increases the relative importance of nighttime NO_3 chemistry. Second,

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differences in gas–particle partitioning and aqueous-phase processing may also contribute to the distinct responses of ISO-ONs and MT-ONs during cloud events. Previous studies have demonstrated that certain ISO-ONs can be efficiently taken up by aqueous particles and undergo rapid hydrolysis in the condensed phase, whereas MT-ONs generally exhibit longer hydrolytic lifetimes (Vasquez et al., 2020; Wang et al., 2021). As a result, ISO-ONs are removed more rapidly than MT-ONs during cloud processing, leading to an enrichment of MT-ONs in the remaining organic nitrate pool. These findings suggest that cloud processing not only reduces the overall abundance of biogenic ONs through wet scavenging but also alters their chemical composition by preferentially removing ISO-ONs relative to MT-ONs.

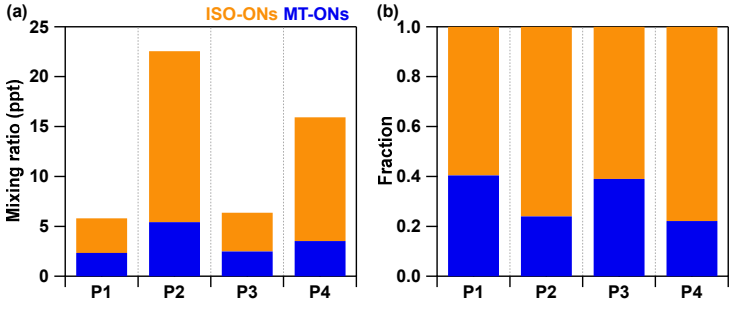

Figure 6: (a) Mixing ratios and (b) relative contributions of isoprene-derived organic nitrates (ISO-ONs) and monoterpene-derived organic nitrates (MT-ONs) during the four periods.

3.4 Source apportionment of OOMs

3.4.1 Daytime OH-initiated BVOC oxidation

Among the nine PMF-resolved factors, two factors were associated with fresh daytime oxidation of BVOCs, namely Daytime ISO oxidation and Forenoon ISO+MT oxidation. Both factors were characterized by abundant low-carbon-number oxygenated products, including $C_3H_6O_3$, $C_4H_6O_3$, $C_4H_8O_3$, $C_5H_8O_3$, and $C_5H_8O_4$, which are widely recognized as first-generation oxidation products of isoprene (Wennberg et al., 2018). These compounds are typically formed through OH-initiated oxidation of BVOCs followed by reactions of RO_2 with HO_2 and NO, producing hydroxy carbonyls, hydroxy acids, and multifunctional oxygenated compounds (Berndt et al., 2019) . The Daytime ISO oxidation factor exhibited a pronounced midday maximum (Fig. 7c), consistent with peak solar radiation and OH radical concentrations (Fig. 1). In contrast, the Forenoon ISO+MT oxidation factor peaked during the morning and contained both oxygenated products and organic nitrate species, including $C_4H_9NO_5$, $C_{10}H_{15}NO_5$, and $C_{10}H_{15}NO_6$ (Figs. 7a and S7). The coexistence of these compounds suggests a transition period during which residual nighttime oxidation products mixed with newly formed daytime oxidation products after sunrise. The strong correlation between these factors and ambient isoprene concentrations (r=0.75) further confirms the dominant role of biogenic emissions in driving their formation (Fig. S8). Non-parametric wind regression (NWR) analysis revealed that both factors were primarily associated with low wind speeds and local source regions (Fig. S9), indicating rapid formation from freshly emitted BVOCs. Together, these factors represent fresh daytime oxidation processes dominated by OH chemistry and

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local biogenic emissions. During P1 and P2, factors associated with daytime BVOC oxidation dominated the OOM budget (Fig. 8). In particular, the contribution of Daytime ISO oxidation increased substantially during the cloud-influenced P1 period, reaching its maximum around noon and accounting for approximately 39% of total OOMs. This observation suggests that despite enhanced wet scavenging, daytime oxidation of BVOCs remained an important source of gas-phase OOMs under cloud conditions, potentially facilitated by aqueous-phase photochemical processing and subsequent repartitioning of oxidation products to the gas phase.

