We would like to thank the reviewer for their valuable and constructive comments/suggestions that helped improve our manuscript. We have carefully addressed all suggestions and revised the manuscript accordingly. Below you will find our point-by-point responses. Reviewer comments and suggestions are written in black, responses in blue.

RC2: 'Comment on egusphere-2025-141', Anonymous Referee #2, 06 May 2025

This study investigated the molecular-level chemical characteristics of organic aerosols collected from the Amazon rainforest during several seasons in 2018 and 2019. Orbitrap MS data provided extensive information on organic molecules, offering valuable insights for readers in this field. I recommend that the authors address the following comments:

We thank the reviewer for the constructive feedback and the effort dedicated to improving our manuscript.

Main Evaluation:

Although the authors emphasize the use of vertical resolution sampling in the abstract, the main text lacks sufficient comparison and discussion of results at different sampling heights. As shown in lines 366–367 and 390–392, the chemical compositions at different altitudes appear to be largely similar. If this is indeed the case, it is necessary to further explain the rationale for sampling at multiple heights. Currently, the results do not fully demonstrate the scientific value of height-resolved measurements.

We thank the reviewer for the suggestion to provide a more detailed discussion of the height-resolved measurements. Due to the non-targeted approach applied in this study, it was challenging to identify consistent vertical trends in the chemical composition of OA at ATTO, as the results varied across compound classes, height levels, seasons, and between day- and nighttime samples. Nevertheless, we re-evaluated all height-resolved data and adjusted the discussion to reflect the actual observations, without aiming to generalize specific trends.

As a result, we added a new section ("3.2.3 Height-dependency of the background OA characteristics") in line 409ff in the revised manuscript focusing on the vertical distribution of background OA. In addition, Figures 3 and 4 in the main manuscript and Figures S13–S16 in the supplementary information have been revised to display all measured heights. New discussions on the observed vertical differences in OA composition were included in lines 491ff; 532ff; 554ff; 556ff; 576ff, 590ff and 607ff of the revised manuscript.

The authors are advised to strengthen the discussion in the following areas:

1. Are there observable chemical differences between sampling heights under nighttime or specific meteorological conditions? For example, do chemical components above and below the forest canopy exhibit nighttime differences due to aerosol deposition, vertical mixing, or local chemical reactions?

We thank the reviewer for these insightful questions that we also consider to be relevant for our discussion. With regard to nocturnal differences in chemical composition below and above the forest canopy, only samples from the dry season 2019 can be considered, as this was the only period when sub-canopy sampling at 0 m was conducted. Dry season conditions are generally associated with more uniform vertical distributions and enhanced mixing of aged, oxidized compounds, driven by prevailing southwesterly winds, increased surface roughness, and turbulent conditions. Consequently, height-resolved differences in OA composition during the dry seasons of 2018 and 2019 were generally low, due to convective mixing leading to more homogeneous chemical distributions. To better capture vertical gradients under more stable conditions, subsequent wet season campaigns for follow-up studies included sampling both, below and above the canopy.

Nevertheless, notable differences were observed in the dry season 2019 and are discussed in line 607ff of the revised manuscript:

"However, the dry season 2019, which included sampling at three different times and at sub-canopy level (0 m), revealed unique patterns. SV-OOA and CHOS compounds in areas *I* and *II* peaked at 80 m during nighttime, consistent with gas-particle partitioning favored by cooler, stable layers above the canopy. CHON compounds were most abundant at 0 m and 80 m in the morning but diminished at 320 m. These patterns underline the importance of both vertical stratification and local chemical processing in modulating aerosol composition at different heights and times of day. Mendonça et al. (2025) noted that dry season nights at ATTO, characterized by southwesterly winds and enhanced surface roughness, can exhibit deeper but more turbulent boundary layers, allowing complex layering and submesoscale motions to form, which could explain the varied height-dependent signals observed in this campaign. Moreover, the presence of the highest CHOS and SV-OOA signals at 80 m during nighttime suggests a zone of active condensation and SOA formation just above the canopy, where gas-particle partitioning is favored by cooler and more stable stratification. The fact that CHON species were relatively suppressed at 320 m both during morning and daytime indicates limited upward transport of nitrogen-containing precursors or their rapid transformation near the surface. The chemical differences between 0 m and 80 m, particularly for CHON and CHO species in areas *II* and *III*, also suggest that in-canopy processes such as deposition, emissions, and light penetration significantly modulate chemical composition. Together, these observations highlight the sensitivity of nighttime aerosol chemistry to fine-scale vertical structure and suggest that sub-canopy and canopy-top levels may act as chemically distinct compartments in the nocturnal boundary layer during the dry season."

2. If overall differences are minimal, does this indicate strong vertical mixing or a stable boundary layer structure in the study area? Discussion of this would help explain the observed vertical uniformity.

