Reply to comments from Reviewer 1:

Author response for "**Chiral Volatile Organic Compound Fluxes from Soil in the Amazon Rainforest across seasons**", Schüttler et al.

The reviewer comments are included here in ***black****, author responses are in* ***blue****, the original manuscript texts are in* ***purple****, while modifications to the manuscript are underlined and in* ***red****. Line numbers in our response relate to the original submitted document (preprint).*

The paper by Schüttler et al. offer some interesting data on BVOC exchanges between the soil and atmosphere and extends our understanding of these fluxes in tropical systems. As a Biologist, not a Chemist, I found the methods descriptions commendably clear, logical, and easy to follow. I do NOT know enough to comment critically on these methods, but the descriptions made perfect sense to me.

The importance of BVOC fluxes in these systems has been known for over thirty years, but we still have very few data sets of soil fluxes, per se; this study, even though it is based on few chambers in one site, offers some tantalizing insights. The authors need to bear in mind in their statistical models when their samples are truly independent, when they are time series, and when they are pseudo-replicated. I suspect they will want to either re-structure their models or, at the very least, acknowledge when their data violate assumptions of independence. I do not see this as a major issue because the results are so striking.

Response: First, we would like to thank you for taking the time reviewing our work and for the positive words. By pointing us to additional aspects of our work, especially from a biologist point of view, we think we can add substantial improvements to the manuscript.

We thank you for putting our attention to our statistical model. We acknowledge that our data is not independent due to repeated measurement over time from the same soil spots when we compare seasons or soil spots. To address this, we have re-analyzed the data using linear mixed-effects models, which accounts for the structure of our time-series data by including random intercepts for each measurement date. We describe the now used statistical model in the methods, changed the corresponding results for soil spot, seasonal, and chiral ratio differences and adjusted Figure 6 and 8. While some p-values changed slightly under the new statistical model, the overall trends and conclusions were not affected when comparing fluxes and chiral ratios per seasons and soil spots. However, when implementing a mixed-effect model to assess the impact of the environmental parameters after adjusting for diurnal cycles, we note differences to results from Pearson correlations.

2.6 Statistical analysis

Statistical analyses were performed using Python (version 3.12.4) with the following packages: numpy (v.2.0.0), pandas (v.2.2.2), matplotlib (v.3.9.1), seaborn (v.0.13.2), statsmodel (v.0.14.5~~2~~), and scipy (v 1.16.0). Data visualization was conducted using matplotlib and seaborn.

Statistical differences were assessed using linear mixed-effect models, because the dataset contains repeated measurements over time from the same soil chambers and ambient sampling points, which violates assumptions of independence of simpler tests. Local time was included as a fixed effect in all models, because we expected a diurnal pattern for the measured VOC fluxes and mixing ratios. ~~between soil fluxes measured in different seasons and from different soil plots~~ were ~~determined using the Tukey HSD (Honestly significant difference) test following a significant result from ANOVA~~ To assess seasonal differences in fluxes, a linear mixed-effects model was implemented with season, chamber spot location and local time as fixed effects and the sampling date spot as random effects. Differences between soil spots within a single season were assessed with chamber spot location and local time as fixed effect and the sampling date as random effect. Using the Holm–Bonferroni method, p-values were adjusted for multiple comparisons afterwards in both cases.

For comparisons of enantiomeric ratios between atmospheric and soil chambers and between seasons, a linear mixed-effect model with fixed effect for local time and a random effect for the sampling date and chamber spot or ambient air sampling location was used. Ratios in both cases were log-transformed prior to analysis to stabilize variance and improve residual normality. To assess the effect size (β coefficient) of environmental parameters on fluxes, mixed-effects models were fitted with fixed effect of local time and adjusting for random effects of measurement date and chamber spot location. ~~, the non-parametric Mann-Whitney U test was used due to non-normality of the data~~. ~~For correlations between the fluxes and environmental parameter Pearson coefficients were calculated.~~

Statistical significance was accepted for $p < 0.05$.

3.3 Diurnal and seasonal dynamics of soil terpenoid exchanges

Line 272: The fluxes showed strong seasonal variation, with higher uptake fluxes in the dry seasons compared to the dry-to-wet and wet seasons (~~Tukey test~~ Holm–Bonferroni adjusted $p < 0.001$ for comparing October 2024 and $p < 0.01$ for comparing with October 2023).

