Responses to reviewer

Responses: Answer to reviewer 3

Reviewer 3' comments in blue

Responses Answers from authors in black

Suggested new text blocks in italic

Reviewer 3

The manuscript by D. Pinheiro-Oliveira does an attempt to quantify CH4 and BVOC emissions from different forest ecosystems in the Amazon. Doing so gas samples were collected at one point in time (December 2021), along duplicated transects in three different forest types. Along with BVOC and CH4 data, data of potential drivers were collected.

In principle this are interesting data. Despite no major methodological flaws are presented in the paper/with the data set, I have several concerns. These concerns are listed below, both in general and specifically.

First, the data set has a very limited temporal coverage, i.e. one time point that has been repeated the next day for a spatially duplicated transect in one specific period, i.e. December 2021. As a result, one forest type has 12 samples from a very specific period. This also is the case for dynamic parameters, such as soil moisture and temperature, which are used as drivers to explain the observed BVOC and CH4 fluxes. As a result, this rather long paper is loaded with sections in the discussion that are very speculative (see examples below) that are not fully supported by data. A next step is than a danger of overstating some conclusions (see examples below) in the discussion. Indirectly the authors mention this limitation in the description of the statistical methods where they reduce the number of explanatory variables due to low amount of data per forest type, i.e. 12. In addition to this, it is also unclear using the PCA in figure 7, how predictor variables were finally selected/retained.

We appreciate the careful review and the concerns raised by the Reviewer regarding the limited temporal coverage of our dataset and its implications for dynamic parameters, as well as for the explanatory power of statistical analyses. This feedback is very constructive and has enabled us to revisit key points in the manuscript to improve clarity and to outline our study's limitations more explicitly.

Below we address each comment:

On the limited temporal coverage and sample size: We recognize that our study was conducted over a very specific period, with data collected during two consecutive days (for each forest type) in December 2021. This limited temporal (and spatial) coverage was partly due to fieldwork constraints: the measurements were physically and logistically challenging, as the team had to carry sampling material over long distances and difficult terrain.

We are aware that this restricted temporal coverage presents limitations, particularly for dynamic parameters, which can vary significantly across seasons and weather conditions. However, these measurements managed to capture spatial variability across forest types, while controlling for interseasonal variability under the same meteorological conditions. Thus, while this study does not cover large temporal variability (e.g., diurnal and seasonal) replicability, which might pose some limitations to the study's conclusions, this does not compromise the consistency of the distinct spatial patterns observed within and across forest types.

To the best of the authors' knowledge, this is the first study comparing different forest types regarding net soil/litter–atmosphere exchange of BVOCs and methane in Amazonian forest types, and can therefore be seen as an exploratory study focusing on the main differences and drivers of gas fluxes across forest types within the same season. A follow-up study could extend it through additional and longer field campaigns, or even long-term measurements. In the revised manuscript, we suggest discussing our temporal limitations in more detail; details on our revisions are given below.

On the speculation in the discussion: While it is true that some points raised in the discussion are exploratory and attempt to broaden the implications of the observed BVOC and CH_4 fluxes, care has been taken to base our arguments on previous literature and the best available interpretation of our dataset. Nevertheless, we agree with the Reviewer that this aspect can be improved. To address this concern, we have reviewed the manuscript and revised speculative sections in the discussion to ensure that all statements are fully supported by the data. Details on our revisions are provided below.

On the PCA and Linear Models: For the PCA, we included all variables available in our dataset to explore the relationships between forest types and environmental predictors without imposing prior restrictions. While the PCA explained 48.5% of the total variance (PC1: 31.6%, PC2: 12.6%), the forest types did not separate completely in the biplot. This limited separation suggested that the relationships between drivers and fluxes were not fully captured by the PCA. Consequently, we applied linear regression models to identify specific drivers for each gas and forest type, as these models allow for a more targeted understanding of the variables influencing the fluxes.

To address the limitation of sample size and to maximize the statistical power of our linear regression models, we followed a systematic approach:

A maximum of two predictor variables was allowed for each gas and forest type to ensure sufficient degrees of freedom. An automated model selection process was performed using the *ols_step_all_possible* function from the *olsrr* package in R, which generated up to ten possible combinations of predictor variables for each forest type and gas flux. The combinations suggested by the function were evaluated based on statistical criteria (Adjusted R^2, AIC, and VIF < 2.5). From these candidate combinations, the model with the best statistical parameters (highest adjusted R^2 and lowest AIC) was selected. The chosen variables were then tested for normality and evaluated individually for statistical significance (p-value), effect size (Cohen's f^2), and overall model fit (R^2). This methodology allowed us to identify strong links between drivers and fluxes.