3.4.2 Aged photochemical oxidation and SOA precursor formation

Two additional PMF factors, Afternoon ISO oxidation and Afternoon ISO+MT oxidation, were characterized by pronounced afternoon maxima and a higher degree of oxidation (Fig. 7), indicating more advanced photochemical processing of BVOCs. The Afternoon ISO oxidation factor was distinguished by the presence of isoprene epoxydiols (IEPOX, $C_5H_{10}O_3$) and showed strong correlations with MVK+MACR (r=0.77, Fig. S8), two well-established oxidation products of isoprene. This factor also contained $C_3H_6O_3$, $C_4H_8O_3$, $C_4H_7NO_5$, and $C_5H_9NO_4$. Bates et al. (2014) has demonstrated that under low-NO conditions, ISOPOO radicals preferentially react with HO_2 to form ISOPOOH, which is subsequently oxidized to IEPOX. The relatively low afternoon NO concentrations observed at SH favour this pathway, resulting in enhanced production of IEPOX-related compounds. The delayed afternoon peak relative to the fresh oxidation factors reflects the multigenerational nature of this oxidation process. Notably, this factor exhibited a strong correlation with the IEPOX-SOA factor resolved from ToF-ACSM measurements (r=0.59), suggesting that the compounds associated with this factor serve as important gaseous precursors for SOA formation. The linkage between gas-phase OOMs and particle-phase IEPOX-SOA highlights the importance of multiphase processing and gas–particle partitioning in the evolution of BVOC oxidation products. The Afternoon ISO+MT oxidation factor was characterized by highly oxygenated products from both isoprene and monoterpenes, including $C_4H_6O_4$, $C_5H_6O_4$, $C_5H_8O_4$, $C_9H_{14}O_4$, $C_9H_{16}O_5$, and $C_{10}H_{16}O_5$. Compared with the fresh oxidation factors, NWR analysis indicated a greater influence of regional transport on the Afternoon ISO+MT oxidation factor. This result, combined with its highly oxygenated molecular composition, suggests that the factor represents relatively aged BVOC oxidation products that have undergone prolonged atmospheric processing before reaching the site. These aged photochemical factors were most pronounced during the warm and cloud-free P2 period (Fig. 8), when elevated temperatures and strong solar radiation favoured BVOC emissions and sustained photochemical processing. Together with Daytime ISO oxidation, they constituted the major fraction of OOMs during P2, consistent with the enhanced importance of secondary formation pathways under clear-sky conditions. Collectively, these two factors reflect the progression of BVOC oxidation from early-generation products to more oxidized species that contribute to SOA formation, providing evidence for the important role of photochemical aging in shaping the OOM composition at the SH site.

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3.4.3 Nighttime BVOC oxidation