3.4 Effects of the soil properties on terpenoid soil fluxes

Line 289: For isoprene, in the dry-to-wet season 2023 and wet season 2024 no significant differences in fluxes were found ($p > 0.05$) (Fig. 4a) between the measured soil chambers. However, in the ~~other three~~ two dry seasons there was a significantly higher isoprene uptake by spot 1 than spot 5 (Holm–Bonferroni adjusted $p < 0.01$ for dry season 2023 and $p < 0.001$ for dry season 2024 ~~all~~) and in the dry season 2024 also in spot 5 than spot 4 (Holm–Bonferroni adjusted $p < 0.001$).

Comparing fluxes of MTs from different soil spots, we note clear monoterpene speciation differences (Fig. 4b). The highest emission rates were observed for soil spot 1 in the dry-to-wet transition season 2023. Here, the flux was significantly higher compared to the other two spots (Holm–Bonferroni adjusted $p < 0.0001$).

3.4.1 Effect of litter removal

Line 289: When litter was removed from the soil plot, in the two seasons dry-to-wet season 2023 and dry season 2024, no significant difference was found in the fluxes for isoprene and total MTs ($p > 0.05$).

3.4.2 Soil fluxes VS environmental conditions

Isoprene, MVK and MACR have an ~~strong~~ ~~negative~~ ~~correlation (Fig. 6)~~ ~~with their~~ estimated change in flux of -1.2 to -1.9 nmol m^{-2} h^{-1} per ambient atmospheric concentration increase in pptv after accounting for diurnal cycles, repeated chamber spot location measurements and dates. Although this result was not significant ($p > 0.05$), it is indicating the uptake rates were higher when the available concentrations in the air above the soil were higher.

Total MTs have an estimated change in flux of more uptake for environmental parameter increasing. The highest effect was found with photosynthetic active radiation (PAR) where the total MT flux decreases an estimated -31 nmol m^{-2} h^{-1} per µmol m^{-2} s^{-1}($p < 0.001$) and soil temperature ($p < 0.01$). At the same time ocimene flux is increasing with increased PAR ($p < 0.01$).

Total SQTs did not show a significant result, however β-caryophyllene, α-copaene and (+)-cyclosativene were uptaken more by soil, when air temperature increased ($p < 0.05$, $p < 0.05$ and $p < 0.01$ respectively).

~~Different MT species like α-phellandrene, 3-carene, γ-terpinene, limonene, and β-ocimene, also show negative correlation with their mixing ratios (-0.21 to -0.82; p <0.001), while β-myrcene had positive correlation with the ambient concentration (0.54; p <0.001).~~ ~~In general, the correlations with the environmental conditions like air and soil temperature and soil water content were stronger for isoprene and its oxidation products. The correlation with the photosynthetic active radiation (PAR) was highest for ocimene (0.29; p <0.01) and the total SQTs, as well as α-copaene (0.26 and 0.24; p <0.001).~~

