

We thank the two reviewers for their thoughtful and constructive comments, which have helped us improve the manuscript. We have revised the manuscript in response to the comments. Our point-by-point responses are provided below.

Response to Referee #1

Major comments:

While the overall conclusions are generally well supported, several key mechanistic interpretations rely primarily on observational correlations. For example, attributing the observed differences among the four periods mainly to cloud processing is inherently challenging because cloud occurrence is accompanied by substantial changes in temperature, solar radiation, precursor concentrations, and air-mass characteristics. Although these factors are discussed individually, the manuscript would benefit from a more balanced assessment of their combined influences and the associated uncertainties. In particular, it would strengthen the paper to more clearly distinguish conclusions that are directly supported by the observations from those that represent reasonable but less constrained interpretations.

Cloud occurrence was accompanied by concurrent changes in temperature, solar radiation, precursor concentrations, and air-mass characteristics, making it difficult to isolate the effects of cloud processing from field observations alone. We have revised the manuscript to clarify that the differences among the four periods likely resulted from the combined effects of cloud processing, atmospheric oxidation conditions, precursor availability, and meteorological variability, rather than from cloud effects alone.

Specifically, we have added the following discussion in Sect. 3.2:

“It should be noted that cloud occurrence coincided with concurrent changes in temperature, solar radiation, precursor concentrations, and air-mass characteristics. Therefore, the observed differences between cloud-influenced and cloud-free periods

cannot be attributed to cloud processing alone. Rather, the observed OOM composition likely reflects the combined effects of cloud-related processing, precursor availability, atmospheric oxidation conditions, and meteorological variability, with these factors potentially interacting throughout the cloud-influenced periods.”

We have also added a discussion of organic nitrates in the second paragraph of Sect. 3.3.2:

“Although the decrease in ISO-ONs and MT-ONs during cloud periods is consistent with enhanced cloud-related removal, changes in precursor abundance and oxidation conditions may also contribute to the observed variability. Therefore, the observed changes in biogenic organic nitrates cannot be attributed to cloud processing alone and should be interpreted in the context of these concurrent atmospheric changes.”

In addition, the manuscript attributes the formation pathways of several OOM factors primarily to OH- and NO₃-initiated oxidation based on molecular fingerprints, diurnal variations, and estimated oxidation rates. These interpretations are generally convincing and well motivated. However, they would be further strengthened by a more explicit discussion of the uncertainties associated with the PMF factor assignments and the potential overlap among different oxidation pathways. Since several characteristic compounds can be produced through multiple oxidation mechanisms, acknowledging this limitation more explicitly would provide a more balanced interpretation and enhance the robustness of the conclusions.

We agree with the reviewer that the assignment of individual PMF factors involves some uncertainty because OOMs with similar molecular characteristics can be formed through different oxidation pathways. We have clarified this point in the revised manuscript and added a discussion in Sect. 3.4:

“It should be noted that the oxidation pathways represented by the PMF factors are not necessarily mutually exclusive, as individual OOMs may be formed through multiple oxidation mechanisms. Thus, the PMF factors represent dominant chemical signatures rather than uniquely resolved oxidation pathways, and some overlap among pathways

is expected.”

We have also clarified that the proposed oxidation pathways are based on the combined evidence from molecular composition, diurnal variations, precursor characteristics, and estimated oxidation rates, rather than on individual marker compounds alone.

Specific comments:

L49–51. The authors summarize previous I-CIMS observations in forest environments very well. However, since the present study focuses on a mountain site, it would be beneficial to briefly mention previous molecular-level OOM observations conducted at similar atmospheric conditions or high-altitude stations to better highlight the novelty of the present work.

Following reviewer’s suggestion, We have expanded the Introduction to include recent I-CIMS observations from mountain and high-altitude sites, including the southeastern Tibetan Plateau (Yu et al., 2025) and at the Chacaltaya station in the Bolivian Andes (Zha et al., 2024). These studies show that OOM composition at high-altitude sites can be influenced by regional transport, anthropogenic emissions, and free-tropospheric air masses.