We agree with the reviewer that the discussion would be improved by strengthening it regarding to boundary layer dynamics. A recent study of Mendonca et al., 2025 showed that the boundary layer dynamics at ATTO can vary significantly depending on the seasonal conditions. If prevalent southeasterly winds direction are prevalent, what is typical for dry seasons at ATTO (Fig S4), higher surface roughness and increased turbulence can be observed, leading to more uniform vertical distributions and mixing of aged, oxidized OA. Contrarily, under wet season conditions, when the wind predominantly arrives from the northeast (Fig S5) and the surface roughness is relatively low, the nocturnal boundary layer is shallow (typically 80–120 m), limiting vertical exchange and favoring accumulation of semivolatile species near the canopy top and allowing upper levels (e.g. 320 m) to be decoupled and enriched in aged or transported aerosol components.

We included these points in our discussion in the revised manuscript in lines 494ff, 557ff, 608ff.

3. Does height-resolved sampling still provide value in identifying potential source regions, reaction mechanisms, or deposition processes? The authors are encouraged to further discuss this issue in their results.

We agree with the reviewer that pointing out the value of height-resolved sampling for identifying potential source regions, reaction mechanisms, or deposition processes would improve the discussion. We consider the newly included height-resolved interpretations of the chemical composition of OA in the revised manuscript as very insightful regarding the topics mentioned.

The revised manuscript underlines potential source regions in lines 495ff, 537f, 555f, 577ff. Furthermore, the influence of reaction mechanisms is pointed in lines 534f, 557, 611f and deposition processes are taken into account in lines 590f, 615f.

Specific comments:

Line 80: Although the study includes sampling at multiple heights, the introduction does not clearly articulate the scientific rationale or objectives of this vertical sampling design. Given that atmospheric composition, photochemical processes, and pollutant transformations vary significantly with altitude, it is essential to clarify why different altitudes were chosen and how this contributes to the overall research objectives.

We thank the reviewer for this valuable comment. The rationale for the vertical sampling design has now been clarified in the introduction section (lines 82ff in the revised manuscript) as follows:

“This height-resolved sampling strategy was designed to capture the influence of biogenic emissions near the forest canopy, photochemical transformation processes above the canopy, and the impact of regionally transported, aged aerosol in the upper boundary layer. In particular, sub-canopy and near-canopy samples reflect local sources and early secondary organic aerosol formation, whereas the 320 m platform provides insight into regional and long-range transport contributions. These data enable a more detailed separation of local and regional influences on OA composition. It is important to note, however, that vertical differences are strongly influenced by seasonal and diurnal meteorological variability, including boundary layer dynamics, atmospheric mixing, and air mass history. Thus, height-dependent measurements must be interpreted within the broader context of meteorological conditions.”

Lines 105–110: How many filters were collected at each altitude for each season? Please add this information.

We thank the reviewer for this suggestion. We have added the requested information to line 111 (track-changes version):

“Ambient PM2.5 filter samples were collected at three different heights at the tower (wet season 2018: 42 m – 15 filters + 2 blank filters, 150 m – 14 filters + 2 blank filters, 320 m – 15 filters + 2 blank filters; dry season 2018 : 80 m - 18 filters + 2 blank filters, 150 m – 18 filters + 2 blank filters, 320 m – 18 filters + 2 blank filters; wet season 2019: 80 m – 22 filters + 2 blank filters, 150 m – 22 filters + 2 blank filters, 320 m – 22 filters + 2 blank filters ; dry season 2019: 0 m – 16 filters + 2 blank filters, 80 m – 14 filters + 2 blank filters, 320 m – 16 filters + 2 blank filters,) using borosilicate glass microfiber filter bonded with PTFE (Pallflex® Emfab, 70 mm diameter).”

Lines 185–186: The manuscript defines “background compounds” as those observed in over 75% of the samples. However, it is unclear how this classification was determined. Is it based solely on matching molecular formulas, or does it also consider MS² data to confirm structural similarity? Since compounds with the same molecular formula may have different structures and properties, clarifying the criteria used for this definition is crucial. I recommend that the authors clearly describe this aspect in the Methods section to ensure transparency and reproducibility.

We thank the reviewer for pointing out the missing information. Background compounds were defined as those detected in more than 75 % of all samples, based on their presence rather than signal intensity. As the analytical setup included an LC system upstream of the ESI-HR-Orbitrap-MS, molecular formula assignment was supplemented by retention time information. This additional dimension reflects compound polarity and allows for improved differentiation of chemical structures in cases of identical molecular formulas, and even enables the distinction between isomers.