In summary, we used the PCA as an initial exploratory tool to provide an overview of variable clustering and forest type differentiation. However, the limited explanatory power and moderate variance explained (48.5%) made it insufficient to delineate specific relationships between gas fluxes and their drivers. The subsequent linear regression models therefore complemented the PCA, providing robust, quantitative insights into the predictors associated with specific fluxes for each forest type.

Second, the method used to calculate BVOC/CH4 fluxes, i.e. collecting a large volume of gas and using a blank chamber is unusual, but not wrong per se. Likely this is needed for the large volumes that need to be collected to detect BVOCs with mass spectrometry? This could be better explained/justified in the text.

We acknowledge that it was not clearly explained why a large volume of air was collected. This is clarified below.

The large gas volume collected was necessary to ensure sufficient air for the different BVOC and GHG analyses conducted using multiple instruments:

- **PTR-QMS:** Measurements of BVOCs by the PTR-MS required a sufficiently large sample volume to capture BVOC concentrations with high precision.

- **Los Gatos:** Due to its relatively high sample flow (0.1 L min^{-1}), at least 0.5 L of gas was needed to determine CH_4 and CO_2 concentrations.

- **Offline GC-MS (cartridges):** In addition to the two on-site instruments, cartridges were sampled to enable specific compound identification, which required at least 2 L of sample air. Results from these analyses are provided in the Supplementary Materials.

The blank chamber was used as a control to (i) account for any non-soil/litter contributions to gas concentrations, (ii) ensure that the measured fluxes originated solely from biogenic sources inside the chamber, and (iii) exclude possible interferences from the chamber itself (background measurement). To ensure identical conditions between the sample and the blank chamber, the exact same gas volumes were collected.

We have revised part of our methodology to clarify this section more effectively. The revised text is suggested to be:

"After 20 minutes of chamber closure with continuous flow, a sampling bag was connected to the outlet of the Teflon pump, and a 5 L sample was collected over 10 minutes. By the end of the 30-minute process, a total of 15 L of air had flowed through the chamber, of which the last 5 L was used for subsequent analyses.

PTR-QMS: Measurements of biogenic volatile organic compounds (BVOCs) using proton-transfer-reaction quadrupole mass spectrometry (PTR-MS) necessitated a sufficiently large sample volume to capture BVOC concentrations with the required precision, especially considering their typically trace levels.

Los Gatos Analyzer: Due to its relatively high sample flow of approximately 0.1 L min^{-1}, a minimum of 0.5 L of gas was needed to ensure stable and accurate determination of methane (CH_4) and carbon dioxide (CO_2) concentrations.

Offline GC-MS (cartridges): For specific compound identification and qualitative analysis through thermal-desorption gas chromatography time-of-flight mass spectrometry (TD-GC-TOF-MS), at least 2 L of sample air was required to effectively load the adsorbent cartridges. (Results from these analyses are further detailed in the Supplementary Materials)."

We improved the 2.4 Sampling design section with details about blank measurements:

"Chambers were installed directly in the field with minimal disturbance to the surrounding environment. To account for potential background signals and chamber interferences, three blank

chambers—featuring completely bottom-sealed collars—were deployed per transect and measured simultaneously with the sample chambers (Fig. 2b).”

Third, another issue is the way nutrients were extracted, i.e. using nitro perchloric solution. The latter is HNO3+HCl. This suggests total nutrient contents were measured and not bio-available levels. There is also a poor discussion on why these nutrient levels are what they are (section 4.1).

We thank the Reviewer for raising the important point regarding nutrient extraction and the interpretation of nutrient levels.

The nitro-perchloric acid digestion method we employed measures total nutrient contents by releasing nutrients bound in both mineral and organic fractions, rather than the immediately bioavailable pools. This method is a well-established standard for comprehensive nutrient quantification in soils and plant tissues (Shaw, 1959; Malavolta et al., 1997; Marschner et al.,2012). While total nutrient content does not represent the labile pool available to plants and microbes at a given moment, it provides fundamental insight into the overall nutrient reservoirs and long-term soil fertility status. These total nutrient contents are critical for understanding ecosystem nutrient cycling and nutrient supply capacity, and they provide important information on the overall nutrient stocks within the system (Sarto et al., 2011; Fontes et al., 2021; Dietrich et al., 2018). Therefore, for our purpose of characterizing differences across forest types, the use of total nutrient content in soil and litter was considered appropriate.

