Dear Editor,

Following the reviewers' comments and your suggestions, we have thoroughly revised the manuscript. The main changes include:

• Major revisions to the figures: Several figures have been updated to improve clarity, readability, and better represent the key findings.

• Substantial modifications throughout the text: We have revised the manuscript for improved structure, clarity, and consistency. We addressed specific reviewer comments point-by-point (see attached response document).

• Clarification of methods and data analysis: We added details in the Methods section, including clarification of the data treatment and justification for certain experimental choices.

• Inclusion of additional references and discussion: Recent studies were integrated to strengthen the scientific context and support our interpretations.

• Minor corrections: Grammatical, typographical, and formatting issues have been corrected throughout the manuscript.

We believe that these revisions have significantly improved the quality of the manuscript and hope that it is now suitable for publication.

Sincerely,

Manon ROCCO

Reviewer #1

We sincerely acknowledge Reviewer 1 for the insightful comments and thorough review. Please find below our point-by-point responses to the reviewer comments (comments in black, responses highlighted in blue).

This study investigates how litter biomass influences soil biogenic volatile organic compound (VOC) fluxes in a Mediterranean deciduous forest dominated by *Quercus pubescens* at the Observatoire de Haute Provence (O3HP) in southern France. The authors measured in situ VOC fluxes using dynamic soil chambers coupled with a PTR-ToF-MS. The experiment compared bare soil with soils amended with four different amounts of fresh litter over daily 24-hour measurement cycles. Additionally, phospholipid fatty acid (PLFA) analyses were conducted to characterize the microbial communities associated with each treatment. The results show a high diversity of VOCs (over 135 compounds) and indicate that for some compounds—such as methanol, acetone, oxygenated monoterpenes, cyclohexanecarboxylic acid, and sesquiterpenes—the net flux shifts from negative (a sink) in bare soil to positive (a source) with increasing litter mass. The experimental design is generally sound and the manuscript is well presented, there are several key points that may require further clarification.

Major Comments

1- The authors filter VOC ions using a Welch t-test with a threshold p-value of 0.001. Conventionally, a p-value below 0.001 would be considered significant, so it is unclear whether the intended criterion was $p < 0.001$. In addition, given the large number of comparisons made across numerous VOC ions, it is important to know whether any corrections for multiple testing (e.g., Bonferroni or FDR adjustments) were applied.

Answer: Since 710 ions were detected by PTR-ToF-MS, we wanted to focus on VOCs that are emitted of deposited inside the chambers. For this purpose, the Welch's t-test was used to compare the VOC concentrations from ambient air and inside the chambers, in order to keep only compounds that show high differences between ambient air and chamber concentrations (and then positive or negative fluxes, see Equation 1). The reviewer is correct, we used a $p < 0.001$ (not of 0.001), which means that the concentration differs strongly between ambient and inside chambers measurements.
It is now in the text: "A holistic approach was used to investigate the emissions, i.e. all VOCs detected by PTR-ToF-MS (710 ions in total) were considered in the data analysis steps described as follows. First, a Welch t-test was used to select only ions showing significant differences between ambient and chamber measurements. The dataset was filtered to retain ions showing a significant flux difference between ambient and chamber measurements."

2- The use of a 20-meter Teflon tube to connect the chambers to the PTR-ToF-MS could potentially lead to VOC adsorption or saturation on the tube walls, especially for compounds with high boiling points or sticky properties. I would like know if there were any measures taken to mitigate these effects and to prevent residual contamination between measurements. Moreover, the flux calculation formula referenced around line 125 is a critical part of the method. Including the full formula, along with a more detailed description of the calibration procedure and the role of the 14 calibration gases, would greatly enhance reproducibility.

Answer: The schematic representation of the setup shown in Figure 1 can be misleading. Each chamber is actually equipped with its own 20-meter long Teflon tube that is connected to the multivalve (i.e. each outlet arrow should connect to the multivalve and not to a common line as suggested on figure 1). This specific valve features a shared outlet that enables continuous flushing of the non-selected lines via a vacuum pump, while the selected line is drawn to the PTR-MS reaction chamber. This configuration is expected to minimize the equilibration time between position switches by keeping each line tubing equilibrated with the incoming air from

their respective chamber over the whole diurnal cycles. To further improve the response delay, the internal surface of the valve and of the reaction chamber are surface passivated with a functionalized hydrogenated amorphous silicon coating and heated to 120°C.

The mixing ratios in ppbV were calculated using the equation below.

$$R = \frac{RH^+}{H_3O^+} \times \frac{Tr_{H3O^+}}{Tr_{RH^+}} \times \frac{U_{drift} \times T_{drift}^{\cdot}}{k \times p_{drift}^2}$$

Where the RH$^+$ and H$_3$O$^+$ are the signal intensity in counts per second (cps) of the VOC and the reagent ions corrected according to their respective relative transmissions (Tr). U$_{drift}$, T$_{drift}$, and p$_{drift}$ are the voltage (in V), temperature (in K), and pressure (in mbar) in the drift tube, and k is the reaction rate coefficients (cm^3/s) between the VOC and the reagent ion.

The relative transmission in the range of 21–181 amu was determined experimentally with a calibration gas mixture (TO-14A Aromatic Mix, 100 ppb each in nitrogen, Restek Corporation, Bellefonte, USA) at the end of the measurement campaign. The composition of the calibration gas mixture, transmission and sensitivities are summarized in Table S3. Uncertainty associated to the calibration is ± 10%. All these details are now in the text.

Component	full concentration (ppb)	mass	k-rate (cm³/s)	Sensitivity (cps/ppb) - frequency 25 kHz	mass concentration (ppb)	Transmission
Benzene	110	79	1.93	316	103.03	0.672
Toluene	110	93	2.06	335	101.93	0.742
Chlorobenzene	110	113	2.48	420	78.13	0.826
Ethylbenzene	110	107	2.18	393	100.81	0.803
O-xylene	110	107			100.81	
M-xylene	110	107			100.81	
P-xylene	110	107			100.81	
Styrene	98	105	2.16	384	89.83	0.794
1,2,4-Trimethylbenzene	110	121	2.29	453	99.71	0.855
1,3,5-Trimethylbenzene	110	121			99.71	
1,2-Dichlorobenzene	110	147	2.21	485	59.40	0.938
1,3-Dichlorobenzene	100	147			54.00	
1,4-Dichlorobenzene	110	147			59.40	
1,2,4-Trichlorobenzene	100	181	2.18	381	40.81	1

Table S.3. Composition of calibration bottle with the respective concentration (ppb), mass (m/z), k-rate, sensitivity and transmission.

3- Since the fresh litter was used and replaced daily (if I understand this correctly), the study only captures a snapshot of VOC emissions from fresh litter. One of the conclusions drawn is that no clear relationship between litter accumulation and VOC fluxes can be established, which should be considered with caution. A time series analysis covering the litter decomposition process would be necessary to fully evaluate how VOC emissions evolve over time (could be at least mentioned in the conclusion for future suggestions).

Answer: We thank the reviewer, who correctly understood the process, for this suggestion. We now mention it in Section 3.2: "Only a few numbers of compounds have shown a significant relationship with the variation of litter

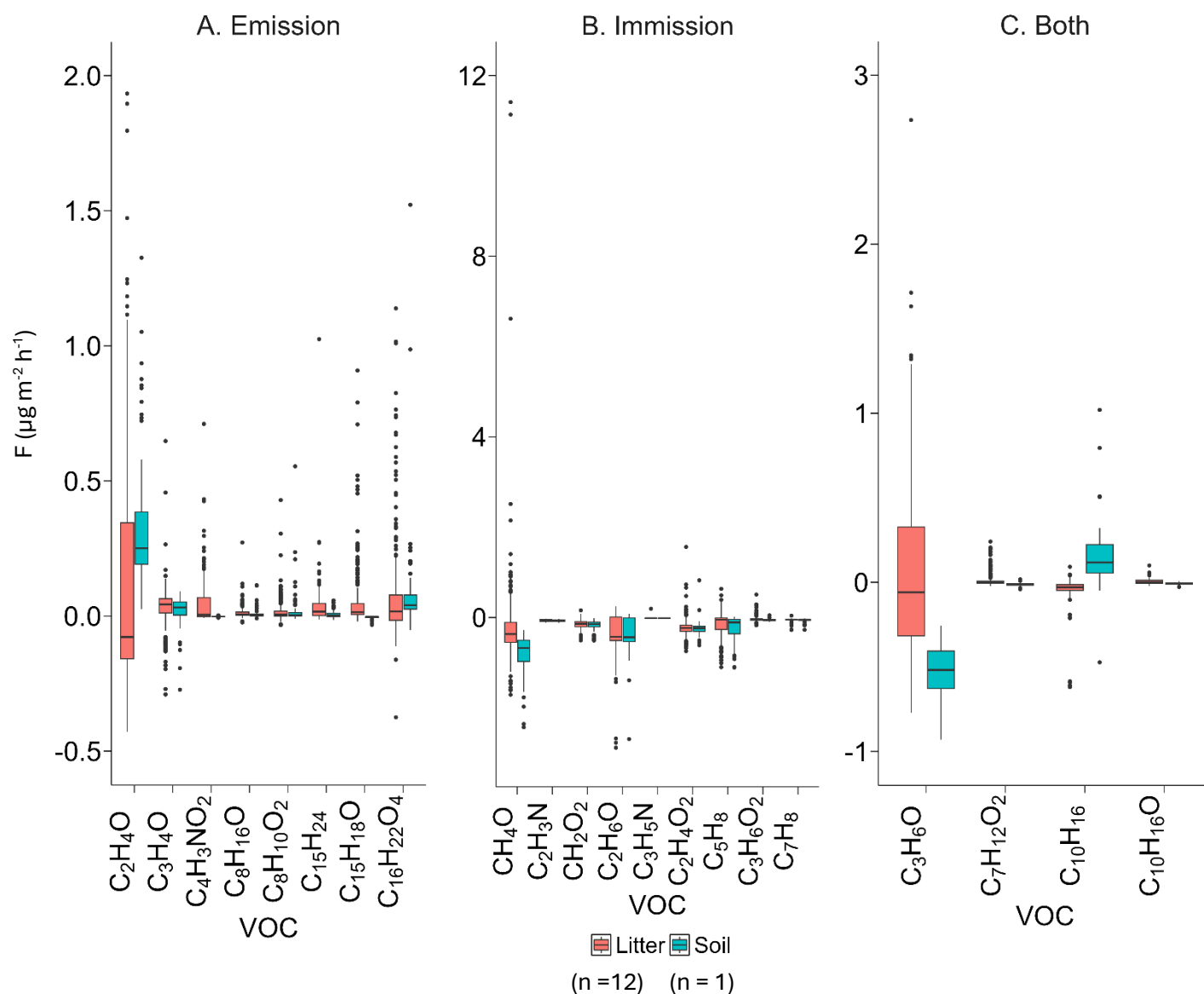
mass. Further tests with longer time series are needed to complete our observations." and in the Conclusion section: "We recommend that further experiments be conducted under varying environmental conditions, and that time series analysis be conducted to fully evaluate the evolution and seasonality of VOC emissions. Finally, experiments in different locations are required to gain a deeper understanding of the role and impact of litter accumulation on VOC fluxes.".