We have revised the sentence in line 195 (track-changes version) as follows:

“Only compounds that were observed in more than 75 % of all samples based on their presence (identical molecular formula + retention time) were defined as background compounds. They presumably describe the local OA characteristics, as it is assumed that they are not dependent on individual emission events. For the variable OA characteristics, the evaluation was carried out by subtracting the peak areas of the previously determined background compounds from the peak areas of the total number of identified compounds (= background compounds + variable compounds). The remaining compounds are attributed to irregular atmospheric events, presumably caused by different meteorological conditions. Compounds that were only detected once in the respective data set were excluded as they were not considered representative.”

Lines 196–198: Is this description a summary? What figure or table does the conclusion refer to?

We thank the reviewer for pointing out the lack of information. We changed the paragraph in the track-changes version in line 204 ff as follows:

"The chemical composition of the SOA samples was mainly influenced by seasonal effects during the measurement campaigns. A total of 2336 molecular formulas could be assigned, of which 699 were in the range of < 250 Da, 1309 between 250 Da and 450 Da, and 328 above > 450 Da. Typical mass spectra are shown in Fig. S 20. Molecular weights (MW) in the range below 250 Da could be assigned to the majority of observed substances in both seasons, while the aerosol composition in the dry season additionally showed signals in the oligomeric range between 300 and 450 Da with lower intensity."

Furthermore, a typical mass spectra were included in Fig S20.

Lines 208–210: It would be preferable to include specific contributions from composite subpopulations from remote/suburban/urban environments in the literature.

We agree with the reviewer and have included the subgroup contributions of CHON and CHONS (negative ion mode) from selected studies across remote, suburban, and urban environments. The revised sentence in line 218 (track-changes version) now reads:

"This trend is in good agreement with similar studies from remote environments (e.g. Amazonia, Brazil: $CHO^{(-)}$ with 58-63 %, $CHON^{(-)}$ with 25-30 %, $CHOS^{(-)}$ with 10 %, $CHONS^{(-)}$ with 2 %, Kourtchev et al., 2016; Hyytiälä, Finland: $CHO^{(-)}$ with 54.8 ± 2.2 %, $CHON^{(-)}$ with 21 ± 3 %, $CHOS^{(-)}$ with 16 ± 3 %, $CHONS^{(-)}$ with 5.4 ± 2.2 %, Kourtchev et al., 2013), while studies from a suburban and urban environment revealed enhanced contributions of CHON and CHONS compounds (Pearl River Delta region, China: $CHON^{(-)}$ with 34 %, $CHONS^{(-)}$ with 8 %, Lin et al., 2012; Cambridge, UK: $CHON^{(-)}$ with 33 %, $CHONS^{(-)}$ with 21-26 %, Rincón et al., 2012; Shanghai, China: $CHON^{(-)}$ with 21-23.7 %, $CHONS^{(-)}$ with 11.2-16.6 % , Wang et al., 2017), proving an increased relevance of nitrogen and sulfur chemistry in more polluted areas."

Lines 246–247: Given that CHONS account for only 1%, classifying them as major components seems questionable.

We agree with the reviewer and revised the sentence in line 257ff of the track-changes version as follows:

"The molecular formulae in the wet seasons are predominated by the CHO subgroup (90 ± 7) %, followed by CHOS with (8 ± 7) %, CHONS (1 ± 1) %, and CHON (1 ± 2) %. The dry seasons show a comparable predominance of the CHO subgroup (93 ± 3) % and an equal contribution of CHONS compounds (1 ± 1) % but an increased fraction of CHON compounds (4 ± 1) % and a decreased fraction of CHOS compounds (3 ± 2) %."

Lines 275–280: The manuscript discusses the effects of different NOx conditions on reaction mechanisms or product distributions but does not clearly define the criteria used to distinguish between high NOx and low NOx conditions. Additionally, the actual NOx concentrations observed in this study are not specified in the main text. I recommend that the authors clearly specify the classification criteria and provide the NOx data used in this work to enhance the scientific rigor and reproducibility of the discussion.

We thank the reviewer for this valuable suggestion. We agree that providing a clearer definition of the NO_x regimes and including actual concentration data enhances the transparency and reproducibility of our discussion.

In the revised manuscript, we now explicitly define the classification of low-NO_x and high-NO_x conditions based on observed NO and NO_2 mixing ratios during the different campaigns in line 290 as follows:

"As shown in Figure S8, NO and NO_2 mixing ratios were generally <0.5 ppb and <1 ppb at 73.3 m and <2 ppb and <0.5 ppb at 0.05 m for the dry season 2018. For the wet seasons 2018 and 2019 NO mixing ratios were <0.25 ppb at 79.3 m and <1.5 ppb at 0.05 m whereas NO_2 mixing ratios were <0.05 ppb at 79.3 m and <0.1 ppb at 0.05 m. NO_x data for the dry season 2019 are lacking due to instrument issues. These conditions are consistent with what is commonly defined as low-NO_x regimes in previous chamber studies (e.g., Krechmer et al., 2015; Paulot et al., 2009; Nagori et al., 2019)."