Specifically, we added the following sentence to the Introduction:

“Recent measurements at high-altitude sites, including the southeastern Tibetan Plateau and the Chacaltaya station in the Bolivian Andes, have shown that OOM composition in mountain environments is influenced by anthropogenic emissions, regional transport, and free-tropospheric air masses. (Yu et al., 2025; Zha et al., 2024a).”

L118–126. The semi-quantitative calibration approach is only briefly described in the main text. Although detailed information is provided in the Supplement, one or two additional sentences summarizing how the relative sensitivity and transmission efficiency were determined would help readers unfamiliar with this method.

We have added two sentences to Sect. 2.2.1 to briefly describe the calibration approach. Instrument sensitivities were constrained using voltage-scanning experiments to

characterize the relative sensitivity of individual OOMs, while the dependence of ion transmission efficiency on analyte mass was parameterized to account for mass-dependent transmission effects. The resulting sensitivity and transmission-efficiency relationships were then applied to convert the measured ion signals into semi-quantitative OOM mixing ratios. Detailed calibration procedures and equations are provided in Text S1.

L200. When discussing the lower volatility of CHON-OOMs, the authors may also cite laboratory studies demonstrating that organic nitrates preferentially partition into the particle phase due to their relatively low volatility.

We have added Aruffo et al. (2022) to the relevant discussion. This laboratory study showed that the gas–particle partitioning of organic nitrates from α -pinene photo-oxidation is strongly influenced by volatility, with lower-volatility ONs preferentially partitioning into the particle phase. We added the following sentence to Sect. 3.2:

“Lower-volatility organic nitrates have also been shown to preferentially partition into the particle phase, consistent with their enhanced condensability (Aruffo et al., 2022).”

L235-236. In Sect. 3.3, the authors estimated OH and NO₃ radical concentrations using the steady-state approach. Is the steady-state assumption still valid under cloud conditions?

We sincerely thank the reviewer for raising this important point. The steady-state assumption may not be strictly valid under cloud conditions. Cloud formation introduces additional multiphase processes and potential sources and sinks of atmospheric radicals that are not fully accounted for in our simplified calculation. We therefore regard the estimated OH and NO₃ concentrations as approximate values with relatively large uncertainties, rather than as direct quantitative measurements.

The estimates are nevertheless useful for the purpose of this study because they are used primarily to compare the relative oxidation rates of different BVOCs by OH, O₃, and NO₃, rather than to determine absolute radical concentrations. In addition, the estimated

OH concentration is of the same order of magnitude as the subsequent direct HOx measurements at the SH site, which provides an independent constraint on the estimate. We have clarified these points in the revised manuscript and added the following statement to Text S3:

“It should be noted that the steady-state assumption may not be strictly satisfied under cloud conditions because cloud-related multiphase processes can introduce additional sources and sinks of atmospheric radicals. Therefore, the estimated OH and NO₃ concentrations (Text S4) should be regarded as approximate values with relatively large uncertainties. In this study, these estimates are primarily used to assess the order of magnitude and relative importance of competing oxidation pathways, rather than to derive precise absolute oxidation rates.”

L272–291. The discussion of cloud impacts on organic nitrates focuses mainly on wet scavenging and hydrolysis. The authors may consider mentioning that differences in aqueous solubility among different classes of organic nitrates could also contribute to the observed compositional changes during cloud events.

We have expanded Sect. 3.3.2 to consider the role of aqueous solubility in addition to wet scavenging, gas–particle partitioning, and hydrolysis. We also added Zare et al. (2019), which showed that isoprene-derived nitrates can contribute substantially to aqueous and in-cloud organic nitrate pools because of their relatively high water solubility.

The following discussion has been added:

“Differences in aqueous solubility among ONs may further affect their uptake into cloud droplets and subsequent removal. Previous modelling and observational studies have shown that isoprene-derived nitrates are generally more water-soluble and can contribute substantially to aqueous and in-cloud organic nitrate pools (Zare et al., 2019).”