Additionally, measuring total nutrients is particularly relevant for our study because it provides a foundation for understanding nutrient pools that contribute to long-term processes in forest soil and litter. Much of the focus in Section 4.1 is on how these nutrients influence BVOC and GHG fluxes, as well as microbial biomass. Since these fluxes are not solely influenced by immediately available nutrients but can also be affected by larger nutrient reservoirs, assessing total stocks allows us to capture a broader perspective on nutrient–flux relationships. For example, nutrient release from organic matter decomposition contributes to both bioavailable and total pools, thereby influencing overall ecosystem processes.

Regarding why nutrient levels vary across forest types, the observed differences reflect distinct biogeochemical processes related to soil parent material, organic matter input and decomposition, nutrient leaching, mineral weathering, and biological uptake and resorption in each forest ecosystem. For instance, the elevated potassium and phosphorus in the ancient river terrace forest likely indicate greater nutrient retention and cycling efficiency, whereas the iron dominance in upland soils aligns with the intense leaching characteristic of highly weathered tropical soils (Mosquera et al., 2024; Li et al., 2023). The white-sand forest’s unexpectedly high nutrient concentrations may result from dissolved organic nutrients and root mat effects enhancing nutrient retention beyond classical fertility expectations (Lange et al., 2024; Draper et al., 2014).

We agree with the reviewer that not all aspects were sufficiently discussed. We have revised Section 4.1 to expand the discussion, following the feedback of the reviewer

“4.1 Differences in soil and litter nutrient contents across forest types

Soil and litter properties showed strong differences between forest types, particularly concerning their total nutrient contents. These total nutrient pools reflect the long-term nutrient availability and reservoirs within each ecosystem, shaped by distinct biogeochemical processes. The ancient river terrace forest stood out for its high litter K and P total contents. These elevated levels likely indicate robust nutrient retention and efficient cycling mechanisms within this forest type, potentially influenced by its historical flooding patterns and allisols (Andreae et al.,2015) , which are generally younger and richer in nutrients.

In the upland forest, the dominance of soil iron total content is likely related to the intense leaching common in its ferrasols (oxisols), resulting in iron enrichment due to the removal of other nutrients (Mosquera et al., 2024). In addition, the formation of iron oxides can reduce the mineralization of organic matter, promoting iron accumulation in the leaf litter (Li et al., 2023). Overall, the white sand forest exhibited distinct soil properties compared to the other studied forest types. Despite its well-documented low fertility (Mendonça et al., 2015; Demarchi et al., 2022) and arenosol characteristics, this forest type showed unexpectedly high soil nutrient and carbon total concentrations (Fig. 4). Phosphorus total levels, for instance, were up to four times higher than in upland and ancient river terrace forests. This observation may be explained by the significant role of dissolved organic nutrients in mitigating nutrient limitations (Lange et al., 2024), or by the efficient capture and retention of nutrients within the forest's extensive root mats, which can enhance carbon storage and nutrient cycling in structurally analogous ecosystems (Draper et al., 2014). Iron total concentrations in the soil of the white sand forest were lower than expected (Cornu et al., 1997), possibly due to spatial variability and seasonal dynamics. During the dry season, low water retention in sandy soils induces drought stress, while wet-season leaching redistributes iron, aluminum, and magnesium (García-Villacorta et al., 2016). This process can form cemented horizons, impeding drainage and elevating water tables (Franco & Dezzeo, 1994; Demarchi et al., 2022). Additionally, differences in tree species composition between forest types may influence the total stocks of nutrient levels (García-Villacorta et al., 2016; Gomes Alves et al., 2022) further contributing to the observed variations."

Fourth, if living roots are also a potential source of BVOCS (line 508-511) why wasn't a root exclusion experiment added as an additional treatment? This would have made the data set, that has a very limited temporal resolution, more interesting.