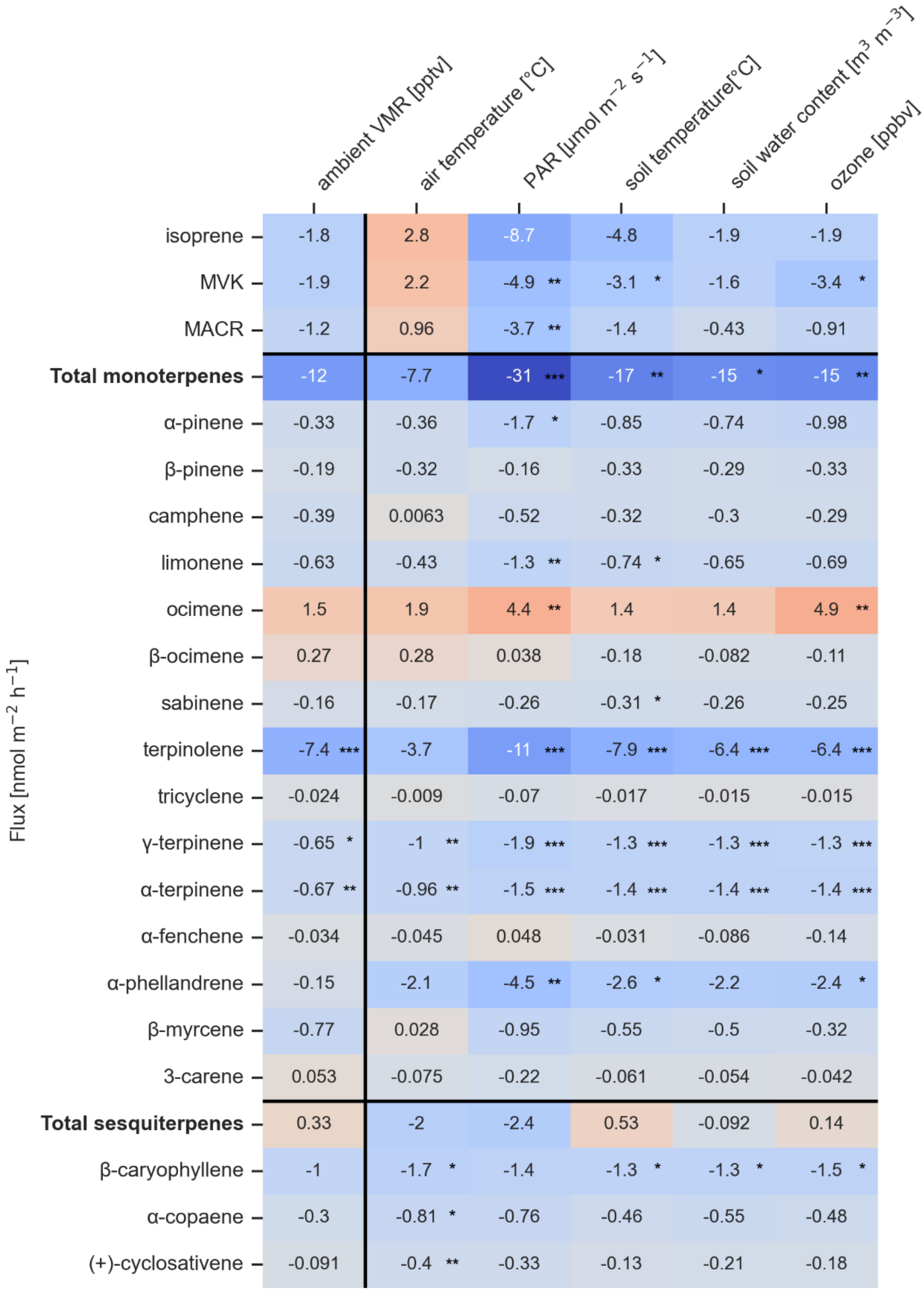

Figure 6 Heatmap of ~~correlations between the~~ β coefficients from linear mixed-effects models quantifying the change in flux of measured compounds ~~and~~ per unit change in environmental variables, after adjusting for the fixed effect of local time and random effects for measurement date and chamber spot location. ~~various e~~ Environmental variables are: ambient mixing ratio (VMR) of each compound in pptv, air temperature at 26 m in °C, incoming photosynthetically active radiation (PAR) at 81 m in µmol m^{-2} s^{-1}, soil temperature in °C and soil water content at 10 cm depth in m^3 m^{-3}. Statistical significance of the ~~Pearson correlation~~ β coefficients is indicated by asterisks: (*) for $p < 0.05$, (**) for $p < 0.01$ and (***) for $p < 0.001$.

3.6 Chirality

Line 352: The (−)-α-pinene was significantly more enriched ~~($p < 0.05$)~~ inside the soil chamber than in the ambient air in the dry-to-wet season 2023 ($p < 0.001$), dry season 2023 ($p < 0.05$), and in the wet season 2024 ($p < 0.01$) (Fig. 8).

Line 357: When only comparing the ambient enantiomeric ratios across the season, they are in most cases significantly different from each other (Fig. 8 e)-h)), especially when comparing both dry ~~wet~~ season 2024 ~~with the dry season~~ and 2023 it was significantly different for all chiral MTs, except for camphene.