We have also revised the subsequent discussion to indicate that the stronger decrease in ISO-ONs may result from the combined effects of aqueous uptake, wet scavenging,

and hydrolysis, rather than from a single removal mechanism.

L347–348. The manuscript attributes the nighttime enhancement of the Nighttime ISO+MT oxidation factor primarily to NO₃ chemistry. Since gas-particle partitioning can also influence the abundance of condensable oxidation products, it would be worthwhile to briefly discuss whether partitioning changes between daytime and nighttime could contribute to the observed variations.

Gas-particle partitioning may contribute to the temporal variation of condensable oxidation products, so we examined the TDLIF measurements to evaluate this possibility. We calculated the particle-phase fraction of ONs as $p\text{ONs}/(p\text{ONs} + g\text{ONs})$. During P2, this fraction reached a maximum at approximately 16:00 and then decreased after sunset, rather than increasing during nighttime. Thus, the nighttime enhancement of the Nighttime ISO+MT oxidation factor cannot be explained solely by increased partitioning of ONs into the particle phase.

We have added this analysis and discussion to Sect. 3.4.3:

“Gas-particle partitioning may also influence the temporal variation of condensable ONs. However, analysis of the TDLIF measurements showed that the particle-phase fraction of ONs, calculated as $p\text{ONs}/(p\text{ONs} + g\text{ONs})$, did not increase during nighttime in P2. Instead, the ratio reached a maximum at approximately 16:00 and decreased after sunset (Fig. S11). This pattern suggests that the nocturnal enhancement of the Nighttime ISO+MT factor cannot be explained solely by increased partitioning to the particle phase and is more consistent with enhanced nighttime chemical production, particularly through NO₃-initiated oxidation.”

We have also moderated the interpretation to acknowledge that partitioning may contribute to the observed variability. The nighttime increase, together with the molecular composition, temporal behavior, NO₃ chemistry, and agreement with laboratory-generated NO₃ oxidation products, is more consistent with enhanced nighttime chemical production as the main driver.

L447-448. The terms "warm periods" and "cool periods" are used throughout the manuscript. For clarity, I suggest indicating the approximate mean temperatures when these periods are first introduced.

We have added the approximate mean temperatures when the terms “warm periods” and “cool periods” are first introduced in the manuscript. The warm periods had a mean temperature of approximately 20 °C, while the cool periods had mean temperatures below 15 °C.

Response to Referee #2

Section 3.3.1: Following the discussion of the diurnal variations of non-nitrate biogenic OOMs in Fig. 4, kinetic calculations are further used to evaluate the relative roles of OH- and O₃-initiated oxidation. Given that OH concentrations were estimated rather than directly measured, the atmospheric meaning of the calculated reaction-rate ratios could be further clarified. For example, do these ratios primarily represent the relative reaction rates of the precursor VOCs with different oxidants, or can they be further interpreted in terms of the relative importance of different oxidation pathways? In addition, please discuss whether the observed diurnal patterns of the OOMs in Fig. 4 provide additional observational support for the proposed oxidation pathways.

We thank the reviewer's comments. The calculated rate ratios primarily describe the relative reaction rates of the BVOC precursors with OH and O₃ under the assumed atmospheric conditions. Because OH concentrations were estimated rather than directly measured, these ratios should not be interpreted as quantitative contributions of the corresponding oxidation pathways to OOM formation. We have clarified this point in Sect. 3.3.1 and added the following statement:

“Because the OH concentrations were estimated rather than directly measured, the calculated rate ratios are best interpreted as relative reaction rates of the precursor VOCs with OH and O₃ under the observed conditions, rather than as quantitative contributions of the corresponding oxidation pathways to OOM production.”

We have also compared the calculated rate ratios with the observed diurnal variations in Fig. 4. The pronounced daytime enhancement of biogenic oxidation products is consistent with active photochemical oxidation, while the temporal behavior of monoterpene-derived products suggests an additional contribution from ozonolysis. We have therefore clarified that the kinetic calculations and the observed diurnal patterns provide complementary qualitative evidence rather than independent quantitative constraints on the oxidation pathways.