Lines 409–411: Isoprene-derived organic sulfates (OS) are typically formed through photochemical oxidation, resulting in higher concentrations during the day than at night. However, in this study, the observed CHOS compounds showed higher abundances at night. I recommend that the authors more clearly emphasize the primary formation pathways of isoprene OS to strengthen the underlying principles and credibility of the conclusion that nighttime concentrations exceed daytime levels.

We thank the reviewer for this valuable comment and the opportunity to clarify our interpretation. It is well established that isoprene-derived organosulfates are primarily formed via photochemical oxidation mechanisms, involving reactive intermediates such as ISOPOOH and IEPOX under low-NO conditions, often leading to enhanced production during the daytime.

However, in our study, we observed consistently higher CHOS signal intensities at night across all seasons. To address this apparent contradiction, we have revised the discussion to more clearly distinguish between formation processes and partitioning behavior in line 483ff as follows:

"It is well established that isoprene-derived organosulfates are primarily formed via photochemical oxidation mechanisms, involving reactive intermediates such as ISOPOOH and IEPOX under low-NO conditions, often leading to enhanced production during the daytime (Surratt et al., 2007; Surratt et al., 2008). However, in our study, we observed consistently higher CHOS signal intensities at night across all seasons. While OS formation is photochemically driven, the nocturnal enhancement in signal intensities is likely not indicative of in situ nighttime production, but instead reflects more efficient partitioning into the particle phase during cooler nighttime conditions. This explanation is consistent with the findings of Gómez-González et al. (2012) and Kourtchev et al. (2014b), who also reported strong diurnal differences driven by temperature-dependent gas-particle partitioning. "

Lines 416 and 430: Please specify in the appendix the number of standard compounds used and which standard compounds were used, and indicate which substances each standard identified or confirmed.

We thank the reviewer for the helpful suggestion. As requested, we have included a specification of the standard compounds used in the analysis in Table S5 in the supplementary information of the revised manuscript. Since LC was used upstream the ESI-HR-Orbitrap-MS system, compounds could be assigned unambiguously by comparing the exact mass and retention time of the compound to be identified and the authentic standard used.

Lines 598–600: Previous studies have shown that organic sulfur emissions from soil increase with soil moisture, suggesting that forest soil sources may be stronger during the rainy season. Therefore, it is recommended that the authors further explore whether the vertical distribution of CHOS and CHONS is influenced by soil emissions—especially during nighttime or stable boundary layer conditions. A decreasing concentration gradient from bottom to top could support this hypothesis and strengthen the discussion on the formation and source attribution of CHOS/CHONS compounds.

We appreciate the reviewer's suggestion to further explore the potential influence of forest soil emissions on the vertical distribution of CHOS and CHONS compounds. Indeed, previous studies have highlighted the role of soil-derived organic sulfur emissions under moist conditions. However, the scope of this study is to provide a comprehensive, seasonally averaged overview of the organic aerosol (OA) composition at the ATTO site. As shown in Table I (background OA characteristics) the wet season 2018 revealed 11-18 % of CHOS compounds whereas the contribution for the wet season 2019 is only 2-4 % and for the dry season 2018 4-5 %. The dry season 2019 had almost no significant contribution of CHOS compounds (0-1 %). CHONS compounds showed more or less the same contribution for all seasons (0-2 %). For the total OA characteristics (background+variable compounds), the wet seasons 2018 and 2019 showed the lowest contribution of CHOS compounds (9-11 % and 17-19 %) whereas the dry seasons 2018 and 2019 exhibited values from 22-23 % and 17-19 % respectively. Therefore, the effects of enhanced soil emissions should be studied event-based and may be masked by temporal averaging. Multiple sources and formation pathways contribute to CHOS/CHONS compounds. For instance, anthropogenic emissions and biomass burning, which are more prevalent during the dry season, lead to elevated CHOS/CHONS levels and complicate a source-specific interpretation based on seasonally averaged data. Therefore, a more targeted approach focusing on specific marker compounds and stratified by meteorological parameters such as rainfall or boundary layer stability would be more appropriate to assess soil-driven emissions.

In fact, such a targeted dataset with rain-event-resolved sampling and focus on selected CHOS compounds has already been collected and will be the subject of a dedicated follow-up publication. This future work will aim to directly address the role of forest soil emissions under varying hydrometeorological conditions and their vertical distribution.

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Author comment:

We hope that the revised manuscript and the responses provided here fully address the reviewer's concerns. We would be happy to clarify any remaining points.