4- The study presents a correlation matrix to explore relationships among VOC fluxes, environmental factors, and microbial parameters. It is not clear whether the analysis was performed using individual replicate values or chamber averages. Clarification on how replicates were handled would provide insight into how variability across measurements was managed.

Answer: To explore the relationship among VOC fluxes, the 3 days of experiments were used (not averaged) with 1-hour VOC fluxes. For this matrix, n = 345 and not 360 (24 hours * 3 days * 5 chambers) as some data was missing between experiments. This is now specified in the text: "For this purpose, a correlation analysis was performed based on hourly fluxes merging the data of the 15 chambers (n=345) and presented in Figure 6."

It is also specified in the caption of Figure 6: "Correlation matrix between BVOC fluxes and abiotic (air temperature and humidity, litter humidity) and biotic (litter mass and microbial biomass) factors merging the data of the 15 chambers (n = 345)."

5- Additionally, Figure 3 may require improvement in its presentation. It would be beneficial to highlight key compounds described around line 195 and consider splitting the figure into subfigures (e.g., categorizing compounds as emission-only, immission-only, or fluctuating, or grouping them by source/sink characteristics). Also, please include the number of replicates in the figure captions and consider presenting statistical analyses comparing soil versus litter treatments.

Answer: Figure 3 has been revised according to the suggestion of the reviewer by keeping only emission/immission/both categories and applying number of points used for plotting:

Furthermore, the previous Figure now presents in Supplementary material as new Figure S1.

Minor Comments

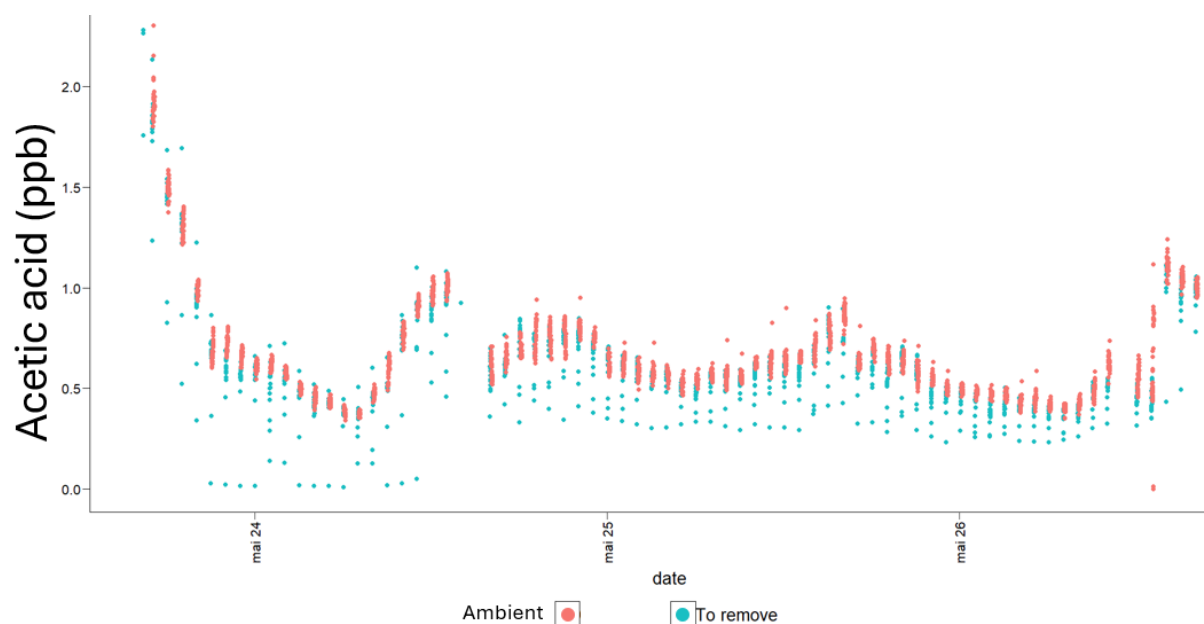
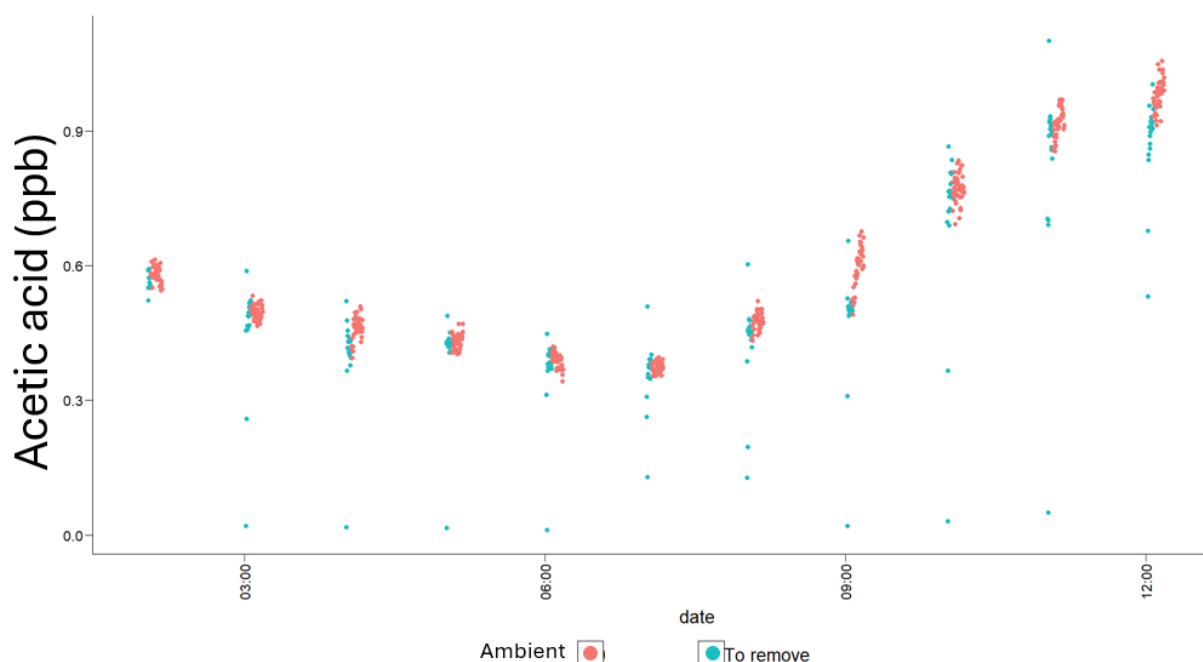
Line 107: "Time of Life" vs. "Time-of-Flight"

Answer: We thank the reviewer for noticing this typo mistake. It has been changed in the text.

Line 100: Please specify the origin of the ambient air used for the measurements (e.g., is it drawn from within the forest canopy?) and provide details on the background VOC levels and their temporal fluctuations.

Answer: Yes, ambient air was provided from the forest canopy, at ca. 0.5 m aboveground level, in a central position with respect to the chambers. It is now added to the text with background values: "Ambient concentrations varied from 0.001 to 3.660 ppbv. Diurnal variations were observed for most of the compounds and are related to transported air masses and VOC emissions from the canopy.". In addition, a table containing ambient VOC concentrations was added to the Supplementary Material as new Table S2.

Line 130: How the outlet concentration was calculated? And curious to know how stable it was? (e.g., whether the outlet concentrations initially increased or decreased before stabilizing).

Answer: Outlet concentrations (from the chamber) were calculated as the average concentration of the last 7 minutes of each ambient measurement step. In other words, we switched between each chamber and the ambient air every 10 minutes, recording a mass spectra every 10 seconds. Then, from the 10-minute measurement step corresponding to ambient air (and for each chamber step), we get rid of the first 3 minutes where concentration equilibrate in the lines. Since a flow through valve was used, the stabilization time was rather short, even with 20 m long tubing. Then, the 10-second data of the last 7 minutes were averaged to provide an average ambient concentration on an hourly time scale, which was later used to calculate fluxes. To illustrate this stability during the selected 7 minutes, the time series of one compound (sticky compound such as acetic acid) is shown below at two temporal scales, highlighting the excluded data (in blue) and those included for the average ambient concentration calculation.