We agree with the Reviewer that the inclusion of BVOC measurements from living roots would have made the data set more interesting. While we agree that such an experiment would provide valuable insights, implementing this methodology in the context of our study would have presented significant methodological and logistical challenges, as outlined below:

1. Methodological differences and complexity: Working with root BVOC emissions requires approaches that differ significantly from those used to measure fluxes from the litter-soil system, which was the focus of our study. A root exclusion experiment would require separating roots from the soil and litter layers, which involves substantial physical disturbance. This process could itself alter BVOC fluxes due to mechanical damage to roots, enhanced microbial activity, and the introduction of artificial hotspots for biogenic emissions (Arellano et al., 2013; Brilli et al., 2011). Additionally, isolating root contributions without affecting microbial and litter processes simultaneously is not straightforward, as roots interact dynamically with the surrounding soil and microbial communities (Peñuelas et al., 2014).

2. Logistical challenges: Our experimental design already involved long sampling and analyzing days to ensure the collection of BVOCs, CH?, and CO? fluxes across multiple forest types. Adding a root exclusion treatment would have required separate chambers, additional time-intensive preparation, and better lab infrastructure in the field. As our main goal was to detect the net soil/litter gas exchange with the atmosphere, having this extra experiment with isolating roots was beyond the scope of this study. Moreover, separating roots from litter and soil for such experiments in tropical forests with complex root systems is particularly challenging and requires prolonged field manipulations (Lang et al., 2021). These logistical demands would have further reduced the temporal and spatial coverage of our sampling efforts.

3. Root BVOCs as a distinct research topic: Research on root BVOCs is an important but highly specialized area within BVOC studies. Fluxes from roots are driven by distinct physiological pathways, including interaction with rhizosphere microbes, exudation processes, and stress-induced responses. Addressing root contributions to BVOCs would require a different experimental framework designed specifically for that purpose. While our study focused on the soil-litter compartment, future work could complement our findings by targeting root emissions using specific methods.

Fifth, I think more efforts could have been done resolve this issue with m/z 42. Was this not solvable?

Unfortunately, with the PTR-QMS, resolving this specific mass fragment is not achievable due to the inherent limitations of the quadrupole-based mass spectrometer. The PTR-QMS excels at real-time detection of VOCs but has reduced selectivity when it comes to distinguishing between molecules with the same m/z value. In the case of m/z 42, this peak is often associated with multiple isobaric compounds such as acetonitrile and fragments of larger VOCs, making it impossible to deconvolute these contributions without additional mass resolution. Since the PTR-QMS does not possess high-resolution capabilities, resolving the exact identity of m/z 42 is beyond its capacity. To resolve this issue, a PTR-Time of Flight (Tof) - MS would have been required, but unfortunately, at the time of this study, we did not have access to a PTR-ToF-MS in our laboratory setup. As the m/z 42 presented interesting results, we encourage future studies to further explore it and with better technical and analytical resources.

Some specific comments:

Line 71: I wonder that you can really generalise that CH4 fluxes are higher from sandy soils? Or do you refer to CH4 uptake fluxes (i.e. CH4 oxidation)?

We acknowledge that the original statement is too specific for the cited study and that CH_4 dynamics are generally more complex than indicated.

While sandy soils typically exhibit higher diffusivity, which can enhance CH_4 diffusion and oxidation and potentially lead to increased CH_4 uptake, the reality is more nuanced. Besides soil texture, soil structure also plays a role. For example, microaggregates can create local anaerobic zones, causing anaerobic gas production, such as methanotrophic CH_4 production. In the revised text, we chose to discuss gas dynamics with relation to soil structure and texture more broadly rather than focusing specifically on CH_4.

For the revised manuscript, we suggest the following text:

Soil flux dynamics are influenced by multiple, interacting factors. Soil texture affects gas diffusivity—for example, higher porosity in sandy soils can enhance oxidation processes, such as found by Cai et al (1999)—while soil structure can create localized anaerobic conditions that promote anaerobic gas production (Sey et al 2008). Consequently, the effects of soil moisture on CH_4 fluxes depend on both texture and structure, highlighting the complex interplay of physical soil properties in regulating soil flux dynamics.

Line 78: How can you state the Amazon is the largest source of BVOCS, without existing data from the Congo basin? Mention also the role of BVOCs for O3 and NOx dynamics.