The Nighttime ISO+MT oxidation factor was dominated by ISO-ONs and MT-ONs and exhibited a pronounced nocturnal maximum at approximately 20:00 local time (Fig. 7). Characteristic compounds included a series of ISO-ONs and MT-ONs identified in Sect. 3.3.2, indicating that this factor represents nighttime oxidation chemistry involving reactive nitrogen species. The temporal behaviour of this factor closely followed the evening increases in O_3 and NO_2, which favour the formation of NO_3 radicals. As discussed previously, monoterpenes react rapidly with NO_3 radicals, while both NO_3-initiated oxidation and ozonolysis contribute to the formation of ONs. The pronounced nighttime peak therefore suggests that NO_3-dominated oxidation is the primary chemical pathway controlling this factor. NWR analysis showed that this factor was mainly associated with local source regions (Fig. S9), consistent with the short atmospheric lifetime of NO_3 radicals and the rapid formation of ONs near emission sources. Further evidence for the assignment of this factor to NO_3-initiated oxidation is provided by comparison with laboratory oxidation experiments (Zhang et al., 2026a). As shown in Fig. S10, after subtraction of the reagent ion, the characteristic mass spectrum of the Nighttime ISO+MT oxidation factor exhibits strong similarities to the products generated from monoterpenes + NO_3 reactions in flowtube experiments, particularly within the *m/z* range of 200–300. Several major species, including $C_{10}H_{15}NO_5$, $C_{10}H_{17}NO_5$, $C_{10}H_{15}NO_6$, and $C_{10}H_{17}NO_6$, were observed in both spectra. These compounds are generally formed through the initial addition of NO_3 radicals to the double bonds of monoterpenes, followed by rapid O_2 addition and subsequent RO_2 radical reactions, yielding multifunctional ONs (Shen et al., 2021; Draper et al., 2019). The close agreement between the ambient PMF factor and laboratory-generated NO_3 oxidation products provides strong evidence that active nighttime oxidation of biogenic terpenes by NO_3 radicals occurred at the SH site and contributed substantially to the formation of nitrogen-containing OOMs. The importance of nighttime BVOC oxidation was particularly evident during the warm and cloud-free P2 period, when isoprene and monoterpene concentrations were comparable (Fig. S4). Under these conditions, daytime OOM production was dominated by isoprene oxidation, whereas the contribution of Nighttime ISO+MT oxidation increased substantially after sunset, highlighting the growing importance of monoterpene oxidation via NO_3 radicals during nighttime.

Overall, the five biogenic PMF factors reveal a continuum of BVOC oxidation processes ranging from fresh daytime OH oxidation, through photochemical aging and SOA precursor formation, to nighttime NO_3-initiated oxidation. Their distinct temporal behaviours and source characteristics demonstrate the strong influence of oxidant availability, precursor emissions, and atmospheric processing on the formation and evolution of OOMs at the SH mountain site.

3.4.4 Anthropogenic and regional transport factors

In addition to the five BVOC-related factors discussed above, four PMF factors were attributed primarily to anthropogenic emissions and regional transport processes. Compared with the biogenic factors, these factors exhibited less pronounced diurnal variability and stronger transport signatures, highlighting the influence of anthropogenic activities on the molecular composition of OOMs at this high-altitude background site.

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The first anthropogenic factor, termed Nitrogen-containing species, was characterized by abundant nitrophenols, ONs, and related nitrogen-containing compounds, including $C_6H_5NO_3$, $C_7H_7NO_3$, and $C_7H_{13}NO_5$. The factor exhibited a pronounced nighttime maximum and showed moderate correlations with aromatic hydrocarbons (Fig. S8). Nitrophenols are well-established tracers of anthropogenic influence and can originate from both primary emissions and secondary atmospheric processing (Harrison et al., 2005). Previous studies have identified biomass burning, residential combustion, and vehicle exhaust as important sources of nitrophenols, while secondary formation through the photooxidation and NO_3-initiated oxidation of aromatic hydrocarbons has also been widely reported (Wang et al., 2020; Wernis et al., 2022). The coexistence of nitrophenols and ONs within this factor therefore suggests mixed contributions from combustion-related emissions and subsequent atmospheric oxidation processes. The NWR analysis further revealed clear transport characteristics, indicating that this factor was not solely associated with local emissions but was also influenced by regional transport of anthropogenic pollutants.