Line 143: "actinobacteria" should be italicized.

Answer: "*Actinobacteria*" is now in italic.

Lines 166–167: The description in these lines is unclear; additional details explaining what is being measured or described would improve understanding.

Answer: To enhance understanding, this paragraph has been rewritten: "Dataset was filtered to keep ions that present a significant flux difference between ambient and chamber measurements. The BVOCs of interest are summarized in Table S.4. VOC data were filtered to keep the most abundant VOC fluxes in each chamber by applying a filter and removing all fluxes > 0.002 µg m^{-2} h^{-1} (in absolute value).".

Line 312 – I've noticed that several sections (e.g., also around Line 353) suggest that the observed flux patterns might be due to different environmental conditions. Could the authors be more specific about this reasoning? Which could be the environmental factors/mechanisms driving these patterns?

Answer: Ambient air injected into the chambers is dependent on environmental factors such as temperature and light, as these concentrations are linked to canopy emissions. Depending on the injected concentrations, the concentrations inside the chambers and then the fluxes induced can be modified. In addition, temperature and humidity can affect emission/deposition by stimulating microbial activity, or promoting surface deposition and volatilization.

This is now mentioned in section 2.1: "Diurnal variations were observed for most of the compounds and are related to VOC emissions from the canopy. The most abundant ambient VOC concentrations are listed in Table S.2."

And corrected in VOC emission section:

"Given the environmental conditions (i.e. humid) inside the chambers, we hypothesize that carboxylic acid deposition processes linked to the soil moisture dominate, resulting in net deposition (further discussed in section 3.4)."

Section 3.2: "For other compounds, the lack of correlation may be due to a high variability, or other environmental factors (such as temperature and humidity inside the chambers) that are more important drivers of emission/deposition."

Section 3.3: "For litters masses ~350 g m^{-2}, the environmental conditions showed few differences with higher temperature and then lower humidity during the measurements (temperature and humidity inside the chambers in Figure 5), which can explain differences in observed fluxes."

"However, temperature and humidity were strongly different and the soil was not subjected to the same constraints, which explains the differences observed between our fluxes and this previous study."

Conclusion: "We performed correlations between VOC fluxes, environmental parameters (temperature and humidity) and microbial biomasses."

Abstract: Species' Latin names should be italicized, and spell out PTR-ToF-MS.

Answer: Latin names are now italicized, and PTR-ToF-MS spelt out.

Reviewer #2

The authors thank the reviewer for his/her positive and constructive suggestions and comments to help to improve our paper. The reviewer can find below the answer (colored in blue) to all his/her comments (in black).

General comments

In their study "Litter biomass as a driver of soil VOC fluxes in a Mediterranean forest" Rocco et al. investigated a highly relevant and timely topic in the field of ecosystem-atmosphere interactions. By using PTR-TOF-MS they deployed a state-of-the art technique to analyze VOC emission from soils covered by different amounts of litter in a Mediterranean downy oak forest. For evaluation of VOC fluxes the authors have chosen an untargeted approach, which in my opinion is an appropriate method for investigating soil VOC emissions, since many compounds emitted from soils still remain uncharacterized. Data were complemented by phospholipid fatty acid analysis of soil and litter samples and environmental parameters (air temperature and relative humidity), which is a strength of this study, as the effect of litter can thus be related to environmental variables that change with the thickness of the litter layer. The results were discussed and presented in a structured manner, based on a comprehensive literature review. Still, I would recommend the authors to have a closer look at the following three studies:

- o Mu Z., Asensio D., Llusià J., Filella I., Ogaya R., Yi Z., Peñuelas J. (2022) Annual and seasonal variations in soil volatile organic compound concentrations in a Mediterranean shrubland and holm oak forest. *Geoderma*, 405, 115401.
- o Meischner, M., Haberstroh, S., Daber, L. E., Kreuzwieser, J., Caldeira, M. C., Schnitzler, J. P., & Werner, C. (2022). Soil VOC emissions of a Mediterranean woodland are sensitive to shrub invasion. *Plant Biology*, *24*(6), 967-978
- o Pugliese G, Ingrisch J, Meredith LK, Pfannerstill EY, Klüpfel T, Meeran K, Byron J, Purser G, Gil-Loaiza J, van Haren J, et al. 2023. Effects of drought and recovery on soil volatile organic compound fluxes in an experimental rainforest. Nature Communications 14: 5064.

These articles have been considered and added throughout the text.

While I believe the study can be a valuable contribution to the field, there are quite a few major aspects that require further consideration.

Major comments

1. In view of the conclusion "based on the results of this study, we can conclude that no clear relationship between litter accumulation and VOC fluxes could be established [...]" (L508ff), I feel the title is misleading. It suggests to be a main result of the study (=litter as a driver of VOC emissions), instead of a research goal (= to investigate litter as a driver of VOC emissions). Please revise the title for more clarity.

Answer: Title has been revised according to the suggestion of the reviewer: "Is litter biomass a driver of soil VOC fluxes in Mediterranean forest?"

2. In my opinion, the relatively short sampling time of three days and few replicates per litter mass (0, 8, 16, 32 and 48 g, n=3) is a major drawback of this study and limits the conclusions that can be drawn from it. The study would have benefited significantly from a longer measurement period under various environmental conditions (e.g. measurements campaigns in spring, summer, autumn and winter) to capture a broader spectrum of temperature, litter degradation phases, soil moistures etcetera. Furthermore, the three replicates are not independent, as only the litter was exchanged, but not the position of the open-bottom-chambers. Consequently, the bare soil remained the same in all three replicates and for the treatment "bare soil" only technical replicates are provided in this study. This is, in my opinion, not enough for statistical hypothesis testing.

Answer: The authors acknowledge that the number of 24-h BVOC measurements (15 in total covered a litter dry mass of *Q. pubescens* gradient ranging from 0 to 449.7 g m^{-2}) and the duration of the experiment (during 3 days) are limitations of the study. Nevertheless, this study was designed to test the hypothesis that litter accumulation affects soil VOC emissions in the short term. Extending the measurements to a longer period and measuring more litter VOC emissions would certainly be of great interest and will be the purpose of future studies. The fact that the chamber localization did not change from one sample to another during the 3 days of experiment is a choice, as it may induce a strong variability due to the high heterogeneity of the studied Mediterranean soils (Santonja et al. 2023), and consequently limit our interpretation of the effect litter accumulation, if we additionally surimpose a confounding effect due to the soil heterogeneity.

Therefore, we decided to limit the effect of soil heterogeneity. We systematically measured all abiotic and biotic parameters, including soil and litter microbial biomasses, and performed correlations between all measured variables as an exploratory approach to link VOC fluxes, environmental and biological parameters. In addition, we did not attempt to parametrize the fluxes with the measured abiotic and biotic parameters, using for example a structural equation modeling approach, due to a lack of statistical power.

Longer measurements are planned and mentioned in Conclusion section: "This study represents only a first step toward understanding the relationship between litter and VOC fluxes. It is not sufficient to conclude that litter mass has no effect on VOC emissions. We recommend that further experiments be conducted under varying environmental conditions, and that time series analysis be conducted to fully evaluate the evolution and seasonality of VOC emissions. Finally, experiments in different locations are required to gain a deeper understanding of the role and impact of litter accumulation on VOC fluxes.".

Santonja, M., Pereira, S., Gauquelin, T., Quer, E., Simioni, G., Limousin, J. M., ... & Baldy, V. (2022). Experimental precipitation reduction slows down litter decomposition but exhibits weak to no effect on soil organic carbon and nitrogen stocks in three mediterranean forests of southern France. Forests, 13(9), 1485. https://doi.org/10.3390/f13091485

Specific comments

Abstract

1. L9: Please specify "litter accumulation" to clarify that not only the effect of litter on soil

VOC emissions was investigated in this study (which was also addressed in several of the studies cited, e.g. Gray et al. 2010, Isidorov & Jdanova 2002, Isidorov et al. 2024, Leff and Fierer et al. 2008, Meischner et al. 2022), but, importantly, different amounts of litter, which in my understanding, is the novelty of this study and, thus, should be emphasized with more clarity throughout the manuscript. The same applies to the sentence: "However, the influence of litter biomass on soil VOC fluxes in Mediterranean forests has never been investigated" in line 71/72.

Answer: The authors thank the reviewer for these suggestions, and it is true that the novelty is the litter accumulation and not the presence/absence of litter.

The text have been changed accordingly:

In the Abstract: "However, previous studies have so far neglected the role of litter accumulation (here considered as the amount of litter) on soil BVOC fluxes, and most of them refer to coniferous and evergreen forests, while litter emissions from Mediterranean deciduous forests remain poorly explored."

In the introduction: "However, the influence of the amount of litter biomass on soil VOC fluxes in Mediterranean forests has never been investigated.".

And conclusion: "Finally, experiments in different locations are required to gain a deeper understanding of the role and effect of the amount of litter accumulated on VOC fluxes.".

2. L22/23: The fact that microbial abundance was analyzed in this study, should be stated earlier in the abstract, i.e. in the method description (L12-17)

Answer: The authors agree with the reviewer. The sentence was changed to: "To fill these gaps, the present work aimed to study BVOC fluxes in a Mediterranean deciduous forest, with a particular attention to the relationship between soil BVOC fluxes, microbial abundance and litter biomass accumulation on soils. ".