We acknowledge that other tropical forests, such as those in the Congo Basin, also make important contributions to the global BVOC budget, which remains poorly investigated. However, our statement is based on previous studies showing that the Amazon Basin is widely regarded as the

largest source of BVOCs to the atmosphere, supported by a combination of satellite-derived estimates, field measurements, and atmospheric modeling (e.g., Wells et al., 2022). We have rephrased the statement in the manuscript to clarify this point as follows:

"The Amazon rainforest alone contributes about 40% of global BVOC emissions, playing a critical role in the global carbon cycle (Guenther et al., 2012; Wang et al., 2024; Tripathi et al., 2025)."

In addition, following the comments of the reviewer, we have rewritten the introduction with the role of BVOC, Ozone and NOx:

"*Biogenic Volatile Organic Compounds (BVOCs) play critical roles across scales, from cellular processes to global climate regulation. While primarily emitted by plants, BVOCs can also be produced and consumed by soils, litter and microorganisms. Once released into the atmosphere, they actively participate in atmospheric chemistry and physics, influencing climate dynamics. BVOCs react with key atmospheric oxidants—including hydroxyl radicals (OH), ozone (O_3), and nitrate radicals (NO_3)—to form secondary organic aerosols (SOAs) (Artaxo et al., 2022; Yáñez-Serrano et al., 2020). SOAs, in turn, have a major influence on cloud properties, enhancing cloud condensation nuclei (CCN) concentrations, which impacts precipitation patterns and alters cloud lifecycles (Liu and Matsui, 2022). Depending on their chemical composition, SOAs can also influence the Earth's radiation budget by scattering incoming solar radiation (resulting in a cooling effect) or absorbing outgoing longwave radiation. Additionally, BVOCs contribute to the formation of tropospheric ozone—an important greenhouse gas and a major air pollutant (Vella et al., 2025) . Given these large-scale impacts, accurately quantifying BVOC fluxes in terrestrial ecosystems is essential for advancing our understanding of forest–atmosphere interactions and for improving Earth system models—thereby improving climate predictions.*

Global emissions of BVOCs from terrestrial vegetation are estimated at approximately 760 Tg C yr^{-1}, with isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) accounting for around 70% and 11% of these emissions, respectively (Tripathi et al., 2025). Isoprene is a simple building block compound emitted in large quantities, particularly by tropical forests, whereas monoterpenes—such as α-pinene, β-pinene, and limonene—are structurally more complex (Guenther et al., 2012; Gomes Alves et al., 2016). The Amazon rainforest alone contributes about 40% of global BVOC emissions, playing a critical role in the global carbon cycle (Guenther et al., 2012; Wang et al., 2024; Tripathi et al., 2025). However, these global estimates primarily consider emissions from plants, neglecting potential contributions from soil and litter, which might also include a large variety of BVOC chemical species. This gap is particularly significant given recent evidence that the soil–litter together is a compartment that can also play a crucial role in BVOC emissions (Fan et al., 2020, 2024; Bourtsoukidis et al., 2018; Peñuelas et al., 2014; Tang et al., 2019). Within this compartment, multiple biological and physical processes influence BVOC dynamics. These include plant-related processes such as intra- and inter-organism communication, herbivore defense, and symbiotic interactions (Gfeller et al., 2013; Lin et al., 2007; Rasheed et al., 2021; Steeghs et al., 2004; Tang et al., 2019; Trowbridge et al., 2020). Additionally, soil microorganisms produce and consume BVOCs for communication and ecological interactions (e.g., defense and competition), with these compounds also being released as residual metabolic products (Isidorov & Jdanova, 2002; Leff & Fierer, 2008; Liu et al., 2024; Monard et al., 2021).

Greenhouse gases (GHGs), such as methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) are also produced and consumed by soil microorganisms through key metabolic processes, including methanogenesis, methanotrophy, and respiration (Conrad, 2009; Hofmann et al., 2016). Greenhouse gases (GHGs), such as methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) are also produced and consumed by soil microorganisms through key metabolic processes, including methanogenesis, methanotrophy, and respiration (Conrad, 2009; Hofmann et al., 2016). While CO2, but also methane, are not classified as a BVOC, theyplay a crucial role in the overall gas exchange and are included in this study alongside BVOCs to

provide a broader perspective of soil-litter gas (carbon) fluxes. This inclusion is also important because environmental factors such as soil moisture, temperature, and nutrient availability influence both BVOC and GHG fluxes, albeit through distinct-but interconnected-biological and physical mechanisms (Greenberg et al., 2012; Tang et al., 2019; Asensio et al., 2007). These interconnected processes drive the net ecosystem exchange of gases between the soil-litter compartment and the atmosphere, making methane and CO_2 key components for understanding processes driving BVOC flux dynamics.