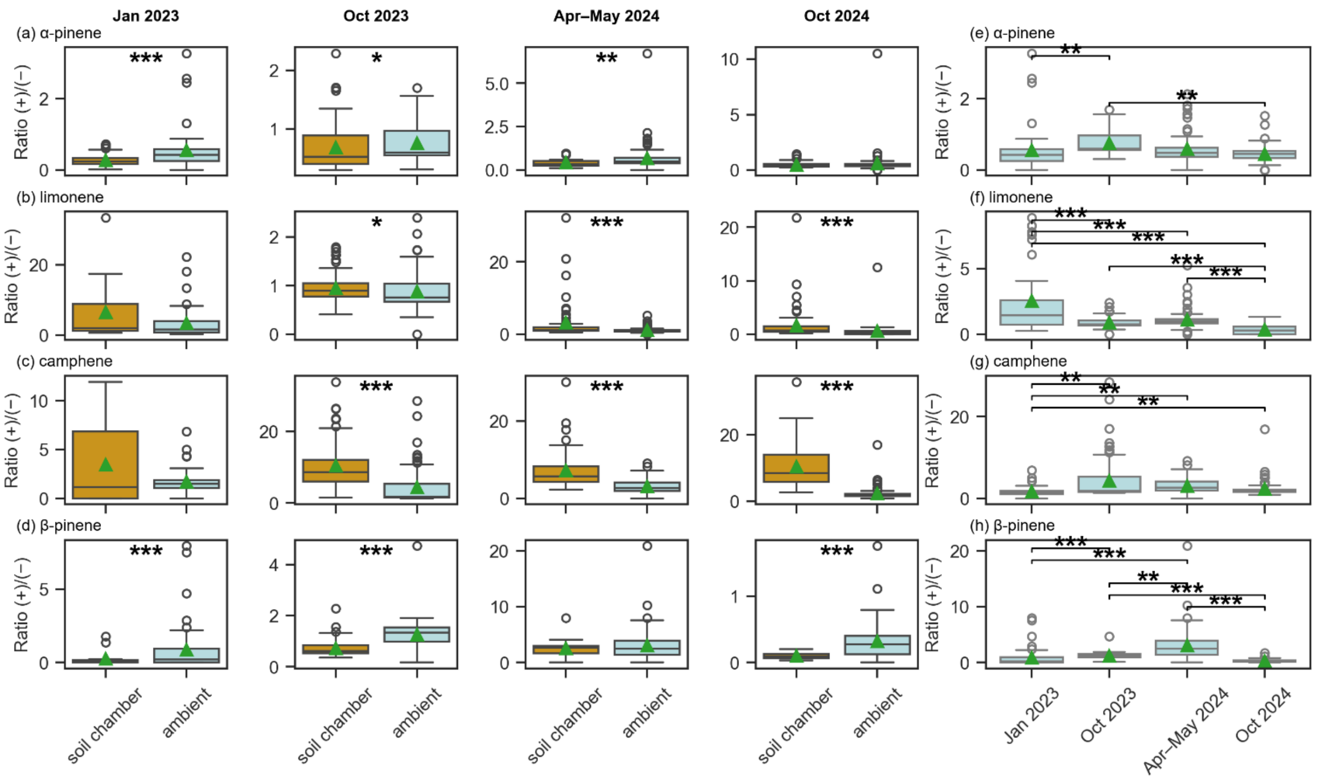

Figure 8 Boxplots show the ratio of the (+)- to (−)-enantiomers for (a) α-pinene, (b) limonene, (c) camphene and (d) β-pinene in both ambient air (light blue) and soil chamber air (dark orange) across different seasons. The rightmost panels display the seasonal distribution of ambient air enantiomeric ratios for (e) α-pinene, (f) limonene, (g) camphene and (h) β-pinene. The boxes represent 25% to 75% of the dataset. Mean values are indicated by green triangles, while the median values are indicated by the central lines. Whiskers indicate the minimum and maximum data points at 1.5 times the interquartile range. Circles represent the outliers. Significance was assessed using linear mixed-effect model accounting for local time as fixed effect; sampling date and chamber spot as random effect. A single asterisk (*) denotes statistically significant differences between groups ($p < 0.05$), double asterisks (**) indicate highly significant differences ($p < 0.01$), and (***) indicate very high significant differences ($p < 0.001$). For improved visualization, in plot (e), two outliers with a ratio of (+)/(−) greater than 5 and in plot (f) one outlier with the ratio greater than 10 are not displayed. They are still included in the statistical analysis.