Introduction

3. L32/32: This argumentation neglects, that the emission factors used in MEGAN (Guenther et. al 2012) reflect the net emission (= emission minus uptake) of VOCs to the atmosphere. This means, that the loss of primary emissions on their way into the above canopy atmosphere, e.g. by consumption on canopy or soil surfaces, is already taken into account (Guenther et. al 2012). Furthermore, it is questionable whether the models underestimate emissions due to the proposed neglect of soil processes, or whether the exclusion of soil processes leads to an overestimation of emissions due to the sink function of VOCs. I fully agree, that there is a scarcity of studies addressing the dynamics of soil VOCs emission and uptake, however, I would strongly recommend to check the argumentation and put a focus more on the understanding of processes, rather than on atmospheric VOC models.

Answer: Thank you for this constructive comment. We changed the argumentation to focus on the understanding of processes rather than on models: "Numerous studies have documented BVOC emissions from the aerial parts of terrestrial plants - at the canopy, branch and leaf scales (Artaxo et

al., 2022; Gros et al., 2022; Mu et al., 2022; Rinnan, 2024), and they are estimated to release between 300 and 1000 Tg (C) yr^{-1} on a global scale (Guenther et al., 2012; Sindelarova et al., 2014; Wang et al., 2024). However, the contribution of soil (bare soil covered by litter) VOC exchange processes (emission and immission) is still unclear due to the scarcity of studies." The processes involved in the VOC exchange at the soil-atmosphere interface are further introduced at Lines 57-80.

4. L58-59: Uptake of VOCs by soils was also recently investigated by Pugliese et al. 2023 (see general comments).

Answer: This reference has been added in the text: "[...] as they can be assimilated through microbial metabolism as a source of carbon and energy for certain heterotrophic microbes (Jiao et al., 2023; Kramshøj et al., 2018; McGenity et al., 2018; Pugliese et al., 2023; Shennan, 2006; Zhang et al., 2020)."

5. L66-L68: It is not clear to me, why limited soil functioning limits BVOC exchange between soil and atmosphere. Please explain this statement in more detail. Alternatively, I suggest rephrasing the sentence as followed to make it more general: "[] and thus affects BVOC exchanges between soil and atmosphere."

Answer: Sentence has been modified as suggested by the reviewer: "[...] and thus affects BVOC exchanges between soil and atmosphere".

6. L80: The aspect of microbial communities is rather brief in the introduction and should be explained in more detail.

Answer: Soil microbial contributions to VOC emission or consumption are already mentioned in several parts of the Introduction section (e.g. Lines 46-47; 49-56; 59-60). However, as suggested, we better introduced the aspect of microbial communities in the Introduction section at Lines 68-71:

"Indeed, Mediterranean ecosystems are strongly affected by increasing warming and aridity (Peñuelas, 2008), which can alter soil microbial communities (i.e. diversity, biomass and activity, Aupic-Samain et al. 2021; Santonja et al. 2017; Shihan et al. 2017), limit soil functioning (e.g. litter decomposition, soil organic carbon sequestration, nutrient release, Quer et al., 2022; Santonja et al. 2017, 2022), and thus affect BVOC exchanges between soil and atmosphere (Peñuelas et al., 2017; Yang et al., 2024b)."

7. Please consider to close the introduction with a clear hypothesis or research question, which should be mentioned again in the conclusions, to improve the general structure and clarity of the article.

Answer: We close the introduction by the following sentence "In this context, the present study aimed to investigate in situ BVOC emissions from soils in a Mediterranean deciduous forest dominated by the downy oak (Quercus pubescens Willd.), the predominant deciduous forest in the Southern Mediterranean part of France. In particular, we sought to verify the hypothesis that litter BVOC fluxes is affected by litter biomass accumulation on the soil surface, and the associated microbial communities", that link to this conclusion's sentence: "Based on the results of this study, we can conclude that, on a short term, no clear relationships between litter accumulation and VOC fluxes could be established, except for a few compounds such as acetone, sesquiterpenes, CHC acid or methanol.":

Methods

8. The flow rate (Q) is an important variable in the quantification of VOC fluxes (F). In line 100 it was stated that all chambers were flushed with 0.6 L min^{-1}. However, in line 110 it says, that there was a flow rate of "around 0.3 L min^{-1}" from the chamber to the PTR-TOF-MS. Please explain, where this difference originates from. Additionally, it is very important for a correct quantification to use the precise flow rate trough the chamber, as it has a direct effect on the VOC concentrations. Please clarify, if the precise flow rates are available for each chamber and if they were used for the calculation of F. If Q varied between the chambers, please report the variance (standard error or standard deviation).

Answer: There was a typo error, all chambers were flushed at 0.3 L min^{-1}, the flow being regulated by a mass flow controller. This error has been corrected through the text.

9. A Welsh t-test was used to identify compounds that differed between ambient air and chamber measurements. Which method or work-flow was used to remove water clusters and fragments? This is an important step in untargeted approaches which should be described with more detail to avoid an overestimation of detected compounds.

Answer: The Welsh t-test is used as a first filter to only include ions with significant fluxes (either positive or negative). Then, among the remaining ions, the chemical formula and trends are carefully checked to remove potential clusters and fragments that are then manually summed with the parent molecule. In particular, fragments were identified based on their correlations with original ions (i.e. if the r^2 between potential fragment (e.g. fragment at *m/z* 81 for monoterpenes) the correlation was very close to 1). The GLOVOCS database (https://glovocs.creaf.cat/, last updated version of 12/11/2024) and its referenced sources were used to assist in identifying fragments and water clusters.

10. An issue that I missed in the section methods and/or discussion is the collinearity of environmental factors in the correlation analysis. Collinearity refers to the non independence of predictor variables, in this case air temperature, relative humidity, fungi biomass etcetera. One example: The predictor variables for VOC fluxes "fungi", "gram_pos" and "gram_neg" are all strongly correlated between each other and with "relative humidity" and "masses", which from an ecological point of view makes perfect sense. However, it is not possible to statistically separate the effect of the individual variables on the VOC fluxes. For further reading on this topic I recommend: Dormann et al. 2012 (https://doi.org/10.1111/j.1600-0587.2012.07348.x)

Answer: We thank the reviewer for this reference recommendation.

As specified previously, we systematically measured all abiotic and biotic parameters and performed correlations between all measured variables as an exploratory approach to link VOC fluxes, environmental and biological parameters. As stated in our manuscript, it is hard to solve the problem of collinearity, and we did not attempt to parametrize the fluxes with the measured abiotic and biotic parameters, using for example a structural equation modeling approach, due to a lack of statistical power. We agree that is not possible to statistically separate the effect of the individual variables on the

VOC fluxes, and by consequence we also refrained an over interpretation of our correlation analyzes, despite a good fit from an ecological point of view.

We stated, at multiple stage of the manuscript (cf citations below), that both increased BVOC measurements and longer studies are required to comfort but also to provide a better mechanistic understanding of our main conclusions:

In the Abstract: "However, previous studies have so far neglected the role of litter accumulation (here considered as the amount of litter) on soil BVOC fluxes, and most of them refer to coniferous and evergreen forests, while litter emissions from Mediterranean deciduous forests remain poorly explored."

In the introduction: "However, the influence of the amount of litter biomass on soil VOC fluxes in Mediterranean forests has never been investigated.".

And conclusion: "Finally, experiments in different locations are required to gain a deeper understanding of the role and effect of the amount of litter accumulated on VOC fluxes.".