These GHGs and BVOCs can also be linked to litter decomposition. In the litter decomposition process, physical factors, such soil moisture, temperature, and nutrient availability greatly affect microbial activity that drives these fluxes (Greenberg et al., 2012; Tang et al., 2019; Mäki et al., 2017; Asensio et al., 2007). N_2O can be produced and consumed by soils through microbial nitrification and denitrification processes (Butterbach-Bahl et al., 2013; Snyder et al., 2009). These microbial processes, like those affecting other soil gases, are strongly influenced by environmental factors such as soil moisture, temperature, and nutrient availability (Saggar et al., 2013; Butterbach-Bahl et al., 2013). Together, these processes drive the net ecosystem exchange of BVOCs and GHGs between the soil-litter compartment and the atmosphere, and the magnitude and direction of this exchange may vary across different ecosystem types.

The Amazon Basin is a mosaic of diverse forest types (Oliveira-Filho et al., 2020), each with distinct plant species compositions (Ter Steege et al., 2013), shaped by the region's highly variable soil properties (Quesada et al., 2011; Quesada et al., 2012). Although Amazonian heterogeneity is known to play a critical role in regulating biogeochemical cycles, comparative studies across forest types—especially at the soil–litter interface—are still scarce. Distinct interactions between vegetation and soil can lead to highly variable patterns of BVOC and GHG exchange, making forest type-specific measurements essential for accurately representing the Amazon in atmospheric budgets. This lack of representation underscores the urgent need for studies that account for the region's ecological diversity to better capture the unique contributions of each forest type to biogeochemical processes. Quantifying this variability is key to improving both regional and global models, as gas fluxes are unlikely to be uniform even within the Amazon

To address these gaps, we investigated soil-litter BVOC (acetaldehyde, methanol, m/z 42, dimethyl sulfide, isoprene and monoterpenes) and GHG (CH_4 and CO_2) fluxes, soil and litter nutrient content and microbial biomass, and soil temperature and moisture from three forest types in central Amazonia: (i) ancient river terrace forest - a forest that was flooded in the past and is no longer flooded due to changes in the river course (paleoigapó); (ii) white sand forest (locally called campinarana) - a less common forest type that occupies about 5% of the Amazon basin (Adeney et al., 2016); and (iii) upland forest (locally called terra-firme) - the most common forest in Amazonia, with the highest plant species richness (Emidio et al., 2016; Luize et al., 2018). While methane and CO_2 are not classified as BVOCs, they play a crucial role in the overall gas exchange and are included in this study alongside BVOCs to provide a broader perspective of soil-litter gas fluxes. This inclusion is important because environmental factors such as soil moisture, temperature, and nutrient availability influence both BVOC and GHG fluxes, albeit through distinct biological and physical mechanisms (Greenberg et al., 2012; Tang et al., 2019; Asensio et al., 2007). These interconnected processes drive the net ecosystem exchange of gases between the soil-litter compartment and the atmosphere, making methane and CO_2 key components for understanding the full scope of these dynamics. With this approach, we aimed to answer the following questions: (i) what is the emission/consumption of BVOCs, CO_2, and CH_4 in magnitude and chemical diversity, and; (ii) what are the main drivers of soil-litter gas exchanges across these three forest types in central Amazonia (specifically, soil moisture and temperature, nutrient content, and microbial biomass from soil and litter)?"

Line 225: no good fit for acetone, ethanol and formaldehyde,… what does this exactly mean?

What we mean by "no good fit" for acetone, ethanol, and formaldehyde in the calibration process is that we encountered challenges inherent to their detection using PTR-QMS. The calibration curves for these compounds—generated as normalized counts per second (ncps) against their mixing ratios—did not yield consistent or accurate results.

These difficulties are linked to known challenges associated with the PTR-QMS when analyzing these specific compounds. For example, formaldehyde detection is particularly affected by the instrument's sensitivity to humidity. The proton affinity of formaldehyde is comparable to that of water vapor, leading to proton transfer reactions that can reverse or be suppressed under humid conditions, introducing inaccuracies. Because our calibration required humidified air to mimic ambient conditions, water vapor interactions likely interfered with formaldehyde detection, preventing the formation of reliable calibration curves. This limitation has been previously described, with formaldehyde detection by PTR-QMS showing poor linearity and sensitivity (Vlasenko et al., 2010; Warneke et al., 2011).