4.1.1 Isoprene and the oxidation products MACR and MVK

Line 380: For isoprene, MACR, and MVK, ~~correlations~~ β coefficients between soil fluxes and ~~both~~ ambient mixing ratios ~~(-0.74 to -0.81; p < 0.001~~) and key environmental parameters such as PAR, soil water content ~~(0.54 to 0.63; p < 0.001)~~ and temperature ~~(-0.48 to -0.56; p < 0.001)~~ (Fig. 7) were negative meaning the uptake rates got higher with higher light intensity and temperature ~~are found. The correlation with the environmental parameters like temperature hint either to the higher ambient concentrations of isoprene at higher temperatures (Alves et al., 2016) or to more efficient uptake rates at higher temperatures.~~ This hints towards a connection of uptake rates with the simultaneous light- and temperature dependent emission of isoprene. Jiao et al., (2023) found that the size of the BVOC sink in soils was proportional to the atmospheric availability of the compound, indicating that higher uptake rates are driven by higher ambient concentrations.

4.1.2 Monoterpenes and sesquiterpenes

Line 400: ~~Different~~ MTs showed negative and positive effects on their fluxes by increasing ~~correlated negatively or positively with~~ ambient concentrations, PAR and the other environmental variables (Fig. 7), indicating there are different processes responsible for the soil fluxes of each MT.

4.2 Effect of litter

Line 420: Although this result was not statistically significant (~~ANOVA t-test~~ p>0.05, sample size with litter n=23, without litter n=8) it gives directional evidence towards the role of litter on total soil terpenoid fluxes.

A few results stood to me, with respect to the underlying Biology. I hope the authors find these useful as they revise.

1. the lack of isoprene uptake in the litter layer suggests that litter microbes have not adapted to this carbon source. Given the earlier described role of litter microbes in methanol and terpene consumption, this result is worth highlighting.

Response: Thank you for pointing out this additional aspect of our results. We will highlight this result in our discussion and conclusion:

4.2 Effect of litter

Line 418: This suggests that microorganisms residing in the soil layer beneath the litter are primarily responsible for metabolizing these compounds, while at the same time indicating that litter microbes here have not adapted to isoprene as a carbon source.

5. Conclusion

Line 538: For the uptake of isoprene, MACR, and MVK ambient concentrations and temperature seem to be the primary drivers, while the litter layer here did not have an effect on the consumption of these compounds.

2. the difference in enantiomeric variability between the monoterpenes and the sesquiterpenes is congruent with earlier ideas that the sesquis come from the MVA pathway while the monoterps are made by the DOX-P pathway.

Response: We thank the reviewer for this insightful comment. While there is a tendency that in plants monoterpenes (MT) are made by the 2-C-methyl-d-erythritol 4-phosphate (MEP/DOX-P) pathway in plastids and sesquiterpenes (SQT) derive from the mevalonate (MVA) pathway in the cytosol, this classical apportionment has been shown to be an oversimplification (Hemmerlin et al., 2012). Isotope-labeling and inhibitor studies show substantial cross-contribution of MEP and MVA to both MTs and SQTs in several species (Dudareva et al., 2005; Yu and Utsumi, 2009; Opitz et al., 2014; Bergman et al., 2020). In general, finding both enantiomers of a SQT is more rare than for MTs, still several SQTs occur in both (+) and (−) forms, sometimes within the same genus or even the same species (Finefield et al., 2012). The enantiomeric outcome of a terpenoid arises at the level of terpene synthases (stereoselective enzymes) downstream from the pathway supplying precursors (Schwab et al., 2002). It was shown by Byron et al. (2022) that MT enantiomers can be produced de novo, while the other enantiomer can be attributed to storage emissions and therefore decoupled from the time of biosynthesis and therefore partly decoupled from precursor pathways.
Thus, observing both enantiomers for some MTs but only one for SQTs in our dataset reflects more on the differences in expressed synthase isoforms and tissue/temporal regulation, rather than indicating distinct precursor pathways.

We would therefore choose not to include discussing the pathways of the precursors in this manuscript, as our study in its design does not give additional insights towards understanding MT and SQT pathways in plants.