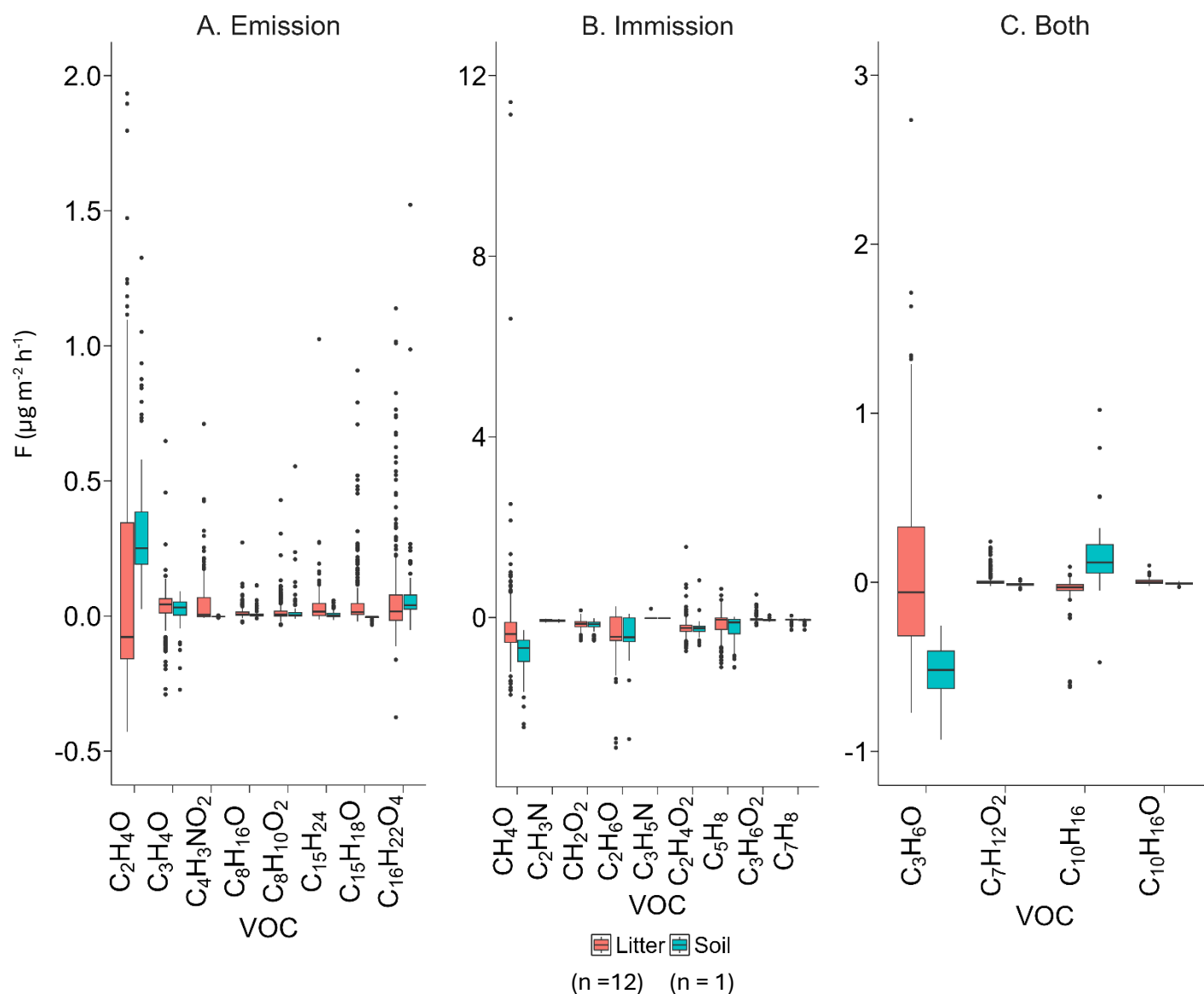
Results and discussion

11. Please take into consideration, that not all of the 135 compound detected necessarily originate from the soil. As ambient air was used to flush the chambers and there were VOCs which were taken up by the soil, these compounds were already present in the measuring air from outside the chambers and hence might be released by vegetation instead of soil.

Answer: The authors agree with the reviewer, the VOCs may originate from many other sources than the soil. This is more specifically the case for those which were deposited on the soil. Indeed, that is the reason at L. 185 we were discussing the diversity of fluxes, not emissions.

We revised the sentence to make it clearer for the reader. The sentence is now: "Considering all treatments, more than 135 compounds were identified that may originate from different sources as ambient air was flushed into the chambers. However, these, numerous measured VOC are reflecting the high diversity of VOC exchanged (emission or deposition) by *Q. pubescens* litter which is much more than in previous studies focusing VOC fluxes from litter soil (Asensio et al., 2007b; Legros et al., 2025; Viros et al., 2020; Yang et al., 2024b)."

12. Figure 3 could, in my opinion, be improved, by presenting the different groups of compounds according to the structure of the subsections (emission, immisson, both) in separate panels or figures.

Answer: Figure 3 has been revised according to the suggestion of the reviewer by keeping only emission/immission/both categories and applying number of points used for plotting (as also suggested by reviewer #1):

Furthermore, the previous Figure is now in supplementary material.

13. Please elaborate, how the assignment of specific compounds to measured masses was verified. Statements like "1H-pyrrole-2,5-dione was identified here for the first time in litter VOC fluxes" (L226) should be supported by measurements of corresponding standards to verify the
compound assignment. If the compound was not present in the calibration standard, it should be made transparent, that the compound was tentatively assigned as [...].

Answer: The reviewer is right; it was not possible to perform calibration with this compound. The sentence has been modified: " $C_4H_3NO_2$ was tentatively assigned as 1H-pyrrole-2,5-dione is observed for the first time in litter VOC fluxes."

Minor comments and technical corrections

Line	Comment
8	It is not ideal to state the importance of a factor with a double negation ("not negligible". Positive alternatives are "substantial", "considerable", "significant" …

Answer: The sentence has been modified as suggested: "Soil biogenic volatile organic compound (BVOC) emissions have been studied in different biomes, showing that their emissions are considerable."

| 13 | Latin species names should be written in italics. Please change to "*Quercus pubescens* Willd." |

Answer: Latin species names is now in italic: "in the downy oak (*Quercus pubescens* Willd.) forest"

| 14 | Please spell out the acronym "PTR-TOF-MS" |

Answer: PTR-ToF-MS have been spelt out in the text: "Measurements were performed in southern France, in the downy oak (Quercus pubescens Willd.) forest of the Observatoire de Haute Provence (O3HP), during the late spring of 2023, using dynamic chambers coupled to an on-line proton transfer reaction – time of flight – mass spectrometer (PTR-ToF-MS).".

| 15 | soil alone → bare soil |

Answer: changed in the text: "We investigated in-situ daily BVOC fluxes from bare soil and different litter biomasses mimicking low [...]"

| 19 | Suggesting that soil […] uptakes compounds → Suggesting that soil […] is taking up/takes up compounds |

Answer: changed : "The results showed a high BVOC diversity with more than 135 emitted compounds. For a large majority of the measured compounds, the BVOC fluxes were negative, suggesting that soil (bare soil covered by litter) **is taking up** compounds through biochemical and/or physical processes."

| 69 | Punctuation: (Asensio et al 2007) → (Asensio et al., 2007) |

Answer: corrected: "While bare soil appears to be a sink for VOCs in Mediterranean ecosystems and other biomes (Asensio et al., 2007),"

| 75 | (around 1855-1870) → (in the years around 1855-1870) |

Answer: changed: "Moreover, greening policies and gradual abandonment (in the years around 1855-1870"

| 85 | Please explain, what an AnaEE in situ platform is. |

Answer: AnaEE is now explained in the text: "AnaEE is a European network providing ecosystem data, research tools, and experimental facilities to study real ecosystems under environmental stress."

| 87 | Please specify the mean air temperatures and precipitation rates of "dry and hot summers" |

Answer: These details have been added: "The climate is typical of the Mediterranean region, characterized by a dry and hot summer (mean air temperature between 5.4°C in January to 20.2°C in July and precipitation rates of ~500 mm/year, Rameau et al., 2008)."

| 87-91 | Please split the sentence into two parts for better readability |

Answer: the sentence has been modified: "The O₃HP site was created in 2009 in order to

study the *Q. pubescens* forest ecosystem (≈ 90 % of the biomass and ≈ 75 % of the trees) at the soil and tree scales. A rainfall exclusion device (an automated, monitored roof that deploys during rain events) is installed over part of the O3HP canopy to study both natural and intensified water stress conditions in this forest."

89 What is meant with "soil and tree scales"? Is there a difference in scale, or are different compartments of the ecosystem being analyzed?
Answer: Different compartments of the ecosystem were analyzed (soil, leaves, canopy). Sentence has been changed: "the Q. pubescens forest ecosystem (≈ 90 % of the biomass and ≈ 75 % of the trees) at different compartment (soil, leaves and canopy scales)."

98 Please report the weight of litter in the unit [g m^2] for better comparability
Answer: Values have been converted in the unit [g m^{-2}].

98,104 Please explain with more detail what is meant with "fresh litter". Where was the litter collected? To which proportion did the understory contribute to the litter composition? Was the weight of the added litter determined from fresh or from dry litter?
Answer: Details have been added in the text: "Fresh litters were removed from the soil, weighted and installed for the experiment. Aliquots were made to calculate equivalent dry masses of the 12 litter biomass pools used in this experiment (Table S1). Chamber 1 covered bare soil (i.e. 0 g m-2 of litter), while chambers 2 to 5 circled bare soil fully covered by litter dry mass of Q. pubescens ranging from 92.5 to 449.7 g m-2 over the 3 days of experiment (Table S1, Figure 1)."

100 Just a suggestion: Why not name the treatments according to the actual weight of added litter?
Answer: You are right, this improvement will facilitate the extrapolation of our results for the readers. Consequently, the different treatments are not named LM1, LM2, LM3 and LM4 anymore. The authors simplified the text by using directly units of masses of litter per area (g m^{-2}).

For example please find here the New version of the Figure 4:

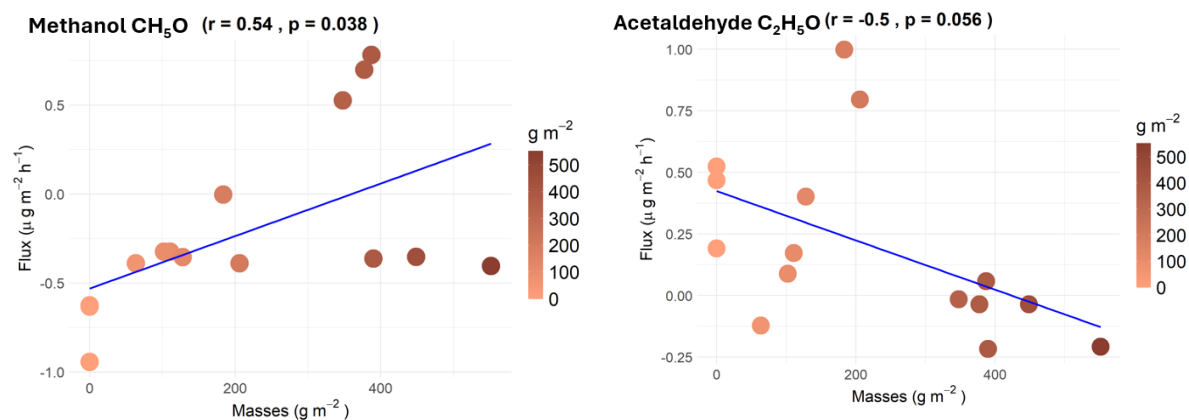
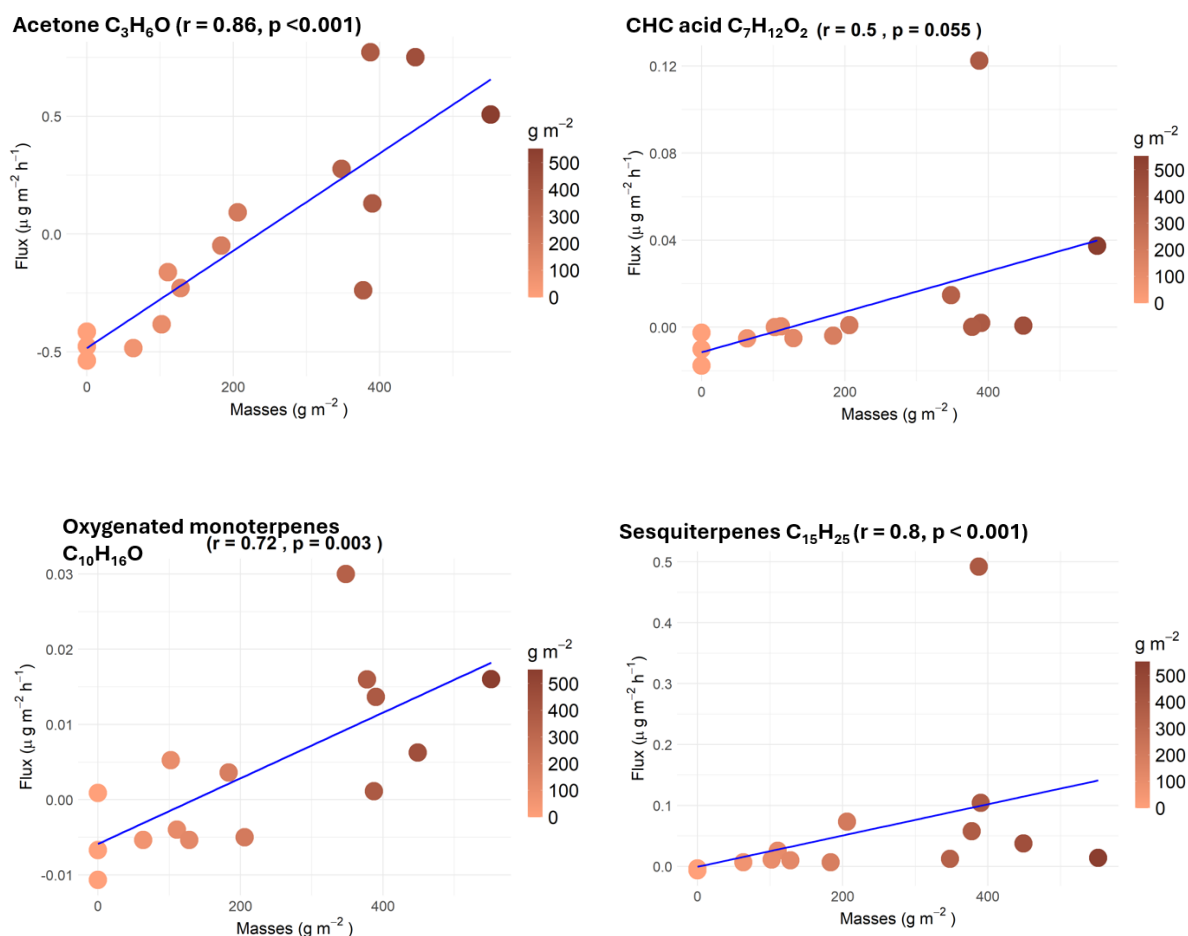



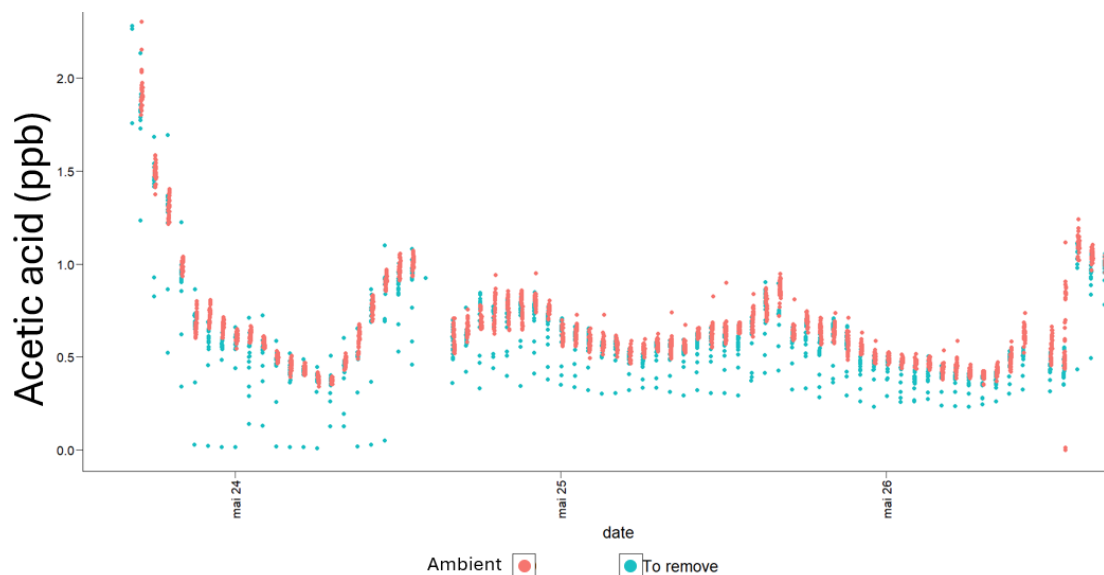
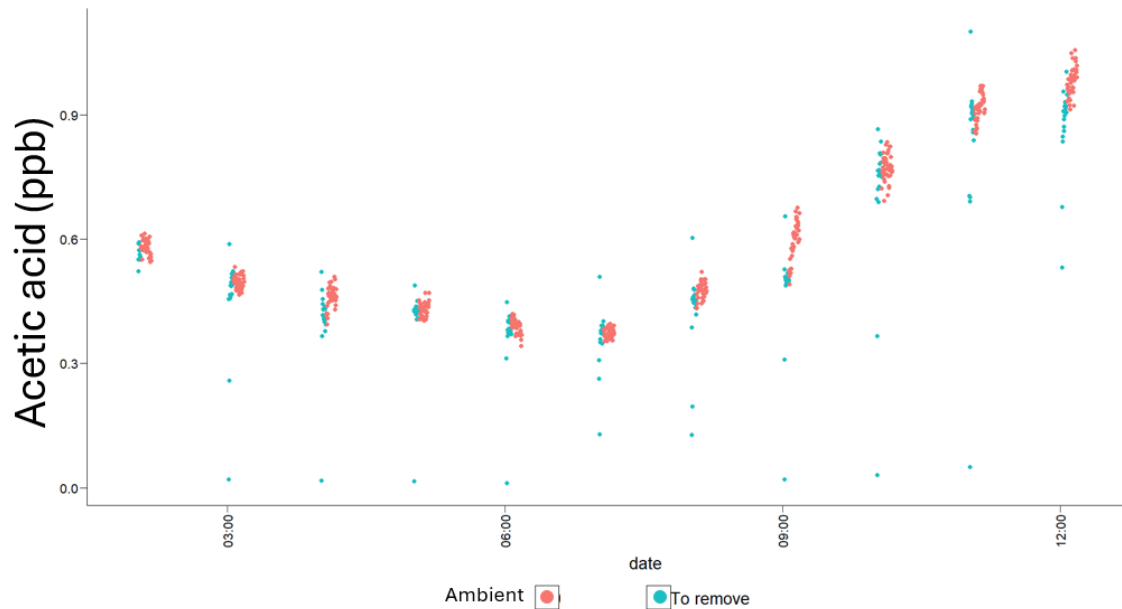
Figure 4. Correlation plots of methanol, acetaldehyde, acetone, oxygenated monoterpenes, CHC HC acid and sesquiterpenes fluxes (µg m^{-2} h^{-1}) with litter masses per area (0 in bare soil in g m^{-2}).

107   Time-of-life → time-of-flight
        Answer: changed.

109   Please standardize the specification of products and companies (usage of capital letters, indication of city and country names)
        Answer: Product name and company has been added in the text: "[…] and the ambient inlet were connected to a flow through multivalve (Valco Instruments Co. Inc, VICI VALCO, Huston, USA) placed inside", and has been homogenize.

110   A suggestion for better readability:
        "Parameters of the PTR-TOF-MS were set to a reaction chamber pressure of x mbar, a drift tube voltage of x V and a temperature of 120°C, corresponding […]
        Answer: The sentence has been changed as suggested: "Parameters of PTR-ToF-MS were set to a reaction chamber pressure of 2.6 ± 0.001 mbar, a drift tube voltage and temperature of 450 V and 120 °C, respectively corresponding […]"

110   Please specify which temperature is meant. The temperature of the reaction chamber?
          Answer: It is the drift tube temperature: "drift tube voltage and temperature of 450 V and
          120 °C, respectively […]"

113   How stable were the measurements during these 10 minutes? Was there a peak at the
          beginning?
          Answer: Over these 10 minutes, the first 3 minutes after the switch were removed to avoid
          accounting for any initial peak involved by the short pressure drop during valve switching,
          or any memory effect. The potential memory effect is reduced thanks to the flush of all the
          inlets at any time. It is also depending on many factors, e.g. temperature, concentration of
          the VOC, polarity of the compound, etc. Considering this, we checked the trend of some
          ions with high concentration and known to be sticky such as acetic acid to be sure that the
          concentration is at equilibria during the 7 minutes. This is now stated in the text: "Each of
          the 15 samples (bare soil or soil covered by litter) and ambient air were sequentially
          monitored every 10 min during 24 h, leading to a one-hour cycle. Over these 10 minutes,
          the first 3 minutes after the switch were removed to avoid accounting for the initial peak or
          memory effect, the following 7 minutes being stable or fluctuating following a natural
          pattern." To illustrate this stability during the selected 7 minutes, the time series of one
          compound (acetone) is shown below at two temporal scales, highlighting the excluded data
          (in blue) and those included for the average ambient concentration calculation.