Specifically, we added the following statement to Sect. 3.3.1:

“The observed diurnal variations in Fig. 4 provide additional qualitative evidence for these contrasting oxidation regimes. The pronounced daytime enhancement of both isoprene- and monoterpene-derived products is consistent with active photochemical oxidation, while the sustained abundance and delayed maxima of monoterpene-derived products, particularly during P2, suggest an additional contribution from ozonolysis. Taken together, the kinetic calculations and observed temporal patterns suggest that isoprene oxidation at the SH site was predominantly associated with OH chemistry, whereas monoterpene oxidation involved both daytime OH oxidation and O₃-initiated ozonolysis.”

Section 3.3.1: P1 and P3 were both influenced by clouds but showed distinctly different responses of biogenic OOMs. Although the effects of temperature, solar radiation, and precursor availability have been well discussed, it remains less clear how meteorologically regulated OOM production and cloud-related removal jointly determine the observed OOM responses. Please further discuss how the interplay between these processes leads to the contrasting responses of biogenic OOMs during P1 and P3.

The different responses of biogenic OOMs during P1 and P3 are unlikely to be explained by cloud occurrence alone. The two periods differed substantially in temperature, solar radiation, and precursor availability, which affected both BVOC emissions and atmospheric oxidation, while cloud processing and precipitation provided additional pathways for uptake and removal. We have expanded Sect. 3.3.1 to discuss these processes together.

During P1, the relatively high temperature and solar radiation favored BVOC emissions and photochemical oxidation, which appeared to sustain OOM production despite concurrent cloud-related uptake and removal. In contrast, the substantially lower temperature and solar radiation during P3 suppressed BVOC emissions and photochemical production. Persistent precipitation and cloud processing may have further enhanced the removal of soluble OOMs and their precursors. The much lower

OOM concentrations during P3 therefore likely resulted from the combined effects of reduced precursor supply and oxidation and enhanced cloud- and precipitation-related losses.

We added the following discussion to Sect. 3.3.1:

“During the cloud-influenced period P1, nearly all oxidation products exhibited pronounced afternoon maxima. This pattern was likely driven by enhanced biogenic emissions under relatively high daytime temperature and solar radiation, which increased the availability of isoprene and monoterpenes (Fig. 1) and promoted their photochemical oxidation despite the presence of clouds. In addition, the high humidity and persistent cloud droplets during P1 may have facilitated aqueous-phase oxidation of water-soluble intermediates, contributing to the formation of oxygenated products through cloud processing (Altieri et al., 2006). Thus, although cloud-related uptake and removal occurred concurrently, the relatively strong precursor supply and oxidation conditions during P1 appear to have sustained net OOM production and the pronounced daytime enhancement.

In contrast, P3 was also strongly influenced by clouds and precipitation but occurred under substantially lower temperature and solar radiation. The resulting suppression of biogenic emissions (Hakola et al., 2006) reduced the availability of isoprene and monoterpenes and limited the formation of their oxidation products. Persistent precipitation and cloud processing may have further enhanced the removal of soluble OOMs and their precursors through aqueous-phase uptake and wet scavenging. Consequently, the much lower OOM concentrations in P3 likely resulted from the combined effects of reduced precursor emissions, weaker photochemical oxidation, and enhanced cloud- and precipitation-related removal. These contrasting responses indicate that the effects of clouds on OOM abundance cannot be considered independently of the meteorological conditions governing precursor emissions and atmospheric oxidation.”

Section 3.4.4: The enhancement of the sulfur-containing factor during cloud events,

together with its relationship with RH, provides useful evidence for aqueous/multiphase processing. However, organosulfur compounds may also be affected by precursor availability and transport. I suggest slightly moderating the relevant wording and describing these observations as being “consistent with” or “supporting” aqueous/multiphase formation, rather than implying a unique formation pathway.