3. the idea of terpene emission from leaf litter, *per se*, rather than microbial activity during decomposition, could be developed a bit. The reason for pursuing this distinction is that a fair bit is known about the distribution of different terpenes in different plant taxa, so the direct leaf-contribution to BVOC fluxes should be predictable if the plant species composition is known.

Response: We appreciate this suggestion and agree that distinguishing direct (abiotic) volatilization from leaf litter and microbially mediated production and consumption is important. In our study site, the plant community is highly diverse (Andreae et al., 2015), and the leaf litter in each soil spot consists of a mixture of species whose individual terpene profiles are unknown. This makes it difficult to predict the contribution of direct litter emissions based on species composition alone.
Many studies on litter BVOCs have focused on temperate forests with coniferous trees that are known to emit terpenes in higher quantities and for longer time periods from their resin ducts as they decompose slower (Greenberg et al., 2012; Tang et al., 2019; Viros et al., 2021; Isidorov et al., 2024). Most tropical leaf litter is from deciduous plant and has more labile storage pools. However, we lack information on the residence time of isoprene, MTs, and SQTs in leaf litter (Tang et al., 2019). We expect abiotic emissions from leaf litter at our site to be transient and likely minor compared to microbial activity, especially over the time scale of our measurements with (visibly) limited fresh litter additions during the measurement period.

So, we would expect abiotic emissions from leaf litter at our measurement site to be less prominent, emitted only in a short period after leaf fall, and not reliably predictable.

4.2 Effect of litter
Line 422: The alteration could be attributed to the abiotic degradation of storage pools within the litter material and/ or to the ~~activity of~~ production and consumption by microorganisms inhabiting the litter surfaces. Abiotic litter emission varies according to decomposition stages as terpenes volatilize from storage pools. As in a tropical forest most plant species are deciduous, storage pool emissions are expected to a lower degree than in litter from coniferous trees (Greenberg et al., 2012; Viros et al., 2021; Isidorov et al., 2024). Previous studies have shown that biotic VOC emissions from litter in California can be 5 to 10 times higher compared to abiotic processes (Gray et al., 2010), indicating that the microbial community on the litter surfaces plays a significant role in VOC fluxes. Similar findings have been reported in soil terpenoid VOC flux shifts following litter removal in other ecosystems, such as an eucalyptus plantation (Mu et al., 2023), in Boreal forests (Mäki et al., 2017, 2019), and in a Mediterranean forest (Yang et al., 2024). However, very limited information is available for leaf litter volatiles contribution over time (Tang et al., 2019), especially in tropical ecosystems. Litter VOCs were found to have an influence in microbial community structures (McBride et al., 2020) and are known to mediate many microbe–microbe, microbe–plant, and microbe–animal interactions (Bitas et al., 2013; Schmidt et al., 2015; Schulz-Bohm et al., 2017). So, the very local litter structure could be responsible for the different MT and SQTs in the studied soil spots. The highest litter fall rates are usually observed at the end of the dry season and can be increased during an El Niño dry season (Martius et al., 2004; Barlow et al., 2007; Brando et al., 2008), so also the seasonal differences observed for MTs and SQTs could be partly attributed to the litter layer.

4. For over 30 years, thanks to Carleton White, we've been aware of the importance of soil microbes as consumers of BVOCs. When the flux is net upward, as Schüttler et al. found here for the 10 and 15 C terpenes, then the consumption processes are smaller than the production ones. The results of this manuscript suggest that it is time for some more process-based studies of soil BVOC fluxes so that we can begin to estimate gross fluxes also.

Response: We thank the reviewer for highlighting the long-standing evidence that soils can act as a microbial sink for monoterpenes (White, 1991, 1994). We have revised the Introduction and Discussion to acknowledge this work and clarified in the manuscript that our measurements report net fluxes as production minus consumption.

1 Introduction
Line 50: MTs can also be metabolized by soil microbes as a carbon source and can have an effect on pathways such as methanotrophy, nitrification, and denitrification in soil microbes (White, 1991, 1994).

4.1.2 Monoterpenes and sesquiterpenes

Line 407: So, the roots, as well as the microbiome, could have contributed to the different MT species net fluxes.