116   Please revise this sentence and put it into context.
Answer: This sentence has been revised and moved in this section: "A large range of BVOC has been identified with mass to charge (m/z) up to m/z 500. PTR-ToF-MS data were post-processed with IDA […]"

128   BVOC fluxes from dynamic chambers were calculated → BVOC fluxes from soil were calculated (the origin of the VOCs is the soil, not the chamber)
Answer: Is it now changed as suggested: "BVOC fluxes (F) from soil were calculated as […]"

130   "circled by the chamber" can be removed
Answer: It is now removed.

143   Is there missing a word? "[…] because they are markers for Gram-positive bacteria"
Answer: Indeed, there is a missing word. It is now corrected.

153   Please explain briefly what "i-buttons" are.
Answer: The i-buttons are sensors for temperature and humidity monitoring. It is now stated as: "continuously monitored by sensors (i-buttonsLink, Whitewater, WI 53190 USA)."

162   Which version of R was used?
Answer: Version of R is RStudio (version 2024.12.0).

190   Only a suggestion: Exchange "assimilation" with "degradation" to avoid confusion with Photosynthesis
Answer: It is now changed into degradation: "[…] covered by litter through degradation or adsorption processes, […]"

239   Please check presentences
Answer: All references have been revised in whole manuscript.

295   Please revise the sentence, it seems that something is missing. I would suggest to remove the "As" at the beginning or to close the sentence differently.
Answer: it is now removed from the sentence: "Toluene, acetonitrile (C_2H_3N) and

propanenitrile (C_3H_5N) are mainly known to be emitted from anthropogenic sources, and more particularly from biomass burning (Holzinger et al., 1999; Sarkar et al., 2016; Yang et al., 2016)."

344   4 → four
Answer: Changed.

345   Any ideas how this follow-up study could be designed?
Answer: The idea is to increase the number of replicates for bare soil and litter chambers: "However, a deeper study dedicated to separate the respective contribution of soil and litter by increasing the number of replicates in different location will be necessary to fully elucidate this point."

Figures 1,4 & 6   In the main text abbreviations for the treatments were introduced as LM1 – LM4. In the figures different names were used (M1-M4; Mass 1 –Mass 4); please standardize the treatment names throughout the manuscript. I also suggest to rename the treatment "Soil" to "Bare soil", as soil covered with litter, is also soil.
Answer: Figures 4 have been modified in order to directly provide the litter masses expressed in g m^{-2} for the readers:

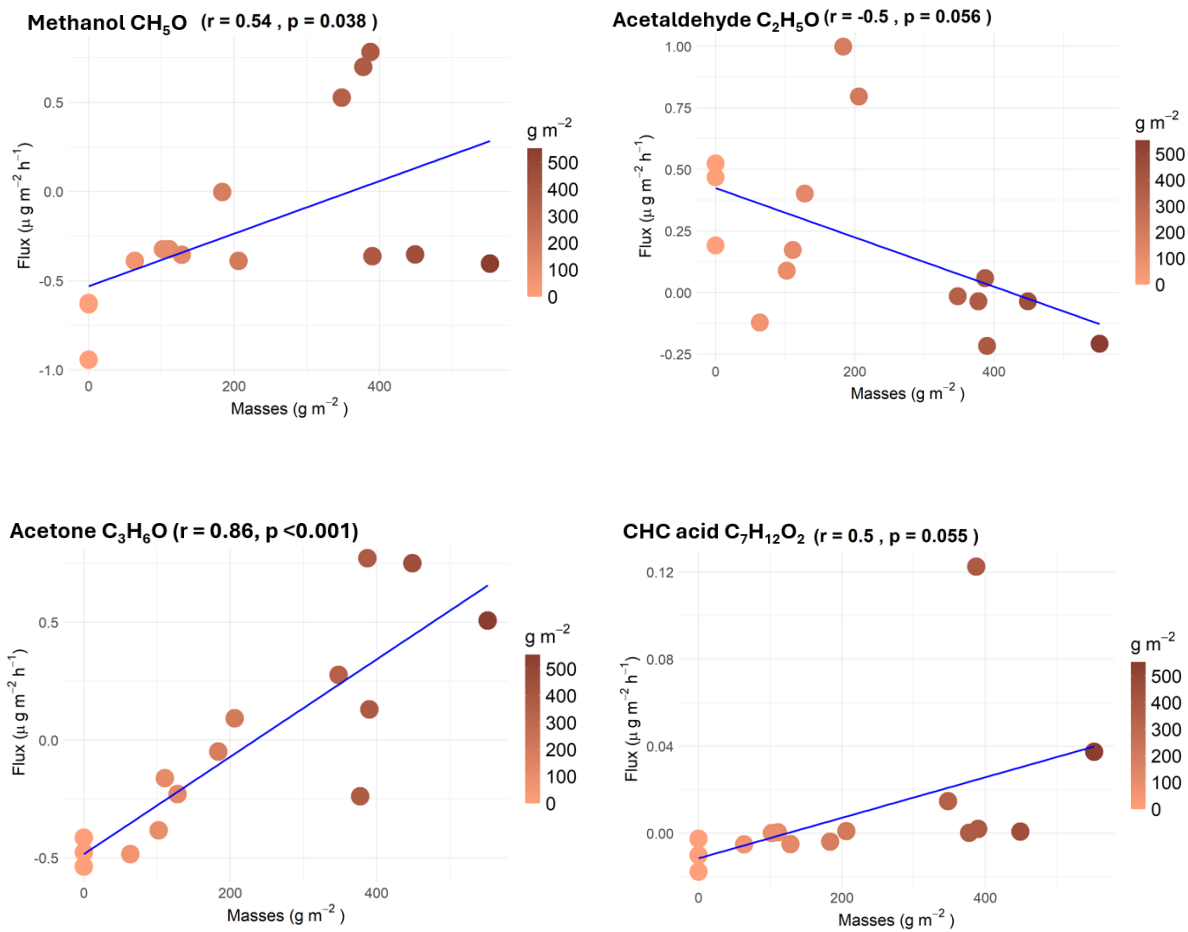
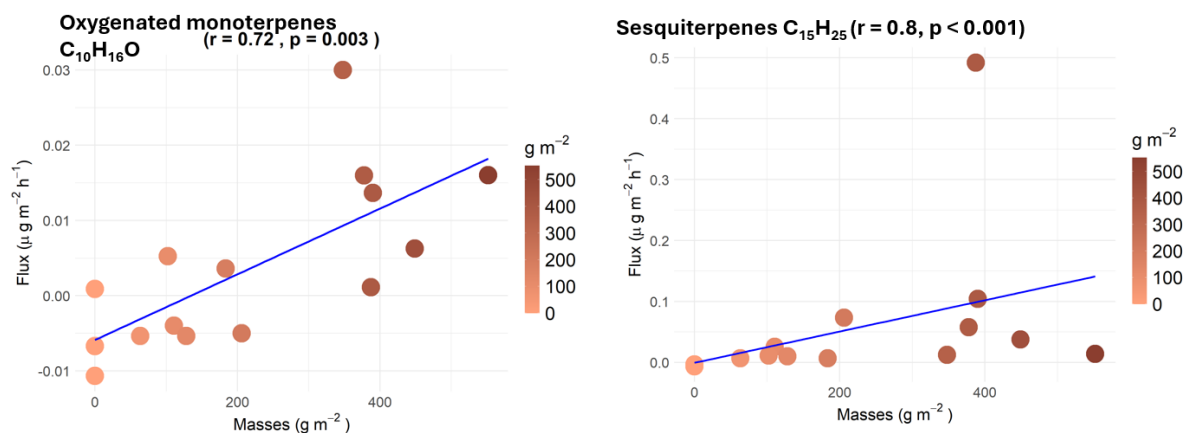
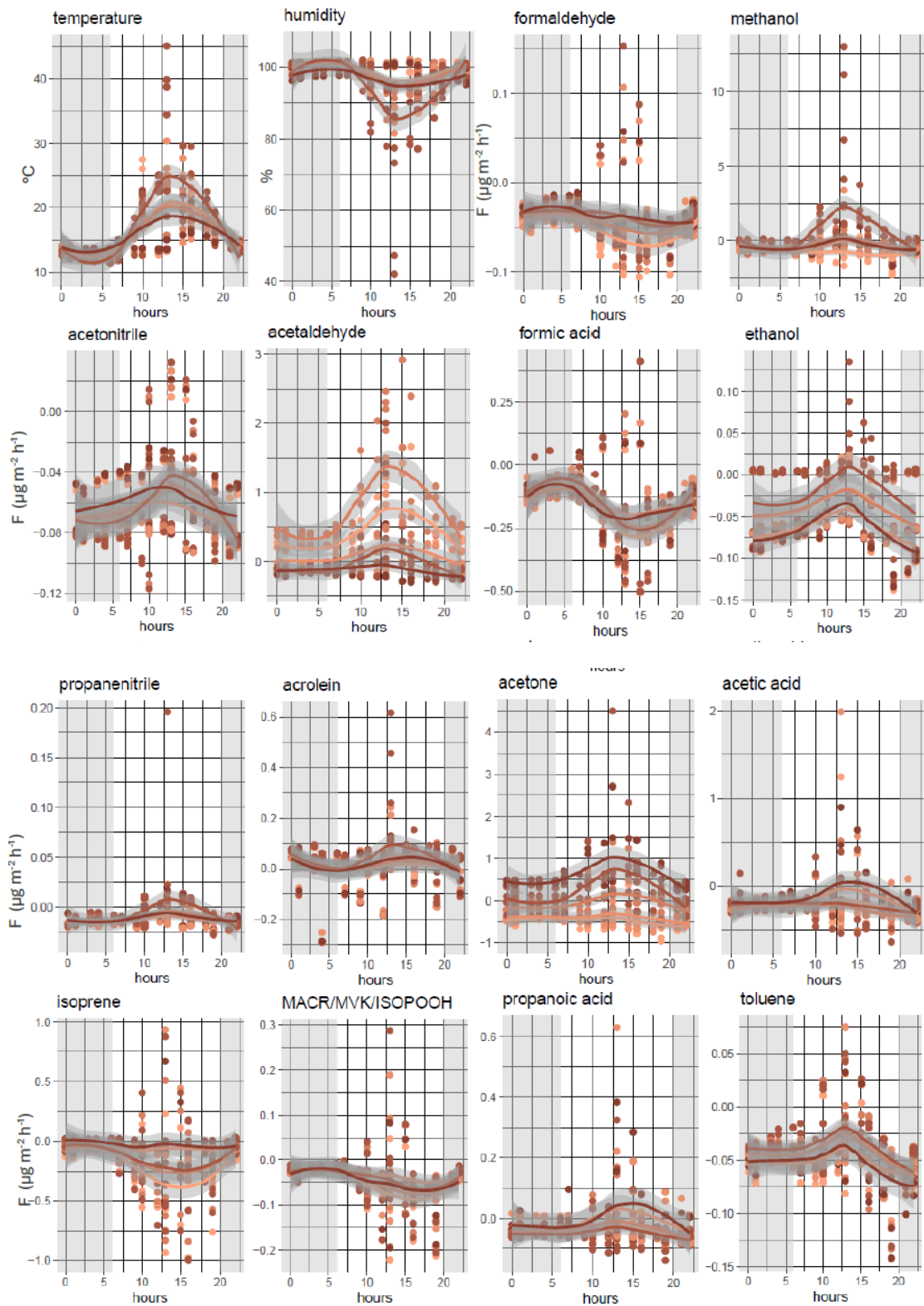
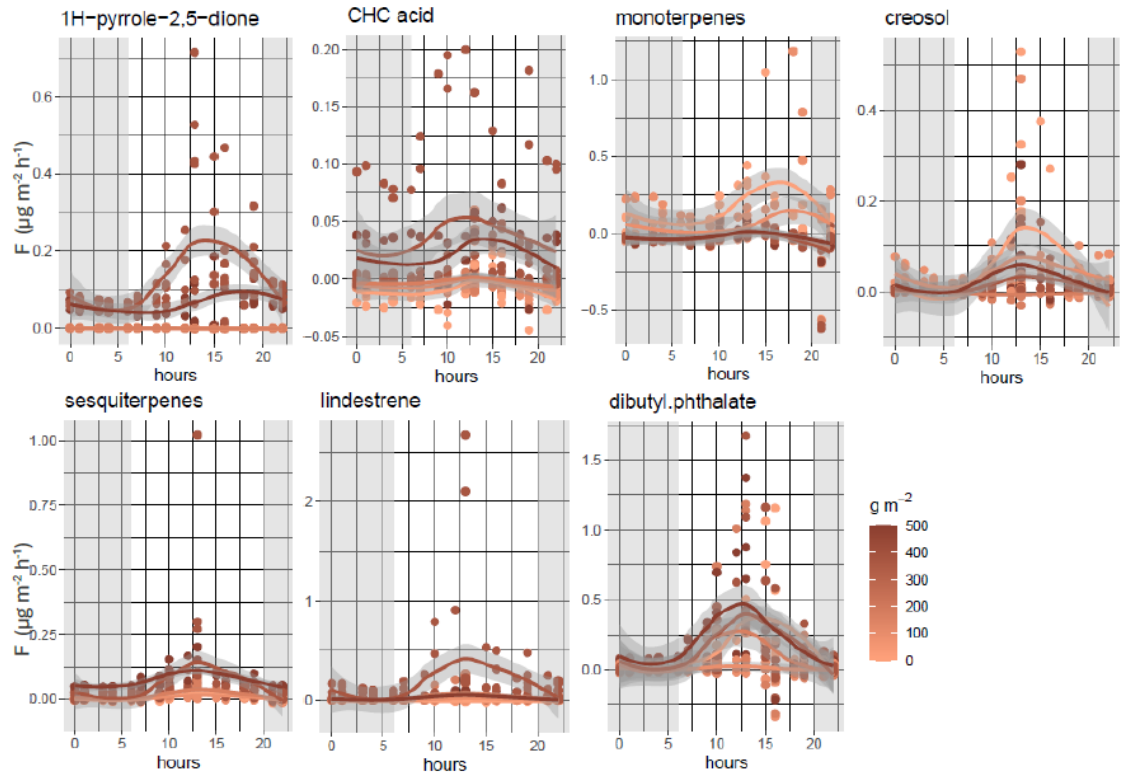