The Sulfur-containing species factor was characterized by organosulfur compounds, including C_3H_8OS, $C_9H_{10}OS$, and $C_9H_{10}O_8S$. Organosulfur species have attracted increasing attention because they can be formed through both primary emissions and secondary atmospheric processes. In particular, compounds such as $C_9H_{10}O_8S$ are likely related to organosulfate formation through multiphase reactions occurring in aerosol liquid water or cloud droplets (Li et al., 2024; Yang et al., 2025). The frequent cloud events observed at the SH site may therefore provide favorable conditions for the aqueous-phase production of organosulfur compounds. Notably, the sulfur-containing species factor exhibited its highest contribution during the rainy P3 period and was also enhanced during nighttime in P1 (Fig. 8). A comparison of factor contributions before, during, and after cloud events further revealed a clear increase in this factor during cloud events (Fig. 9), suggesting that aqueous-phase processing plays an important role in the formation of organosulfur compounds. Cloud droplets and aerosol liquid water can provide reactive media for the uptake and transformation of sulfur-containing precursors, thereby promoting organosulfur formation through multiphase reactions (Mcneill, 2015; Brüggemann et al., 2020). The interpretation of aqueous-phase formation is further supported by the observed relationship between sulfur-containing species and ambient humidity (Fig. S11). The summed concentration of sulfur-containing molecules increased with RH, indicating that humid conditions favoured their production. Elevated RH enhances aerosol liquid water content and promotes cloud droplet formation, thereby facilitating the uptake and transformation of sulfur-containing precursors through multiphase reactions. These observations provide additional evidence that cloud and aerosol liquid water played an important role in regulating organosulfur formation at the SH site.

The Anthropogenic organic nitrates factor was characterized by $C_4H_7NO_5$, $C_5H_9NO_5$, $C_7H_{13}NO_5$, and $C_9H_{15}NO_5$. Unlike the biogenic organic nitrate factor discussed in Section 3.4.3, this factor exhibited relatively weak diurnal variation, indicating a more aged and regionally mixed source. The factor showed strong correlations with MO-OOA ($r = 0.67$) and particulate nitrate ($r = 0.63$), suggesting that it was associated with highly oxidized air masses and secondary aerosol formation. Previous studies have shown that anthropogenic ONs can be produced through the oxidation of anthropogenic VOCs under elevated NO_x conditions and subsequently partition into regional aged aerosol (Lee et al., 2019; Zhu et al., 2025). The close relationship between this factor and MO-OOA therefore implies that both species may share similar source regions and atmospheric aging

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histories. Consistent with this interpretation, NWR analysis revealed a clear transport signal from the northwest, indicating that regional transport played a major role in controlling the abundance of this factor. The final factor, Regional transport, was characterized by $C_6H_4N_2$, $C_6H_5NO_3$, and $C_8H_{11}NO_2$. The presence of nitrogen-containing aromatic compounds, together with its strong correlation with MO-OOA (r = 0.62) and weak diurnal variability, suggests an association with aged anthropogenic air masses transported to the site. The similarity between the source characteristics of this factor and those of the Anthropogenic organic nitrates factor suggests that both originated from transported anthropogenic air masses that had undergone extensive atmospheric processing before arriving at the site. In contrast to P1 and P2, the relative contribution of anthropogenic-related OOM factors increased markedly during P3 and P4, accounting for approximately 63% of total OOMs (Fig. 8). The decrease in temperature and BVOC precursor concentrations reduced the importance of biogenic oxidation pathways, whereas the contributions from sulfur-containing species, anthropogenic organic nitrates, and regional transport became increasingly prominent. This finding highlights the importance of long-range transport of anthropogenic pollutants in shaping the chemical composition of OOMs and secondary organic aerosol at high-altitude background sites.