Acetone and ethanol exhibited issues likely related to proton-transfer reactions within the instrument's drift tube. Ethanol, for instance, has been shown to undergo competing reactions with H_3O^+ ions, leading to incomplete or inconsistent protonation, which can compromise measurement accuracy (Sémon et al., 2017). Because we could not achieve good fits in the calibration curves (i.e., high R^2 values), we decided to exclude these compounds from the analysis, as they could not be reliably quantified.

Line 308-309 (as example): no need to use 3 decimals here.

Thanks for pointing that out. We removed the excessive number of decimals in the flux values for BVOCs and GHGs.

Line 329-332: You cannot make a "translation" to "soil moisture available to plants" without soil physical data such as a Pf curve.

We acknowledge that a precise determination of soil moisture available to plants requires specific soil physical data, such as water retention curves (Pf curves) or field capacity measurements, which were not part of our dataset.

To address this, we revised the text in the result section. We ensured we did not overinterpret the soil moisture data as directly representative of plant-available water. Instead, we highlighted that soil texture significantly modulates how measured soil moisture translates into water accessibility for plants and microbes.

Below follows the sentence that we rewrote:

"*The substantial differences in soil texture (see supplementary material, Table S1) between sites modulate how measured soil moisture corresponds into water available to plants and microbes. However, since individual transects were measured on different consecutive days, distinguishing temporal from spatial effects remains challenging."*

Line 462: higher than anticipated, how much higher?

In this study, we found much higher BVOC emission fluxes compared to those reported by previous studies in tropical soils. Several studies investigating soil BVOC emissions in tropical forests have suggested relatively low emissions under undisturbed conditions. For example: Bourtsoukidis et al. (2018) measured sesquiterpene emissions in Amazonian soils and reported fluxes of sesquiterpenes around 0.01–0.02 mg m^{-2} h^{-1}, which are significantly lower than, for instance, the acetaldehyde fluxes (29.911 mg m^{-2} h^{-1}) or dimethyl sulfide (0.924 mg m^{-2} h^{-1}) emissions observed in our study for the white sand forest. Llusià et al. (2022) observed monoterpene emissions of 0.0104 mg m^{-2} h^{-1} in unfertilized plots and 0.0390 mg m^{-2} h^{-1} in fertilized plots. In comparison, monoterpenes emissions in our study were higher (1.164 mg m^{-2} h^{-1}), especially in the white sand forest.

Line 516: I think this is rather a diffusion into the soil, then an effective (microbial) or (physical) uptake.

We agree with the Reviewer that diffusion of plant-emitted isoprene into the soil via deposition is a plausible explanation that complements our suggestion of microbial activity. To address this, we will add to the discussion the possibility of isoprene diffusion and subsequent interactions in the soil, including both microbial and physical uptake, as these processes may occur simultaneously.

"The lower isoprene uptake by the soil observed in the upland forest (-0.1 mg m^{-2} h^{-1}) compared to the higher uptake fluxes in drier conditions (~ -2.38 mg m^{-2} h^{-1}) reported by Pugliese et al. (2023) may reflect the combined effects of diffusion of isoprene emitted by plants into the soil and subsequent microbial and physical absorption processes. Diffusion acts as a transport mechanism, allowing isoprene to enter the soil matrix, where microbial communities metabolize it as a carbon source (Cleveland and Yavitt, 1998). In addition, physical processes such as adsorption or dissolution can influence isoprene loss, especially under variable soil moisture conditions (Mu et al., 2023). Thus, diffusion and microbial/physical uptake likely occur simultaneously, controlling the net isoprene fluxes observed in the soil."

Line 695-696: how can a forest type with an aerial coverage of 5% offset all carbon losses from other forest types?

We understand the Reviewer's concern regarding the relatively small area coverage of white-sand forests and their potential role in compensating carbon losses from other forest types. We would like to clarify that our intention was not to imply that white-sand forests serve as a carbon offset mechanism for the entire Amazon Basin. Rather, we aimed to highlight their unique ecological roles and the biogeochemical processes they influence. This illustrates that even in relatively small areas, such as those occupied by white-sand forests, the biogeochemical and atmospheric processes affected by BVOCs and CH_4 may differ substantially, reinforcing the heterogeneity of the Amazon's diverse forest types.