5. Conclusion

Line 539: MT and SQT net emissions and uptake showed to be governed on the litter layer and season, as well as showing very local differences from spot to spot in the composition of the total flux.

Line 552: By taking up isoprene and the net emission of MTs and SQTs the soil will exert partial control over near-surface ambient atmospheric ozone and OH.

5. I applaud the authors for their wet & dry season measurements, but I think the link to El Nino is rather tenuous, and, imo, they should de-emphasize this point. But I leave this to the editor's discretion.

Response: We appreciate the reviewer's point of view and agree that the link to El Niño could be de-emphasized, as we cannot prove that the observed higher rates of sesquiterpene (SQT) emission by the soil spots in the dry season 2023 was caused by the El Niño event.

4.1.2 Monoterpenes and sesquiterpenes

Line 411: In ~~Only i~~n the El Niño-influenced dry season 2023 the emission of SQT was more pronounced ~~was an emission pattern of SQT evident.~~

5. Conclusion

Line 541: ~~An El Niño drought period caused~~ Enhanced SQT emissions from soil were observed during the El Niño-influenced dry season 2023.

6. the authors make the important point that soil fluxes could result from microbes and/or roots. There have been similar observations on volatile sulfur fluxes in tropical systems. Distinguishing plant from microbial sources of production and consumption is crucial for developing predictive modeling. If the authors choose to discuss this, they should bear in mind McDonald and Falls's older work showing microbial consumption on the leaf surface, which could look like leaf consumption.

Response: We thank the reviewer for raising this important point. Distinguishing between root and microbial contributions to soil VOC fluxes is indeed critical for improving predictive models of biogenic emissions. However, our current dataset does not allow us to partition these sources, as both roots and rhizosphere microbes can produce VOCs, and their activities may be tightly coupled. However, there is no evidence that roots do consume VOCs. Future studies could distinguish roots and free-living/rhizosphere microbes VOC emissions via stable isotope labeling e.g., by pulse-labeling plants with $^{13}CO_2$ or adding ^{13}C labeled substrates to the soil (Gkarmiri et al., 2017; Cabugao et al., 2022; Pugliese et al., 2023; Meischner et al., 2025). Another approach could be sterilization in microcosms, root exclusion, having root-free controls or depth-resolved studies (Raza et al., 2021; Wannenmacher et al., 2025). However, such manipulations are difficult to implement without disturbance of natural conditions.

While our study focused on terpenoid soil VOCs, not specifically on volatile sulfur compounds, we recognize the relevance of prior work on volatile sulfur fluxes in tropical ecosystems (Andreae and Andreae, 1988; Kesselmeier et al., 1993; Jardine et al., 2015; Pugliese et al., 2023), where differentiating plant and microbial contributions is also a major challenge (Kesselmeier and Hubert, 2002).

We agree with the reviewer's caution regarding microbial consumption potentially masking root-derived emissions analogous to observations of methanol uptake by leaf-surface microbes (MacDonald and Fall, 1993; Fall and Benson, 1996). While our study did not measure methanol or leaf processes, we focused on net soil-atmosphere fluxes integrating both root and microbial activity. This approach provides insights into overall soil VOC dynamics, but underscores the need for targeted experiments to resolve source contributions in future work.

4.1.1 Isoprene and the oxidation products MACR and MVK

Line 396: Therefore, a consumption of these compounds by roots and/or microorganisms in the soil is a possible explanation for the observed net uptake rates.

Line 404: Roots have also been implicated as sources of MTs from soils (Asensio et al., 2008a), and both plant roots and microbial communities are responsive to climatic variation and drought stress (Bourtsoukidis et al., 2014; Byron et al., 2021; Honeker et al., 2023; Pugliese et al., 2023). So, the roots, as well as the microbiome, could have contributed to the different MT species fluxes. With our measurement we can only make assumptions about the net exchange between the soil-sphere and the atmosphere.

4.6 Limitations of this study and future directions

Line 532: Additionally, isotopic labelling and on-line measurements with a greater time resolution between samples, could further strengthen the understanding of soil BVOC exchange processes, especially in regards to resolving roots and/ or microbiome sources.

In short, this is a fine contribution and one that I look forward to citing when it appears in the literature.

Thank you!

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