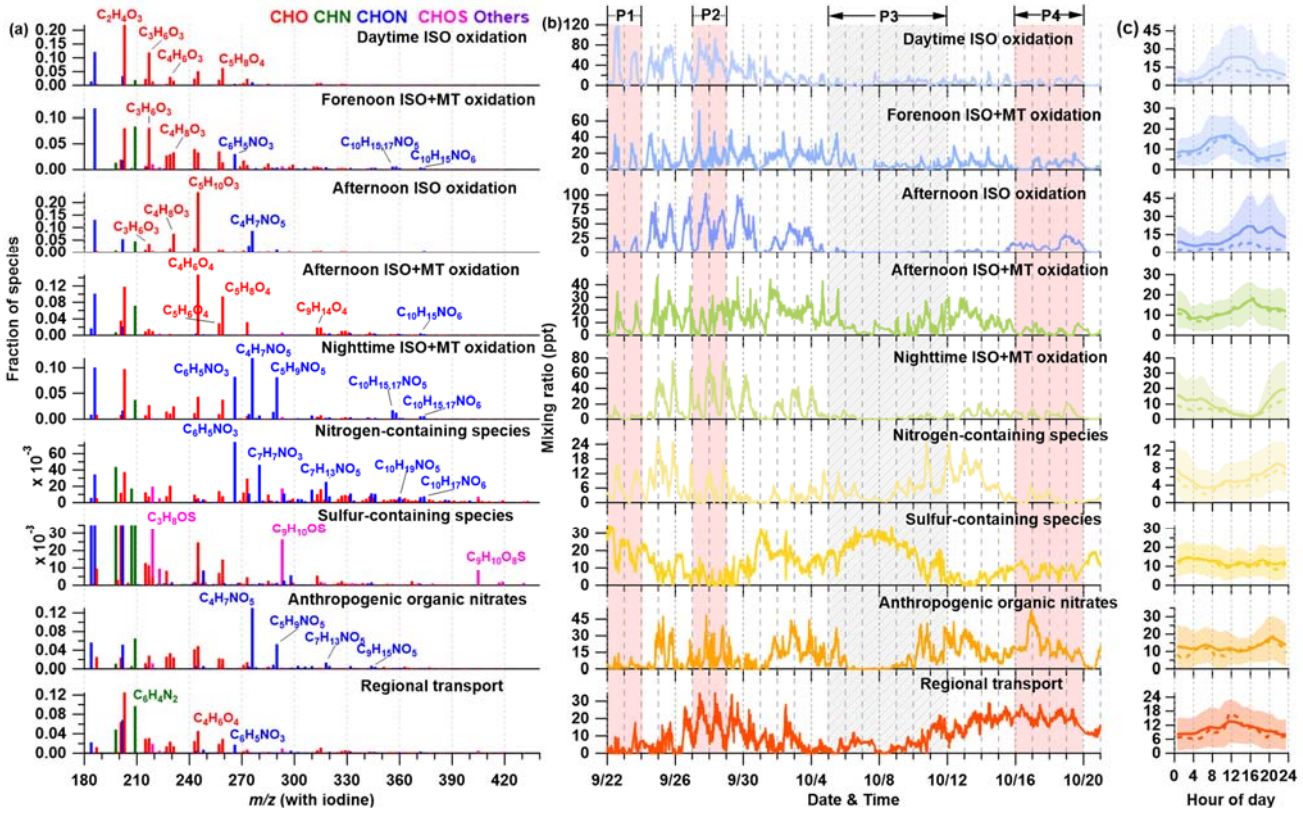

Figure 7: (a) Mass spectra of the nine resolved OOMs factors. (b) Temporal variations and (c) diurnal patterns of the PMF-resolved OOM factors. For the diurnal patterns shown in panel (c), solid lines and dashed lines denote the mean and median values, respectively; and the shaded areas represent ±1 standard deviation around the mean.

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Overall, the factor contributions reveal a pronounced meteorological control on OOM sources and formation pathways. Warm conditions favoured local BVOC oxidation and the production of biogenic OOMs, whereas lower temperatures and changes in air-mass origin enhanced the influence of anthropogenic emissions and regional transport. Cloud events not only reduced OOM concentrations through wet scavenging but also altered their chemical composition by promoting aqueous-phase formation pathways, particularly for sulfur-containing organic compounds. These results demonstrate that the molecular composition of OOMs at the SH mountain site is jointly regulated by biogenic emissions, anthropogenic influences, and cloud-driven multiphase processing.