The revised sentence:

"In these areas, higher productivity under dry conditions may maintain relatively stable carbon dynamics, presenting a contrasting response to the substantial carbon losses typically observed in deep water table - upland forests - during drought."

Examples of “speculation”: lines 482, 487, 507, 530, 550-559 (the entire soil moisture and temperature issue as drivers for CH4 and BVOC fluxes, cannot be covered with this limited temporal data set!), 575-577 (idem), 582-584 (idem), line 675 (due to the low temporal coverage the extreme conditions of especially the white sand soils could not be covered),...

Examples of “overstating”: lines 36, 468, 568-569, 692,…

We acknowledge your concern that our limited temporal dataset for soil moisture and temperature might lead to speculation or overstatement regarding these factors as drivers for CH4 and BVOC fluxes. While our measurements represent a snapshot in situ investigation rather than continuous long-term monitoring, the statistical analyses performed allowed us to identify significant correlations and patterns within the context of our study. We view these findings as valuable indications and hypotheses that warrant further, more extensive research, particularly given the scarcity of such data from Amazonian ecosystems like the white sand forest. As noted in our conclusion (Lines 714-715), this research represents a pioneering investigation aimed at establishing initial insights into these ecosystems.

To address your specific points regarding "speculation" and "overstating," we have carefully revised the identified lines to employ more cautious and precise language.

Here is a summary of the revisions:

Line 36 - "...WS can be a significant ecosystem for BVOC and methane fluxes, where these fluxes are influenced by soil moisture and temperature

Line 468 - Revision: "...key observations related to BVOC and CH4 fluxes and their drivers..."

Line 482 Revision: "...possibly reflecting the role of dissolved organic nutrients in mitigating nutrient limitations (Lange et al., 2024)."

Line 487 - Revision: "...possibly attributed to spatial variability and seasonal dynamics."

Line 507 - Revision: "...the observed high emissions might indicate contributions from the activity of microorganisms living in the soil and litter (Carruthers & Lee, 2021; Hernandez-Arranz et al., 2019)."

Lines 550-559- Revision: "A principal component analysis (PCA) was performed to identify variables that could collectively differentiate forest types and their gas fluxes. As the PCA showed a limited capacity for differentiation due to overlapping ellipses, a further investigation was carried out using linear models (LMs). The LMs suggested that soil temperature and soil moisture were influential physical factors for all three forest types, particularly for the white sand forest. The white sand forest, with its relatively open canopy, shorter trees, and shallow water table (Adeney et al., 2016; Rossetti et al., 2019), often experiences dynamic conditions, which was reflected in the highly variable temperature and soil moisture values measured across its two transects over two subsequent days. In the following sections, we discuss the observed roles of soil temperature and moisture, and other potential factors influencing gas fluxes."

Regarding lines 575-577, we suggest underlining that we are limited by a small temporal dataset as follows:

“However, since high soil moisture often coincides with low temperatures, and since our conclusions are based on a limited temporal dataset, it remains challenging to ascertain whether low temperatures or high moisture levels drive increased fluxes under field conditions.”

Line 568-569 - Revision:

“However, in the white sand forest, high BVOC emissions were observed in the wetter transect, while low emissions and uptake were observed in the drier transect. While based on limited data, it indicates that Amazonian soil emissions may respond differently to soil moisture depending on the soil and forest type.”

Line 675: The original sentence states that few studies exist partly due to

"*challenging conditions... such as flooding and extreme temperatures.*"

This line describes the inherent nature of white sand forests, not an assertion that our study fully captured these extreme conditions. While our interpretation throughout the discussion focuses on the potential impact of such conditions, acknowledging our own temporal limitations, we fully agree with the reviewer's valid point that it is indeed important to explicitly state that our study, with its current temporal coverage, could not comprehensively observe the full range of these extremes.

To address this, we have revised line 675 by adding a clarifying sentence that explicitly states this limitation. The updated text now reads:

“This can partly be explained by the challenging conditions of this forest type, such as flooding and extreme temperatures, which require specific infrastructure for data collection. While our observations constitute one of the first characterizations of VOCs in this unique forest type, their capacity to capture the full spectrum of extreme conditions is inevitably limited by the short temporal coverage of the dataset..

Line 692 - Revision: "Our results suggested a stronger link between white sand forest gas fluxes and physical factors (more than other forest types), which indicates a possible sensitivity to upcoming climate extremes."

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