We have revised the discussion in Sect. 3.4.4 to distinguish evidence consistent with aqueous/multiphase processing from evidence for a specific formation pathway. The increase in the sulfur-containing factor during cloud events and its positive relationship with RH support a contribution from aqueous/multiphase processes, but precursor availability and changes in air-mass transport may also affect the observed sulfur-containing compounds. These factors cannot be fully separated from cloud-related effects in the present observations.

The corresponding statement in the Conclusions has also been revised to maintain the same interpretation. The revised discussion in Sect. 3.4.4 reads:

“The frequent cloud events observed at the SH site may provide favorable conditions for aqueous/multiphase processing and potentially enhance the formation of organosulfur compounds. A comparison of factor contributions before, during, and after cloud events revealed an increase in this factor during cloud events (Fig. 9), consistent with enhanced aqueous/multiphase processing (McNeill, 2015; Brüggemann et al., 2020). The positive relationship between sulfur-containing species and ambient humidity (Fig. S12) provides further evidence for the possible involvement of aqueous/multiphase processes. The summed concentration of sulfur-containing molecules increased with RH, indicating that their abundance was enhanced under more humid conditions. Elevated RH can increase aerosol liquid water content and promote cloud droplet formation, potentially facilitating the uptake and transformation of sulfur-containing precursors through multiphase reactions. However, precursor availability and changes in air-mass transport may also influence the abundance of sulfur-containing species, and these effects cannot be fully separated from those of cloud and

humidity in the present observations. Therefore, the observed enhancement during cloud events and its positive relationship with RH are consistent with an important contribution from aqueous/multiphase processing, rather than providing evidence for a unique formation pathway.”

Section 3.4.2: The Afternoon ISO oxidation factor shows a moderate correlation with IEPOX-SOA ($r = 0.59$), which is interpreted as evidence for a linkage between gas-phase OOMs and particle-phase SOA formation. However, both gas-phase isoprene oxidation products and IEPOX-SOA are also expected to respond to common controlling factors, such as isoprene precursor abundance and photochemical activity. Please briefly discuss whether these common influences may partly contribute to the observed correlation, in addition to direct gas-to-particle processing.

The correlation between the Afternoon ISO oxidation factor and IEPOX-SOA ($r = 0.59$) may partly reflect their common dependence on isoprene precursor abundance and photochemical activity, in addition to gas-to-particle processing. We have revised Sect. 3.4.2 to make this point explicit and to avoid interpreting the correlation as a direct quantitative precursor–product relationship.

The revised text reads:

“Notably, this factor showed a moderate correlation with the IEPOX-SOA factor resolved from ToF-ACSM measurements ($r = 0.59$), suggesting a link between gas-phase isoprene oxidation products and particle-phase IEPOX-SOA formation. This correlation may partly reflect gas-to-particle processing of isoprene oxidation products, but it may also arise from their common dependence on isoprene precursor abundance and photochemical activity. Therefore, the correlation should not be interpreted as direct evidence of a quantitative precursor–product relationship. Nevertheless, the concurrent variation of the Afternoon ISO oxidation factor and IEPOX-SOA is consistent with a role for gas–particle processing in the evolution of isoprene oxidation products and SOA formation at the SH site.”

Texts S5–S6: Several equations describing the oxidation-rate calculations appear to

contain inconsistent reactant concentrations or rate coefficients. For example, [ISO] appears in the monoterpene oxidation equations. Please carefully verify these equations, clarify whether these inconsistencies are typographical errors, and explicitly provide the reaction-rate coefficients used in the calculations so that the reported rate ratios can be readily followed.

We have carefully rechecked the oxidation-rate calculations in Texts S5–S6. The inconsistent reactant concentrations in the equations, including the appearance of [ISO] in the monoterpene oxidation equations, were typographical errors in the presentation and did not affect the calculations or the reported rate ratios. We rechecked the reactant concentrations, reaction-rate coefficients, and calculated oxidation rates to ensure consistency.

Texts S5–S6 have been revised to simplify and reorganize the equations and make the calculation procedure easier to follow. We have also added a table listing all reaction-rate coefficients used in the calculations, allowing the oxidation rates and rate ratios to be checked and reproduced more readily.

References

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