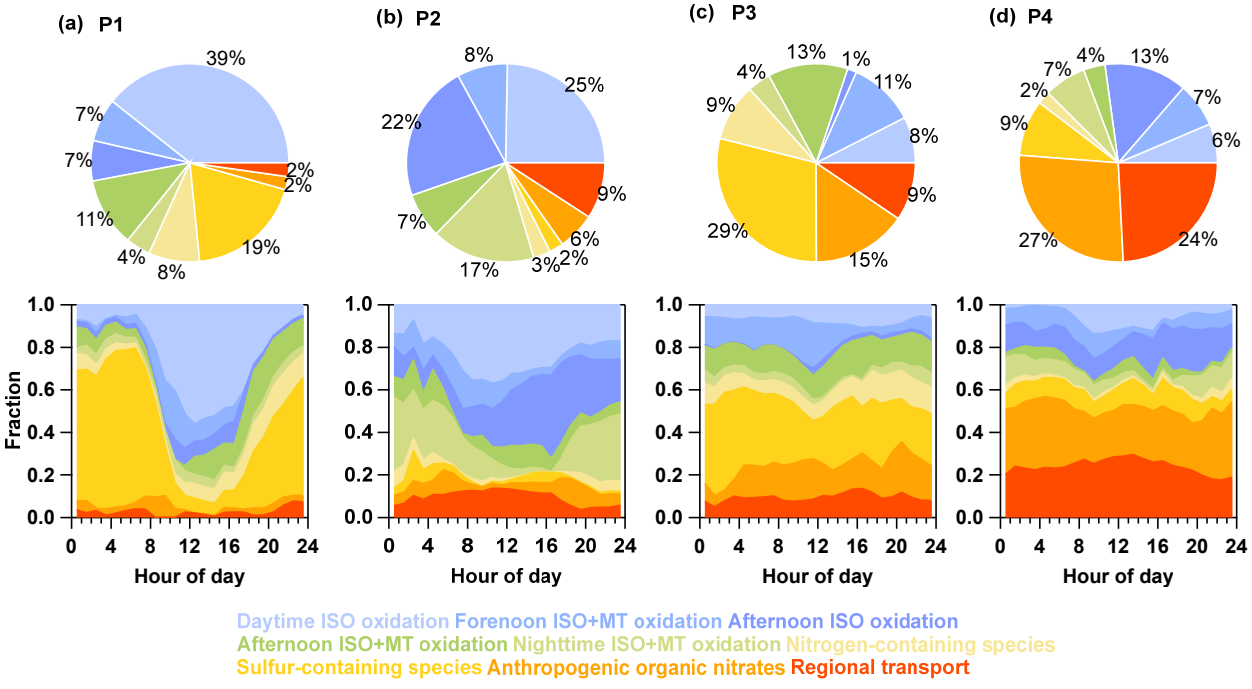

Figure 8: Average contributions and diurnal variations of the PMF-resolved OOM factors during the four periods.

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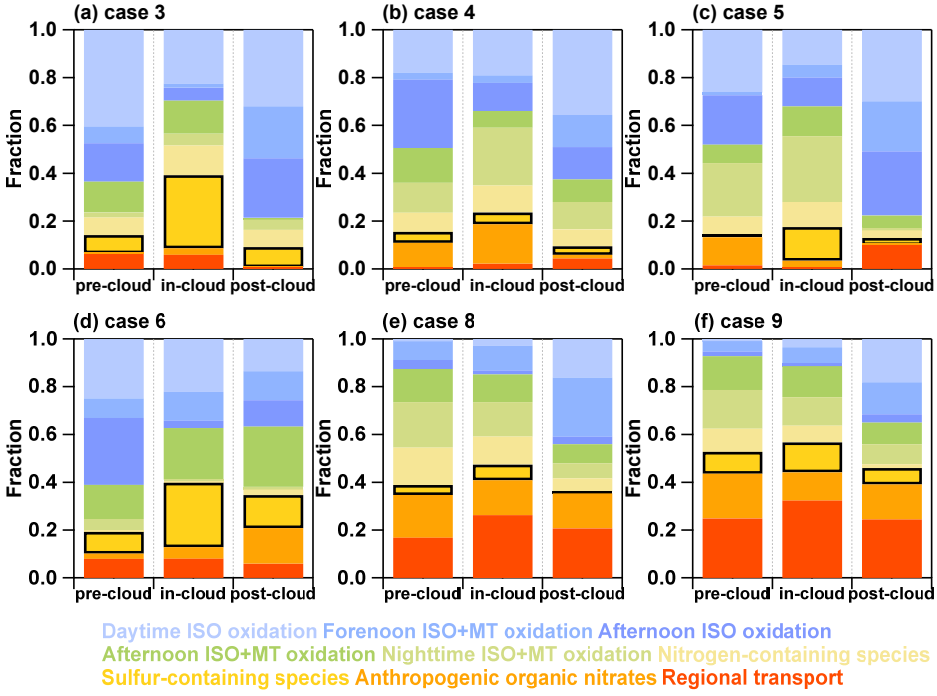