Figure 4   Please revise p-values displayed for acetone and sesquiterpenes and exchange p=0 with p<0.01 as in the main text
Answer: Revised.

385   "Formic acid, acetone and formaldehyde were especially sinked by the soil during night"→ suggestion: "The uptake of formic acid, acetone and formaldehyde by the soil was particularly high at night."
Answer: Changed as suggested: "The uptake of formic acid, acetone and formaldehyde by the soil was particularly high at night when the humidity increased and reached 100 % (-0.052 ± 0.023 µg m^{-2} h^{-1}"

Figure 5   Please arrange the panels on a vertical page not horizontally
Figure 5   Please add a y-axis label to the "humidity" panel (%?), like it was done for temperature
Figure 5   Just a suggestion: Night times could be indicated in the figure by adding a light grey background to each panel.
Answer: Figure 5 has been modified as suggested:

418   Please format the title to bold
Answer: Title is now in bold.

427   Remove "e" after "soil"
Answer: Removed.

427   Fungi are at the origin of monoterpene emissions → Fungi are producers of monoterpenes
Answer: Changed.

429   "Compounds observed in cluster 2 were positively related to the temperature inside the chambers, and logically negatively related to relative humidity". Please mention the negative correlation between relative humidity and temperature explicitly here, to explain why the negative correlation between the compounds of cluster 2 and relative humidity is "logic".
Answer: Correlation between temperature and humidity have been added in the text: "Compounds observed in cluster 2 were positively related to the temperature inside the chambers, and logically negatively related to relative humidity (r(humidity/temperature) = -0.85)."

432, 437, 442   Please remove asterisks, if possible
Answer: Asteriks have been removed.

451   "Emission from dead leaves" → "emission from plant tissues"
Answer: Changed.

460 ff	Please check grammar
	"Surprisingly, isoprene fluxes were negatively correlated with temperature (r = -0.35, pvalue < 0.001), and so does for their oxidation products MACR/MVK/ISOPOOH (r = - 0.24, pvalue < 0.001) and formic acid (r = -0.43, pvalue < 0.001)." →
	"Surprisingly, isoprene fluxes were negatively correlated with temperature (r = -0.35, pvalue < 0.001), and so were their oxidation products MACR/MVK/ISOPOOH (r = -0.24, pvalue < 0.001) and formic acid (r = -0.43, pvalue < 0.001)."
	Answer: Corrected.

467	"between themselves" can be removed
	Answer: Corrected.

Figure 6	Please standardize the font of the figure caption
Figure 6	"* ≧ 0.05, 0.01 < ** < 0.05 and 0.001< *** < 0.01" →
	"p ≧0.05 (*), p < 0.01 (**), p<0.001 (***)"
	Answer: Done and changed.

492	"with some fluxes appearing to be independent on litter mass": Please name some Examples
	Answer: We give examples of toluene and formaldehyde.

494	"the most uptaken compounds were […] → The compounds with highest uptake rates were [….]
	Answer: Corrected.

495	"Thanks to holistic methodology" → "By a holistic approach"
	Answer: Corrected.

496	Was the identification of these compounds verified by the measurements of standards? Otherwise the measured mass should be reported together with the tentatively assigned compound name
	Answer: Changed.

499	Please mention the environmental factors that were correlated with the local time.
	Answer: Changed : "10h and 15h local time".

510	A suggestion: "This study represents only a first step toward the relationship between litter and VOC fluxes" → "This study contributes to a better understanding of the relationship between litter and VOC fluxes"
	Answer: Changed.

References	There are some references listed in the bibliography, that were not mentioned in the main text: Inomata et al. 2014; Meischner et al. 2022
	Please revise the references carefully and ensure, that all cited articles appear in the bibliography and *vice versa*.
	Answer: Inomata et al. (2014) and Meischner et al. (2022) have been cited in the supplementary material for identification of compounds. References have been added in the text.

Figure 2	Please revise the x-axis of Fig. 2, hard to read. E.g. 01/22 instead of Jan. 22,..
Figure 2	No heading is needed for a figure, this information should be in the figure caption
	Answer: Changed.