435 **Figure 9: Variations in the contributions of PMF-resolved OOM factors during the pre-cloud, in-cloud, and post-cloud stages.**

4 Conclusions

In this study, gas-phase oxygenated organic molecules (OOMs) were comprehensively characterized at a forested mountain station in southeastern China using an iodide-adduct chemical ionization time-of-flight mass spectrometer (I-CIMS). A total of 1503 iodide-adduct ions were identified, with CHO and CHON compounds constituting the dominant fraction of detected
440 OOMs. Volatility analysis showed that intermediate-volatility organic compounds dominated both classes, while CHON compounds exhibited lower volatility than CHO compounds, indicating a stronger tendency for gas-to-particle partitioning. Distinct diurnal patterns of biogenic oxidation products were observed under different meteorological conditions. Kinetic analyses suggested that OH oxidation dominated the atmospheric processing of isoprene, whereas both NO_3 and OH oxidation pathways contributed substantially to monoterpene oxidation, resulting in contrasting formation mechanisms for non-nitrate
445 and nitrate-containing biogenic OOMs.

Positive matrix factorization resolved nine physically meaningful OOM factors, including five biogenic oxidation factors and four anthropogenic-related factors. Biogenic oxidation was the dominant source of OOMs during warm periods, contributing 68–79% of total OOM abundance, whereas anthropogenic influences became increasingly important during cooler and more polluted conditions. The resolved factors revealed clear temporal segregation among daytime photochemical oxidation,
450 afternoon-aged oxidation, and nighttime NO_3-radical-driven chemistry. Correlation analyses and wind-regression results

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further indicated that most biogenic factors were primarily associated with local formation, while aged anthropogenic OOMs exhibited stronger signatures of regional transport.

Cloud processes exerted a substantial influence on OOM abundance and composition through wet scavenging and multiphase chemical processing. During cloud periods, concentrations of isoprene-derived and monoterpene-derived organic nitrates decreased by 75% and 46%, respectively, while the relative contribution of monoterpene organic nitrates increased from 23% to 40%, suggesting distinct cloud-processing mechanisms and hydrolysis behaviours. At the same time, the enhanced contribution of sulfur-containing OOMs during cloud events highlighted the importance of aqueous-phase formation pathways. Overall, these findings demonstrate that cloud processing not only removes OOMs from the atmosphere but also selectively alters their molecular composition and source contributions, emphasizing the coupled roles of BVOC emissions, anthropogenic pollutants, and multiphase chemistry in shaping the evolution of atmospheric organic matter in forested mountain environments.

Data availability

The data are available upon request from the corresponding author Yele Sun (sunyele@mail.iap.ac.cn).

Author contributions

YS designed the research. YiZ, YuZ, WX, WZ, YL, ZZ, BS, NZ, JW, EA and PDC conducted the measurements. YiZ, ZZ, YL, and YuZ analysed the data. LL, XP, EA and ZW reviewed and commented on the paper. YZ, WZ and YS wrote the paper.

Competing interests

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

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